PAC investigations of ferromagnetic spinel semiconductors

Von der Fakultät für Chemie und Physik

der Technischen Universität Bergakademie Freiberg

genehmigte

DISSERTATION

zur Erlangung des akademischen Grades

doctor rerum naturalium

(Dr.rer.nat.)

vorgelegt von Dipl.-Ing. Veaceslav Samohvalov

geboren am 28. August 1976 in Chișinău, Moldova

Gutachter: Prof. Dr. rer. nat. habil. Sepp Unterricker, FreibergProf. Dr. rer. nat. habil. Tilman Butz, LeipzigDr. rer. nat. Jens Kortus, StuttgartProf. Dr. habil. Ivan M. Tiginyanu, Chisinau

Tag der Verleihung: 25. Juli 2003

Contents

1

1 Ferromagnetic spinels

1.1 Cr	ystal structure	
1.2 Ph	ysical properties	5
1.2.1	Crystal growth	5
1.2.2	Magnetic properties	7
1.2.3	Optical properties	9
1.2.4	Electrical characteristics	9
1.3 Ap	pplications	11

2 Theoretical basis and experimental requisites for PAC

2.1	Introduction	
2.2	Hyperfine interactions	
2.2.	.1 Magnetic dipole interaction	
2.2.	.2 Electric quadrupole interaction	
2.3	Perturbed γ-γ Angular Correlations method	
2.3.	.1 Principles	
2.3.	.2 Magnetic dipole interaction	
2.3.	.3 Electric quadrupole interaction	
2.3.	.4 Combined magnetic and electric interaction	
2.3.	.5 Data reduction	
2.3.	.6 Information obtained from PAC experiments	
2.4	PAC probes	
2.5	Doping procedures	
2.6	Experimental apparatus	

3 Results and discussion

3.1	Imp	lantation defects in ferromagnetic spinels	33
3.2	Site	occupation and behavior of radioactive probes	37
3.2.	1	Introduction	37
3.2.	2	State of the art	37
3.2.	3	Measurements with ¹¹¹ In(¹¹¹ Cd), ^{111m} Cd and ¹¹¹ Ag(¹¹¹ Cd) probes	38
3.2.	4	Measurements with ⁷⁷ Br(⁷⁷ Se) probes	44
3.2.	5	Measurements with ^{199m} Hg probes	47
3.2.	6	Measurements with ¹¹⁷ Cd(¹¹⁷ In) probes	49

3.2	2.7	Measurements with ¹⁰⁰ Pd(¹⁰⁰ Rh) probes	51
3.2	2.8	Summary	53
3.3	Sig	gn determination of internal magnetic fields	60
3.4	Te	mperature dependence of the electric field gradients in spinels	67

4 Theoretical calculations of the hyperfine fields

4.1	Theoretical background	71
4.1.	1 Introduction	71
4.1.	2 Density functional theory	71
4.1.	3 Spin-polarized systems	74
4.1.	4 The full potential LAPW method	75
4.1.	5 The electric field gradient formalism within the LAPW method	77
4.2	WIEN97 program	79
4.2.	1 Flow of programs	79
4.2.	2 Parameters for calculations	79
4.2.	3 Choice of muffin-tin radii	80
4.2.	4 Choice of the other parameters	80
4.2.	5 Convergence criteria	82
4.3	Theoretical determination of anion parameters	83
4.4	Theoretical electric field gradients	85
4.5	Calculations of magnetic properties	91
4.6	Impurity-case calculations	95
4.7	Technical details	102
Summa	ry	

Appendix	
Abbreviations	
References	
Acknowledgements	

Introduction

The second half of the 20th century can be called the era of microelectronics. During that 50-year period, the world witnessed a revolution based on the remarkable developments in the fields of electronics and information technologies. From the earliest transistor to the powerful microprocessors in desktop computers, most electronic devices have employed the flow of electric charges. However, in order to enhance the multi-functionality of devices (for example, carrying out processing and data storage on the same chip), investigators have tried to exploit another property of electrons – a characteristic known as spin. The transmission of spin, like the flow of charge, can also carry information among devices. One advantage of spin over charge is that spin can easily be manipulated by externally applied magnetic fields, a property already in use in magnetic storage technology. Another potentially significant property of spin is its long relaxation time, i.e., once established it tends to stay in this state for a long time, unlike charge states, which are easily destroyed by scattering or collision with defects, impurities or other charges. These characteristics open the possibility of developing devices that could be much smaller, consume less electric power and be more effective for certain types of computations than it is possible with electron-charge-based systems. That will lead to a new generation of electronic devices based on the flow of spin in addition to the flow of charge. However, the semiconductors currently used in integrated circuits, transistors and lasers, such as Si, Ge, and GaAs, are non-magnetic, in which the carrier energy is almost independent of the spin direction. In contrast, in magnetic semiconductors, which have both properties of magnetic materials and semiconductors, these exchange interactions can give rise to pronounced spin-related phenomena. Recently the injection of polarized spins into lightemitting diode structures and the electric-field control of ferromagnetic ordering have been achieved [Ohn99, Ohn00]. This resulted in the emergence of a new field in electronics semiconductor spin electronics (or semiconductor spintronics) - involving the use of spin states inside semiconductor materials [Das01, Ohn02]. Thus, all these events require search, growth and investigations of magnetic semiconductors with properties suitable for spintronics.

The ternary spinel-type compounds CdCr₂Se₄, CdCr₂Se₄, HgCr₂Se₄, and CuCr₂Se₄ with Cr as transition metal form a special group of magnetic semiconductors. These materials are ferromagnetic with Curie temperatures between 84.5 K and 430 K. They were extensively studied several decades ago due to a number of peculiar and intriguing properties like giant magnetoresistance, photoferromagnetic effect, red shift of the optical absorption edge, giant Faraday rotation and others (apart from the coexistence of semiconducting and ferromagnetic properties). Moreover, these materials can be doped in a defined manner to achieve various properties using, e.g., Ag, In, Ga and Br dopants and, thereby, fulfill the basic requirements of a semiconductor material for technical applications. Nevertheless, later interest to these compounds languished because of the difficulties in crystal growth and the inability to incorporate them with established semiconductor device materials. And only recently the epitaxial growth of CdCr₂Se₄ films on both GaAs and GaP substrates has successfully been carried out, thereby providing an unprecedented opportunity to tune and optimize spindependent behavior in semiconductor device heterostructures [Par02]. However, in spite of the rich set of experimental data mainly obtained by conventional macroscopic methods, the knowledge about the ferromagnetic spinels is by far not complete. For instance, the site occupation of the most important dopants Ag and In, which are responsible for p- and n-type conductivity, respectively, as well as for the changes of the Curie temperature, have remained rather ambiguous up to now. To get a deeper insight into some open questions, in this thesis the following problems have been investigated:

- lattice site occupation of doping atoms
- extent and annealing behavior of implantation damage
- role of lattice defects like cation or anion vacancies
- thermal behavior of doping atoms
- implantation induced disordered structures
- experimental hyperfine fields as test quantities for modern *ab initio* calculations.

Hyperfine interactions are a powerful tool for the characterization of different atomic sites in a given sample that can help to answer these questions. Hyperfine parameters describe the interaction of a nucleus with electric and magnetic fields created by the environment of the corresponding atom. By hyperfine interactions of the probe nuclei it is possible to obtain information on the site occupation and the behavior of the corresponding atoms in the substances investigated on an atomic scale. Many experimental techniques such as Mössbauer effect spectroscopy, nuclear magnetic resonance, and perturbed angular correlations (PAC) spectroscopy can access hyperfine parameters in fundamentally different ways. In this work, the perturbed angular correlations technique was employed. An essential advantage of the PAC method is the small number $(10^{10}-10^{12})$ of probe nuclei required to study a sample. A distinguishing feature of this thesis is the use of various implanted radioactive probes ^{111m}Cd(¹¹¹Cd), ¹¹¹In(¹¹¹Cd), ¹¹¹Ag(¹¹¹Cd), ⁷⁷Br(⁷⁷Se), ¹¹⁷Cd(¹¹⁷In), ^{199m}Hg(¹⁹⁹Hg), and ¹⁰⁰Pd(¹⁰⁰Rh) that allowed the thorough and versatile examination of the substances under study. Nearly all of the probes mentioned (except for ¹¹¹In(¹¹¹Cd)) were used for the first time for the investigations of ferromagnetic spinels. The ion implantations were mostly carried out at the on-line separator and implanter ISOLDE at CERN in Geneva, which provides a large variety of radioactive isotopes including short-lived ones (e.g., ^{111m}Cd and ^{199m}Hg) with high isotopic purity. It is worth noting that most of the probes used in this thesis represent either essential doping elements or constituents of the ferromagnetic spinels.

Today powerful methods for the calculation of hyperfine fields in solids are available. In this work the WIEN97 program [Bla99], based on the Linearized Augmented Plane Wave method (LAPW), was employed. The LAPW method proved to be one of the most accurate schemes to determine the electronic structure in ordered solids. The charge and spin density distributions are calculated self-consistently from first principles within density functional theory. From the charge and spin densities the hyperfine interaction parameters, namely, electric field gradients and magnetic hyperfine fields, can be determined, respectively. Thus the measured hyperfine interaction parameters obtain an additional importance as test quantities for *ab initio* calculations especially if a unit cell is as large as that of the spinel structure (56 atoms). The subject of special interest is the theoretical treatment of the so-called "impurity-case", where the probe atom represents an impurity in the host lattice. In general, impurities introduce structural atomic relaxations in the host lattice and modify the electronic structure of the system that makes an adequate theoretical description very difficult. In such a case a considerably enlarged cell (supercell) has to be calculated, taking into account possible relaxations of at least the nearest environment of the impurity atom. Such kind of calculations was practically impossible, say, ten years ago due to the large number of atoms that have to be considered along with the required high accuracy of the charge distribution close to the nucleus as well as due to limited computer performance. In this work, however, the impuritycase calculations have successfully been carried out on a cluster of PCs in excellent agreement with experiment.

1 Ferromagnetic spinels

1.1 Crystal structure

The class of normal spinels can be represented by the general formula unit $A^{2+}B_2^{3+}C_4^{2-}$. The spinel structure named for the mineral spinel MgAl₂O₄ is face-centered cubic (fcc) with a large unit cell containing eight formula units [Lan70]. It can be described as a cubic close-packed array of anions with the cations located in interstitial positions in this array. Two types of interstices are available, one formed by four anions at the vertices of a tetrahedron and the other by six anions at the vertices of an octahedron. These interstices are commonly called the tetrahedral or A-sites and the octahedral or B-sites, respectively.

The space group of the spinel structure is $Fd\bar{3}m$ with the number 227 in the International Tables for Crystallography [Hah96]. It should be noted that for this space group two notations of Wyckoff positions exist: origin choice 1 and origin choice 2 (see Table 1.1). The latter has the origin at the center of symmetry and is more appropriate for *ab initio* calculations. Therefore throughout this work the origin choice 2 has been used.

Multiplicity, Wyckoff letter, Site symmetry			Coor	rdinates		
			Origin choice 1			
8 A	а	$\overline{4}3m$	(0, 0, 0) (3/4 , 1/4 , 3/4)			
16 B	d	3m	(5/8, 5/8, 5/8) (3/8, 7/8, 1/8)	(7/8 , 1/8 , 3/8) (1/8 , 3/8 , 7/8)		
32 C	e	3 <i>m</i>	$\begin{array}{ll} (x, x, x) \\ (-x, -x + 1/2, x + 1/2) \\ (-x + 1/2, -x + 1/2, -x) \\ (x + 1/2, -x, -x + 1/2) \end{array} \qquad \begin{array}{ll} (x + 3/4, x + 1/4, -x + 3/4) \\ (-x + 1/4, -x + 1/4, -x + 1/4) \\ (x + 1/4, -x + 3/4, x + 3/4) \\ (-x + 3/4, x + 3/4, x + 1/4) \end{array}$			
			Origin choice 2			
8 A	а	$\overline{4}3m$	(1/8, 1/8, 1/8) (7/8, 3/8, 3/8)			
16 B	d	3m	(1/2, 1/2, 1/2) (1/4, 3/4, 0) (3/4, 0, 1/4) (0, 1/4, 3/4)			
32 C	е	3 <i>m</i>	$\begin{array}{c c} (x, x, x) & (x + 3/4, x + 1/4, -x + 1/2) \\ (-x + 3/4, -x + 1/4, x + 1/2), -x + 3/4) & (x + 3/4, -x + 1/2), (-x, -x, -x) \\ (x + 1/2, -x + 3/4, -x + 1/4) & (x + 1/2, -x + 3/4), (-x + 1/2) \end{array}$			

Table 1.1. Wyckoff positions for the space group $Fd\overline{3}m$ (No. 227). The whole unit cell of 56 atoms can be obtained by translations using the following vectors (0, 0, 0); (0, 1/2, 1/2); (1/2, 0, 1/2); (1/2, 1/2, 0) [Hah96].

The conventional unit cell contains 56 atoms: 8 A-atoms, 16 B-atoms and 32 C-anions. The corresponding point symmetries are $\overline{4}3m$ for the A-sites, $\overline{3}m$ for the B-sites and 3m for the C-sites, respectively. For the electric quadrupole interaction (see section 2.2.2) the point



Fig 1.1: Crystal structure of normal spinels: a) the conventional unit cell of 56 atoms; b) schematic representation of two octants of the unit cell showing the tetrahedral and octahedral environments.

symmetry of the atom positions is essential. Atoms at A-sites have a cubic environment. They possess four threefold axes that results in a vanishing electric field gradient. Atoms at B- and C-sites have only one threefold axis, which leads to axially symmetric electric field gradients. A complete picture of the spinel cell with 56 atoms and a schematic representation of two octants of the unit cell are shown in Fig. 1.1. However, the essential symmetry of the structure is simpler to distinguish with only part of the spinel cell along the body diagonal <111> (Fig. 1.2). The small cubes of the dimension a/4 illustrate the tetrahedral coordination of the A-atoms (centers of selected cubes) and the octahedral coordination of the B-atoms (corners of some cubes). Each anion connects an A-cation with three B-cations.

The positions of the cations are fixed by the symmetry of the structure, but the anion positions are variable and are specified by the internal anion parameter u. The value u = 1/4 (or 3/8 in the case of the origin choice 1) corresponds to perfect close-packing of the anions with an exact fcc arrangement. But for real substances u > 1/4 and the anions are shifted



Fig 1.2: Part of the spinel unit cell near the body diagonal <111> showing the essential symmetry properties of the structure. The A- and B-atoms with framing exhibit the tetrahedral (triangle) and octahedral (square) coordination of the anions. In the case of u >1/4 the anions are shifted along the body diagonals of the small cubes (arrows).

along the body diagonals away from the A-cations. Thereby the tetrahedrons get enlarged while maintaining their overall $\overline{4}3m$ point symmetry, whereas the octahedrons become distorted and assume $\overline{3}m$ (rather than m3m) symmetry.

One distinguishes two possible distributions of the cations among the available sites. If the tetrahedral sites are occupied by divalent ions and the octahedral sites by trivalent ions, the structure is *normal*. If the tetrahedral sites are occupied by trivalent ions and the octahedral sites by a random arrangement of divalent and trivalent ions, the structure is *inverse*. Intermediate arrangements are also possible and the general form of the structural formula may be represented as $(A_{1-x}B_x)[A_xB_{2-x}]C_4$, where x is the degree of inversion, equal to zero and unity for the normal and inverse structure, respectively. In this work only spinels with the normal structure are considered.

Spinel substances have rather complicated bonding character. Based on the concept of lattice compression it was found that for Cd(Cu) containing compounds the covalent anionanion bonds are formed in addition to the ionic cation-anion bonds [Miy80]. X-ray and neutron diffraction data revealed that magnetic cation-anion (B-C) bonds have predominantly an ionic character in contrast to the highly covalent nonmagnetic cation-anion (A-C) bonds [Gog86, Zar86].

1.2 Physical properties

The following overview of general chromium chalcogenide ferromagnetic spinels and their properties is mainly based on that carried out in [Nik99].

1.2.1 Crystal growth

Chromium chalcogenide ferromagnetic spinels (FMS) were first synthesized by Passerini *et al.* [Pas31] and later by Hahn and Schroeder [Hah52]. But ferromagnetic ordering in FMS was discovered only later [Lot65, Bal65, Men66] and this resulted in more active research studies. The investigations of FMS required single crystals of acceptable size (1-2 mm), high purity and perfection, and controlled doping. However, at an early stage of experiments polycrystalline samples prepared by solid state reaction processes [Pin68, Tre72] have been used, since the growth of the corresponding monocrystals is complicated. All known FMS have been found to decompose below the melting point [Ple78], therefore the basic methods for growing single crystals have been limited to the following [Phi71]:

- flux growth
- closed-tube vapor transport
- liquid transport
- vapor-liquid transport
- open-tube vapor transport (intended for the growth of thin single-crystalline films)



Fig 1.3: Single crystals of the ferromagnetic spinels investigated in this work. All single crystals were grown by the closed–tube vapor transport.

The single crystals of FMS used in this work have been grown by the closed-tube vapor transport (see Fig. 1.3), which proved to be a successful method for growing high quality crystals¹. In order to carry out the optimal growth, knowledge of the thermodynamic parameters for the basic transport reactions is required. Lack of these parameters led to the necessity of empirical studies of transport kinetics. That is why different halogen or chloride carriers at various concentrations, different temperatures gradients and ampoule dimensions have been tried by a number of authors with different results [Phi71]. The most effective transport agents were found to be CrCl₃ (for CdCr₂Se₄, CdCr₂S4 and HgCr₂Se₄) and I₂ (for CuCr₂Se₄). Vapor transport turned out to be also suitable for growing single crystals of solid solutions or with special doping materials such as Ag, Au, Cu, In, Ga or Br [Min71, Pro74, Oka74, Rad80].

In [Tre72, Ple78] it was shown that no incorporation of excess chalcogen into a crystal lattice of FMS is possible, whereas nonstoichiometric anion vacancies are easily formed. In contrast to oxide spinels it was found [Tre72] that such significant deviations from stoichiometry in FMS are not accompanied by a change of the lattice parameters. Experimental data from [Buz86] revealed that the maximum chalcogen deficiency in CdCr₂Se₄ can be reduced by a factor of three by doping with Ag or In.

¹ The monocrystals of FMS used in this work were grown at the Academy of Sciences of Moldova by Dr. V. Tezlevan from the group of Prof. I.M. Tiginyanu and Dr. V.V. Tsurkan.

Paramatar		Dof			
	CdCr ₂ Se ₄	CdCr ₂ S ₄	HgCr ₂ Se ₄	CuCr ₂ Se ₄	Nel.
Crystallochemical parameters					
Lattice constant Å	10.75	10.244	10.753	10.334	[Lan70]
Lattice constant, A	10.748(1)	10.244(1)	10.742(1)	10.337(1)	this work ²
Anion parameter	0.265	0.265	0.265	0.25756	[Lan70]
Density, g/cm ³	5.675	4.243	6.670	5.818	[Lan70]
Decomposition temperature, °C					
in vacuum	564	528	300	532	[Wad71]
	650 542	680	- 240	- 700	[Gri75]
in air	542 560	800 650	540 _	/00	[wad/1] [Gri75]
Magnetic parameters	200				[011,0]
Ferromagnetic Curie temperature, K	129	84.5	106	430	[Lan70]
Paramagnetic Curie temperature, K	204	152	200	465	[Lan70]
Magnetization at 4.2K, T	0.4490	0.4986	0.4458	_	[Nik99]
Optical parameters					
Absorption edge, eV					
at 300 K	1.32	1.57	0.80	-	DU1-001
at 4.2 K	1.12	1.80	0.27	_	[[N]K99]
Index of refraction	3.17	2.84	3.36	_	[Lee71]
Electrical parameters	-				
Conductivity type	semicond.	semicond.	semicond.	metallic	[Lan70]
Resistivity, Ω·cm					
at 300 K	10 ²	10 ³	0.7	$2 \cdot 10^{-4}$	[L on 70]
at 4.2 K	10 ⁵	10 ⁶	10 ²	_	[Lan/0]

Table 1.2. Some general properties of the FMS under consideration.

In Table 1.2 some general crystallochemical, magnetic, optical and electrical properties for the FMS under study are collected.

1.2.2 Magnetic properties

First physical studies of FMS revealed the coexistence of ferromagnetic ordering and semiconductor properties [Bal65, Men66]. Analysis of the ferromagnetic state in these compounds [Bal66] showed that due to the large distances between Cr ions a negative exchange caused by direct overlapping of Cr d orbitals is negligible. As a result, the 90° superexchange interaction between nearest neighbor Cr ions via the chalcogen anions is predominant.

The possibility of changing the valency of some Cr ions by doping or deviation from stoichiometry is the main characteristic feature of FMS [Miy80, Nik81]. The ferromagnetic

² The X-ray measurements were kindly carried out by Dipl.-Phys. G. Schreiber (TU Bergakademie Freiberg, Institut für Metallkunde).

resonance (FMR) studies in FMS revealed that the anisotropy of the resonance field and resonance linewidth depend on the type of doping or thermal treatment conditions [Ber67, Bai77, Nik82]. Gurevich *et al.* [Gur74] indicated that CdCr₂Se₄ doped with Ag gives rise to a magnetic anisotropy, which is negative and associated with the appearance of tetravalent Cr ions. Vacuum annealing at 650°C/50h created Se vacancies, which resulted in a repeated change in sign of the magnetic anisotropy for the same CdCr₂Se₄:Ag crystals caused by Cr transformation from the tetravalent to the divalent state (Fig. 1.4). Nuclear magnetic resonance studies of CdCr₂Se₄ carried out in [Abe86, Pro92] confirmed that doping by Cu, Ag or In results in a change of the valency states of the Cr ions.



Fig 1.4: Angular dependencies of resonance field and FMR linewidth for $CdCr_2Se_4$ doped by 1.5 at. % Ag before (1) and after (2) annealing in vacuum at 650°C/50h [Bai77].

As a result of the superexchange interaction via nonmagnetic ions the ferromagnetic Curie temperature of the FMS was found to depend on the type and concentration of the doping. Minematsu *et al.* [Min71] and Vinogradova *et al.* [Vin76] showed that the doping of CdCr₂Se₄ and HgCr₂Se₄ with In or Ga diminishes the Curie point, whereas the doping with Ag has the opposite effect (Fig. 1.5 a, b). Miyatani *et al.* [Miy71] found a dramatic decrease of the Curie temperature (from 430 to 130K) by bromine substitution in CuCr₂Se₄ (Fig. 1.5 c).

The most interesting and principally new properties of the FMS are specified by interactions between electron and spin systems. Veselago *et al.* [Ves72, Ves90] found that in



Fig 1.5: Ferromagnetic Curie temperature versus doping contents of: (a) Ag and Ga in CdCr₂Se₄ [Vin76]; (b) Ag and In in HgCr₂Se₄ [Min71]; (c) Br in CuCr₂Se₄ [Miy71].

 $CdCr_2Se_4$ illumination causes the change of magnetic permeability, coercive force and magnetization. Such an effect strongly depends on the level of doping by Ga (or In) and was found to be maximal at about 0.1 at. % Ga.

1.2.3 Optical properties

The most widely recognized influence of magnetic ordering on the electron system in the FMS is the so-called red shift of the optical absorption edge with a reduction in temperature (Fig. 1.6). The total effect of magnetic ordering on the energy band gap was estimated to be 0.27 eV for CdCr₂Se₄ and 0.66 eV for HgCr₂Se₄ [Har66, Leh70, Ara73, Kun76]. The application of an external magnetic field at the Curie temperature shifts the absorption edge to lower energy as well (e.g., about 10% for HgCr₂Se₄ at 0.7 T) [Ara73]. In contrast to other FMS in this context CdCr₂S₄ is remarkably different and exhibits a blue shift of the absorption edge, which is typical for nonmagnetic semiconductors [Kun76]. It was suggested that the red shift in the FMS is caused by s-d exchange splitting of the conduction band, whereas in $CdCr_2S_4$ the internal *d*-*d* transitions between Cr levels (or narrow bands) lie at lower energy and are responsible for the usual blue shift [Met68].



Fig. 1.6: Optical absorption edge versus temperature for the general FMS compounds [Har66, Leh70, Ara73, Kun76].

Magnetooptical properties of the FMS have intensively been studied as well [Bon68, Mos71, Lee71]. For instance, for CdCr₂S₄ in the ferromagnetic state the Faraday rotation was found equal to 10^4 deg/cm near the absorption edge and 10^5 deg/cm at higher energy (corresponding to Cr *d*-*d* transitions) [Mos71].

1.2.4 Electrical characteristics

Studies of the influence of nonstoichiometry and doping on the electrical properties of the FMS revealed that the electrical behavior of *n*- and *p*-type materials are strikingly different. The *p*-type specimens have electro- and magnetoresistance typical for nonmagnetic semiconductors. In contrast, the *n*-type specimens are characterized by anomalies in the electro- and magneto-resistance. Lehmann [Leh67] demonstrated that the conductivity of CdCr₂Se₄ doped with In increases by a factor of 10^4 with decreasing temperature from 150 to 77 K (Fig. 1.7). In the system CuCr₂Se_{4-x}Br_x electrical resistivity clearly revealed the change in magnitude going from metallic to semiconductor-type as bromine substitution increased [Miy71].

Another interesting feature found in the FMS is the negative magnetoresistance. For instance, the transverse magnetoresistance of $CdCr_2Se_4$ [Leh67] as a function of magnetic



Fig. 1.7: (a) Electrical conductivity of three different samples of $CdCr_2Se_4$ as a function of reciprocal temperature [Leh67]; (b) electrical resistivity for the system $CuCr_2Se_{4-x}Br_x$ versus composition [Miy71].

field at different temperatures with different doping is shown in Fig. 1.8. For *p*-type samples at the highest temperature measured (166 K) $\Delta \rho / \rho_0$ is positive and proportional to H^2 , whereas at lower temperatures no simple relationship between $\Delta \rho / \rho_0$ and *H* can be observed. At sufficiently low temperatures the magnetoresistance becomes negative and shows saturation. The magnetoresistance of the *n*-type samples, in contrast, is always negative and has a maximum at T_C. For CdCr₂S₄:In crystals Nikiforov *et al.* [Nik78] also observed that an external magnetic field of 0.5 T reduces electroresistivity near the Curie temperature by a factor of 100. Such anomalies were found to depend on the nature and concentration of the donor doping as well as on the thermal treatment conditions [Rad78].



Fig. 1.8: Transverse magnetoresistance $\Delta \rho / \rho_0$ of CdCr₂Se₄: (a) 1 % Ag as a function of magnetic field at different temperatures; (b) 1 % In as a function of magnetic field at different temperatures [Leh67].

1.3 Applications

Summarizing the reviewed experimental data, one can state that FMS are without doubt very promising materials for microelectronics. As a result of the unique properties found in these compounds, diverse practical applications were proposed, some of which are discussed below:

- $CdCr_2Se_4$ based photo-detectors, which convert the input (light emission amplitude) to a proportional change of the output signal frequency. Its transformation coefficient has a value of $10^{10}-10^{12}$ Hz/W at 20-50 K for an emission wavelength of 1150 nm [Vin83].
- HgCr₂Se₄ based infra-red-emission modulators with a modulation level, which is linearly dependent on the applied magnetic field. A 30 % modulation is achieved at B = 0.4 T [Los89].
- Cd(Hg)Cr₂Se₄ based Schottky-barrier diodes. For an Au-*n*-HgCr₂Se₄ structure the magnetic-field-dependent capacitance was found to increase by 7 12 % at B = 1.25 T [Kog80], whereas for an Ag-CdCr₂Se₄ structure the capacitance increases even by 20 % at 98 K and B = 0.6 T [Rad78]. For Pt-*n*-CdCr₂Se₄ the photo-induced voltage reached 0.35 V at 77 K with a light intensity of 50 mW/cm². The sign of the voltage depends on the direction (side) of the illumination [Tsu87].
- magnetic-field-dependent laser diodes based on CdCr₂Se₄ [Rad78]. An applied external magnetic filed of 0.8 T changes the wavelength of the laser emission from 0.947 to 0.954 μ m at 130 K.
- FMS are promising candidates for magnetooptic memory, acoustic devices, ultrahigh frequency devices, devices for detection and modulation of electromagnetic emission, devices in magnetooptics based on the Faraday and Kerr effects, etc [Rad78].
- in [Osi98] the injection of polarized charge carries in FMS-semiconductor heterostructures *n*-HgCr₂Se₄-*n*-InSb and *p*-HgCr₂Se₄-*n*-InSb was observed that provides new opportunities for building various millimeter and submillimeter highly sensitive narrow-band devices (like generators, receivers, photodetectors, transducers of frequency, etc.) tunable by magnetic field.

Moreover, ferromagnetic semiconductors give rise to the construction of devices based on quite new principles. Whereas in the conventional semiconductor electronics the essential mechanism is the manipulation of electronic charge, an intriguing alternative is the transport of spins in the corresponding process. The combination of both transport mechanisms can result in new electronic devices with various technical applications. Such a new field of electronics is referred to as *spintronics* [Das01, Ohn02]. Recently an essential step in the development of spintronics has been done by several groups, which have realized the injection of polarized spins from layers of ferromagnetic semiconductors used as a spin aligner (Be_xMn_yZn_{1-x-y}Se [Fle99] and Ga_{1-x}Mn_xAs [Ohn99] with T_C \leq 100 K) into *p-n* junctions. In this context it is worth noting a turning-point for the FMS based on the

successful epitaxial growth of *n*-type CdCr₂Se₄ (001) films on both GaAs and GaP (001) substrates [Par02] that provides an excellent opportunity to tune and optimize spin-dependent behavior in semiconductor device heterostructures. One of the most attractive properties of the FMS is the potential to obtain them either *n*- or *p*-type by aimed doping. In addition, ferromagnetic order is stabilized even in non-doped materials. This is in marked contrast to the A^{III}-Mn-B^V ferromagnetic materials, which are *p*-type only, since Mn acts as both the magnetically active element and an acceptor in the A^{III}B^V host, and a high hole density is critical in stabilizing of the ferromagnetic ordering. Therefore in this system it is not possible to control the ferromagnetic ordering and carrier type (or concentration) independently.

That is why FMS have a good chance to be the next candidates for applications in the promising fields of spintronics, since their magnetic, optical and electrical properties can be adjusted in a wide range by doping.

2 Theoretical basis and experimental requisites for PAC

2.1 Introduction

Among the numerous experimental techniques available to study solids, techniques focused on hyperfine interactions (HI) form a subclass that probes a material at the smallest possible length scale. Perturbed Angular Correlations (PAC) spectroscopy, NMR (Nuclear Magnetic Resonance), ME (Mössbauer Effect) spectroscopy, Perturbed Angular Distribution (PAD) and Nuclear Orientation (NO) belong to the same family of nuclear hyperfine techniques. They are based on the observation of the electric and magnetic nyperfine interaction between the nuclear moments of specific probe nuclei and the magnetic or electric fields induced by the surroundings of the probes (valence electrons, conduction electrons, neighbor atoms or ions, neighboring defects). The high sensitivity combined with only a small number of required probe atoms make them ideal tools for studying structural, electronic and dynamical properties of host atoms, single impurities, and impurity-defect complexes on an atomic scale. Among the hyperfine interaction techniques mentioned above the PAC spectroscopy is especially outstanding due to various advantages such as [Ler87a]:

- 1. The amount of the material under study can be small (normally 1-100mg).
- 2. The sensitivity of the method is temperature independent (no Debye-Waller-Factor as in ME, no Boltzmann-Factor as in NMR).
- 3. Insensitivity with respect to mechanical vibrations (in contrast to ME).
- 4. In principle, no magnetic field and no high frequency is required as in NMR.
- 5. Normally, weak nuclear quadrupole interactions can be better resolved than in ME.
- 6. The amount of radioactive nuclei, which is needed, is orders of magnitude lower than for conventional ME and NMR (an absolute amount of 10^{10} - 10^{12} PAC probes is sufficient).
- 7. PAC-probes can serve as a valuable complement of available isotopes in the other HI techniques.

2.2 Hyperfine interactions

The hyperfine structure originates from the fact that a nucleus is not point-like. The simplest non-trivial example is the description of the charge density within the nucleus as a deformed sphere (prolate or oblate), which is characterized by the nuclear quadrupole moment Q. In addition, the nucleus possesses a nuclear magnetic dipole moment μ . The interaction of these moments with the electromagnetic fields in a solid produced by electrons and nuclei in the vicinity of the nucleus is called a hyperfine interaction. Besides, external fields, for instance an externally applied magnetic field, may also be present. A hyperfine structure has the nuclear energy levels on a scale of some neV. Detection of hyperfine interactions is the goal of the PAC spectroscopy used in this work.

2.2.1 Magnetic dipole interaction

The nuclear magnetic dipole moment $\mu = \gamma \hbar I$, where $\gamma = g \mu_N / \hbar (\mu_N - \text{nuclear magneton};$ g - g-factor) is the gyromagnetic ratio and *I* is the nuclear spin operator, interacts with the magnetic flux density at the position of the nucleus, called the magnetic hyperfine field B_{hf} . The interaction energy is [Sch96]

$$E_{magn} = - \boldsymbol{\mu} \cdot \boldsymbol{B}_{hf} \tag{2.1}$$

This extra energy lifts the degeneracy of the nuclear M states producing the energetically equidistant Zeeman splitting (see Fig. 2.1) and induces a precession of the nuclear spin. Choosing the z-axis parallel to B_{hf} , one obtains

$$E_{magn} = -\gamma B_z^{hf} \hbar M , \qquad \qquad M = -I, \dots, +I \qquad (2.2)$$

The energy difference between adjacent M levels is

$$E_{magn}(M+1) - E_{magn}(M) = -\gamma \hbar B_z^{hf} = -g \mu_N B_z^{hf} = \hbar \omega_L$$
(2.3)

where ω_L is the Larmor frequency given by

$$\omega_L = -\gamma B_z^{hf} = -\frac{g\mu_N B_z^{hy}}{\hbar}$$
(2.4)

The internal magnetic field B_{hf} can be separated in the following way [Sch96]

- $\boldsymbol{B}_{hf} = \boldsymbol{B}_{ext} + \boldsymbol{B}_{dem} + \boldsymbol{B}_{L} + \boldsymbol{B}_{dip} + \boldsymbol{B}_{orb} + \boldsymbol{B}_{Fermi}$ (2.5)
- B_{ext} is the external magnetic field (in this work $|B_{ext}| = 0.5(1)$ T, see section 2.6).
- B_{dem} is the demagnetization field due to the magnetic poles on the surface. It depends on the form of the sample. For instance, for a sphere

$$\boldsymbol{B}_{dem}(sphere) = -\frac{1}{3}\mu_0 \boldsymbol{M}$$
(2.6)

where M is the macroscopic magnetization of the sample. In this work nearly all samples (except CuCr₂Se₄) had a regular octahedron shape (see Fig. 1.3), which can be considered in a good approximation as a sphere.

• B_L is the Lorentz field - the field at the center of a hypothetical spherical hole (Lorentz sphere). It has the value

$$\boldsymbol{B}_{L} = \frac{1}{3} \boldsymbol{\mu}_{0} \boldsymbol{M}_{s} \tag{2.7}$$

where M_s is the saturation magnetization. M_s can be determined in a macroscopic measurement. In the case of a spherical sample and with an external polarizing field large enough to reach the saturation magnetization the sum $B_{dem} + B_L = 0$.

- B_{dip} is the field due to individual dipoles within the Lorentz sphere. The dipolar term is zero at sites with cubic symmetry (like at the A-site in the spinel structure).
- B_{orb} is the orbital contribution originating from orbital motion of electrons around the nucleus (the Biot-Savart law). However, normally this contribution is very small and can be neglected.



Fig. 2.1: (a) Pure magnetic splitting and (b) electric quadrupole splitting by an axially symmetric efg ($\eta = 0$) of a nuclear level with spin I = 5/2.

• B_{Fermi} is called the Fermi contact field which describes a nucleus embedded in a homogeneous magnetic medium due to the net *s*-electron spin density at the nucleus (in a relativistic approach also *p*-electrons can penetrate the nucleus). In the ferromagnetic materials the main contribution to the internal magnetic field at a nucleus is given by the Fermi contact field.

Thus, taking into account the factors mentioned above Eq. (2.5) reduces to

$$\boldsymbol{B}_{hf}^{eff} = \boldsymbol{B}_{ext} + \boldsymbol{B}_{Fermi}$$
(2.8)

2.2.2 Electric quadrupole interaction

The electric hyperfine interaction is a purely electrostatic effect and stems from the fact that the nucleus is not point-like. For an extended but completely spherical nucleus this difference results in a shift in energy, whose magnitude depends on the overlap of the nuclear and electronic charges [Kar95]. Thus isotopes of the same element with different charge radii show a shift in their spectral lines relative to each other. This is known as the isotope shift.

Nuclei with spin $I \ge 1$ also have a quadrupole moment Q, which describes their deviation from sphericity. If such a nucleus is placed in an inhomogeneous electric field, its electrostatic energy will depend on the orientation of the nuclear spin I with respect to the symmetry axis of the electric field. This will lead to another splitting of the energy levels. In a solid a nucleus is surrounded by electrical charges which produce a potential $V(\mathbf{r})$. Classically, the interaction energy of a nuclear charge distribution $\rho(\mathbf{r})$ in an external potential $V(\mathbf{r})$ is given by [Sch96]

$$E_{electr} = \int \rho(\mathbf{r}) V(\mathbf{r}) d^3 r \tag{2.9}$$

where

$$\int \rho(\mathbf{r}) d^3 r = Ze \tag{2.10}$$

is the total nuclear charge. The electric potential can be expanded in a Taylor series around r = 0. After some mathematical transformations (e.g., see [Sch96]) one can extract the term of the electric quadrupole interaction

$$E_{Q} = \frac{e}{6} \sum_{\alpha} V_{\alpha\alpha} Q_{\alpha\alpha}$$
(2.11)

where

$$Q_{\alpha\alpha} = \frac{1}{e} \int \rho(\mathbf{r}) (3x_{\alpha}^2 - r^2) d^3r \qquad (2.12)$$

For $x_{\alpha} = z$ expression (2.12) is equal to the classical definition of the quadrupole moment of the nucleus.

 $V_{\alpha\alpha}$ is called the electric field gradient (efg). The efg is a traceless tensor, which is specified by the components V_{xx} , V_{yy} and V_{zz} . The efg depends on the symmetry of the electron charge distribution near the nucleus and is equal to zero only if the symmetry around the nucleus is high (spherical or cubic). Due to $\sum V_{\alpha\alpha} = 0$ the efg is completely described by two parameters. By appropriate choice of the principal axis system, one can have $|V_{zz}| \ge |V_{yy}| \ge |V_{xx}|$. Generally one chooses to describe the efg by V_{zz} , the largest of the three principal components, and the asymmetry parameter η

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad (0 \le \eta \le 1)$$
(2.13)

which expresses the deviation of the tensor from the axially symmetric case $V_{xx} = V_{yy}$.

Thus the electric field gradient tensor interacts with the tensor of the electric quadrupole moment Q, whereby the nuclear spin I points along the symmetry axis of the quadrupole moment. Analogous to the magnetic interaction, a reorientation of the electric quadrupole moment inside the electric field gradient leads to a spin precession about the field axis. In the quantum-mechanical representation the quantity E_Q for the case of axially symmetric electric filed gradients ($V_{xx} = V_{yy}$ or $\eta = 0$) is given by [Sch96]

$$E_{Q} = \frac{3M^{2} - I(I+1)}{4I(2I-1)} eQV_{zz}$$
(2.14)

A comparison with the magnetic interaction reveals two differences: the degeneracy of the *M*-states is only lifted with regard to |M| and the energy splitting ΔE is not equidistant (Fig. 2.1). This means that the energy splitting and also the number of observable spin precession frequencies ω - being usually more than one - depend on the particular spin value *I*. The transition energy between two sublevels *M* and *M'* is

$$E_{Q}(M) - E_{Q}(M') = \frac{3eQV_{zz}}{4I(2I-1)} |M^{2} - M'^{2}|$$
(2.15)

Thereby the smallest observable spin precession frequency is

$$\omega_0 = \frac{3eQV_{zz}}{4I(2I-1)\hbar} \text{ (for integer nuclear spin)}$$
(2.16)

$$\omega_0 = \frac{6eQV_{zz}}{4I(2I-1)\hbar} \text{ (for half-integer nuclear spin)}$$
(2.17)

and the other observable frequencies are integer multiples of ω_0 . The strength of the electric quadrupole interaction is defined by the spin independent product, called the nuclear quadrupole coupling constant

$$v_{Q} = \frac{eQV_{zz}}{h}$$
(2.18)

In Fig. 2.1 the quadrupole splitting of an I = 5/2 state is shown. The transition frequencies ω_1 , ω_2 , and $\omega_3 = \omega_1 + \omega_2$ are given by $\omega_1 = \omega_0$, $\omega_2 = 2\omega_0$, and $\omega_3 = 3\omega_0$. In this case the quadrupole coupling constant is

$$v_{\mathcal{Q}} = \frac{10}{3\pi}\omega_0 \tag{2.19}$$

The calculation of the electric field gradient in a solid is difficult, since one has to calculate the contributions to the efg from neighboring ionic cores, electrons of the probe core, valence and conduction electrons. Such a problem requires very accurate band-structure calculations. Self-consistent molecular cluster calculation, in which the solid is approximated by a small atomic cluster (up to 30 atoms), is an alternative approach (e.g., [Lin86]). In the past one often could do no better than use a phenomenological model. In this model [Ste54, Bar64] the efg is assumed to be a sum of two parts: one from the neighboring ion cores (lattice) and one from the electrons

$$V_{zz} = (1 - \gamma_{\infty}) V_{zz}^{lattice} + (1 - R) V_{zz}^{el}$$
(2.20)

Amplification factors $(1-\gamma_{\infty})$ and (1-R) are supposed for the lattice and electronic contribution, respectively. Thus the efg at a nucleus in a solid is a quantity, which depends not only on the geometrical arrangements of the surrounding atoms (considering a point charge model), but also on the amplification of the "point charge efg" by electric-field-induced distortions of the inner shells of the probe atom. This type of amplification was first calculated by Sternheimer [Ste50], therefore the factor γ_{∞} is called the Sternheimer antishielding factor. The index ∞ means that the efg sources are completely outside the probe atomic shell that, of course, is not rigorously valid. Commonly one obtains γ_{∞} values of the order of 10 to 100 [Gus95], which increase with the mass of the atom. The amplification is very large and therefore it determines the magnitude of the efg.

A special case is the situation when impurity probe atoms enter the host lattice substitutionally, and the point symmetry at such sites is the same as that for the host atoms. The efg at the nuclei of impurity atoms depends on the local electronic structure around these centers as well as on the symmetry and distances to the charged ion cores in the host crystal. The efg in this case cannot straightforwardly be predicted from the parameters determined in a usual band-structure calculation for the host lattice, since such a calculation would require a detailed knowledge of the wave-functions in the vicinity of the impurity atom. In such a situation a theoretical approach based on a simulation of the "impurity + nearest host atoms" by a sufficiently large supercell (so-called "impurity-case") should be considered. Formerly such calculations were too time-consuming. Therefore an intermediate treatment was used: first *ab initio* calculations of the host structure were carried out and then the results were estimated with the help of the Sternheimer corrections [e.g., Die00, Die01]. Thus, if the efg at

the host atom A is known from the calculations then the efg at the impurity atom B, which substitutes the atom A in the lattice, can be estimated using the ratio

$$V_{zz}^{B} = \frac{\left(1 - \gamma_{\infty}^{B}\right)}{\left(1 - \gamma_{\infty}^{A}\right)} V_{zz}^{A}$$

$$(2.21)$$

It is obvious that this approach is also not always appropriate. However, nowadays with development of the Density Functional Theory methods and computer technique the impurity-case calculations even with 56 atoms in the supercell have become feasible (see section 4.6).

2.3 Perturbed γ-γ Angular Correlations method

Perturbed γ - γ angular correlations method has been established in the past three decades as a powerful tool for the microscopic investigation of solid state properties. It was originally developed and applied to the determination of magnetic dipole and electric quadrupole moments of excited nuclear states, a domain of nuclear physics. The possibility to obtain information about internal magnetic fields or electric field gradients, which interact via a hyperfine interaction with the nuclear moments, opened up the field to solid state physics. Today, the precise determination of these electromagnetic fields in the local environment of radioactive probes constitutes the main application of this nuclear method [Wic86].

2.3.1 Principles

The basic idea of γ - γ angular correlation stems from the fact that the probability of photon emission from a radioactive nucleus depends, in general, on the angle between the nuclear spin axis and the direction of emission. Normally, the radiation from a radioactive sample is isotropic, because all spins are randomly oriented in space. An anisotropic radiation pattern can only be observed from an ensemble of nuclei, whose spins are not randomly oriented. In the case of the angular correlation technique, an effective spin alignment can be established by picking out only those nuclei, whose spins happen to lie in a preferred



Fig. 2.2: Schematic representation of a γ - γ cascade with initial spin I_i, intermediate spin I, and final spin I_f.

direction. In a successive emission of two γ -quanta (see Fig. 2.2) the observation of the first one determines the preferred spin direction and thereby selects an ensemble of aligned nuclear spins, so that the correlated second γ -quantum of the cascade displays an anisotropic radiation pattern. In general, such an angular correlation is described by [Sch96]

$$W(\theta) = \sum_{k \text{ even}}^{k_{\text{max}}} A_{kk} P_k(\cos \theta)$$
(2.22)

Here θ denotes the angle between the emission directions of γ_1 and γ_2 ; *k* is a summation index that has the values $0 \le k \le$ minimum of (2*I*, 2*L*₁, 2*L*₂), where *I* is the spin of the intermediate



Fig. 2.3: Principles of the PAC-method. (a) In a semi-classical picture the hyperfine interactions can be described as a precession of the nuclear spins. The atomic nuclei behave like small multipole antennas with anisotropic emission characteristics of γ -quanta. The precession of the nuclear spin rotates the angular correlation function $W(\theta)$. (b) The time-dependent coincidence count rate between γ_1 and γ_2 is registered by two arrangements of detectors (180°/90°). (c) By combination of these two spectra one can calculate the PAC-spectrum, which reflects pure modulation. (d) The following Fourier transformation reproduces the frequency spectrum. From these frequencies electric field gradients as well as internal magnetic fields can be determined.

nuclear state and $L_{1,2}$ are the multipolarities of the transitions. The angular correlation coefficients A_{kk} describe the deviation of the coincidence probability from the isotropic case $W(\theta) = 1$. Their values can be positive, negative or zero, and are governed by the spin sequence and the multipolarities of the γ -radiations. The Legendre polynomials $P_k(\cos\theta)$ reflect the spatial angular distribution of the involved γ -rays. Since the transition probabilities between nuclear states decrease with increasing angular momentum of the emitted ray, one usually deals with L = 1 or 2, so that k_{max} does not become larger than 4.

In a semi-classical picture the hyperfine interaction between the nuclear moments of the probe nuclei and magnetic fields or electric field gradients results in a precession of the probe atoms' nuclear spins about the field direction. The precession frequency ω is proportional to the strength of the field at the site of the nucleus. In the PAC-technique the change of the spin orientation with time is directly observable by detecting two γ -rays in coincidence, which are

emitted during the decay of the unstable probe atom. The conservation of angular momentum connects the orientation of the nuclear spin with the angular distribution of the emitted γ -rays, i.e. with the probability to detect γ -rays along a certain space direction. The precession of the nuclear spins results in a rotation of the anisotropic radiation pattern as well. In this case the γ - γ angular correlation function becomes time-dependent or *perturbed* $W(\theta) \rightarrow W(\theta, t)$. Therefore, the successive detection of a γ - γ cascade allows a direct observation of the change in spin orientation during the time interval between the emission of the γ -rays. The change of the spin orientation within that time interval reflects the spin precession frequency. Thus, whenever a radioactive probe atom decays, information about the field strength at its lattice site is delivered to the experimentalist via this frequency ω . In Fig. 2.3 the principle of the PAC-method is sketched. One registers the time dependent coincidence count rate between γ_1 and γ_2 , which is modulated, by two arrangements of detectors normally in 180° and 90°geometry. By combination of these two spectra the PAC-spectrum, which reflects pure modulation, can be calculated. The following Fourier transformation reproduces the frequency spectrum. From these frequencies electric field gradients as well as internal magnetic fields can be determined. The information obtained in that way is microscopic and local in its nature, since the field strength decreases rapidly with increasing distance from the probe atom. Therefore, contributions originating from the nearest shells of surrounding lattice atoms are mainly observed. This holds especially for the case of the electric field gradient.

The general theory of angular correlations is mathematically quite complex. For instance, the rigorous form for the time-dependent γ - γ angular correlation function is [Sch96]

$$W(\mathbf{k}_{1},\mathbf{k}_{2},t) = \sum_{k_{1},k_{2},N_{1},N_{2}} A_{k_{1}}(1)A_{k_{2}}(2)G_{k_{1},k_{2}}^{N_{1},N_{2}}(t)\frac{1}{\sqrt{(2k_{1}+1)(2k_{2}+1)}}Y_{k_{1}}^{N_{1}*}(\theta_{1},\phi_{1})Y_{k_{2}}^{N_{2}}(\theta_{2},\phi_{2})$$
(2.23)

where \mathbf{k}_1 and \mathbf{k}_2 are the emission directions of γ_1 and γ_2 , A_{k_i} are coefficients, $Y_{k_i}^{N_i}(\theta_i, \phi_i)$ are spherical harmonics with θ_i and ϕ_i denoting the polar and azimuthal angles of the vector \mathbf{k}_i . The perturbation factor $G_{k_1,k_2}^{N_1,N_2}(t)$ contains full information on the nature, intensity and direction of the hyperfine interactions. Thus the determination of $G_{k_1,k_2}^{N_1,N_2}(t)$ is the essence of the PAC-method. For practical applications and understanding it is useful to derive analytic expressions for some common cases.

2.3.2 Magnetic dipole interaction

1. Transverse geometry. In the transverse geometry [But89a], the external magnetic field is applied perpendicular to the detector plane in the $180^{\circ}/90^{\circ}$ arrangement (see Fig. 2.4, a), i.e. $\theta_{l} = \theta_{2} = 90^{\circ}$ and $\theta = \phi_{2} - \phi_{l}$. In this case one obtains for the angular correlation function with $k_{max} = 2$

$$W(\theta,t) = 1 + A_{22}P_2[\cos\left(\theta - \omega_L t\right)]$$
(2.24)

where $A_{22} \equiv A_2(1) A_2(2)$ and ω_L is the Larmor frequency.



Fig. 2.4: Detector arrangements for measurement of the magnetic hyperfine interaction: (a) transverse geometry; (b) Raghavan's geometry, (c) sign-sensitive geometry; (d) zero-field geometry.

If one forms the ratio

$$R(t) = \frac{W(180^{\circ}, t) - W(90^{\circ}, t)}{W(180^{\circ}, t) + W(90^{\circ}, t)} = \frac{3 \cdot A_{22} \cdot \cos 2\omega_L t}{4 + A_{22}}$$
(2.25)

a time modulation with twice the Larmor precession frequency is obtained. The sign of the Larmor frequency ω_L cannot be measured in this geometry because of the even cosine function.

2. Raghavan's geometry. Raghavan *et al.* [Rag71] was the first who found that it is possible to observe the Larmor frequency rather than twice the Larmor frequency by a suitable orientation of the external magnetic field. The field should be in the detector plane and make an angle of 45° or 135° with the two detectors (see Fig. 2.4, b). In this case one obtains

$$R(t) = \frac{W(180^\circ, t) - W(90^\circ, t)}{W(180^\circ, t) + W(90^\circ, t)} \approx \frac{3}{4} A_{22} \cos \omega_L t$$
(2.26)

Normally the transverse geometry is more in use for practical reasons. But if the Larmor frequency is very large then the limited time resolution of PAC-apparatus can impede the measurement of $2\omega_L$. Therefore in this case the Raghavan's geometry is more appropriate.

3. Sign-sensitive geometry. The sign of the internal magnetic field can be determined in the transverse geometry by placing the detectors $+135^{\circ}/-135^{\circ}$ apart (see Fig. 2.4, c). In this case one obtains the ratio

$$R(t) = \frac{W(135^\circ, t) - W(-135^\circ, t)}{W(135^\circ, t) + W(-135^\circ, t)} = -\frac{3 \cdot A_{22} \cdot \sin 2\omega_L t}{4 + A_{22}}$$
(2.27)

which depends on the sign of ω_L .

4. Zero-field geometry. In this case the 180°/90°-geometry is used, but no external polarizing magnetic field is applied [Wic86], i.e. the internal magnetic fields are randomly oriented so that the perturbed angular correlation function becomes

$$W(\theta,t) = \sum_{k \text{ even}}^{k_{max}} A_{kk} G_{kk}(t) P_k(\cos \theta)$$
(2.28)

with a simplified form of the perturbation factor

$$G_{kk}(t) = \frac{1}{2k+1} \sum_{N=-k}^{+k} \cos(N\omega_L t)$$
(2.29)

In this case the R(t) ratio with $k_{max} = 2$ is given by

$$R(t) = \frac{W(180^{\circ}, t) - W(90^{\circ}, t)}{\frac{1}{2}W(180^{\circ}, t) + W(90^{\circ}, t)} = A_{22}G_{22}(t) = A_{22}\frac{1}{5}(1 + 2\cos\omega_{L}t + 2\cos2\omega_{L}t)$$
(2.30)

where averaging over all field directions leads to the occurrence of ω_L and $2\omega_L$.

2.3.3 Electric quadrupole interaction

For a pure electric hyperfine interaction, which is axially symmetric, the perturbation factor $G_{k,k_2}^{NN}(t)$ can be rewritten as [Sch96]

$$G_{k_1k_2}^{NN}(t) = \sum_n s_{nN}^{k_1k_2} \cos(\omega_n t)$$
(2.31)

where the number of frequencies in the sum depends on the nuclear spin *I*. The weight factors $s_{nN}^{k_1k_2}$ depend on the angles (θ, ϕ) chosen by the detectors with respect to the crystal axis as well as on the direction of the principal axis (V_{zz} component) of the efg tensor at the site of the probe atom. In the case of the polycrystalline sample (statistical distribution of efg orientations) the angular correlation function becomes

$$W(\theta, t) = \sum_{\substack{k \text{ even}}}^{k_{\text{max}}} A_{kk} G_{kk}(t) P_k(\cos \theta)$$
(2.32)

where

$$G_{kk}(t) = \sum_{n=0}^{n_{\text{max}}} s_{kn} \cos(\omega_n t)$$
(2.33)

For $k_{max} = 2$ and I = 5/2 the angular correlation function is given by

$$W(\theta, t) = 1 + A_{22}G_{22}(t)P_2(\cos\theta)$$
(2.34)

with the perturbation factor

$$G_{22}(t) = s_{20} + \sum_{n=1}^{3} s_{2n} \cos(\omega_n t)$$
(2.35)

Thus in this case each efg is characterized by three frequencies ($\omega_1 + \omega_2 = \omega_3$) with the ratio 1:2:3. In a single crystal the coefficients s_{2n} depend on the orientation of the efg tensor with respect to the detector directions. By forming the ratio R(t) one obtains

$$R(t) = \frac{W(180^\circ, t) - W(90^\circ, t)}{\frac{1}{2}W(180^\circ, t) + W(90^\circ, t)} = A_{22}G_{22}(t)$$
(2.36)

2.3.4 Combined magnetic and electric interaction

In magnetically ordered materials with non-cubic symmetry for the probe atom both electric and magnetic hyperfine interactions contribute to the nuclear level splitting. If one interaction is dominant, the other one may be treated as a perturbation: for instance, a weak magnetic splitting of the terms $\pm M$ in the quadrupole doublets considered in Fig. 2.1 (b). If they are of the same order of magnitude, a complete quantum-mechanical treatment with diagonalization of the interaction Hamiltonian is necessary. The splittings will be functions of the magnetic parameter B_{hf} and the electric parameters V_{zz} and η . Often this leads to complicated PAC-spectra. The shape of the spectra depends on the angle between the local



Fig. 2.5: Frequencies contained in PAC spectra for an I = 5/2 nucleus with a combined magnetic and electric interaction consisting of a symmetric efg and a magnetic hyperfine filed (a) coaxial with and (b) perpendicular to the symmetry axis of the efg. The abscissa axis shows the ratio of the Larmor frequency ω_L to the quadrupole frequency $\omega_0 = 6\omega_E$ over the range from zero to one. To cover all possible values of this ratio, it is continued by curves for ω_0/ω_L from one to zero [Kar95].

magnetic and electric fields as well as on the detector angles chosen for the observation. Here only the special case with coaxial magnetic and electric fields is considered, since the coaxial case is the simplest combined interaction. The eigenvalues of the coaxial hyperfine Hamiltonian are then (for $\eta = 0$) [Kar95]

$$E_{M} = \hbar \omega_{E} \left[3M^{2} - I(I+1) \right] + \hbar \omega_{L} M$$
(2.37)

where

$$\omega_E = \frac{eQV_{zz}}{4I(2I-1)\hbar} \tag{2.38}$$

For I = 5/2 the energy eigenvalues are split as shown in Fig. 2.5 (a). The following eight frequencies can then appear in the PAC spectrum (considering that in this case $\omega_0 = 6\omega_E$):

 $3\omega_0 \pm 2\omega_L \quad 2\omega_0 \pm \omega_L \quad \omega_0 \pm \omega_L \quad \omega_0 \pm 2\omega_L \quad (\text{for } \omega_0 \ge \omega_L)$ (2.39)

or

 $2\omega_L \pm 3\omega_0 \quad 2\omega_L \pm \omega_0 \quad \omega_L \pm 2\omega_0 \quad \omega_L \pm \omega_0 \quad (\text{for } \omega_L \ge \omega_0) \tag{2.40}$

from which it is clearly seen how a magnetic field perturbs the pure electric fields frequencies, and vice versa. The intensities of the frequency components depend on the detector geometry chosen. In Fig. 2.5 (b) the splitting in the case of perpendicular magnetic and electric fields is also presented for comparison. It is obvious that the PAC spectra in this case would be essentially different. In particular, for weak efg ($\omega_L \gg \omega_0$) the lines in the Fourier spectrum are split much less than in the coaxial case so that it is practically impossible to distinguish them from the frequency distribution caused by deviations of the internal magnetic field.

2.3.5 Data reduction

For an observation of spin precession through an angle $\Delta \theta$, the emission of γ_2 has to be delayed by a time $\Delta t = \Delta \theta / \omega$ with respect to γ_1 . Therefore, the intermediate nuclear state of the probe atom has to exist for some time, which is characterized by the mean lifetime τ_N . The larger τ_N ("exploration time") the more oscillations are observable and, hence, the better the frequency resolution. It should be noted that in an experiment one deals with an ensemble of statistically decaying nuclei, that is why the decay of a large number of probe atoms has to be detected in order to establish the spin precession frequency. The differential coincidence count rate at time *t*, where *t* is the elapsed time between the emission of γ_1 and γ_2 , is given by

$$N_{ij}(\theta, t) = N_{ij}^0 \cdot e^{-\frac{t}{\tau_N}} \cdot W(\theta, t) + B$$
(2.41)

where *B* is the time-independent background (random coincidence count rate); $W(\theta, t)$ represents the time-dependent angular correlation; θ is the angle between the two detectors. A PAC measurement is normally performed using four detectors simultaneously recording up to 12 coincidence spectra $N(\theta, t)$, which correspond to the different detector combinations enclosing the angle θ (normally 180° and 90°). After correcting these spectra for accidental coincidences, one can form the following ratio

$$R(t) = \frac{N(180^\circ, t) - N(90^\circ, t)}{N(180^\circ, t) + N(90^\circ, t)} = \frac{y - 1}{y + 1}$$
(for magnetic interaction) (2.42)

and

$$R(t) = \frac{N(180^\circ, t) - N(90^\circ, t)}{\frac{1}{2}N(180^\circ, t) + N(90^\circ, t)} = \frac{2y - 2}{y + 2}$$
(for quadrupole interaction) (2.43)

where

$$y = \frac{N(180^{\circ}, t)}{N(90^{\circ}, t)} = \frac{\left(N_{13}N_{31}N_{24}N_{42}\right)^{1/4}}{\left(N_{12}N_{21}N_{23}N_{32}N_{34}N_{43}N_{14}N_{41}\right)^{1/8}}$$
(2.44)

By forming the ratio R(t) the exponential decay factors cancel and the detector efficiencies are eliminated to first order. In order to extract information from R(t) a least-squares procedure is used for fitting the theoretical perturbation function to the experimental data. In this work the programs UNCPAC [Hof93] and DEPACK [Lin96] have been utilized.

2.3.6 Information obtained from PAC experiments

1. Site occupation.

The R(t)-function is characteristic for a specific environment "felt" by the probe nucleus. If two or more distinct environments are present, the measured R(t) is a sum of the R(t)functions due to each environment. The distinct sites can be inequivalent lattice positions: a substitutional or/and an interstitial position. Unraveling a measured R(t)-spectrum into the partial R(t)-functions, from which it is built, and assigning these to a specific position in the sample makes it possible to track their occupation by probe atoms. This enables a study of the probe behavior (substitution and migration) as a function of temperature and thermal treatments. The lattice site of an impurity atom, particularly in semiconductors, determines its electrical, optical and magnetic properties as well as its interaction with other impurities or defects. Thus the determination of the lattice site after doping and annealing is of utmost importance.

Moreover, radioactive isotopes are not only employed to identify the lattice sites of impurity atoms, but some of them can also be used for a well-defined, site-selective doping of the crystal lattice, thereby the efficiency of the doping process can substantially be increased. This approach is based on the fact that by implanting radioactive host atoms or isovalent impurity atoms into the semiconductor the radioactive isotopes are localized on regular, substitutional lattice sites. After the radioactive decay the daughter isotopes are forced to occupy selectively only one lattice site, provided that the recoil energies involved in the radioactive decay are low enough to prevent lattice site changes. Transmutation doping is mainly applied to semiconductors, and the P doping of Si, in reactors exploiting the thermal neutron capture reaction ³⁰Si (n, γ) ³¹Si and the subsequent β^- decay of ³¹Si \rightarrow ³¹P, represents the best known example of the industrial application of this doping technique [New82].

2. Distributions.

The measured R(t)-function sometimes shows a damped amplitude. The reason is that the hyperfine fields and hence the frequencies forming R(t) are not an infinitely sharp determined quantity. If some perturbations of the environments are present (e.g., lattice defects, vacancies, impurities, etc.), they will show up as a damping of R(t) described mainly by lorentzian or gaussian distributions of the frequencies in its Fourier spectrum. Thus, determination of the parameters of distribution can give additional information about "purity" of the probe environment on an atomic scale.

3. Implantation damage.

With the exception of diffusion all other doping techniques like nuclear activation, recoil-, off-line or on-line implantation involve the formation of radiation-induced lattice damage. The extent of radiation damage is indicated by a distribution of the measured hyperfine frequencies. In the case of amorphized probe environments this frequency distribution is very broad. The radiation damage can be annealed by a thermal treatment. Typically, investigations in this context are focused on the nature of the induced radiation defects, their interaction with other defects or impurity atoms, their diffusion mechanisms and their annealing behavior.

4. Theoretical understanding of hyperfine fields.

A very important problem, when using any nuclear technique, is to relate a measured hyperfine field (which is a very local quantity) to particular chemical and physical properties of the neighborhood of the probe nucleus and even of the material as a whole. Thus, since the hyperfine fields are very sensitive to electronic structure, PAC experiments provide a possibility to test *ab initio* electronic theories. For a long time this question has been dealt with in a rather crude, phenomenological way. It took until the early nineties when *ab initio* methods with quantitative predicting power were developed within the framework of Density Functional Theory (DFT). By using the full potential felt by the electrons and solving the resulting Kohn-Sham equation by, e.g., the Linearized Augmented Plane Wave (LAPW) method, the tails of the electron wave functions near the nucleus can be calculated with a sufficient accuracy to obtain the hyperfine fields. The method has been implemented in the computer code WIEN97, which is discussed in Chapter 4.

2.4 PAC probes

The choice of a radioactive atom for a specific experiment is determined on the one hand by its chemical nature and on the other hand by its nuclear properties. A source nuclide must satisfy several requirements, which are seldom fulfilled simultaneously:

- easy available;
- high intensity populating and depopulating the intermediate level;
- a non-zero anisotropy in the angular correlation of the γ rays involved;
- energies of the γ rays should be of a few hundred keV and energetically well separated to allow effective detection;

- the isomeric quadrupole moment and the magnetic dipole moment should be large enough for electric field gradient and magnetic investigations, respectively;
- a lifetime of the intermediate level of 10-1000 ns is the most favorable.

But the most important feature is dictated by the half-life of the employed parent isotope [For99]:

- *Half-lives of the order of days* are often preferred since they permit laboratory experiments, where one sample can be systematically studied as a function of different parameters such as the annealing conditions, measuring temperature or external pressure. In the case of PAC spectroscopy the number of suitable, long-lived probe atoms is rather limited, but their application is widespread. The most commonly used isotope is ¹¹¹In(¹¹¹Cd) (T_{1/2} = 2.81 d).
- *Half-lives of the order of hours* require a reactor, an accelerator or an on-line mass separator to provide probe atoms during the experiment on a regular basis with a repetition rate of a few hours. The possibilities for sample treatments are limited and normally only one measurement can be taken per sample. Typical example of the short-lived isotopes of this kind is ^{111m}Cd ($T_{1/2} = 49$ min).
- *Half-lives of less than 10 min* require so-called on-line experiments. The experimental setup of PAC is directly connected either to an accelerator or an on-line mass separator. Probe atoms of short half-life are repetitively implanted into the samples. The options for subsequent sample treatment using these short-lived isotopes are very limited. In this work such kind of the radioactive isotopes has not been used.

All the relevant parameters for the probes used in this thesis are given in Table 2.1.

Table 2.1. Properties of the PAC-isotopes used in this work. The following quantities are listed: mother-
daughter isotope with decay type, $T_{1/2-mother}$ – half-life of the mother isotope, E – energy of the intermediate level,
$I-spin \ of \ the \ intermediate \ level, \ Q-quadrupole \ moment, \ \mu-magnetic$
moment, $E_{\gamma 1}$ and $E_{\gamma 2}$ – cascade energies, A_{22} – maximal experimental anisotropy. Taken from [Fir96] except
¹⁾ [Ler87b, But96], ²⁾ [Haa93], ³⁾ [Moh88].

Probe	T _{1/2} mother	E [keV]	I	T _{1/2} [ns]	Q [b]	μ [μ _N]	Ε _{γ1} [keV]	Ε _{γ2} [keV]	A ₂₂ [%]
111 Ag (111 Cd) [β^{-}]	7.45 d				1)		95.5		-13
^{111m} Cd(¹¹¹ Cd) [IT]	49 m	245	5/2+	85.0(7)	+0.83(13)	-0.7656(25)	150	245	+16
¹¹¹ In(¹¹¹ Cd) [EC]	2.81 d						171		-18.0(2)
¹¹⁷ Cd(¹¹⁷ In) [β ⁻]	2.49 h	660	3/2+	53.6(7)	(-)0.59(1)	+0.938(10)	89	345	-36
^{199m} Hg(¹⁹⁹ Hg) [IT]	42.6 m	158.4	5/2-	2.45(2)	+0.95(7)	+0.88(3)	374.1	158.4	+18.4(6)
⁷⁷ Br(⁷⁷ Se) [EC]	57.0 h	250	5/2-	9.68(6)	0.76(5) ²⁾	+1.12(2)	755	250	-45 3)
¹⁰⁰ Pd(¹⁰⁰ Rh) [EC]	3.63 d	75	2+	214	0.076(20)	+4.324(8)	84	75	+16

2.5 Doping procedures

The radioactive isotopes for the measurements are produced at reactors or accelerators. Some combinations of probe atoms and host lattices allow one to dope the samples directly via nuclear reactions inside the material. Typical examples are the doping of cadmium compounds with ¹¹¹In via the ¹¹⁰Cd(d, n)¹¹¹In and ¹¹¹Cd(d, 2n)¹¹¹In reactions (e.g., at the Research Center Rossendorf). However, research in nuclear solid state physics demands a much larger variety of possible combinations of probe atoms and host lattices. Long-lived isotopes like the commercially available ¹¹¹In are produced at cyclotrons and radio-chemically separated from the target material. Then these isotopes can be either diffused or implanted via an off-line separator into the material under study. Doping by diffusion is sometimes hampered by the surface barrier of the material or by small diffusion coefficients.

In contrast, the implantation technique is more versatile: the radioactive atoms can be implanted into any host lattice. Off-line implanters dedicated to this application are available, e.g., at the universities of Göttingen and Bonn and the maximum implantation energies are 400 and 160 keV, respectively. For obvious reasons both diffusion and off-line implantation are restricted to radioactive atoms with half-lives of the order of days or longer.

Another doping possibility is based on recoil implantation at the heavy ion accelerator (e.g., HMI ISL-Berlin [Sie98]). A heavy ion beam strikes a thin target and induces nuclear reactions. The reaction products are knocked out of the target with recoil energies up to several MeV and implanted into the host material (catcher foil). Due to the high recoil energy the implantation range is of the order of some μ m. This doping technique also permits the use of short-lived isotopes and enables a rather large variation in the combinations of probe atoms and host lattices. However, the catcher samples may be contaminated by atoms from the target material or by products from competing nuclear reactions. Secondly, the production rate of the probe atoms is not very high and thus the beam time necessary for these types of experiments is rather long.

The most versatile tool, however, is represented by an on-line isotope separator facility such as ISOLDE (Isotope Separator On-Line DEvice) at CERN in Geneva. Here the production, the chemical separation, the mass separation and the implantation of radioactive isotopes are integrated into one device, whereas off-line separators only cover mass separation and implantation. At ISOLDE the radioactive ions are produced by spallation, fragmentation or fission reactions in thick solid or liquid targets hit by an external high-energy proton beam, which is nowadays delivered by CERN's PS Booster. The pulsed proton beam of 1.0 GeV energy and a mean intensity corresponding to about 2 μ A DC beam is delivered to one of the two ISOLDE target stations: the General Purpose Separator (GPS) or the High Resolution Separator (HRS). Depending on the radioactive isotope, that has to be produced, the target material may consist of metal foils (e.g. tantalum), liquid metals (e.g. lanthanum), oxides like calcium oxide or carbides like uranium carbide. The target is kept at a temperature between 700 and 2000 °C permitting the rapid diffusion of reaction products into the ion source. This

can be either a surface, plasma or laser ionization source, where a further chemical separation of elements is performed. After ionization the ion beams are accelerated to 60 keV energy and mass-separated by the GPS or HRS separator. The mass resolution $m/\Delta m$ is 2000 for the GPS and potentially 30000 for the HRS. The intensities of the separated ISOLDE beams as they are sent into the ISOLDE beam line system and thus to the experiments are up to 10^{11} ions/s and are most often higher than produced with any other technique at any other facility. The implantation energy of 60 keV results in a projected range for the isotopes of several tenths of nanometers below the surface. Up to 600 different isotopes of 70 elements can be produced by about 60 different combinations of target material and ion sources, providing a wide range of short-lived isotopes in almost all regions of the nuclide chart. The wide range of isotopes, the isotopically clean ion beams and the high beam intensities have made ISOLDE the most important facility for solid state physics with radioactive isotopes. Numerous combinations of probe atoms and host lattices are possible, because the isotopes are implanted into the samples within a few seconds after their production. A more detailed description of the ISOLDE separators can be found in [Kug00].

In this work as doping procedure the ion implantation was used exclusively. All radioactive probes except ¹¹¹In were obtained at the ISOLDE implanter. The implantation parameters and conditions (e.g., implantation intensities, dose, time, etc.) can be found in [Die98a]. For measurements with ¹¹¹In the implantation possibilities at the Research Center Rossendorf and at the University of Bonn were utilized.

2.6 Experimental apparatus

The essence of a PAC experiment is the recording of the coincidence count rate as a function of time between the emission of γ_1 and γ_2 at fixed detector angles. This is usually carried out by so-called *fast-slow* coincidence electronics. Two signals are derived from each detector. The anode signal is transformed to a standardized timing pulse by a constant fraction discriminator. The role of the fast coincidence part is to establish the time relationship between the two photons: γ_1 provides the start signal of a time-to-amplitude converter (TAC), while γ_2 gives the stop signal. Thus the output of the TAC is a measure of the time elapsed between the two events.

The slow coincidence unit selects via single channel analyzers the detector dynode signals arising from the detection of the photons of energy $E_{\gamma 1}$ on the start side and of energy $E_{\gamma 2}$ on the stop side. The energy-coincident signal triggers a gate that allows the TAC output to enter a multichannel analyzer ADCAM (Analog to Digital Converter And Memory), where the height of an analog signal from the TAC is converted into a digital value and stored. An event is accepted only when the selected energy criteria and the appropriate time requirement are met simultaneously. Thus by this fast-slow principle, energy selection (whether γ_1 or γ_2) and time measurement are performed separately. A simplified schematic diagram of the apparatus used in Freiberg is represented in Fig. 2.6.



Fig. 2.6: Simplified scheme of the PAC-apparatus used in Freiberg illustrating the fast-slow principle.

Usually, one uses four detectors in $180^{\circ}/90^{\circ}$ -geometry. Each detector can be used as both a start and stop detector. These combinations lead to a total of 12 possible coincidence spectra. However, an arrangement with 6 detectors is also possible that results in 30 detector combinations (6 combinations with $\theta = 180^{\circ}$ and 24 combinations with $\theta = 90^{\circ}$) [But89b].

In general, PAC spectrometers should fulfil the following requirements [But96]:

- proper choice of the detectors for the γ-quanta involved. High detection efficiency is imperative, because one deals with *coincidence* measurements rather than with single counts;
- large solid angles per detector progressively wipe out the angular part of the perturbation function. Hence, multi-detector arrangements are preferable;
- the energy resolution of the detectors should be sufficiently good to distinguish between γ_1 and γ_2 and possibly between other decay-quanta not associated with the cascade of interest;
- the time resolution should also be as good as possible, preferably better than 1 ns.

All experiments in this work were carried out using the following PAC-apparatus:

- two four-detector PAC-setups (with four start-stop detector combinations) in Freiberg, where one is supplied with NaI-detectors (good energy resolution ~ 9%) and the other is with BaF₂-detectors (good time resolution ≤ 1ns). The detailed schemes of the setups with time calibrations, parameters for adjustments of electronics and other information can be found in [Die98a].
- two four-detector PAC-setups (with 12 start-stop detector combinations) with BaF₂-detectors at ISOLDE from the group of Dr. M. Deicher, University of Konstanz.
- in several cases a six-detector PAC-apparatus (30 start-stop detector combinations) with conically shaped BaF₂-detectors at ISOLDE from the group of Prof. T. Butz, University of Leipzig, was utilized.

In this work the measurements were carried out below and above room temperature (RT). For the measurements above RT up to 1200 K a special furnace was used [Die98a]. However, for the investigation of magnetic semiconductors measurements below Curie temperatures are very essential as well. Measurements at 77K could be carried out using special Dewar vessels filled with liquid nitrogen. At ISOLDE also a cryostat with a closed cycle working principle is available, where temperatures down to 10 K can be realized. It has a special cooling head with low attenuation for the γ -radiation of the sample, which is positioned in the center of a four detector arrangement.

The FMS are soft ferromagnets and magnetic saturation is possible with relatively low external magnetic fields (0.3 - 0.5 T). Therefore, for the measurements in the ferromagnetic state magnetically polarized samples were used. This considerably simplifies the interpretation of the measured spectra and it is just necessary if one intends to carry out sign-sensitive measurements with 135°-geometry (see section 3.3). It is obvious that in this case the polarizing magnets must be small and magnetically well shielded. Thus for such purposes special well-shielded pot magnets, which contain two cylindrical pieces of FeNdB permanent magnets, with magnetic field of 0.5(1) T for measurements at 77 K were constructed (see Fig. 2.7). Additionally the mini pot magnets for measurements in the close-cycle cryostat even at 10 K have been designed and tested. The magnet covers are made from low-carbon iron, so that the whole magnetic field remains inside. The sample is positioned in the center between the two permanent magnets.



Fig. 2.7: Pot magnets for external magnetic polarization: (a) for measurements at 77 K in special Dewar vessels; (b) cylindrical pieces of FeNdB permanent magnets showing their dimension in comparison with a 1 Pfennig coin; (c) mini pot magnet for measurements in the close-cycle cryostat. The magnet covers are made from low-carbon iron, so that the whole magnetic field remains inside. The sample is positioned in the center between the two permanent magnets.
3 Results and discussion

3.1 Implantation defects in ferromagnetic spinels

Nowadays, ion implantation is a primary technology, which is used in the semiconductor industry to introduce impurities into semiconductors in order to form various devices and VLSI (Very Large Scale Integration) circuits. All VLSI manufacturing includes ion implantation steps. The technology has universal acceptance because of the accuracy of the number of implanted atoms, and the uniformity of the implantation across large semiconductor wafers [Zie92].

However, particle penetration in matter leads to the loss of their energy within the target, and thus results in the creation of radiation damages. Such defect structures around the implanted atoms are not yet well understood as compared with periodic crystal structures. The PAC method has a large advantage, since it can examine the environment of the implanted probes *in situ* directly after implantation. Therefore, it is interesting to study the extent of the short-range order in defect areas around implanted atoms and its behavior after different thermal treatments.

Implantation defects lead to broad distributions of the interaction frequencies measured with hyperfine interaction methods. In the case of the quadrupole interaction these distributions are caused by different electric field gradients (efg) V_{zz} and anisotropy parameters η . At first sight, it seems that there is no connection between the symmetry of the undisturbed lattice and the formation character of the damaged zones. In order to check this statement a structure with different types of lattice symmetry (e.g., cubic and non-cubic) should be taken. The spinel structure is especially suitable for such investigations, since it has a site with cubic environment with vanishing efg (A-site) and sites with non-cubic symmetry, namely, with axially symmetric efg (B, C-sites).

In Fig. 3.1 (a, c) the as-implanted measurements of the magnetic spinel semiconductors $CdCr_2Se_4$ with ^{111m}Cd and $CdCr_2S_4$ with ¹¹¹In(¹¹¹Cd) are shown. ^{111m}Cd probes are substituted at the cubic A-site and ¹¹¹In probes mostly at the B-site with axially symmetric efg (see section 3.2.3). In both cases the as-implanted spectra indicate that probes are situated in heavily damaged regions without any defined quadrupole interaction. However, the Fourier spectra show that for the cubic A-site the frequency distribution has a maximum at very small frequencies, whereas at the B-site with pronounced non-cubic symmetry the frequency distribution has its maximum at higher frequencies, which correspond to the quadrupole interaction of the undisturbed lattice. The measurements with not completely annealed samples (Fig. 3.1 b, d) confirm the tendency of development for the A- and B-site environments. These investigations point out that the environments of the implanted probes cannot be described by a statistical arrangement of atoms, but the bonds of atoms create some preferred arrangements. Therefore, one can conclude that the frequency distribution of the



Fig 3.1: PAC spectra R(t) and their Fourier transforms $F(\omega)$ showing the character of the implantation damage for the sites with different symmetry: ^{111m}Cd implanted in CdCr₂Se₄ (a) as-implanted and (b) partly annealed at 200°C / 10 min; ¹¹¹In(¹¹¹Cd) implanted in CdCr₂S₄ (c) as-implanted and (d) partly annealed at 300°C / 20 min. All measurements were carried out at RT in the paramagnetic state.

quadrupole interaction is correlated with the symmetry of the undisturbed lattice and, in addition to vacancies and interstitial defects, the implantation defects express themselves by distributions of the bond lengths and bond angles.

The measurements described above were carried out in the paramagnetic state. However, it would be interesting to examine the same as-implanted samples in the ferromagnetic state, where the magnetic interaction dominates. For such measurements ^{111m}Cd is the most suitable probe because of the following reasons:



Fig. 3.2: PAC spectra R(t) and their Fourier transforms $F(\omega)$ for ^{111m}Cd implanted into CdCr₂Se₄: quadrupole interaction at RT (a) as-implanted and (b) annealed (500°C / 20 min); magnetic interaction at 77K with an external magnetic field perpendicular to the detector plane (c) as-implanted and (d) annealed (500°C / 20 min).

- For many spinel compounds under consideration it is a host atom.
- ^{111m}Cd is unambiguously substituted in all magnetic spinel semiconductors at the A-site with cubic symmetry, where no combined interaction is expected. This considerably facilitates the interpretation of results.
- ^{111m}Cd can be implanted at ISOLDE with high isotopic purity.
- The decay proceeds without additional consequences such as EC (electron capture) that excludes possible undesirable effects like *decay after effect* [Kar95].

In Fig. 3.2 a series of measurements for $CdCr_2Se_4$ is shown. After implantation of ^{111m}Cd probes RT-measurements (above T_C) display only strongly damaged environments around the probes with broad frequency distributions. By a thermal treatment at 500°C/20 min the probe environments can be annealed to a large extent and the typical spectrum for cubic environments, as expected in the paramagnetic state at the A-site, is observed. The remaining defects (slow decay of R(t)) are no more in the direct probe proximity, so-called distant non-correlated defects, e.g., exchanges of A- and B-atoms, vacancies, etc.

Measurements at 77K (below T_C) should clarify how the magnetic interaction manifests itself in the case of implantation defects (Fig. 3.2, c). The samples were magnetically polarized perpendicular to the detector plane by an external magnetic field of 0.5(1) T. Surprisingly, the spectra show directly after the implantation a defined magnetic dipole interaction. Although the defect areas cause a damping of R(t) that is reflected in the Fourier spectrum as a frequency distribution (magnetic field distributions) and the Larmor frequency is somewhat larger than in the case of completely annealed samples, but the spin ordering can clearly be distinguished. After annealing at 500°C/20 min (Fig. 3.2, d) a perfect spin ordering is observed.

Similar experiments were carried out for $CdCr_2S_4$, $HgCr_2Se_4$ and $CuCr_2Se_4$ as well, where the same behavior was detected. This fact suggests that it is not just a random coincidence, but a real effect. Thus, one can conclude that the spin ordering is not influenced to such an extent by implantation defects as the lattice ordering or, in other words, the "efg ordering".

3.2 Site occupation and behavior of radioactive probes

3.2.1 Introduction

The development of semiconductor technique requires the invention and design of new semiconductor devices with unique properties. These new properties can usually be obtained by means of a doping procedure. Therefore, it is of great importance to have knowledge about the site occupation of doping impurities and their behavior. For ferromagnetic spinels (FMS) such doping impurities are In and Ag, which are responsible for n- and p-type conductivity, respectively [Leh67]. By favorable coincidence ¹¹¹In and ¹¹¹Ag are PAC-probes, which do not differ from the stable In and Ag in terms of properties, but allow investigations of their behavior by PAC on an atomic scale. Moreover, ¹¹¹In is considered to be the best PAC-probe that stimulated the interest of this research additionally. Apart from the technological importance to the site occupation there is also interest from the point of view of basic research. The experimental hyperfine fields, especially measured at the impurity site, can serve as test quantities for modern theoretical calculations, since they are very sensitive to the quality of a theoretical charge and spin density distribution, which are the fundamental descriptions of solids.

3.2.2 State of the art

PAC investigations of FMS were started about 20 years ago and a number of experiments was carried out [Unt80, Vai81, Jha87, Rod93]. However, in all former PAC experiments the probe ¹¹¹In(¹¹¹Cd) was used exclusively. Other PAC-probes were hardly or not available at all. It is worth noting that one of the most important factors for these investigations is the quality of the crystals. Since the growing procedure of the FMS monocrystals is not so simple and time consuming (a complete growing cycle takes about two months or more), the samples investigated were powders in most cases that casts doubt on the quality of the materials. One should also take into account that the doping procedures were different and not very appropriate for such experiments:

- Addition of ¹¹¹In during growing the substances [Vai81, Jha87].
- Diffusion of ¹¹¹In into polycrystalline samples [Rod93].
- Recoil implantation of ¹¹¹In following nuclear reactions with Cd-nuclei of single crystalline host materials [Unt80, Unt83, Unt91].

Disadvantages of these procedures are the following: (i) the production of polycrystalline materials with stoichiometric deviations and large defect contents; (ii) the diffusion at relatively high temperatures can change the stoichiometry and the defect chemistry; (iii) in the case of recoil implantation other interfering radioactivity is also produced (especially from Cr and Se nuclei) that is very unfavorable for precise measurements. All these facts led to inconsistent results in terms of the hyperfine fields. The site occupation has also remained as an open question until now.

In contrast, in this work the ion implantation of radioactive probes was used exclusively, thereby the crystallinity and stoichiometry of the crystals were not destroyed. Of course, radiation defects are produced during implantation, but they can be annealed at relatively low temperatures (~ 500°C for 15 min). In addition to popular ¹¹¹In(¹¹¹Cd) probes, also ^{111m}Cd, ¹¹⁷Cd(¹¹⁷In), ¹¹¹Ag(¹¹¹Cd), ^{199m}Hg, ⁷⁷Br(⁷⁷Se) and ¹⁰⁰Pd(¹⁰⁰Rh) were available that allowed thorough investigations and reliable interpretations of the results. Another advantage of the current PAC-investigations is the improvement of the time resolution due to BaF₂-scintillators as compared to the former used NaI-scintillators. This is especially important for measurements of large magnetic hyperfine fields with high Larmor frequencies. In addition, a four-detector arrangement (up to 12 subspectra available) was implemented that resulted in much better statistics. And last but not least, in this work only high quality single crystalline materials were utilized¹.

3.2.3 Measurements with ¹¹¹In(¹¹¹Cd), ^{111m}Cd and ¹¹¹Ag(¹¹¹Cd) probes

In Fig. 3.3 a series of measurements for CdCr₂Se₄ with ¹¹¹In(¹¹¹Cd) probes is presented. The measurement at RT shows a dominating quadrupole interaction after annealing of the implantation damage. However, there is also a part of probes in cubic environment, which is visible by the time independent part of the PAC-spectrum that amounts to 11(3) %. At higher temperature ($T_{meas} = 500^{\circ}$ C) up to 60(7) % probes are positioned at the site with nearly cubic environment with distant defects only (slow decay of R(T)). This process is reversible and the PAC-spectrum measured at RT after the high temperature measurements turned out to be identical with that measured before. This suggests that the ratio between the part of probes with non-cubic and with cubic surroundings can be changed by a thermal treatment of the sample. In order to verify this statement one can try to freeze in the distribution of the probes between two nonequivalent sites by quenching of the sample in H₂O. The result of this procedure is displayed in Fig.3.3 (c), where 40(4)% of ¹¹¹In probes are observed at cubic sites.

The former investigations showed similar results [Unt91]. The experiments at that time were interpreted in the following way. For the site occupation of ¹¹¹In probes the A-site with cubic environment was suggested exclusively. The presence of the axially symmetric efg was explained by a high concentration of defects in the samples caused by radiation damages. As the origin of the defects, anion vacancies, which remain even after annealing and have an attractive interaction with the In impurity atoms at the A-site, were suggested. At elevated temperatures the defects, due to their mobility, leave their sites, thereby the distribution of probes between two nonequivalent sites is changed.

However, the observed axially symmetric efg can also be explained by the occupation of the B-site, where according to the point group symmetry an axially symmetric efg is expected.

¹ The monocrystals of FMS were grown at the Academy of Sciences of Moldova by Dr. V. Tezlevan (from the group of Prof. I.M. Tiginyanu) and Dr. V.V. Tsurkan. The quality of the crystals was independently checked by Dipl.-Phys. G. Schreiber (TU Bergakademie Freiberg, Institut für Metallkunde) using X-ray and microprobe analysis.



Fig. 3.3: PAC spectra R(t) and their Fourier transforms $F(\omega)$ for ¹¹¹In(¹¹¹Cd) probes implanted into CdCr₂Se₄: normal annealing (a) at RT (paramagnetic state, PM) and (b) at 77K (ferromagnetic state, FM); annealing with quench in H₂O (c) at RT (paramagnetic state) and (d) at 77K (ferromagnetic state). All measurements at 77K were carried out with an external magnetic field perpendicular to the detector plane.

Moreover, the experimental value of the efg is in good agreement with the theoretical one calculated at the B-site (see section 4.4). In order to clarify this situation measurements in the ferromagnetic state were carried out, where the magnetic dipole interaction dominates. Two internal magnetic fields corresponding to two nonequivalent positions were found with fractions of 12(3) % and 88(3) %, respectively. A thermal treatment with successive quench increased the fraction of the probes with the lower magnetic field. This magnetic field agrees with NMR measurements for the A-site (10.71 T [Sta69]). The higher magnetic field is by a



Fig. 3.4: Decay scheme for ¹¹¹Ag(¹¹¹Cd), ^{111m}Cd and ¹¹¹In(¹¹¹Cd) showing that these three probes decay via the same excited level of ¹¹¹Cd with $I = 5/2^+$, $T_{1/2} = 85$ ns and Q = 0.83 b.

factor of 2.3 larger. A Se vacancy can not cause such a drastic change of the internal magnetic field. The NMR result for B_{hf} at the Cr-site is also by a factor of 1.4 larger in comparison with that of the Cd-site. Thus, there are more facts in favor of the A- and B-site occupations.

Another approach to determine the site occupation is based on the fact that the three PACprobes ¹¹¹Ag, ^{111m}Cd and ¹¹¹In, which originally have quite different properties (valency, doping character), have the same daughter nucleus ¹¹¹Cd and decay via the same exited level of ¹¹¹Cd (5/2⁺) (see Fig. 3.4). Therefore one can directly compare final experimental results. As discussed in section 3.1, ^{111m}Cd probes occupy only the site with cubic environments and no other fraction with the efg was detected. The same behavior was observed for ¹¹¹Ag probes, i.e., they are mostly substituted at the A-site (Fig. 3.5, a). No influence of the thermal treatment, especially quenching was found. However, because of incomplete annealing in this measurement, the impact of remaining defects is present that is reflected by the decay of R(t). It is interesting that in the corresponding magnetic case only a small damping is observed. The situation here is similar to that in ^{111m}Cd-mesureaments discussed in section 3.1.

In Fig. 3.5 (b-d) the measurements with ¹¹¹Ag, ^{111m}Cd and ¹¹¹In probes at 77K with an external magnetic field perpendicular to the detector plane are presented for comparison. For ^{111m}Cd and ¹¹¹Ag probes only the one site occupation, namely, the A-site and for ¹¹¹In probes the two sites are observed. From the Fourier transformation one can see that for all three spectra the first Larmor frequency $\omega_{L1} = 166$ Mrad/s and the corresponding magnetic field $B_{hf1} = +11.3(1)$ T is exactly the same and agrees well with the NMR result ($B_{hf} = +10.71(2)$ T at 77 K [Sta69]; note that in the PAC-experiments at 77 K B_{ext} of 0.5(1) T was applied that resulted in increase of the measured hyperfine fields by this value). Hence it is an additional proof that the first Larmor frequency indeed corresponds to the magnetic field at the A-site



Fig. 3.5: PAC spectra R(t) and their Fourier transforms $F(\omega)$ for ¹¹¹Ag, ^{111m}Cd, and ¹¹¹In probes implanted into CdCr₂Se₄: (a) ¹¹¹Ag probes, at RT (paramagnetic state); (b) ¹¹¹Ag probes, at 77K (ferromagnetic state); (c) ^{111m}Cd probes, at 77K; (d) ¹¹¹In probes, at 77K. All measurements at 77K were carried out with an external magnetic field perpendicular to the detector plane.

and the second one conforms to the magnetic field at the B-site. Thus, by combination of measurements in the paramagnetic and ferromagnetic state with ¹¹¹Ag, ^{111m}Cd and ¹¹¹In probes the problem of the site occupation for CdCr₂Se₄ was unambiguously solved.

The analogous procedure was applied for other magnetic spinels, namely, for CdCr₂S₄, HgCr₂Se₄ and CuCr₂Se₄. It would be logical to suppose the same behavior of the PAC probes in these compounds, since all these materials belong to the same family and have similar lattice constants and anion parameters.



Fig. 3.6: PAC spectra R(t) and their Fourier transforms $F(\omega)$ for ¹¹¹In(¹¹¹Cd) implanted into: CdCr₂S₄ (a) at RT (paramagnetic state, PM) and (b) at 77K (ferromagnetic state, FM); HgCr₂Se₄ (c) at RT (paramagnetic state) and (d) at 77K (ferromagnetic state). The measurements at 77K were carried out with an external magnetic field perpendicular to the detector plane. The samples were annealed at 500°C / 15 min with slow cooling.

For CdCr₂S₄ and HgCr₂Se₄ the same behavior of the probes as in the case of CdCr₂Se₄ was observed, namely, for ^{111m}Cd and ¹¹¹Ag probes solely the A-site occupation and for ¹¹¹In probes the two-site occupation. In Fig. 3.6 the measurements with ¹¹¹In probes for CdCr₂S₄ and HgCr₂Se₄ in the paramagnetic and in the ferromagnetic states are presented. However, in these materials the A-site substitution after "normal" annealing is larger than that for CdCr₂Se₄ and amounts to 30(4) % for CdCr₂S₄ and 62(3) % for HgCr₂Se₄. The annealing with successive quench, in turn, did not result in drastic changes of the probes distribution and comes to 44(6) % for CdCr₂S₄ and 77(4) % for HgCr₂Se₄.



Fig. 3.7: PAC spectra R(t) and their Fourier transforms $F(\omega)$ for ^{111m}Cd and ¹¹¹In probes implanted into CuCr₂Se₄: (a) ^{111m}Cd probes, at 77K (ferromagnetic state); (b) ¹¹¹In probes, at 77K (ferromagnetic state); (c) ¹¹¹In probes, annealed at 650°C / 15 min with quench in H₂O, T_{meas} = 300°C (paramagnetic state). The measurements at 77K were carried out with an external magnetic field perpendicular to the detector plane.

The measurements for CuCr₂Se₄, in contrast, revealed solely the A-site occupation for all three probes. For ^{111m}Cd and ¹¹¹Ag probes this result was expected on the basis of the measurements on other ferromagnetic spinels, but for ¹¹¹In probes it was surprising. This fact was proved both by comparison of the measurements with the three probes and by the measurements in the paramagnetic and ferromagnetic states. In Fig. 3.7 the measurements carried out with ^{111m}Cd and ¹¹¹In probes are shown. The origin of the splitting in the Fourier spectrum for ^{111m}Cd probes is discussed in section 3.2.8. In the paramagnetic state no quadrupole interaction was detected. The annealing with successive quench led to a weak perturbation of the cubic environment only and resulted in slow decay of R(t) for the measurement in the paramagnetic state (T_{meas} = 300°C) (see Fig. 3.7, c) and small damping for the measurement in the ferromagnetic state. High temperature measurements (T_{meas} = 500°C) did not reveal any changes in the probe distribution.



Fig. 3.8: Summary-chart of the A-site substitution for the ferromagnetic spinels investigated by ¹¹¹In probes and their behavior with respect to different thermal treatments.

3.2.4 Measurements with ⁷⁷Br(⁷⁷Se) probes

In order to consider the investigations of the spinel compounds to be complete all three available sites have to be examined. The use of the probes discussed above (¹¹¹In, ¹¹¹Ag and ^{111m}Cd) was intended for the investigation of the cation sites. As to the anion site, it has not been studied by the PAC-method until now. However, the ⁷⁷Br(⁷⁷Se) probe, which is available at ISOLDE, is ideally suited for this purpose. Moreover, unstable ⁷⁷Br decays to ⁷⁷Se, which is a host atom in the Se-spinels.

Apart from the methodological interest from the point of view of PAC, Br is considered to be an important doping material for changing the magnetic and electrical properties of the FMS. For instance, in the system CuCr₂Se_{4-x}Br_x [Miy71] the Curie temperature decreases from 430 K for x = 0 to 130 K for x = 1. Moreover, electrical studies of this system have indicated that the resistivity behavior changes from a metallic to a semiconductor one as xincreases from zero to one. Thus, by changing x, the Curie temperature can be adjusted in such a way so that this system can be a suitable candidate for magneto-optical recording media utilizing a low power laser for thermo-magnetic writing and erasing [Tan94].

One of the advantageous properties, which distinguishes ⁷⁷Br(⁷⁷Se) from other probes, is its large anisotropy $A_{22} = -0.45$ [Moh88] that results in a larger amplitude of R(t). However, it has a half-life of the intermediate level of 9.3 ns that leads to an effective PAC-spectra time range of about 60 ns. Thus, for systems with small efg ($v_Q \le 40$ MHz) or small magnetic fields it is difficult to determine the modulation frequency with a high precision. Another disadvantage of this probe is the small probability of the decay via the proper γ_1 - γ_2 cascade utilized for the PAC-measurements that results in relatively insufficient statistics.

The measurements carried out for the FMS in the paramagnetic state revealed an axially symmetric efg (e.g., see Fig. 3.9, a), which is expected for the C-site. The experimental values of the efg are comparable with the theoretical ones. However, the situation in the ferromagnetic state is much more complicated. As discussed in section 1.1, in the normal



Fig. 3.9: PAC spectra R(t) and their Fourier transforms $F(\omega)$ for the FMS measured with ⁷⁷Br(⁷⁷Se) after annealing of the implantation damage (500°C / 15 min): (a) CdCr₂Se₄ at RT (paramagnetic state, PM); (b) CdCr₂Se₄ at 77K (ferromagnetic state, FM), pronounced combined interaction; (c) CdCr₂S₄ at 77K (FM); (d) CuCr₂Se₄ T_{meas} = 200°C (PM); (e) CuCr₂Se₄ at 77K (FM). All measurements at 77K were carried out with an external magnetic field and principal axis of the efg (<111> direction) perpendicular to the detector plane.

spinel structure the A-site has a vanishing efg, whereas the B- and C-sites possess axially symmetric efg. The case, where the strength of the electric quadrupole and magnetic interactions is comparable, is referred to as a combined interaction (see section 2.3.4). The interaction frequencies of the magnetic hyperfine fields at the B-site are much higher than those of the efg. e.g., for CdCr₂Se₄ $2\omega_I/\omega_0 \approx 14$. In this situation the combined interaction manifests itself by a slight broadening of the Fourier peak because of the small splitting. Therefore in this case the consideration of the combined interaction can be omitted. However, this is not the case at the C-site, where one has a pronounced combined interaction (e.g., for CdCr₂Se₄ $2\omega_1/\omega_0 \approx 3$). The treatment of the combined interaction is complicated. In principle, such a case can be evaluated using the program DEPACK [Lin96]. However, for an evaluation of the measurement the exact orientation of both B_{hf} and efg in a given coordinate system is required. Theoretically, the mutual orientation, which dramatically influences the appearance of the PAC-spectra, is feasible to fit, provided that either the orientation of the efg or that of the applied magnetic field is available. The orientation of the external magnetic field is known (perpendicular to the detector plane), but in the PAC-experiments normally 5-8 monocrystals with random orientation have been used. Here the simplified approach of the DEPACK program can not be applied, since the perturbing Hamiltonian is different for the monocrystals randomly oriented with respect to the external magnetic field. In order to overcome this problem, measurements with a defined orientation of the efg were carried out. In principle, for such experiments one monocrystal with a defined orientation would be enough, but practically it is difficult to realize implantation in a single crystal of the FMS due to its small dimensions. Therefore several monocrystals per compound oriented with a <111>direction (direction of the principal axis of the efg) perpendicular to the detector plane, i.e., coaxial with an external magnetic field, were used. For this purpose first the single crystals with a good octahedron shape were selected, where every facet in an octahedron is a (111) plane, and hence, its normal has a <111> direction. Then the samples were glued with one of the (111) planes down to a small disk, thus providing the <111> direction to be perpendicular to the plane. For the evaluation of the measured spectra all four equivalent <111> directions were taken into account using the DEPACK program (see Fig. 3.9 b, c).

In contrast to CdCr₂Se₄, CdCr₂S₄ and HgCr₂Se₄, the situation for CuCr₂Se₄ is quite different. In Fig. 3.9 (d) a measurement at 200°C (paramagnetic state) is presented. From the character of R(t) one can conclude that it is a quarter of the period corresponding to the quadrupole interaction. The quadrupole coupling constant amounts to $v_Q = 10(5)$ MHz that corresponds to $|V_{zz}^{exp}| = 0.6(4) \cdot 10^{21}$ V/m². According to theoretical calculations (section 4.4) $|V_{zz}^{theo}| = 1.2 \cdot 10^{21}$ V/m² that is in reasonable agreement with experiment. Taking into account that V_{zz} at the C-site for CuCr₂Se₄ is by a factor of 10 less than that for CdCr₂Se₄, the manifestation of the combined interaction is less expected in this case. These expectations were confirmed in practice (Fig. 3.9, e), where the pronounced magnetic interaction was observed. Since in this case for the measurement a single plate with a defined orientation was

used, the mutual orientation of the efg and B_{hf} is known, namely, it is coaxial perpendicular to the detector plane. This case can be evaluated by DEPACK. In the Fourier spectrum next to the main frequency a peak with smaller amplitude appears as well. However, the quadrupole interaction is so weak ($2\omega_L/\omega_0 \approx 39$) that it practically should not disturb the magnetic one. Therefore, one can conclude that the additional peak has quite another origin, which will be discussed in section 3.2.8.

3.2.5 Measurements with ^{199m}Hg probes

As pointed out in section 3.2.1, In and Ag impurities in FMS are responsible for n- and ptype conductivity, respectively. However, taking into account that compounds with the general formula ACr_2X_4 are magnetic, the search for new doping impurities, which change the magnetic properties and consequently result in the design of new devices, is required as well. Hg is a representative of this type of impurity. A number of experiments in terms of general properties have already been carried out for solid solutions with Hg (e.g., Hg_{1-x}Cu_xCr₂Se₄ [Oko77, Tsu97]). Thus, the site occupation and behavior of implanted ^{199m}Hg is of special interest. Nevertheless, such PAC-experiments have not been carried out so far because of difficulties to introduce such a short-lived probe.

With the establishment of ISOLDE the realization of such experiments became in principle feasible. However, a special feature of this probe is a very short half-life of 2.45 ns in the intermediate state that allows observing a hyperfine modulation only within a very short time range of about 20 ns. That is why ^{199m}Hg has only been used for substances with very high electric field gradients, mostly for organic compounds with $v_0 = 1000-1500$ MHz [Sol98], and never for FMS, since for such a short time range the internal magnetic fields of more than 30 T are required. Moreover, such large modulation frequencies make higher demands to PAC-apparatus first of all in terms of the time resolution, which should be better than 1 ns. It is interesting to note that ^{199m}Hg probes have never been applied even to such well investigated ferromagnetic metals as Fe, Ni and Co. The hyperfine fields in these materials have been measured mostly with ¹⁹⁸Hg by the integral PAC (IPAC) and with ¹⁹⁷Hg by the $e^{-\gamma}$ TDPAC [Kri73]. Although some attempts to measure B_{hf} at ¹⁹⁹Hg were also undertaken [Rag73], they were carried out with ¹⁹⁹Tl(¹⁹⁹Hg) probes, which have a half-life of 7.4 h of the mother nuclei. The results remained in some cases rather contradictory, which may be connected with different doping procedures and limited accuracy due to the short half-life of the intermediate state. All these facts suggest that ^{199m}Hg is a difficult probe even for simple compounds. Nevertheless, in spite of all difficulties mentioned above, the measurements with ^{199m}Hg in the FMS were successfully carried out in this work.

In Fig. 3.10 (a, b) the spectra for $HgCr_2Se_4$ at RT (paramagnetic state) and at 77K (ferromagnetic state) are presented. The existence of only one interaction frequency in the ferromagnetic state and solely a time independent part in the paramagnetic state unambiguously indicates the A-site occupation. Analogous results were obtained both for $CdCr_2Se_4$ and $CdCr_2S_4$ (Fig. 3.10 c, d). Annealing with successive quench has not led to



Fig. 3.10: PAC spectra R(t) and their Fourier transforms $F(\omega)$ for ^{199m}Hg after annealing of the implantation damage (500°C / 15 min): (a) HgCr₂Se₄ at RT (paramagnetic state); (b) HgCr₂Se₄ at 77K (ferromagnetic state); (c) CdCr₂Se₄ at 77K; (d) CdCr₂Se₄ at 77K; (e) CuCr₂Se₄ at 77K. All measurements at 77K were carried out with an external magnetic field perpendicular to the detector plane. For the measurements (b) and (d) the samples were annealed with successive quench.

any probe distribution between the A- and B-sites, but only to slight damping of R(t) and corresponding broadening of the Larmor frequencies in the Fourier spectra.

In contrast to the other substances, for CuCr₂Se₄ a quite opposite behavior of ^{199m}Hg was found. A series of experiments suggests the occupation of two non-equivalent sites with 40(4) % and 60(4) % for the low and high field site, respectively (Fig. 3.10, e). Surprisingly, in CuCr₂Se₄ for all other probes only the one site occupation (A-site) was observed, even for ¹¹¹In probes, which for all other FMS showed the A- and B-site occupation. On the basis of the experiments for other FMS one can assume that the lower Larmor frequency corresponds to the A-site and the higher one to the B-site, respectively. However, in this case it is difficult to answer this question unambiguously even with the help of the measurements in the paramagnetic state. According to theory (see section 4.4) the efg at the B-site in CuCr₂Se₄ is by a factor of about four smaller than that in the other FMS. Using Sternheimer factors one can estimate v_Q at the B-site measured with ^{199m}Hg probes, which would amount to 30 MHz. Such a relatively small frequency is practically impossible to detect within the given time range of 20 ns and to distinguish it from the time independent (cubic) part, which is also present. Thus, the measurements for CuCr₂Se₄ have to be considered as preliminary for more detailed investigations in the future.

While a ^{199m}Hg probe is an impurity for most of the FMS investigated, for HgCr₂Se₄ it is a host atom. This fact can be used to test the quality of the theoretical charge and spin density distribution in modern *first principles* calculations for the host system (see section 4.5). The theoretical value of $B_{hf}^{theo} = +44.3$ T turned out to be in good agreement with the experimental one of $B_{hf}^{exp} = +41.6(9)$ T (T_{meas} = 10 K).

3.2.6 Measurements with ¹¹⁷Cd(¹¹⁷In) probes

In the case of the ¹¹¹In(¹¹¹Cd) probe the parent ¹¹¹In is implanted and decays to ¹¹¹Cd, which for Cd-spinels is a host atom. The behavior of this probe was discussed in section 3.2.3. With ¹¹⁷Cd(¹¹⁷In) one can observe the opposite situation, where ¹¹⁷Cd, being a host atom in CdCr₂Se₄ and CdCr₂S₄, decays to ¹¹⁷In creating a so-called antisite defect In_{Cd}. For Cd-spinels, of course, the A-site occupation is expected. However, ¹¹⁷Cd first decays to an excited level of ¹¹⁷In (1/2⁺) with a half-life of 5 ns. Theoretically, it is likely that during this time an exited ¹¹⁷In probe will change its position, taking into account that for ¹¹¹In probes the two-site occupation is not so predictable as in the previous case.

Another special feature of ¹¹⁷Cd(¹¹⁷In) is the spin I = 3/2 in the intermediate state that advantageously distinguishes it from other probes with the spin I = 5/2. This peculiarity results in a simple quadrupole interaction with only one frequency that is especially appreciated in the case of the possible combined interaction in the ferromagnetic state. However, there is also a disadvantage connected with the relatively low energy of γ_1 (E_{γ_1} = 89 keV). Such a small energy leads to absorption of the γ -radiation by heavy atoms like Cd and Hg inside the crystals.



Fig. 3.11: PAC spectra R(t) and their Fourier transforms $F(\omega)$ for ¹¹⁷Cd(¹¹⁷In) after annealing of the implantation damage (500°C / 15 min): (a) HgCr₂Se₄ at RT (paramagnetic state); (b) HgCr₂Se₄ at 77K (ferromagnetic state); (c) CdCr₂Se₄ at 77K; (d) CuCr₂Se₄ at 77K. All measurements at 77K were carried out with an external magnetic field perpendicular to the detector plane. For the measurement (c) the samples were annealed with successive quench.

In Fig. 3.11 some measurements with $^{117}Cd(^{117}In)$ are presented. In the paramagnetic state only a time independent part in R(t) is observed that implies solely the A-site substitution. In the ferromagnetic state the spectra reveal for all substances only a single magnetic interaction with high Larmor frequencies, which are by a factor of two larger than those measured with ^{111}Cd (see Table 3.3, page 59). However, the difference between the internal magnetic hyperfine fields measured at In and Cd lies within 2 T. This phenomenon can be explained by

the fact that the g-factor for ¹¹⁷In is twice as large as that for ¹¹¹Cd. The proximity of B_{hf} for ¹¹⁷In and ¹¹¹Cd can serve as an additional proof of the A-site occupation, since internal magnetic fields at the B-site are expected to be twice as large. The stable behavior of ¹¹⁷Cd(¹¹⁷In) probes demonstrates that in this case no site transition occurs. A thermal treatment with successive quench has not led to any probe distribution.

3.2.7 Measurements with ¹⁰⁰Pd(¹⁰⁰Rh) probes

All probes discussed above are non-magnetic. In contrast, ¹⁰⁰Pd has the electronic configuration [Kr]4d¹⁰ and decays to ¹⁰⁰Rh with the electronic configuration [Kr]4d⁸5s¹, i.e., belongs to the transition metals of the 4d-series. Therefore, it is interesting to investigate the FMS by this transition metal probe. Moreover, ₄₆Pd continues the row of the probe elements ₄₉In, ₄₈Cd, ₄₇Ag, which have successfully been exploited in this work for the investigations of the FMS. Nevertheless, in spite of the big interest there are not so many investigations with ¹⁰⁰Pd(¹⁰⁰Rh) in semiconductors and especially in ferromagnetic semiconductors. This may result from the complicated electronic structure and low solubility of Pd in these materials in contrast to e.g. In.

The isotope ¹⁰⁰Pd can be produced by a number of nuclear reactions. However, in contrast to other various probes, ¹⁰⁰Pd is not available at ISOLDE due to difficulties with ion source and mass-separation. Therefore, the implantation and measurements were carried out using recoil implantation at the heavy ion accelerator at ISL (Ionen-Strahl-Labor) of the Hahn-Meitner Institute (HMI) Berlin². A heavy-ion beam of ¹⁵N with 65 MeV bombarded a thin ⁸⁹Y target foil to produce the desired ¹⁰⁰Pd probes by a nuclear reaction ⁸⁹Y(¹⁵N, 4n)¹⁰⁰Pd. From the reaction mechanism the ¹⁰⁰Pd probes were emitted in a small cone centered on the beam direction receiving the forward momentum of the incoming beam which led to recoil energies of up to 10 MeV and implantation depth of several µm.

Compared to the PAC probes discussed above, ¹⁰⁰Pd has some disadvantages. First of all, the two γ -ray energies (see Table 2.1) are almost the same and cannot be distinguished by NaI or BaF₂ detectors. Since the start and stop γ -rays are not distinguishable, one obtains time spectra in the multichannel analyzer that are symmetric around t = 0, so-called "roof"-spectra. Second, the integer spin (I = 2) in the intermediate state leads to a complicated angular correlation spectrum for non-axially-symmetric ($\eta \neq 0$) quadrupole interactions (10 different transition frequencies and a constant term) [Sch96]. Third, the energies of the γ - γ cascade are relatively low that can cause their absorption in the case of compounds containing heavy metals like Cd or Hg.

In Fig. 3.12 the first experiments with ¹⁰⁰Pd in the FMS are presented. In the paramagnetic state (Fig. 3.12, a) the PAC-spectrum shows a slow decay like in the case of ^{111m}Cd or ¹¹¹Ag (section 3.2.3). Therefore, at first one can suppose only the A-site occupation with some

² The implantation and measurements with ¹⁰⁰Pd(¹⁰⁰Rh) at HMI were kindly supported by Dr. W.D. Zeitz, Dr. H.E. Mahnke and Dipl.-Phys. V. Koteski.



Fig. 3.12: PAC spectra R(t) and their Fourier transforms $F(\omega)$ for ¹⁰⁰Pd(¹⁰⁰Rh) in the FMS after annealing of the implantation damage (450°C / 20 min): (a) CdCr₂Se₄ at RT (paramagnetic state); (b) CdCr₂Se₄ at 77K (ferromagnetic state); (c) CuCr₂Se₄ at RT (ferromagnetic state). All measurements in the ferromagnetic state were carried out in the Raghavan's geometry (see section 2.3.2) with observation of the single Larmor frequency only.

distant non-correlated defects. However, the quadrupole moment of ¹⁰⁰Rh is rather small Q = 0.076(20) barn. For instance, it is by a factor of 11 smaller than that of ¹¹¹Cd. An estimation of the quadrupole coupling constant for ¹⁰⁰Rh at the B-site based on the measurements with ¹¹¹In(¹¹¹Cd) ($v_Q = 58.55$ MHz) and Sternheimer corrections results in $v_Q \approx 5$ MHz. Thus, in this situation it is difficult to determine reliably whether an occupation of one or two sites (as in the case of ¹¹¹In(¹¹¹Cd), section 3.2.3) takes place. Therefore the approach based on the comparison between measurements in the paramagnetic and ferromagnetic state, which was successfully applied earlier, here does not work. On the other hand, such a tiny quadrupole frequency is advantageous in the case of the combined interaction of the combined interaction can entirely be neglected.

Another feature of ¹⁰⁰Rh is its large g-factor g = +2.162(4), which is by a factor of 7 larger than that of ¹¹¹Cd. Thus, in the ferromagnetic state the Larmor frequencies of up to

4000 Mrad/s were expected. Measurements in the transverse geometry would result in twice the Larmor precession frequencies of 8000 Mrad/s ($1/2T_L = 0.785$ ns). Such high frequencies require a PAC-apparatus (first of all detectors) with a very good time resolution. Therefore, in this series of measurements the Raghavan's geometry (see section 2.3.2) was utilized, where one observes the Larmor frequency rather than twice the Larmor frequency. In Fig. 3.12 (b) the measurement for CdCr₂Se₄ in the ferromagnetic state is shown. In spite of the bad statistics and considerable amplitude attenuation because of the finite time resolution, it was feasible to fit two interaction frequencies $\omega_{L1} = 2653(14)$ Mrad/s and $\omega_{L2} = 4017(18)$ Mrad/s that correspond to $B_{hf1} = 25.6(3)$ T and $B_{hf2} = 38.8(4)$ T, respectively. Drawing an analogy from the measurements with ¹¹¹In(¹¹¹Cd) (see section 3.2.3), where also two interaction frequencies were observed, one is tempted to ascribe the occupation of ¹⁰⁰Pd to the A- and Bsite as well. In the case of $CuCr_2Se_4$ (Fig. 3.12, c) only a single interaction frequency $\omega_L = 1590(10)$ Mrad/s with $B_{hf} = 15.4(3)$ T is observed that suggests either the A- or B-site occupation. According to the results obtained with other probes and taking into account that the internal magnetic field measured with ¹⁰⁰Pd in CuCr₂Se₄ is small in comparison with that in CdCr₂Se₄, one can conclude that 100 Pd(100 Rh) probes occupy in CuCr₂Se₄ rather the A-site. However, it should be emphasized that these measurements with ¹⁰⁰Pd(¹⁰⁰Rh) were first and certainly not last experiments opening a new series of investigations of the FMS with magnetic probes.

3.2.8 Summary

The problem of the site occupation of different doping atoms in the FMS arose a long time ago. Such impurities as In, Ag, Br, Hg and others at a certain concentration may drastically change the properties of the host material in a wide range in terms of the conductivity type, Curie temperature, magnetic ordering and optical effects. That is why many scientists have been trying to solve this problem with direct and indirect methods for more than 30 years. This question has emerged not accidentally, since the site occupation of cations depends on many factors [Rad78, Nik81, Wei01]:

- 1. The size of ionic radii. The system of physical ionic radii corresponds to the real characteristic of the electron density distribution. This system gives a good description of interatomic distances in ionic crystals. However, for incompletely ionized divalent and multivalent cations, when the bonds become partly covalent, the physical interpretation of these radii becomes vague. In this case they should be treated more cautiously, rather as formal characteristics.
- 2. The anion displacement parameter u, which differs from substance to substance. It is responsible for the nearest-neighbor tetrahedral bond length (\mathbb{R}^{T}) and the nearest-neighbor octahedral bond length (\mathbb{R}^{O}) of the host compound (see section 4.4). When u increases, the tetrahedral bond lengths increase while the octahedral bond lengths decrease.
- 3. The preference of some cations to form covalent tetrahedral bonds with anions by means of sp³-hybridization directed towards the vertices of tetrahedron. Ions with shallow

occupied *d* orbitals such as Cu^+ , Zn^{2+} , Ga^{3+} , Ge^{4+} , Ag^+ , Cd^{2+} , In^{3+} , and Sn^{4+} tend to occupy the tetrahedral site, whereas $3d^3$ and $3d^8$ ions (Cr^{3+} , Ni^{2+}) have a strong tendency to occupy the octahedral sites.

- 4. The electrostatic interaction, which is characterized by the Madelung constant, has significant influence on the cation distribution (see section 4.4). The Madelung constant M is a dimensionless constant, which solely depends on the geometry of an ionic array and determines the Coulomb energy of an ionic crystal [Kit96]. A larger Madelung constant means a lower (more negative) electrostatic energy. Therefore the configuration with larger M is more stable.
- 5. The valency of ions. The "valency" here implies a formal electrical charge of an ion, which should be ascribed for keeping the electro-neutrality of the whole crystal. In some cases the valency of ions is variable that certainly may influence the site occupation, since the ionic radii decrease with increasing valency.
- 6. In real spinel substances a certain degree of inversions between the A- and B-sites exists [Wei01], which along with intrinsic defects (first of all anion vacancies) should be taken into account.

Probe \ Substance	CdCr ₂ Se ₄	CdCr ₂ S ₄	HgCr ₂ Se ₄	CuCr ₂ Se ₄	
^{111m} Cd(¹¹¹ Cd)	Cd	Cd	Hg	Cu	
¹¹¹ Ag(¹¹¹ Cd)	Cd	Cd	Hg	Cu	
¹¹¹ In(¹¹¹ Cd)	Cd 11(3) % Cr 89(3) % Quench Cd 40(4) % Cr 60(4) %	Cd 30(4) % Cr 70(4) % Quench Cd 44(6) % Cr 56(6) %	Hg 62(3) % Cr 38(3) % Quench Hg 77(4) % Cr 23(4) %	Cu 100 %	
¹¹⁷ Cd(¹¹⁷ In)	Cd	Cd	Hg	Cu	
⁷⁷ Br(⁷⁷ Se)	Se	S	Se	Se	
^{199m} Hg(¹⁹⁹ Hg)	Cd	Cd	Hg	Cu 41(7) % Cr 59(7) %	

Table 3.1. Lattice site occupations for the probe-substance combinations of the FMS investigated.

In Table 3.1 the lattice site occupations for the probe-substance combinations of the materials investigated are shown and in Table 3.3 the measured magnetic hyperfine fields are summarized. Nearly all probes in the FMS, except ¹¹¹In(¹¹¹Cd), occupy solely the A-site (the case of ^{199m}Hg in CuCr₂Se₄ is preliminary and should be investigated further). For some FMS certain probes are host atoms, e.g., ^{111m}Cd in CdCr₂X₄, ^{199m}Hg in HgCr₂Se₄. Therefore the site occupation in these cases was predictable. In the case of ¹¹¹Ag and ^{199m}Hg (where Hg is an impurity) the A-site substitution was expected as well taking into account the factors

mentioned above. Experimental results obtained with other methods [Rad78] also support these findings.

As to ¹¹¹In, the situation with predictions is not so simple. In spite of its valency (In^{3+}), for a long time ¹¹¹In has been supposed to occupy only the A-site, e.g., [Vai81, Jha87, Unt91]. However, the investigations carried out in this work unambiguously showed that in CdCr₂Se₄, CdCr₂S₄ and HgCr₂Se₄ ¹¹¹In can substitute both the A-site and the B-site with a certain ratio depending on the thermal treatment. Moreover, in these materials after "normal" annealing the A-site substitution increases in the sequence CdCr₂Se₄, CdCr₂S₄, HgCr₂Se₄ (Table 3.1). This behavior can not be explained completely taking into account the different relevant factors mentioned above, which can have an influence on it. However, it can qualitatively be understood considering the tetrahedral (R^{T}) and octahedral (R^{O}) bond lengths of the host compounds. The anion parameter *u* increases from CdCr₂Se₄ to HgCr₂Se₄ causing the R^{T} to increase at the expense of the R^{O} , which decreases (see Table 3.2). Therefore the probability of the A-site occupation under other equal conditions should increase as well. This trend was observed experimentally.

Table 3.2. Ionic radii for some cations in connection with the ratio of the tetrahedral and octahedral bond lengths in the FMS.

Compound	и	$\mathbf{R}^{\mathbf{O}}/\mathbf{R}^{\mathrm{T}}$	R-cation, Å [Vai94]						
Compound			Ag	Cd	In	Cu	Hg	Cr	
CdCr ₂ Se ₄	0.26521	0.97096							
CdCr ₂ S ₄	0.26578	0.96491	1+ 1 13	2+ 0.99	3+ 0.92	$\begin{array}{c} 1^{+} \ 0.98 \\ 2^{+} \ 0.80 \end{array}$	2+ 1.12	2^+ 0.83 3^+ 0.64	
HgCr ₂ Se ₄	0.26611	0.96149	1 1.15						
CuCr ₂ Se ₄	0.25778	1.05526							

However, in CuCr₂Se₄ an anomalous behavior of ¹¹¹In probes was found, namely, they solely occupy the A-site. This finding is consistent with other experiments, where in the systems Cu_xIn_yCr₂Se₄ [Oko94] and Cu_xGa_yCr_zSe₄ [Win96] In³⁺ and Ga³⁺ ions in small concentrations also occupy the A-site only. This phenomenon can obviously not be explained in terms of the ratio R^O/ R^T, since in this case R^O/ R^T>1 that suggests the preference of the B-site occupation. However, it may be related to a feature, which distinguishes CuCr₂Se₄ from the other FMS, namely, the presence of Cu⁺ instead of Cu²⁺ that is discussed below.

The results of the site occupation of In and Ag are of interest not only from the point of view of basic research. Already in the sixties it was found that In and Ag are responsible for n- and p-type conductivity [Leh67]. Even after a few first experiments it was clear that the mechanism of the conductivity in the FMS is different from that in Si and Ge. Numerous investigations with different methods have resulted in the following models of the mechanism of conductivity in the FMS, which are summarized in [Rad78]. Let us first consider the nature of acceptors in the FMS doped with Ag on the example of $CdCr_2Se_4$. The usual mechanism of the acceptor conductivity in the "standard" semiconductors like Si, Ge, or $A^{III}B^{V}$ is based on



Fig. 3.13: The scheme illustrating the mechanisms of the p-type conductivity in the FMS doped with Ag: (a) the mechanism, which prevails at high temperatures; (b) at low temperatures.

the substitution of a host atom by an atom with smaller number of valence electrons. This mechanism, as known, results from the fact that at the impurity atom one electron is missing in order to form the strong covalent bond and hence an electron can transit from the valence band to that atom with generation of a hole. Thus the necessary prerequisites for this mechanism are the presence of the strong covalent bonds and a different number of valence electrons at the host and impurity atoms. However, this is not the case in the FMS, where both ions (Cd²⁺ and Ag⁺) have the same filled electron shells. They are connected to their neighbors (Se²⁻) by ionic bonds, which are not destroyed by the Ag^+ substitution of Cd^{2+} , and consequently Ag⁺ can not accept an electron as acceptor. Therefore the electrical neutrality of $CdCr_2Se_4$, because of the substitution of Cd^{2+} by Ag^+ , is compensated according to the formula $Ag_{x}^{+}Cd_{1-x}^{2+}[Cr_{2-x}^{3+}Cr_{x}^{4+}]Se_{4}^{2-}$ by the creation of Cr^{4+} ions, which become again Cr^{3+} by accepting an electron. Thus one can consider the level of the 3*d*-electrons of Cr as an acceptor level. In the stoichiometrical crystals this level is entirely occupied, whereas in the Ag-doped crystals it is occupied incompletely. At temperatures higher than 150 K thermal transitions of electrons from the valence band to the acceptor level (or rather to the narrow acceptor band) occur, thereby Cr^{4+} ions turn into Cr^{3+} and in the valence band the corresponding holes appear (Fig. 3.13, a). The distance from this level to the top of the valence band is the activation energy of the *p*-conductivity at high temperatures. The conductivity at low temperatures (T < 150 K) is due to "impurity conduction", which is characterized by the much lower activation energy, but also by considerably lower mobility of the charge carriers. This mechanism of conductivity can be referred to as "hopping mechanism", where thermoactivated electrons jump from Cr^{3+} ions to Cr^{4+} (Fig. 3.13, b) that can also be considered as the motion of holes in the narrow "acceptor band".

For In-doped FMS one could assume a similar mechanism of the conductivity, namely, according to the formula $In_x^{3+}Cd_{1-x}^{2+}[Cr_{2-x}^{3+}Cr_x^{2+}]Se_4^{2-}$ In³⁺ should lead to the creation of corresponding Cr^{2+} ions, which form the narrow "donor band". However, the temperature dependences of electrical conductivity for *n*- and *p*-type CdCr₂Se₄ are strikingly different [Leh67, Rad78]. The conductivity of the *n*-type material shows a minimum at 150 K and

increases sharply with further decreasing temperature. Moreover, some additional magnetoopto-electrical effects arise as well, e.g, strong red-shift of the absorption band edge, giant negative magnetoresistance, increasing of mobility and carrier concentration at lower temperatures, etc. (see section 1.2). Therefore in this case the situation is much more complicated, since the magnetic ordering plays an essential role. Although there is no definite indication as to the nature of the donor level, there is an indication that it is due to Cr^{2+} , since the magnetization decreases and the anisotropy increases with increasing In substitution [Leh67]. These facts were explained by the presence of Cr^{2+} with their moments aligned antiparallel to the Cr^{3+} moments. The Cr^{2+} ions also act as charge compensators.

Thus the site occupation of In-atoms plays an essential role taking into account that only at the A-sites they are electrically active. According to the results obtained in this work (see section 3.2.3) only 11(3) % of In-atoms substitute the A-site after normal thermal treatment. It is interesting to note that other three-valent impurities like Al, Dy, Ti turned out to be electrically passive in the FMS [Haa67] that suggests solely the B-site substitution.

CdCr₂Se₄, CdCr₂S₄, and HgCr₂Se₄ have more or less similar properties (e.g., semiconducting type of conductivity, saturation magnetization of about $6\mu_B$ per formula unit and relatively low Curie temperatures). In contrast, CuCr₂Se₄ has properties quite different from those of the FMS mentioned above: p-type metallic conductivity, ferromagnetism with high Curie temperature ($T_C = 430$ K) and saturation magnetization of about 5 μ_B per formula unit. For the explanation of the physical properties of CuCr₂Se₄ several models of the electronic structure have been introduced. The assumed valence distributions in this compound are: $Cu^{2+}[Cr_2^{3+}]Se_4^{2-}$ (model of Goodenough) [Goo67], $Cu^+[Cr^{3+}Cr^{4+}]Se_4^{2-}$ and later $Cu^+[Cr^{3+}_{l+\delta}Cr^{4+}_{l-\delta}]Se^{(2-\delta/4)-}_4$ with $\delta = 0.1$ (model of Lotgering) [Lot64, Lot68], the valency of ions obtained from the self-consistent calculation are $Cu^{1.25+}[Cr_2^{1.41+}]Se_4^{1.02-}$ [Oga82]. From X-ray photoelectron spectroscopy it follows that the bonds are of covalent rather than of ionic character and no formal valency can be ascribed from the chemical formula, since charge distribution plays an important role [Win96]. In [Ovc79] it was shown that under certain conditions both Lotgering and Goodenough phases can be realized as well as intermediate phases with unequal concentration of Cr^{3+} and Cr^{4+} ions. Summarizing numerous experimental results one can claim that the Lotgering-based model is dominating. In this model the assumption was made that Cu occurs as a monovalent diamagnetic ion with configuration $3d^{10}$ and the ferromagnetism and conduction were attributed to double exchange between Cr³⁺ and Cr⁴⁺ occupying the octahedral sites of the spinel lattice. The ferromagnetic moment of 5 μ_B per formula unit arises from a parallel alignment of the Cr^{3+} and Cr^{4+} moments.

The PAC-experiments carried out for $CuCr_2Se_4$ in this work have been started with ⁷⁷Br(⁷⁷Se) probes (see section 3.2.4). The results at 77K and RT have revealed the presence of an asymmetric splitting, which manifests itself by an additional peak in the Fourier spectrum

with a lower frequency and amplitude. The presence of these two frequencies may result from the following reasons: (i) a part of the probes, besides Se sites, occupies another position in the lattice: (ii) ⁷⁷Br(⁷⁷Se) probes substitute Se-sites only, but the environment of Se sites is not unique that causes two interactions; (iii) the splitting is caused by a combined interaction, which is expected at the C-site. The first assumption seems to be excluded because of the rather large ionic radius of the Br (1.96 Å), as compared to the size of the cations in the crystal lattice. The combined interaction is unlikely too (see section 3.2.4). It is well known (see section 1.2) that in spinel compounds there are many defects, first of all anion vacancies. In principle, they could produce this effect. However, this phenomenon can not be checked by comparison with the other FMS because of the disturbing combined interaction at the C-site in these cases. Further experiments with ^{111m}Cd and ¹¹¹Ag(¹¹¹Cd) have shown similar results with a pronounced asymmetric splitting that has not been found in the other FMS, where obviously the anion vacancies exist too. It is worth noting that NMR-measurements with ⁵³Cr for CuCr₂Se₄, in contrast to results for the other FMS, also revealed a single strong component with a weak asymmetric contribution extending about 6 MHz to lower frequencies [Ber68]. Thus, with various methods the existence of an asymmetric splitting at the three sites was confirmed. That is why one can claim with high probability that this phenomenon is not connected to any defects, which are also present in the other FMS, but related to the variable valency of the Cr cations that distinguishes CuCr₂Se₄ from the other FMS. Different amplitudes of the peaks can be explained by different concentrations of Cr^{3+} and Cr^{4+} ions that correspond to the mixed model of the electronic structure discussed above. This hypothesis is consistent with the NMR measurements for CdCr₂Se₄ doped with Ag [Abe00] and In [Abe86] with impurity concentrations of about 1.5 at. %. In the case of the Ag-doped crystals two non-equivalent states of ⁵³Cr attributed to Cr⁴⁺ and Cr³⁺ were found, whereas for the In-doped crystals an additional high frequency contribution ascribed to Cr^{2+} was detected.

¹¹¹In(¹¹¹Cd) probes behave in CuCr₂Se₄ anomalously. First, they exclusively substitute the A-site contrary to the results obtained for the other FMS and the ratio R^{O}/R^{T} (see Table 3.2), which preferably suggests the B-site occupation. Second, for ¹¹¹In(¹¹¹Cd)</sup> probes only a single line in the Fourier spectrum was observed and no asymmetric splitting was found. In this case one can only speculate about the reason of this effect. According to the mechanisms of conductivity in CdCr₂Se₄, CdCr₂S₄, and HgCr₂Se₄ discussed above, doping with In leads to the reduction of the Cr valency. Therefore one can suppose that ¹¹¹In probes in CuCr₂Se₄ cause the transition $Cr^{4+} \rightarrow Cr^{3+}$ in the very nearest surrounding of the probes, thereby the spectra look similar to those of the other FMS, i.e., with only one line in the Fourier spectrum. This assumption is supported in [Win96], where it was found that doping with In or Ga (~ 4 at. %) in CuCr₂Se₄ leads to an increase of the amount of Cr³⁺ ions.

Table 3.3. Summary of the measured magnetic hyperfine fields in the FMS with various probes. NMR measurements were carried out at 4.2 K [Lan70]. All PAC measurements at 77 K were carried out with $B_{ext} = 0.5(1)$ T. "A" and "B" imply the A- and B-sites, respectively.

Compound	T _{meas}		¹¹¹ In(¹¹¹ Cd)	^{111m} Cd	¹¹¹ Ag(¹¹¹ Cd)	¹¹⁷ Cd(¹¹⁷ In)	^{199m} Hg	⁷⁷ Br(⁷⁷ Se)		
CdCr ₂ Se ₄	77K	ω_L (Mrad/s)	A 165(1) B 380(3)	165.9(3)	166.1(6)	371.6(2)	671(4)	134(2)		
		B _{hf} (T)	A 11.2(1) B 25.9(3)	11.3(1)	11.3(1)	12.4(1)	39.7(7)	6.3(2)		
	10K	ω _L (Mrad/s)		195.8(3)		440.9(8)	805(4)			
		$\mathbf{B}_{\mathrm{hf}}\left(\mathbf{T}\right)$		13.4(1)		14.7(2)	47.6(7)			
	NMR	$\mathbf{B}_{\mathrm{hf}}\left(\mathbf{T}\right)$		+13.62 (¹¹¹ Cd) -18.	25 (⁵³ Cr) -	9.8 (⁷⁷ Se)			
CdCr ₂ S ₄	7717	ω _L (Mrad/s)	A 149(1) B 228(4)	151.2(2)	151(2)	316(1)	587(5)	100(2)		
	77 K	B _{hf} (T)	A 10.2(1) B 15.5(4)	10.3(1)	10.3(2)	10.6(2)	34.7(8)	4.7(2)		
	10K	ω_L (Mrad/s)		233.3(2)		500(5)	940(6)			
		$B_{hf}(T)$		15.9(1)		17(1)	55.6(9)			
	NMR	$B_{hf}(T)$	+16.7 (¹¹¹ Cd) -19.10 (⁵³ Cr)							
HgCr ₂ Se ₄	77K	ω _L (Mrad/s)	A 137.5(4) B 341(2)	138.0(2)	137(3)	297.1(6)	534(3)	111(6)		
		$\mathbf{B}_{\mathrm{hf}}\left(\mathrm{T} ight)$	A 9.4(1) B 23.2(2)	9.4(1)	9.3(4)	9.9(2)	31.6(6)	5.2(3)		
	10K	ω _L (Mrad/s)	A 174(1) B 499(4)			376(2)	704(6)			
		B _{hf} (T)	A 11.8(2) B 34.0(5)			12.6(3)	41.6(9)			
	NMR	$B_{hf}(T)$	+44.6 (Hg) $-17.9 (^{53}Cr) -9.17 (^{77}Se)$							
CuCr ₂ Se ₄	RT	ω _L (Mrad/s)	A 195.2(2)	182(1) 195.4(4)	195(2)	431.8(8)		108(5) 148(2)		
		$\mathbf{B}_{\mathrm{hf}}\left(\mathrm{T} ight)$	A 13.3(1)	12.4(3) 13.3(1)	13.3(4)	14.4(2)		5.0(4) 6.9(2)		
	77K	ω_L (Mrad/s)	A 255.8(2)	237(1) 255.0(7)		578(1)	A 485(6) B 984(6)	142(6) 193(2)		
		$\mathbf{B}_{\mathrm{hf}}\left(\mathrm{T} ight)$	A 17.4(1)	16.2(3) 17.4(2)		19.3(2)	A 28.7(8) B 58.2(8)	6.6(4) 9.0(2)		
	NMR	$B_{hf}(T)$		+	7.21 ($^{63, 65}$ Cu)	-16.1 (⁵³ C	Cr)			

3.3 Sign determination of internal magnetic fields

In the 1970-ties the ferromagnetic metals Fe, Co and Ni were a subject of intensive and numerous investigations by hyperfine interaction methods. These materials were studied with the help of various probes. The investigations have revealed that the internal magnetic hyperfine fields measured at impurity nuclei of non-transition elements in the ferromagnets vary in a wide range. Besides, the internal magnetic fields change their sign for certain nuclei. This effect was explained by J. Kanamori et al. [Kan81] using *ab initio* calculations. The theoretical results were in good agreement with the experimental ones that implied a great breakthrough in the theoretical understanding of this phenomenon.

Nowadays, around the world there are about a dozen of research groups applying hyperfine interaction measurements for the study of local structural and electronic properties at surfaces and in ultrathin multilayer systems. These experiments focus the interest in particular on local magnetic properties at surfaces, near surfaces and at interfaces. Of special importance are induced magnetic interactions in magnetic multilayer systems, where magnetic interactions are induced into nonmagnetic metals, when they are in contact with a ferromagnet. Modern calculations of the magnetic hyperfine fields for elements in the adatom position on the ferromagnetic surface [Mav98] revealed quite different behavior as compared to bulk materials, namely, for some elements the bulk values are small and negative, whereas the predicted adatom values are large and positive. Later H.H. Bertschat et al. [Ber02] using PAC found that the magnetic hyperfine field (in this case at ¹¹¹Cd on the Ni surface) increases (with change of sign) with respect to the probe position on the surface (e.g., bulk, "terrace", "free step", adatom, etc). However, the sign of the magnetic hyperfine fields was measured only for the bulk value, for the adatom values it was deduced from calculations, although the PACmethod is able to determine the sign using a certain configuration of detectors. All arguments mentioned above suggest that a reliable sign determination of B_{hf} is very important.

As described in section 2.3.2, in the arsenal of the PAC-method there is a detector configuration, which allows sign-sensitive measurements. In the 70-ties for this purpose two detectors with the inter-detector angle of 135° were used [Hun74]. This configuration with only two detectors had a number of drawbacks: (i) bad statistics; (ii) floating zero line, which has to be corrected additionally; (iii) complexity of apparatus connected with the necessity to use either the magnet, which periodically changes the direction of B_{ext}, or a special mechanism changing the location of a detector between +135° and -135°. Because of these shortcomings the 135°-setup with two detectors has been less and less in use until the most efficient 180°/90°-arrangement with four detectors became dominant and later standard.

Theoretically, in order to obtain the R(t)-spectrum, which reflects a pure modulation, one should form for the transverse $180^{\circ}/90^{\circ}$ -geometry (see section 2.3.2) the following ratio

$$R(t) = \frac{W(180^\circ, t) - W(90^\circ, t)}{W(180^\circ, t) + W(90^\circ, t)} = \frac{y - 1}{y + 1} = \frac{3 \cdot A_{22} \cdot \cos 2\omega_L t}{4 + A_{22}}$$
(3.1)

where

$$y = \frac{W(180^\circ, t)}{W(90^\circ, t)}$$
(3.2)

However, in practice, R(t) is expressed not by the angular correlation function, but by the differential coincidence count rate:

$$N_{ij}(\theta, t) = N_{ij}^0 \cdot e^{-\frac{t}{\tau_N}} \cdot W(\theta, t) + B$$
(3.3)

where *B* is the time-independent background (random coincidence count rate), which is subtracted before forming R(t); $W(\theta, t)$ represents the time-dependent angular correlation (θ is the angle between the two detectors); τ_N is the lifetime of the intermediate level. The coincidence count rate N_{ij}^0 at time t = 0 between start detector *i* and stop detector *j* is given by

$$N_{ij}^{0} = \varepsilon_{i}^{start} \cdot \Omega_{i}^{start} \cdot w_{i}^{start} \cdot \varepsilon_{j}^{stop} \cdot \Omega_{j}^{stop} \cdot w_{j}^{stop} \cdot A \equiv \chi_{i}^{start} \cdot \chi_{j}^{stop} \cdot A$$
(3.4)

where *A* is the source activity, ε_i the photopeak efficiencies of the detectors, Ω_i the solid angles normalized to 4π , w_i the coefficients related to the proper adjustments of the energy windows, χ_i^{start} and χ_j^{stop} contain all parameters mentioned above for start detector *i* and stop detector *j*, respectively. Then the R(t)-ratio can be written as:

$$R(t) = \frac{N(180^{\circ}, t) - N(90^{\circ}, t)}{N(180^{\circ}, t) + N(90^{\circ}, t)} = \frac{y - 1}{y + 1}$$
(3.5)

where

$$y = \frac{N(180^{\circ}, t)}{N(90^{\circ}, t)} = \frac{\left(N_{13}N_{31}N_{24}N_{42}\right)^{1/4}}{\left(N_{12}N_{21}N_{23}N_{32}N_{34}N_{43}N_{14}N_{41}\right)^{1/8}} = \frac{W(180^{\circ}, t)}{W(90^{\circ}, t)}$$
(3.6)

One can easily show that in (3.6) the detector efficiencies, solid angles and energy-windows coefficients are cancelled, since they appear in both the numerator and denominator. Thus, in spite of the fact that with the $180^{\circ}/90^{\circ}$ -geometry the sign determination of the Larmor frequency is impossible, because of the even cosine function (see Eq. 3.1), it has a series of advantages such as better statistics (up to 12 start-stop detector combinations available) and independence of the detector and energy-window efficiencies, which are cancelled after forming the ratio R(t). In this work an attempt was made to find the optimal configuration with four detectors for sign-sensitive measurements with as many as possible start-stop detector combinations and taking into account the elimination of the efficiencies mentioned above.

The sign-sensitive detector arrangements are based on the fact that the Legendre polynomial $P_2(\theta, t)$, which is included in the angular correlation function $W(\theta, t)$, for $\theta = \pm 135^{\circ}$ (θ – angle between detectors) contains the sine function of the double Larmor frequency instead of the cosine that leads to

$$R(t) = \frac{W(135^{\circ}, t) - W(-135^{\circ}, t)}{W(135^{\circ}, t) + W(-135^{\circ}, t)} = \frac{y - 1}{y + 1} = -\frac{3 \cdot A_{22} \cdot \sin 2\omega_L t}{4 + A_{22}}$$
(3.7)



Fig. 3.14: Possible four-detector arrangements: (a) conventional 180°/90°-geometry; (b, c, d) 135°-geometries. The last geometry (d) is the optimum, where the coefficients of any kind are cancelled completely.

However, the same expression can be obtained for $\theta = \pm 45^{\circ}$, i.e., W(135°, t) = W(-45°, t) and W(-135°, t) = W(45°, t). Considering this point, three sign sensitive detector arrangements were found (Fig. 3.14, b-d). Every configuration has its advantages and disadvantages in terms of the distances "sample-detector", symmetrical layout, scattering of the γ -radiation, etc. It should be noted that in all these configurations each detector is used as start and stop, where in general $\chi_i^{start} \neq \chi_i^{stop}$. One can show that only in the last configuration (Fig. 3.14, d) all coefficients are cancelled. Therefore, theoretically it seems to be the optimal decision for sign-sensitive measurements:

$$y = \frac{N(135^{\circ}, t)}{N(-135^{\circ}, t)} = \frac{\left(N_{14}N_{31}N_{23}N_{42}\right)^{1/4}}{\left(N_{13}N_{24}N_{41}N_{32}\right)^{1/4}} = \left(\frac{\chi_{1}^{start}\chi_{4}^{stop}\chi_{3}^{start}\chi_{1}^{stop}\chi_{2}^{start}\chi_{3}^{stop}\chi_{4}^{start}\chi_{2}^{stop}}{\chi_{1}^{start}\chi_{3}^{stop}\chi_{2}^{start}\chi_{4}^{stop}\chi_{4}^{start}\chi_{1}^{stop}\chi_{3}^{start}\chi_{2}^{stop}}\right)^{1/4} \cdot \frac{W(135^{\circ}, t)}{W(-135^{\circ}, t)} = \frac{W(135^{\circ}, t)}{W(-135^{\circ}, t)}$$
(3.8)



Fig. 3.15: PAC spectra R(t) and their Fourier transforms $F(\omega)$ for ^{111m}Cd in CdCr₂Se₄ measured in the possible four-detector sign-sensitive arrangements after annealing of the implantation damage (600°C / 10 min). The first geometry (a) is optimal, where the coefficients χ_i are cancelled completely. In contrast, in the configurations (b) and (c) a shift of the zero line of R(t) is observed.

In contrast, in the other two configurations (Fig. 3.14 b, c) the elimination of the coefficients takes place only for the ideal condition $\chi_i^{start} = \chi_i^{stop}$. This can be illustrated by the example of the configuration shown in Fig. 3.14 (b):

$$y = \frac{N(135^{\circ}, t)}{N(-135^{\circ}, t)} = \frac{\left(N_{14}N_{32}N_{12}N_{34}\right)^{1/4}}{\left(N_{41}N_{23}N_{21}N_{43}\right)^{1/4}} = \left(\frac{\chi_1^{start}\chi_4^{stop}\chi_3^{start}\chi_2^{stop}}{\chi_4^{start}\chi_1^{stop}\chi_2^{start}\chi_3^{stop}}\right)^{1/2} \cdot \frac{W(135^{\circ}, t)}{W(-135^{\circ}, t)}$$
(3.9)

In general, it may result in by-effects like shifting of the zero line of R(t) (see Fig. 3.15).

In Fig. 3.16 some examples of sign-sensitive measurements in the FMS are presented. It should be noted that the extraction of the sign of B_{hf} from R(t) is not straightforward and requires additional parameters or rather their signs. In Table 3.4 these parameters for different probes are collected. Some parameters are predefined by probes (e.g., anisotropy, g-factor) and cannot be changed. Others (e.g., the direction of an external magnetic field) can be chosen and influence the final view of R(t)-spectra (positive or negative slope). Anyway, they do not



Fig. 3.16: PAC spectra R(t) and their Fourier transforms $F(\omega)$ for the FMS measured by different probes in the sign-sensitive configuration after annealing of the implantation damage: (a) CuCr₂Se₄ with ¹¹¹In(¹¹¹Cd); (b) HgCr₂Se₄ with ¹¹¹mCd; (c) HgCr₂Se₄ with ¹¹¹In(¹¹¹Cd); (d) CdCr₂S₄ with ^{199m}Hg; (e) CuCr₂Se₄ with ⁷⁷Br(⁷⁷Se). All measurements were carried out at 77K with an external magnetic field perpendicular to the detector plane (upward) in the optimal sign-sensitive geometry.

change the true sign of B_{hf} . This can be illustrated by measurements with ¹¹¹In and ^{111m}Cd probes (Fig. 3.16 a, b). In these experiments the probes occupy the A-site with a positive B_{hf} . However, the slope of R(t) is negative for ^{111m}Cd and positive for ¹¹¹In probes. According to Table 3.4 this is not surprising, because ^{111m}Cd, in contrast to ¹¹¹In, has a positive anisotropy.

D (Probes						
Parameter	^{111m} Cd	¹¹¹ In	¹¹¹ Ag	¹¹⁷ Cd	⁷⁷ Br	^{199m} Hg	
Anisotropy $A_{22} > 0$	+1	-1	-1	-1	-1	+1	
B_{ext} positive ($\uparrow\uparrow z$)	+1	+1	+1	+1	+1	+1	
g-factor > 0	-1	-1	-1	+1	+1	+1	
Right-hand system	+1	+1	+1	+1	+1	+1	
Slope of R(t)	-1	+1	+1		+1	+1	
Sign of B_{hf} $\Pi =$	+1	+1	+1		-1	+1	

Table 3.4. Sign determination of the magnetic hyperfine fields in the FMS by different probes. "+1" stands for a positive answer. The sign of B_{hf} is determined as a sign product of all parameters.

In Table 3.5 the magnetic hyperfine fields of the sign-sensitive measurements with different probes are compared with those of $180^{\circ}/90^{\circ}$ -geomery and with NMR measurements [Lan70]. Good agreement between experiments with 135° - and $180^{\circ}/90^{\circ}$ -geometry proves that the approach used for the sign-sensitive measurements is reliable. For all probes substituted at the A-site a positive magnetic field was found that is in agreement with NMR results. However, the internal magnetic field at the B-site for HgCr₂Se₄ measured by ¹¹¹In(¹¹¹Cd) probes turned out to be positive in contrast to the negative value measured with ⁵³Cr by NMR. It is interesting to note that positive internal magnetic fields at the B-site were also found at ¹¹⁹Sn in configurations ACr_{1.9}Sn_{0.1}X₄ (where A = Cd, Cu; X = Se, S) using Mössbauer spectroscopy [Oka79].

The encouraging results obtained by the sign-sensitive measurements in this thesis proved that it is a promising and valuable tool in PAC, which can and should be used in the areas of solid states physics, where the sign determination of the magnetic hyperfine fields plays a crucial role.

Table 3.5. Summary of the magnetic hyperfine fields measured in the sign-sensitive configuration and compared with those measured in 180°/90°-geometry and by NMR [Lan70]. Note that all PAC-measurements were carried out at 77K, whereas for NMR experiments $T_{meas} = 4.2K$ was used. Here the NMR results are cited to show the sign of B_{hf} only. For the cases marked with "x" no substitution was observed.

Compound				A-site	B-site	C-site	
Compound			¹¹¹ In(¹¹¹ Cd)	^{111m} Cd	^{199m} Hg	¹¹¹ In(¹¹¹ Cd)	⁷⁷ Br(⁷⁷ Se)
CdCr ₂ Se ₄	ωL	135°		+165.0(5)	-664(7)		+134(4)
	(Mrad/s)	90°	165(1)	165.9(3)	671(4)	380(3)	134(2)
	B _{hf} (T)	PAC	11.2(1)	+11.3(1)	+39.7(7)	25.9(3)	-6.3(2)
		NMR	+	13.62 (¹¹¹ Cd)	-18.25 (⁵³ Cr)	-9.8	
CdCr ₂ S ₄	ω _L (Mrad/s)	135°		+147(1)	-580(6)		+101(3)
		90°	149(1)	151.2(2)	587(5)	228(4)	100(2)
	р (т)	PAC	10.2(1)	+10.3(1)	+34.7(8)	15.5(4)	-4.7(2)
	$\mathbf{D}_{hf}(\mathbf{I})$	NMR	+16.7 (¹¹¹ Cd)			-19.10 (⁵³ Cr)	
HgCr ₂ Se ₄	ω _L (Mrad/s)	135°	+137.6(5)	+136(1)	-533(5)	+338(4)	+114(6)
		90°	137.5(4)	138.0(2)	534(3)	341(2)	111(6)
	B _{hf} (T)	PAC	+9.4(1)	+9.4(1)	+31.6(6)	+23.2(2)	-5.2(3)
		NMR	+44.6 (Hg)			-17.9 (⁵³ Cr)	-9.17
CuCr ₂ Se ₄	ω _L (Mrad/s)	135°	+254(1)	+237(1) +254(1)		х	+140(6) +185(6)
		90°	255.8(2)	237(1) 255.0(7)		х	142(6) 193(2)
	B _{hf} (T)	PAC	+17.4(1)	+16.2(3) +17.4(2)		X	-6.6(4) -9.0(2)
		NMR		+7.21 (Cu)		-16.1 (⁵³ Cr)	

3.4 Temperature dependence of the electric field gradients in spinels

In the last 30 years the efg in solids have extensively been investigated with different methods. One of the purposes of such investigations was to find the reason for the temperature dependence of the efg. Here first a short overview about the temperature dependence of the efg in different substances will be given for a better understanding of the problem.

1. $T^{3/2}$ law in metals. In 1975 it was empirically discovered that the $V_{zz}(T)$ data in many metals can well be reproduced by a $T^{3/2}$ dependence [Chr76]:

$$V_{zz}(T) = V_{zz}(0) \cdot \left(1 - B \cdot T^{3/2}\right)$$
(3.10)

Thus, besides the trivial normalization factor $V_{zz}(0)$, the temperature dependence of the efg is described in many cases over the entire temperature range up to the melting points by only one free parameter *B*. This empirical temperature rule was found to be valid for pure noncubic metals, binary alloys, intermetallic compounds and some semiconductors. For instance, in the systems As, InSe and Sb_{1-x}M_x (M_x = Cd, Sn, In; x > 0.2) the efg also follows a T^{3/2} relation [Wit85]. The most surprising feature of (3.10) is its simplicity. In order to explain this behavior several models have been proposed like the "quadrons" approach, Fermi surface electrons approach, Wave function approach, Potential approach, etc., which are summarized in [Chr83]. In these models as the leading source of temperature variation, the thermal lattice vibration, the presence of conduction electrons and to a smaller extent the thermal lattice expansion were considered. Nevertheless, no consistent theoretical model reproducing the analytical form of relation (3.10) has been found so far.

2. Model of thermal lattice expansions. In the $A^{I}B^{III}C_{2}^{VI}$ semiconductors with chalcopyrite structure a surprisingly strong temperature dependence of the B^{III} -site efg measured by $^{111}In(^{111}Cd)$ was related to the anisotropic thermal lattice expansion [Unt96].

3. Model of intrinsic conductivity. In [Bar81] an increase of the efg with temperature for ¹¹¹Cd in Te was interpreted by thermally activated changes of the charge carrier density. Thereby the efg in the region of intrinsic conductivity was described by the expression

$$V_{zz}(T) = V_{zz}(0) + c \cdot e^{-\Delta E/2kT}$$
(3.11)

The alloys Sb_2Te_3 , Bi_2Te_3 [Bar83] and InTe [Bar84] showed an analogous temperature dependence. In contrast, in In_2Te_3 [Bar83, Bar84] the efg was found to be independent of temperature that is not understood.

4. Model of extrinsic conductivity. In $A^{IV}B^{VI}$ semiconductor SnSe measured with 111 In(111 Cd) [Pal99] a similar complex behavior of the temperature dependence of the efg was found. The efg strongly increases between 100 K and 300 K and thereafter remains almost constant. This situation was explained by an assumption that Cd forms very shallow acceptor levels and the thermal population of these acceptor levels saturates at around 300 K, and hence, the efg trend is governed by concentrations of charge carries.

5. General trends for semiconductors. In general, from the studies in semiconductors reported so far, the following trends of efg variation with temperature have been generalized in [Wit85]. In small-gap semiconductors ($E_g < 0.5 \text{ eV}$) the efg increases with increasing temperature and is governed by the conduction electron density, while in large-gap systems ($E_g > 1.5 \text{ eV}$) it is found to be insensitive to temperature variation, reflecting the low conduction electron density at moderate temperatures. Intermediate band gap semiconductors exhibit rather complex behavior. However, these general trends were not always confirmed.

6. Model of the trapping and detrapping of vacancies. In insulating materials pronounced temperature dependences of the efg were found too. For instance, in [Mom00] PAC measurements of tetragonal ZrO_2 with ¹¹¹In(¹¹¹Cd) also showed a clear increase of the quadrupole interaction frequency with increasing temperature. In this case the increase was attributed to the trapping of oxygen vacancies, which are present in the samples, by ¹¹¹Cd probe ions. The trapping and detrapping of vacancies occur on a time scale, which is at least two orders of magnitude faster than the lifetime of the intermediate state of the ¹¹¹Cd probe atom. As a result of the fast motion of oxygen atoms, only average efg for the possible configurations of ¹¹¹Cd probes, i.e. with and without a trapped vacancy, is observed.

7. Model of probe-related dependence. Most of the investigations in regard to the temperature dependence of the efg in solids were carried out using PAC. However, the PAC probe often constitutes an impurity center in the host material. In this case the question arises in terms of the probable influence of the impurity properties on the efg temperature dependence that may be quite different compared to the host atoms and result in a quite different efg behavior. Nevertheless, there are very few cases where the efg has been measured using two different hyperfine probes in the same compound and at the same site. In [Ada94], using two chemically different PAC probes ¹¹¹In(¹¹¹Cd) and ¹⁸¹Hf(¹⁸¹Ta), significant differences in the temperature dependences of the efg parameters in TiO₂ were found in comparison with those measured by NMR with ⁴⁹Ti. Later a systematic investigation of this problem was carried out in oxides with the bixbyite structure, namely, in In₂O₃, Sc₂O₃, Y₂O₃ and $C-R_2O_3$ (R = Sm, Eu, Gd, Dy, Ho, Er, Yb), based both on data already reported in the literature and on new experimental results [Shi98]. For this investigation ¹¹¹In(¹¹¹Cd) and ¹⁸¹Hf(¹⁸¹Ta) probes were utilized. Decay of ¹¹¹In to ¹¹¹Cd results in oxides doped with ¹¹¹Cd²⁺ ions, which represent acceptor ions at cation sites, whereas after the decay of ¹⁸¹Hf to ¹⁸¹Ta the efg is measured at the double donor ¹⁸¹Ta⁵⁺. It was found that the slope sign of the temperature dependence of the efg observed when the hyperfine probe is a single acceptor is opposite to that measured when the probe is a double donor. Thus, these facts suggest that the temperature dependences of the efg observed in rutile and oxides belonging to the bixbyite group are attributed not only to the properties of host materials, but also (and maybe to a larger extent) to the properties of ¹¹¹In(¹¹¹Cd) and ¹⁸¹Hf(¹⁸¹Ta) probes themselves.

8. Temperature dependence of the efg in spinels. In Fig. 3.17 the temperature dependences of the quadrupole coupling constant for various spinels including non-magnetic compounds (like $CdIn_2S_4$, $HgIn_2S_4$, $ZnAl_2S_4$) measured with ¹¹¹ $In(^{111}Cd)$ at the B-site are


Fig. 3.17: Temperature dependences of the quadrupole coupling constant for ¹¹¹In(¹¹¹Cd) at the B-site in various spinel compounds.

presented. The results show a surprisingly strong temperature dependence, which can be fitted by the linear function

$$v_{Q}(T) = v_{Q}(0) \cdot (1 + C \cdot T)$$
 (3.12)

The fitted parameters are collected in Table 3.6. In order to check the influence of the thermal lattice expansion on the efg behavior in spinels, *ab initio* calculations (see Chapter 4) with different lattice constants corresponding to different temperatures have been performed. As an example, in Fig. 3.18 the results for $CdIn_2S_4$ are shown, where one can clearly see that the temperature dependence of the efg due to the variation of the lattice parameters is much too small and, moreover, has even an opposite sign of the slope in order to explain the phenomenon observed.

Spinel	ν _Q (T),	MHz	V _{zz} (T) , 1	C, 10 ⁻⁴ K ⁻¹	
_	T = 0 K	RT	T = 0 K	RT	
CdCr ₂ S ₄	69.6	74.0(2)	3.5	3.7(2)	2.118
HgCr ₂ Se ₄	53.8	61.6(1)	2.7	3.1(2)	5.008
CdCr ₂ Se ₄	52.6	58.6(1)	2.6	2.9(1)	3.899
ZnAl ₂ S ₄	31.5	37.0(2)	1.6	1.8(1)	6.008
HgIn ₂ S ₄	27.2	34.7(2)	1.4	1.7(1)	9.458
CdIn ₂ S ₄	25.5	31.9(2)	1.3	1.6(1)	8.281

Table 3.6. Summary of the fitted parameters using the linear function (3.12). For comparison the results at RT are presented as well.



Fig. 3.18: Variation of the lattice parameter in $CdIn_2S_4$ with temperature (left) [Kis82] and the normalized temperature dependence of the efg for ¹¹¹In(¹¹¹Cd) at the B-site in $CdIn_2S_4$ (right) compared with theoretical values taking into account the thermal lattice expansion only [this work].

In the case of the spinel compounds the explanation of the efg temperature dependence in terms of the intrinsic (Model 3) or extrinsic (Model 4) conductivity discussed above can be excluded, since: (i) in contrast to these cases, in all spinels a linear temperature dependence was found; (ii) in spite of the fact that the spinels investigated have band gaps varying in a wide range, from semiconductors to insulators (ZnAl₂S₄), they all surprisingly revealed a similar efg behavior. The assumption related to anion vacancies (Model 6) is more probable taking into account that in spinels chalcogen vacancies are always present to a certain extent. However, in this case also a non-linear temperature dependence of the efg was found. In the current situation, the speculation proposed for the bixbyite compounds (Model 7) is the most matched to the spinels among all available, since: (i) here like in the spinels, a linear temperature dependence of the efg was observed; (ii) in the bixbyite compounds the probes occupy the sites with an octahedral coordination that is similar to the B-site of spinel compounds. However, from all probes used in this work only ¹¹¹In succeeded in occupying the B-site. Therefore at this level it is impossible to give an unambiguous answer to this question. It would be interesting to compare the results obtained in this work with the temperature dependence of the efg measured by NMR or PAC with other probes, which also occupy the B-site. Unfortunately, such experiments have not been carried out so far.

In general, the variety of the results obtained for the temperature dependence of the efg in non-metals proved that it is really a complex scientific question. Many details and some important general aspects still remain unsolved and require substantial extensions and further developments of the theory. In particular, no general theoretical models for the efg at impurity sites have been proposed so far. This fact suggests that in this situation only precise *ab initio* calculations of the band structure at $T \neq 0$ taking into account electron-phonon interactions can help to explain the efg behavior for a particular system. In this work, however, the calculations from *first principles* were carried out without taking into account thermal effects (see Chapter 4). Therefore, in order to exclude the influence of temperature, extrapolated PAC-values of the efg at 0 K have been taken for comparison with theory.

4 Theoretical calculations of the hyperfine fields

4.1 Theoretical background

4.1.1 Introduction

Over the past decade, the development of the information technologies has become a significant trend, which now touches almost every aspect of life in some way. Most significant for scientists is the emergence of numerical modeling as a powerful and widely used tool. This has been fueled by the availability of relatively inexpensive high performance workstations or PCs. Problems that required the largest supercomputers in the early 1980's can now be solved routinely on desktop machines.

In this environment it is natural that there is a strong interest in using numerical modeling in solid state physics. Historically, progress in solid state physics has almost always occurred through laboratory experimentation. Obtained knowledge was often guided by empirical trends and physical intuition, using the properties of related materials, but rarely by predictions based on numerical modeling. Now this situation is changing.

First principles calculations, using Density Functional Theory (DFT) and particularly the Local Spin Density Approximation (LSDA), proved to be a reliable and computationally tractable tool in condensed matter physics. These calculations have now impacted virtually every area of this broad field. Along with the advances in computing technology that occurred during the last decade, there have been important algorithmic improvements. For certain classes of materials it is now feasible to simulate systems containing 100 or more atoms in a unit cell. This opens the door for the direct application of these techniques in studying of real materials problems. The following brief description of DFT and related methods is mainly based on [Sin94, Bla99].

4.1.2 Density functional theory

An efficient and accurate scheme for solving the many-electron problem of a crystal (with nuclei at fixed positions) is the local spin density approximation within density functional theory. DFT is based on the theorem of Hohenberg and Kohn [Hoh64]. It states that the total energy E of a non-spin-polarized system of interacting electrons in an external potential (for our purposes the Coulomb potential due to the nuclei in a solid) is given as a functional of the ground state electronic density ρ .

$$E = E(\rho) \tag{4.1}$$

Hohenberg and Kohn further showed that the true ground state density is the density that minimizes $E(\rho)$, and that other ground state properties are also functionals of the ground state density. Unfortunately, the Hohenberg-Kohn theorem provides no guidance about the form of $E(\rho)$, and therefore the utility of DFT depends on the discovery of sufficiently accurate approximations. In order to do this the unknown functional $E(\rho)$ is rewritten as the Hartree

total energy plus another unknown functional $E_{xc}(\rho)$, called the exchange-correlation functional.

$$E(\rho) = T(\rho) + E_{Ne}(\rho) + E_{H}(\rho) + E_{NN}(\rho) + E_{xc}(\rho)$$
(4.2)

Here $T(\rho)$ denotes the kinetic energy, $E_{Ne}(\rho)$ is the Coulomb interaction energy between the electrons and the nuclei, $E_{NN}(\rho)$ arises from the Coulomb interaction of the nuclei with each other, and $E_H(\rho)$ is the Hartree component of the electron-electron energy.

$$E_{H}(\rho) = \frac{e^{2}}{2} \int d^{3}\boldsymbol{r} \, d^{3}\boldsymbol{r}' \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$
(4.3)

In the LSDA, $E_{xc}(\rho)$ is written as

$$E_{xc}(\rho) = \int d^{3} \boldsymbol{r} \rho(\boldsymbol{r}) \varepsilon_{xc}(\rho(\boldsymbol{r}))$$
(4.4)

where $\varepsilon_{xc}(\rho)$ is approximated by a *local function of the density*.

Kohn and Sham [Koh65] wrote the electron density as a sum of single particle densities, and used the variational principle to obtain a prescription for determining the ground state energy. In particular, they showed that the correct density is given by the self-consistent solution of a set of single particle Schrödinger-like equations, known as the Kohn-Sham (KS) equations, with a density dependent potential

$$\left[T + V_{Ne}(\mathbf{r}) + V_{H}(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\varphi_{i}(\mathbf{r}) = \varepsilon_{i}\varphi_{i}(\mathbf{r})$$
(4.5)

The density is given by a sum over the occupied orbitals

$$\rho(\mathbf{r}) = \sum_{occ} \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r})$$
(4.6)

Here the highest occupied orbital is determined by the electron count, φ_i are single particle orbitals, ε_i are the corresponding eigenvalues, T is the kinetic energy operator, V_{Ne} is the Coulomb potential due to the nuclei, V_H is the Hartree potential and V_{xc} is the exchange correlation potential. Both V_H and V_{xc} depend on ρ

$$V_{H}(\mathbf{r}) = e^{2} \int d^{3}\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
(4.7)

and

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}(\rho)}{\delta \rho(\mathbf{r})}$$
(4.8)

A calculation entails the self-consistent solution of (4.5 - 4.8). Thus, instead of having to solve a many-body Schrödinger equation, using DFT one has the much easier problem of determining the solution of single particle equations, along with a self-consistency requirement.

DFT based electronic structure methods can be classified according to the representations that are used for the density, potential and, most importantly, the Kohn-Sham orbitals. The choice of representation is made to minimize the computational and human (e.g. programming) costs of calculations, while maintaining sufficient accuracy. Nearly all



Fig. 4.1: Schematic flow-chart for self-consistent density functional calculations.

approaches rely on a basis set expansion for the KS orbitals, i.e. use a basis, in which the KS orbitals are:

$$\varphi_i(\mathbf{r}) = \sum c_{i\alpha} \,\phi_\alpha(\mathbf{r}) \tag{4.9}$$

where $\phi_{\alpha}(\mathbf{r})$ are the basis functions and $c_{i\alpha}$ are expansion coefficients.

Since, given a choice of basis, these coefficients are the only variables in the problem (note that the density depends only on the KS orbitals) and the total energy in DFT is variational, solution of the self-consistent KS equations amounts to determining $c_{i\alpha}$ for the occupied orbitals that minimize the total energy.

The energy can be rewritten using the single particle eigenvalues

$$E(\rho) = E_{NN}(\rho) + \sum_{occ} \varepsilon_i + E_{xc}(\rho) - \int d^3 \boldsymbol{r} \,\rho(\boldsymbol{r}) \left(V_{xc}(\boldsymbol{r}) + \frac{1}{2} V_H(\boldsymbol{r}) \right)$$
(4.10)

where the sum is over the occupied orbitals, and ρ , V_H and V_{xc} are given by (4.6), (4.7), and (4.8), respectively.

In the most common approach to density functional calculations (illustrated schematically in Fig. 4.1), the optimization of $c_{i\alpha}$ and the determination of the self-consistent charge density are separated and performed hierarchically. In this scheme it is necessary to repeatedly determine $c_{i\alpha}$ that solve the single particle equations (4.5) for a fixed charge density. If the true occupied KS orbitals can be expressed as linear combinations of the basis functions, then optimizing $c_{i\alpha}$ will yield the exact self-consistent solution. With a fixed basis the coefficients $c_{i\alpha}$ are the only parameters that can be varied, otherwise there are additional parameters that determine the basis functions. An output charge density is constructed from the eigenvectors using (4.6), and then mixed with the input to yield a refined input for the next iteration. The simplest mixing scheme is straight mixing:

$$\rho_n^{i+1} = (1-\alpha)\rho_{in}^i + \alpha \rho_{out}^i$$
(4.11)

where the superscript refers to the iteration number and α is the mixing parameter. Since the time required to perform a self-consistent calculation is proportional to the number of iterations needed to reach self-consistency, it is important to choose an efficient mixing of input and output charge densities. Therefore considerable effort has been devoted to devising more sophisticated mixing procedures, using information from previous iterations to accelerate the convergence. The most common is Broyden's method [Bro65].

4.1.3 Spin-polarized systems

In the generalization of DFT to spin-polarized systems, the charge density $\rho(\mathbf{r})$ is decomposed into the two spin densities: for spin-up $\rho_{\uparrow}(\mathbf{r})$ and spin-down electrons $\rho_{\downarrow}(\mathbf{r})$.

$$\rho(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) + \rho_{\downarrow}(\mathbf{r}) \tag{4.12}$$

In this case the Hohenberg-Kohn theorem generalizes to state that the ground state total energy is a variational functional of the spin densities.

$$E = E\left(\rho\uparrow, \rho\downarrow\right) \tag{4.13}$$

The energy may be decomposed as in (4.2). The Coulomb terms remain functionals of the total density, but T and E_{xc} become functionals of the two spin densities. The variational principle is invoked to generate the spin-polarized KS equations of spin density functional theory

$$\left[T + V_{Ne}(\mathbf{r}) + V_{H}(\mathbf{r}) + V_{xc,\sigma}(\mathbf{r})\right] \varphi_{i\sigma}(\mathbf{r}) = \varepsilon_{i\alpha} \varphi_{i\sigma}(\mathbf{r})$$
(4.14)

$$\rho_{\sigma}(\mathbf{r}) = \sum_{occ} \varphi_{i\sigma}^{*}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r})$$
(4.15)

and

$$V_{xc,\sigma}(\mathbf{r}) = \frac{\delta E_{xc}(\rho_{\uparrow}, \rho_{\downarrow})}{\delta \rho_{\sigma}(\mathbf{r})}$$
(4.16)

where σ is the spin index. The total energy expression then becomes

$$E = E_{NN} + \sum_{occ} \varepsilon_i + E_{xc} (\rho_{\uparrow}, \rho_{\downarrow}) - \frac{1}{2} \int d^3 \mathbf{r} V_H(\mathbf{r}) \rho(\mathbf{r}) - \int d^3 \mathbf{r} \left[\rho_{\uparrow}(\mathbf{r}) V_{xc,\uparrow}(\mathbf{r}) + \rho_{\downarrow}(\mathbf{r}) V_{xc,\downarrow}(\mathbf{r}) \right]$$

$$(4.17)$$

These equations have to be solved self-consistently as in the non-spin-polarized case. The differences are:

- 1. The density consists of two spin densities.
- 2. There are separate sets of KS orbitals for the two spin components, and two sets of single particle equations need to be solved to obtain them.
- 3. V_{xc} is *spin-dependent*; this is the only term in the single particle Hamiltonian that is explicitly spin-dependent.

4. In the total energy expression E_{xc} is a functional of the two spin densities. E_{xc} favors spinpolarized solutions and T opposes them. Whether or not a material is magnetic, depends on the balance between these terms.

Finally, because of the additional degrees of freedom contained in the spin density, spinpolarized KS equations often have multiple self-consistent solutions corresponding to different stable spin configurations. Determining which of these is the ground (lowest energy) state and if there are any solutions that have been missed may require an exhaustive search.

4.1.4 The full potential LAPW method

The Linearized Augmented Plane Wave (LAPW) method proved to be one of the most accurate methods for the computation of the electronic structure of solids. It is based on the density functional theory and uses the Local Spin Density Approximation (LSDA). Like most "energy-band methods", the LAPW method is a procedure for solving the Kohn-Sham equations (4.5) for the ground state density, total energy, and eigenvalues (energy bands) of a many-electron system (here a crystal) by introducing a basis set, which is especially adapted to the problem.



Fig. 4.2: Partitioning of the unit cell into atomic spheres (I) and an interstitial region (II).

This adaptation is achieved by dividing the unit cell into (I) non-overlapping atomic spheres (centered at the atomic sites) and (II) an interstitial region (see Fig. 4.2). In the two types of regions different basis sets are used:

1. (I) inside atomic sphere t, of radius R_t , a linear combination of radial functions times spherical harmonics $Y_{lm}(\mathbf{r})$ is used

$$\phi_{k_n} = \sum_{lm} \left[A_{lm} \, u_l(r, E_l) + B_{lm} \, \dot{u}_l(r, E_l) \right] Y_{lm}(\hat{r}) \tag{4.18}$$

where $u_l(r, E_l)$ is the regular solution of the radial Schrödinger equation for energy E_l and the spherical part of the potential inside sphere t; $\dot{u}_l(r, E_l)$ is the energy derivative of u_l taken at the same energy E_l . A linear combination of these two functions constitutes the linearization of the radial function. The coefficients A_{lm} and B_{lm} are functions of k_n (see below) determined by requiring that this basis function matches (in value and slope) the corresponding basis

function of the interstitial region; u_l and \dot{u}_l are obtained by numerical integration of the radial Schrödinger equation on a radial mesh inside the sphere.

2. (II) in the interstitial region a plane wave expansion is used

$$\phi_{k_n} = \frac{1}{\sqrt{\Omega}} e^{ik_n r} \tag{4.19}$$

where $k_n = k + K_n$; K_n are the reciprocal lattice vectors and k is the wave vector inside the first Brillouin zone, Ω is the cell volume. Each plane wave is augmented by an atomic-like function in every atomic sphere.

The solutions to the Kohn-Sham equations are expanded in this combined basis set of LAPW's according to the linear variation method

$$\psi_k = \sum_n c_n \phi_{k_n} \tag{4.20}$$

and the coefficients c_n are determined by the Rayleigh-Ritz variational principle. The convergence of this basis set is controlled by a cutoff parameter $R_{mt}K_{max} = 6 - 9$, where R_{mt} is the smallest atomic sphere radius in the unit cell and K_{max} is the magnitude of the largest **K** vector in equation (4.20).

In order to improve upon the linearization (i.e. to increase the flexibility of the basis) and to make possible a consistent treatment of semicore and valence states in one energy window additional (k_n independent) basis functions can be added. They are called "local orbitals" [Sin91] and consist of a linear combination of two radial functions at two different energies and one energy derivative (at one of these energies):

$$\phi_{lm}^{LO} = \left[A_{lm} u_l(r, E_{1,l}) + B_{lm} \dot{u}_l(r, E_{1,l}) + C_{lm} u_l(r, E_{2,l}) \right] Y_{lm}(\hat{r})$$
(4.21)

The coefficients A_{lm} , B_{lm} and C_{lm} are determined by the requirements that ϕ^{LO} should be normalized and has zero value and slope at the sphere boundary.

In its general form the LAPW method expands the potential in the following form

$$V(r) = \begin{cases} \sum_{lm} V_{lm}(r) Y_{lm}(\hat{r}) & \text{inside sphere} \\ \sum_{K} V_{K} e^{iKr} & \text{outside sphere} \end{cases}$$
(4.22)

and the charge densities analogously. Thus no shape approximations are made and the procedure is frequently called the "full-potential LAPW" (FLAPW) method.

Several forms of LSDA potentials exist in the literature. Recent progress has been made going beyond the LSDA by adding gradient terms of the electron density to the exchange-correlation energy or its corresponding potential. This has led to the generalized gradient approximation (GGA) [Per96]. GGA is, in general, considered as a significant improvement over LSDA and nowadays is mostly preferred for such calculations.

More complete information about DFT and the LAPW method can be found in [Wim81], [Bla83] and [Sin94].

4.1.5 The electric field gradient formalism within the LAPW method

For a long time, electric field gradients (efg) in solids were estimated by assigning some effective charges to the ions of the crystal and performing a point charge summation [Wet61]. Since such calculations do not account for any onsite polarization, Sternheimer antishielding factors [Ste54, Shm80, Gus95] were introduced to describe core polarization (which was assumed to be proportional to the external efg), whereas chemical bondings were only roughly estimated (see section 2.2.2). The accuracy of such corrections was often limited.

Development and progress in DFT and in the LAPW method have made it possible to perform calculations for complicated solids or impurity systems [Bla00] and to determine efg from first principles without any assumptions of ionic charges or Sternheimer antishielding factors. From such calculations the origin of the efg can be analyzed and its relation to chemical bonding and the sensitivity to the asymmetry in the charge density can be clarified. Thus, nowadays it is feasible to complement experiment even in complicated cases and gain new insight due to a combination of both experiment and theory.

The efg tensor can be obtained as the second derivatives of the Coulomb potential at the nucleus. The Coulomb potential is determined from the total (electronic and nuclear) charge density in the crystal by solving Poisson's equation. Both the total charge density and the Coulomb potential are vital ingredients of electronic structure calculations and it is therefore straightforward to calculate the efg once the charge distribution has been determined theoretically.

The general expression for the principal component of the efg tensor, arising from a (nuclear plus electronic) charge density $\rho(\mathbf{r})^1$, is defined as

$$V_{zz} = \int \rho(\mathbf{r}) \frac{2P_2(\cos\theta)}{r^3} d^3 \mathbf{r}$$
(4.23)

where P_2 is the second-order Legendre polynomial. Once the charge density of a system is known to high precision, the efg can be obtained numerically from (4.23) without further approximations, since the charge density contains all ionic, covalent, and polarization effects in the solid [Sch92]. No assumptions are made about ionicities or specific charge distributions.

The charge density coefficients $\rho_{LM}(r)$ can be obtained from the wave functions by

$$\rho_{LM}(r) = \sum_{E_{nk} < E_F} \sum_{lm} \sum_{l'm'} R_{lm}(r) R_{l'm'}(r) G_{L l l'}^{M mm'}$$
(4.24)

where $G_{Lll'}^{M\,mm'}$ are Gaunt numbers (an integral over a product of three spherical harmonics, stemming from two wave-functions and the L, M of the density expansion) and $R_{lm}(r) = A_{lm} u_l(r) + B_{lm} \dot{u}_l(r)$ denote the LAPW radial wave functions (of state E_{nk}).

For a given charge density the Coulomb potential is obtained numerically by solving Poisson's equation in form of a boundary value problem using a method proposed by Weinert

¹ Here the electron charge *e* is included in $\rho(\mathbf{r})$.

[Wei81]. This yields the potential coefficients $V_{LM}(r)$. For the efg calculation only the L = 2 terms near the nucleus are needed; in the limit $r \rightarrow 0$ the asymptotic form of the potential $r^L V_{LM} Y_{LM}$ can be used, and this procedure yields

$$V_{2M} = -C_{2M} \int_{0}^{R} \frac{\rho_{2M}(r)}{r^{3}} r^{2} dr + C_{2M} \int_{0}^{R} \frac{\rho_{2M}(r)}{r^{3}} \left(\frac{r}{R}\right)^{5} r^{2} dr + \frac{5C_{2M}}{R^{2}} \sum_{K} V(K) j_{2}(KR) Y_{2m}(\hat{K})$$
(4.25)

with $C_{20}=2(4\pi/5)^{1/2}$, $C_{22}=(3/4)^{1/2}C_{20}$, and the spherical Bessel function j_2 . The first term (called *valence* efg) corresponds to the integral of (4.23) taken over the atomic sphere; after integration over \mathscr{P} and φ a radial integration must be carried out. The second and third terms (called *lattice* efg) arise from the boundary value problem and from charge contributions outside the considered sphere. *It should be noted that this definition of the lattice efg differs from that based on a point charge model*. With these definitions the diagonal terms of the traceless efg tensor with respect to the crystallographic axis *a*, *b*, and *c* are

$$V_{aa} = -1/2 V_{20} + V_{22},$$

$$V_{bb} = -1/2 V_{20} - V_{22},$$

$$V_{cc} = V_{20}.$$

(4.26)

In many simple cases the off-diagonal elements of the efg tensor vanish due to symmetry, but if non-diagonal terms exist diagonalization of the efg tensor is required. By ordering the eigenvalues according to their magnitudes it is defined that $|V_{zz}| \ge |V_{yy}| \ge |V_{xx}|$. The efg tensor is characterized by the largest component V_{zz} and the anisotropy parameter η defined as $\eta = (V_{xx} - V_{yy})/V_{zz}$, where η varies between 0 (axial symmetry) and 1 (see section 2.2.2).

4.2 WIEN97 program

4.2.1 Flow of programs

The WIEN97 package [Bla99] consists of several independent programs, which are linked via C-*SHELL SCRIPTS* (see Table 4.1). First of all one has to carry out an initialization, which consists of running a series of small auxiliary programs generating the inputs for the main programs. Then a self-consistency cycle (scf) should be started and repeated until convergence criteria are met.

Program	Description
Initialization	
NN	a program which lists the nearest neighbors up to a specified distance and thus helps to determine the atomic sphere radii
LSTART	generates free atomic densities and determines how the different orbitals are treated in the band structure calculations (i.e. as core or band states, with or without local orbitals)
SYMMETRY	generates the space group symmetry operations, determines the point group of the individual atomic sites, generates the LM expansion for the lattice harmonics and determines the local rotation matrices
KGEN	generates a k-mesh in the Brillouin Zone
DSTART	generates a starting density for the self-consistency cycle by superposition of atomic densities generated in LSTART
Self-consistency	cycle (SCF)
LAPW0	generates potential from density
LAPW1	calculates valence bands (eigenvalues and eigenvectors)
LAPW2	computes valence densities from eigenvectors
LCORE	computes core states and densities
MIXER	mixes input and output densities

Table 4.1. Programs of the WIEN97 package used in calculations.

4.2.2 Parameters for calculations

There are many input parameters, which one should specify in order to perform calculations. For some of them the input files are automatically generated with some default values, which should be a reasonable choice for most cases. Nevertheless, there are several crucial parameters, which depend on calculated structure and therefore should draw higher attention. In Table 4.2 the most important parameters for calculations are collected.

Parameter	Description
RMT	muffin-tin radius, sphere size
k-points	number of k-points in the whole Brillouin Zone
RKMAX	$R_{mt}K_{max}$ determines the number of basis functions (size of the matrices)
GMAX	magnitude of the largest vector in charge density Fourier expansion
LMAX	maximum l value for partial waves used inside atomic spheres
R0	first radial mesh point
NPT	number of radial mesh points

Table 4.2. Some important parameters for calculations.

4.2.3 Choice of muffin-tin radii

On the one hand, the magnitude of muffin-tin radius R_{mt} is not so crucial as in the Muffintin Approach, since the standard ionic radii are less important in determination of R_{mt} . On the other hand, one should take into account the following points, when choosing the size of R_{mt} [FAQ, WIEN97]:

- choosing them smaller will make the calculations more "expensive", since more plane waves will be needed, but a little bit more accurate (e.g., plane waves are better basis functions, reduced linearization error);
- one should take care so that core charge would not leak out of the spheres. If it is the case, one should either increase the sphere of the atom, where the core charge leaks out, or include some high lying states as valence states by putting an extra LO (local orbitals) in the basis set for that state;
- R_{mt} should not be too different even when geometry would allow, otherwise this will lead to quite different "effective" $R_{mt}K_{max}$ values for these atoms and eventually lead to approximative linear dependencies and resulting "ghostbands".

4.2.4 Choice of the other parameters

It is not simple to define beforehand what value for which parameter should be specified. The only way is to perform a number of calculations for a given structure with different values of parameters in order to find out the optimum in terms of computational time and accuracy. Therefore several test calculations for non-magnetic and ferromagnetic spinels have been carried out. In Fig. 4.3 and 4.4 the influence of the plane wave basis set ($R_{mt}K_{max}$) and the number of k-points in the irreducible wedge of the Brillouin zone (IBZ) on the total energy, the force at the C-site and the efg at the B- and C-sites for CdIn₂S₄ is presented, respectively. One can clearly see that good convergence could be reached for $R_{mt}K_{max} \ge 7.5$ and the number of k-points ≥ 4 . The dependence of the total energy E_{tot} on $R_{mt}K_{max}$ can easily be interpreted in terms of the variational principle: the better the basis set, the lower the total



Fig. 4.3: Total energy (a), force at the C-site (b), efg-values (c) and Matrix Size (d) (number of functions in the plane wave basis set) for $CdIn_2S_4$ versus convergence parameter $R_{mt}K_{max}$.



Fig. 4.4: Total energy (a), force at the C-site (b), efg-values (c, d) for $CdIn_2S_4$ versus number of k-points in the irreducible wedge of the Brillouin zone.

energy. Fig. 4.3 illustrates the importance of a good basis set: a poor basis set can cause qualitatively wrong results. Obviously, the basis set improves by increasing $R_{mt}K_{max}$, but the parameter range is strongly restricted by main memory limitations and computational time. The WIEN97-specific parameters NPT and R0 defining the radial mesh within the spheres were tested as well. However, these parameters have only minor influence on the results and therefore are not reported here. Finally, according to the test calculations the following parameters for the spinel structure were chosen: GGA [Per96], $R_{mt}K_{max} = 8$, 20 k-points in the IBZ, GMAX = 14, LMAX = 12. The values of R_{mt} and effective $R_{mt}K_{max}$ along with matrix sizes for the spinels calculated in this work are listed in Table A.1 (Appendix).

4.2.5 Convergence criteria

There are three convergence criteria used in WIEN97: *total energy convergence*, magnitude of *force convergence* and *charge convergence* [Bla99]. During a calculation only one criterion can be specified. Different systems require quite different limits. The fact that a system has converged according to one quantity does not imply that it has converged using another one, i.e. it can still be changing from iteration to iteration. In this work mostly the charge convergence criterion was used. One should bear in mind that during scf cycles not all terms of the forces are included in order to save CPU time. Therefore the force at the C-site did not converge to zero (see Fig. 4.5, b). When the calculation had converged, an additional final iteration was carried out in order to include an additional force term (so-called "Pulay" force contribution [Pul69]), referred to as an incomplete basis set correction.



Fig. 4.5: Convergence of total energy (a), force at the C-site (b) and efg at the B- and C-sites (c, d) for $CdIn_2S_4$ versus number of iterations.

4.3 Theoretical determination of anion parameters

As mentioned in section 1.1, there are two structural parameters for spinels: the lattice constant a and the anion parameter u. Only the lattice constant a can be determined from the positions of the X-ray reflections with high accuracy. For the evaluation of the parameter u a structure refinement is necessary. The intensities of the reflections must be determined accurately and the corresponding structure amplitudes have to be fitted. Such a procedure has a limited accuracy. Therefore, the u parameter has a larger uncertainty than the lattice parameter a and for some of the substances there are no experimental values available at all. At the same time, the efg strongly depend on the u parameter (see Fig. 4.6 c, d).

With the help of the WIEN97-program it was feasible to determine theoretical u parameters on the basis of the experimental lattice constants a using two different numerical approaches, namely, from the minimum of the total energy or directly using the forces at the nuclei. Fig. 4.6 shows such a dependence of the total energy on the u parameter $E_{tot}(u)$ in the case of CdIn₂S₄. The total energy reveals a nearly quadratic dependence on the u parameter and consequently the force, defined as $F_x = -\delta E/\delta R_x$ (where R_x is the position of atom X), but calculated directly using the wave functions, shows only very small deviations from linearity. The theoretical anion parameters were determined by both minimizing total energies and adjusting for vanishing forces with excellent agreement between these two approaches. The results are illustrated in Fig 4.7, where comparisons between theoretical and experimental values from X-ray diffraction measurements are presented (complete information can be found in Table A.1, Appendix). The spinel compounds are sorted in ascending order with



Fig. 4.6: Total energy (a), force at the C-site (b), efg at the B- and C-sites (c, d) versus anion parameter u for CdIn₂S₄.



Fig. 4.7: Chart of anion parameters u for a number of spinel compounds determined experimentally [Lan70] and theoretically from the minimum of the total energy and using the forces at the nuclei, respectively. The sequence of the compounds is ascending with respect to the lattice constant a.

respect to the lattice constant a. From this chart it is clearly seen that there is no certain direct dependence between the anion parameter u and the lattice constant a.

There are two approaches to the choice of lattice constants for calculations. In the first one, the experimental lattice constants are taken and then only the internal parameter optimization has to be carried out, if necessary. The second one stands for a complete optimization of both the lattice constants and the internal parameters. Of course, it would be desirable to optimize the lattice constant of the spinels by minimization of the total energy in addition to the anion parameters. However, several test calculations for spinels revealed that the efg remain practically the same for a wide range of changes of the lattice constants for a given compound, provided certainly that for every lattice constant the anion parameter is optimized (see Fig. 4.8). In other words, the small deviations in the experimental lattice constants (less than 2 %) play an insignificant role in comparison with well-performed optimizations of the anion parameters. Therefore in this work the experimental lattice constants were taken for the calculations.



Fig. 4.8: Efg at the B-site (left) and optimized anion parameter u (right) versus lattice constant a for CdIn₂S₄. At the left the square and triangle symbols represent the dependences for u = 0.25914 (the optimal u for the structure with $a = a_{exp} = 10.8434$ Å) and u = 0.260, respectively. For the dependence with circles the anion parameter u was optimized for every point (see figure at the right).

4.4 Theoretical electric field gradients

Once the anion parameters are determined, one can calculate the efg at the B- and C-sites. In Table 4.3 the theoretical efg for a number of spinel compounds are summarized and compared with those obtained from PAC and NMR measurements. In the case of NMR measurements one can make direct comparison with calculations, since all measurements were carried out with host atoms. As to PAC measurements, one can either estimate results using rough Sternheimer corrections (see section 2.2.2) or carry out so-called "impurity-case" calculations (see section 4.6). Nevertheless, even with the Sternheimer corrections the experimental results are in good agreement with theory (except In-spinels).

Table 4.3. Theoretical and experimental efg for a number of spinel compounds. The efg values of the PACmeasurements are given for 0 K using an extrapolation of the temperature dependences of efg (see section 3.4). Here ¹ [Sta69], ² [Bab83], ³ [Mae97], ⁴ [Mit96], ⁵ [Men96].

		C – site (η= 0)				
Spinel	WIEN97	PAC	of ¹¹¹ In(¹¹¹	C d), 0K	NMR, 4.2 K	WIEN97
	$\mathbf{v}_{zz}(\mathbf{u}_{E_{min}}),$ 10^{21} V/m^2	ν _Q , MHz	$\frac{ \mathbf{V}_{\mathbf{z}\mathbf{z}} }{10^{21} \text{ V/m}^2}$	V _{zz} corrected	$\frac{ \mathbf{V}_{\mathbf{z}\mathbf{z}} }{10^{21} \text{ V/m}^2}$	$V_{zz}(u_{E_{min}}),$ 10 ²¹ V/m ²
CdCr ₂ Se ₄	-1.21	52.6	2.6	1.2	0.99 ¹⁾	6.39
HgCr ₂ Se ₄	-1.31	53.8	2.7	1.3	1.081)	11.51
CdCr ₂ S ₄	-1.35	69.6	3.5	1.6	1.05 1)	2.54
CuCr ₂ Se ₄	-0.37				0.11 2)	1.20
ZnAl ₂ S ₄	-0.20	31.5	1.6	0.23	0.22(1)	2.97
CdIn ₂ S ₄	-2.16	25.5	1.3	1.2		2.43
HgIn ₂ S ₄	-2.57	27.2	1.4	1.3		4.80
CdIn ₂ O ₄	-5.23	84.8 ⁵⁾	4.2	3.8		1.74
CuCr ₂ S ₄	-0.78				0.66 ²⁾	0.61
CuCr ₂ Te ₄	-0.05					0.51
HgCr ₂ S ₄	-1.42				1.05 1)	4.96
MgAl ₂ O ₄	-0.90				1.03 ³⁾	1.69
ZnAl ₂ O ₄	-0.94				1.02 4)	1.80

A careful analysis of the obtained theoretical results revealed that the absolute value of the efg at the B-site increases following the sequences Cu, Cd, Hg for A-cations; Al, Cr, In for B-cations and Te, Se, S, O for C-anions, respectively. Moreover, it turned out that the calculated efg show a strong linear dependence on the u parameter and can be divided into two groups (see Fig. 4.9). The intersection of the two lines lies at u = 0.2572, where the efg is about zero.



Fig. 4.9: The calculated efg at the B-site versus the u parameter. All spinels turned out to be divided into two groups in terms of the behavior of efg, which is reflected by two linear dependences.

It is well known that the efg is proportional to the anisotropy of the charge density distribution. On the other hand, the actual distance of the nearest neighbors to the site under consideration has an influence on the charge distribution, which in turn significantly changes the efg. That is why it is worth analyzing the behavior of tetrahedral R^{T} and octahedral R^{O} cation-anion distances with change of the *u* parameter. For a value of u = 0.250 the anions form an exactly cubic close packed array, and define a regular tetrahedron around the A-sites (point group symmetry $\overline{4}3m$) and a regular octahedron around the B-sites (m3m). The octahedral cation-anion distance (bond length) in this case is 1.155 times larger than the tetrahedral bond length. As *u* increases, the anions displace along a [111] direction, causing the tetrahedrons to enlarge at the expense of the octahedrons, while the symmetry of the latter degenerates to $\overline{3}m$. The nearest-neighbor tetrahedral bond length R^{O} are given by:



Fig. 4.10: The ratio of the nearest-neighbour octahedral bond length (\mathbb{R}^{O}) and the nearest-neighbour tetrahedral bond length (\mathbb{R}^{T}) versus the *u* parameter.

$$R^{T} = a \cdot \sqrt{3(u - 0.125)^{2}}$$
(4.27)

$$R^{O} = a \cdot \sqrt{(3u^{2} - 2u + 0.375)}$$
(4.28)

Thus the two structural parameters *a* and *u* unambiguously define the tetrahedral and octahedral bond lengths. If one takes the ratio of cation-anion distances R^O/R^T then the lattice parameter is cancelled and only the *u* parameter is variable. The analysis of this dependence (Fig. 4.10) reveals that it is close to a linear one and has a critical point at *u* = 0.2625, where the two bond lengths R^T and R^O are equal. The compounds with $R^O/R^T > 1$ correspond to the Group I in Fig. 4.9 (except ZnAl₂S₄) and the compounds with $R^O/R^T < 1$ to the Group II.

As mentioned above, the Sternheimer corrections for all spinels investigated yield good agreement with theory except for the In-spinels, which form the Group I in Fig. 4.9. The reason of this fact seems to be not understood at first. The Sternheimer corrections are known to work perfectly for compounds with ionic bond characters. In spinels, however, the bonding character represents a mixture of ionic and covalent contributions and the determination of the ratio of these contributions is not so simple. In order to obtain a qualitative picture for the bonding character in the vicinity of the B-sites, the calculations of electron density for each compound were carried out. For clarity, in such calculations only the states of the upper valence band were taken into account. As the area of the electron density plots, the plane depicted in Fig. 4.11, which represents a section of an octahedron, was chosen. The results revealed quite different bonding characters for substances from the different groups (see Fig. 4.12). In the Group I (In-spinels) there is a trend to have more covalent contribution around the B-site, whereas in the Group II more ionic bond character is observed. This may



Fig. 4.11: The plane used for the electron density plots, which represents a section of an octahedron.

qualitatively elucidate the nature of the division of $V_{zz}(u)$ into two groups and explain the disagreement with the Sternheimer corrections for the substances from the Group I.

It is interesting to note that according to band structure calculations carried out with WIEN97 all spinels belonging to the Group I are indirect semiconductors (except Cucompounds, which reveal metallic behavior) and those belonging to the Group II are

direct semiconductors. In Fig. 4.13 some examples of band structures for compounds from the different "groups" are presented. An analysis of the band structures revealed that the bottom of the conduction bands for all spinels is mainly composed of the *s*-orbitals of the A-atoms and has an absolute minimum at the Γ -point (k = 0). This means that the character of the energy gap is defined solely by the position of the maximum in the valence bands: at the Γ -point for direct and at the *K*-point for indirect gap, respectively. It is worth noting that the highest level of the valence bands consists mainly of the *p*-orbitals of the C-atoms (for ferromagnetic spinels *d*-states of transition Cr-atoms contribute as well). These findings are in good agreement with other band structure calculations carried out for various spinels [Con94, Ogu81, Mo96, Lav00, Mel70]. Thus, one can see a direct relation to the anion parameter, since the formation of the bands significantly depends not only on the species of atoms, which compose the spinel structure, but also on the location of the atoms with respect to each other that in spinels is mainly defined by the *u* parameter.



Fig. 4.12: Charge densities of $HgIn_2S_4$ belonging to the Group I (left) and $ZnAl_2S_4$ belonging to the Group II (right) for the upper valence band in the range from 0 to 0.5 *e*/a.u.³.



Fig. 4.13: Examples of band structures for spinel compounds: $HgIn_2S_4$ (left) belongs to the Group I (indirect semiconductors); $ZnAl_2S_4$ (right) belongs to the Group II (direct semiconductors).

In order to understand the meaning of the intersection of the two lines in Fig. 4.9 it is necessary to consider some properties of the spinel structure. One of the interesting features of spinels is a wide range of cation distributions found in this system. Some of the spinels, e.g., $ZnAl_2S_4$, are known to have the "normal" distribution, where 1/8 of the tetrahedral voids in a face-centered-cubic (fcc) close-packed anion sublattice are occupied by the A-atoms and 1/2 of the octahedral voids are occupied by the B-atoms. Other spinels, e.g., FeIn₂S₄, are known to have the "inverse" distribution, where the tetrahedral voids are occupied by the B-atoms and the octahedral voids are occupied by both A- and B-atoms. Intermediate phases with the formula $(A_{1-x}B_x)[A_xB_{2-x}]C_4$ also exist. Here, cations in the square brackets occupy the octahedral sites and cations in the parentheses occupy the tetrahedral sites. The cation inversion parameter *x* ranges from 0 for a normal spinel to 1 for an inverse spinel. For a completely random distribution *x* is equal to 2/3. In fact, the cation distribution in spinels is still a subject of discussion [Wei01]. At the same time, it strongly affects the electronic structure of spinels, which in turn causes the change of such parameters as the band gap, efg, anion parameters, etc.

The electrostatic energy has long been considered to be one of the most important factors in determining the cation distribution in spinels. Therefore, in order to understand the influence of the cation distribution on the anion parameter, electrostatic lattice energy calculations have been carried out by O'Neill and Navrosky [Nei83]. They performed the calculations of the electrostatic energy $E_M = -M(e^2/a)$ of normal and inverse spinels as a function of u. Here, M is the Madelung constant, which in this case is a function of the charges on each ion and also of the anion parameter u. A larger Madelung constant means a lower electrostatic energy. The calculated Madelung constants are plotted in Fig. 4.14, where one can see that for normal spinels the Madelung constant increases with rising u, while for inverse spinels the Madelung constant decreases with increasing u. These calculations show that the intersection point for the normal and inverse curves is at u = 0.2555. For values of u less than this one, the electrostatic energy would favor the inverse distribution, and vice versa. Therefore compounds with large A-atoms, and hence large u tend to have the normal spinel structure. Thus, the Coulomb energy can qualitatively explain this trend.

Later Wei and Zhang [Wei01] systematically studied the site preference of cation distribution in spinels using a first-principle band-structure method within the local density approximation. They found that the critical u value, at which the Madelung constants for the normal and inverse spinels are equal, is shifted from u = 0.2555 to u = 0.258 (see Fig. 4.14).

In section 4.6 it will be shown that a very rough approximation of the inverse spinel structure for CdIn₂S₄, where one A-atom (Cd) is substituted at the B-site, leads to a decrease of the anion parameter from u = 0.25918 for the normal spinel structure to u = 0.25609 for the "inverse" spinel structure. Thus, taking into account that all spinels calculated by WIEN97 in this work were treated as normal and according to the electrostatic lattice energy calculations, one can assume that the value of u = 0.2572 obtained from the intersection of the V_{zz}(u) dependence in Fig. 4.9 is a theoretical minimum for spinels with a normal structure, determined from first principles.



Fig. 4.14: Calculated Madelung constants as a function of the anion displacement *u* for normal (solid line) and inverse spinels: a) by O'Neill and Navrosky [Nei83] (dashed line); b) by Wei and Zhang [Wei01] (dotted line).

4.5 Calculations of magnetic properties

Transition metals and their compounds display a particularly rich set of properties, many of which are related to magnetism. Another reason for interest is related to the wide range of magnetic experimental studies that, until now, have poorly been supported by reliable theoretical calculations. The existing difficulties stem either from problems using LSDA to describe the electronic structure of ferromagnetic materials containing highly correlated electrons, or simply from the difficulty of dealing with very complex crystal structures. A special problem of the magnetic calculations has always been the reliable determination of theoretical magnetic hyperfine fields, since these values are very sensitive to magnetic structure.

The first and the simplest task were calculations of the magnetic hyperfine fields of pure transition metals such as Fe, Ni, Co. In spite of the fact that this problem seemed to be solved already in the eighties, in 1999 it was raised again [Aka99] and new methods for calculations of the magnetic hyperfine fields were suggested. Moreover, it is worth noting that nearly all available calculations of magnetic structures were mostly directed to band-structure calculations, determination of magnetic hyperfine fields. That is why before starting with such a complicated system as the spinel structure, it is reasonable first to test the LAPW method for simple transition metals such as Fe, Ni, Co. This approach can be justified by the following reasons: (i) these ferromagnetic metals have already been investigated; (ii) this task does not require so much computational efforts. In Table 4.4 the theoretical and experimental results of the magnetic hyperfine fields and magnetic moments for Fe, Ni and Co are collected.

Table 4.4. Comparison of the magnetic hyperfine fields and magnetic moments of Fe, Ni and Co calculated by the LSDA, GGA, RPA (Random Phase Approximation), CS (Combined Scheme) with experimental values (EXP). In this work for the calculations of Fe, Ni and Co the following parameters were used: $R_{mt}K_{max} = 8.0$, $R_{mt} = 2.0$, 1050-1540 k-points in the IBZ, GMAX = 14, LMAX = 12.

Matarial		Magnetic	Magnetic moments (μ_B)				
	LSDA (this work)	GGA (this work)	RPA [Aka99]	ACSEXPG499][Aka99][Rao75](this	GGA (this work)	EXP [Hel88]	
Fe	-30.89	-33.16	-32.9	-39.4	-33.1(1)	2.302	2.218
Ni	-10.41	-11.60	-13.5	-13.2	-9.7(1)	0.673	0.605
Со	-26.99	-28.47	-32.3	-33.9	-22.8(1)	1.716	1.71

The next magnetic compound used for test calculations was Fe₃Al, which is a well-studied example of magnetic-component systems. This structure is more complicated than that of the previous ferromagnetic metals. A unit cell of Fe₃Al consists of four face-centered-cubic sublattices *A*, *B*, *C*, and *D*. The iron atom occupies *A*, *B*, and *C* sublattices, while *D* is occupied by Al. The space group of this structure is *Fm3m* (225) [Pea85], which finally

results in three non-equivalent positions with three non-equivalent magnetic hyperfine fields for Fe(1), Fe(2) and Al, respectively. In Table 4.5 the theoretical and experimental results of the magnetic hyperfine fields and magnetic moments for Fe₃Al are presented. For these calculations the following parameters were chosen: a = 5.7923Å, $R_{mt} = 2.0$, $R_{mt}K_{max} = 8.0$, Spinpolarized GGA, 2000 k-points (72 k-points in the IBZ), GMAX = 14, LMAX = 12.

Table 4.5. Comparison of the magnetic hyperfine fields and magnetic moments of Fe₃Al calculated by the GGA with experimental values (EXP).

Atom	Magnetic hy	perfine fields (T)	Magnetic moments (μ_B)		
Atom	GGA (this work)	EXP	GGA (this work)	EXP [Ste71]	
Al	-4.93	-2.7 [Bur70]	- 0.071	_	
Fe(1)	-31.61	-29.37 ± 0.33 [Ste68]	+2.427	$+2.14 \pm 0.1$	
Fe(2)	-26.25	-21.1 ± 0.33 [Ste68]	+1.954	$+1.46 \pm 0.1$	

When examining Tables 4.4 and 4.5 one can observe an acceptable agreement between theory and experiments for not so complex magnetic structures. However, for the binary compound Fe_3Al the deviation between the theoretical and experimental results for magnetic moments is larger than that for the simple ferromagnetic metals.

Nevertheless, the promising results of the test calculations encouraged us to try the magnetic spinel compounds. However, it is worth noting that these calculations take twice as much computational time as compared to non-magnetic spinels, since in this case the spin-polarized calculations have to be performed, i.e. some steps are done for spin-up and spin-down electrons separately (see section 4.1.3). In Table 4.6 the theoretical and experimental PAC and NMR results are collected. An analysis of the table reveals that at the cubic A-site the theoretical magnetic hyperfine fields are of the same order of magnitude as compared to the experimental results. But at the B- and C-sites they are significantly smaller than the experimental ones. Nevertheless, the signs of the magnetic hyperfine fields were determined correctly.

The parameters for the calculations were chosen as discussed in section 4.2.4: spinpolarized GGA, $R_{mt}K_{max} = 8.0$, 20 k-points in the IBZ, GMAX = 14, LMAX = 12. Normally, the number of k-points is a crucial parameter, which in some cases may significantly influence the results of calculations, especially if a magnetic structure is under consideration. In order to exclude a numerical aspect as the cause of the discrepancy, a calculation with *large number of k-points*, namely, 8000 k-points (256 k-points in the IBZ), for CuCr₂Se₄ was carried out². However, this calculation did not improve the values of the magnetic hyperfine fields. Therefore one can conclude that this problem is not related to the chosen parameters. Since the nature of the discrepancy is apparently the same for all magnetic spinels, one can expand this conclusion to all magnetic spinel compounds.

² This very time consuming calculation was kindly performed by Dr. J. Kortus at the Center for Computational Materials Science, Naval Research Laboratory, Washington DC, USA.

Table 4.6. Comparison of the magnetic hyperfine fields of the ferromagnetic spinel compounds calculated by WIEN97 with experimental PAC and NMR results. All spinels at the A- and C-sites were measured by PAC (this work) with host atoms, unless the probe is explicitly indicated. The uncertainties of the PAC results are omitted here, but they can be found in Table 3.3. All PAC measurements at 77K were carried out with an external magnetic field of 0.5(1) T.

S-rimel	$\mathbf{B}_{\mathbf{h}\mathbf{f}}$	(T), A-	site	Bhf	· (T), B-	site	B _{hf} (T), C-site		
Spiner	WIEN97 0K	PAC 10K (77K)	NMR 4.2K [Lan70]	WIEN97 0K	WIEN97 PAC ¹¹¹ Cd NMR WI 0K 10K 4.2K 0 (77K) [Lan70] 0	WIEN97 0K	PAC 10K (77K)	NMR 4.2K [Lan70]	
CdCr ₂ Se ₄	+21.86	+13.4 (+11.3)	+13.62	-3.35	(25.9)	-18.25	-3.56	(-6.3)	-9.8
CdCr ₂ S ₄	+26.98	+15.9 (+10.3)	+16.7	-4.04	(15.5)	-19.10	-2.75	(-4.7)	
HgCr ₂ Se ₄	+44.33	+41.6 (+31.6)	+44.6	-3.38	+34.0 (+23.2)	-17.9	-2.46	(-5.2)	-9.17
CuCr ₂ Se ₄	+10.05	+17.5 ^{Cd}	+7.21	-1.94		-16.1	-0.78	(-9.0)	
HgCr ₂ S ₄	+58.47		+52.43	-4.28		-19.0	-2.27		
CuCr ₂ S ₄	+12.47			-3.39			-2.11		
CuCr ₂ Te ₄	+5.62		+3.99	-0.71		-15.1	-5.42		-18.75

The results of band structures and magnetic moments (see Table 4.7) are similar to those calculated by other groups [Ant99, Con94, Ogu81] also using first principles methods. However, these calculations were restricted only to band structure calculations and determinations of magnetic moments so that no magnetic hyperfine fields were available for comparison. In Table A.2 (Appendix) the calculated magnetic moments for distinct atoms and for a formula unit of magnetic spinels are collected.

It is worth noting that in many transition metal ferromagnets, the non-spin polarized solution is metastable, and self-consistent iterations that do not start close enough to the magnetic solution may not converge to it. In other words, it is not unusual at all to have multiple minima in the Energy(magnetic moment) curve. This may lead to completely wrong results. In order to overcome this problem the Fixed Spin Moment (FSM) procedure [Wil84] was developed, which greatly simplifies the study of magnetic materials, particularly those with ferromagnetic phases. The idea underlying the FSM approach is to do total energy calculations with the total magnetic moment constrained to fixed values. In this way the total energy as a function of the magnetic moment can be mapped out and the local minima can be readily identified and studied. Thus with the FSM procedure, self-consistent spin densities can be obtained for a magnetic moment estimated to be close to that of the magnetic solution and these could be input to an unconstrained calculation. However, the magnetic moments determined in the normal spin-polarized calculations (Table 4.7) are not so far from the experimental values, and therefore FSM-calculations might not be necessary. As supposed,

several attempts with FSM-calculations showed that in the case of spinel compounds this method does not help to solve the problem.

Compound	Atom	WIEN97 (this work)	Other theories	Experiment
	Cu	-0.121	-0.082	0.01 ± 0.13
CuCreSo	Cr	2.652	2.824	2.81 ± 0.11
CuC12564	Se	-0.143	-0.142	-0.25 ± 0.14
			[Ant99]	[Col67]
	Cu	-0.134	-0.089	$\textbf{-0.07} \pm 0.02$
CuCr.S.	Cr	2.501	2.652	2.64 ± 0.04
CuCl ₂ 54	S	-0.126	-0.099	-0.05 ± 0.11
			[Ant99]	[Yam79]
	Cu	-0.076	-0.102	0.05 ± 0.14
CuCr.To	Cr	2.838	3.187	3.11 ± 0.16
	Te	-0.135	-0.213	-0.25 ± 0.14
			[Ant99]	[Col67]
	Cd	0.016	0.02	
CdCroSe	Cr	2.911	2.91	
CuC12564	Se	-0.081	-0.09	
			[Con94]	

Table 4.7. The calculated and experimental magnetic moments (in μ_B) for some ferromagnetic spinels. The experimental values were obtained using the polarized neutron diffraction technique.

All calculations in this thesis were carried out using the scalar relativistic approximation without spin-orbit interaction. However, the spin-orbit term may be important for calculations of magnetic materials as well as materials containing heavy elements. Unfortunately, the spin-orbit term couples spin-up and spin-down wave-functions. This means that if one began (without the spin-orbit coupling) with *n* basis functions (i.e., a $n \times n$ secular equation for each spin) and then included the spin-orbit coupling in the Hamiltonian, one would end up with a $2n \times 2n$ secular equation to solve at each k-point. Because of the cubic scaling of the computing time with the size of the secular equation, this implies that a calculation including the spin-orbit term would require roughly eight times the resources of a scalar relativistic calculation. Moreover, in spin-polarized calculations the presence of the symmetry of the system. Therefore taking all these difficulties into account, the calculations including the spin-orbit term have not been carried out in this work.

4.6 Impurity-case calculations

The electric field gradients discussed in section 4.4 were calculated for host atoms at the lattice sites. But most of the PAC-probes represent doping atoms (impurities) in the substances investigated. For a long time the so-called Sternheimer antishielding correction (see section 2.2.2) has been used for a rough estimation of the corresponding efg. But nowadays it is feasible to carry out *ab initio* "impurity-case" calculations in order to obtain realistic values of the efg.

Nevertheless, from the theoretical point of view, the determination of the efg at an impurity has several difficulties that make a realistic calculation very cumbersome to perform, since:

- the efg is very sensitive to the asymmetry of the charge distribution in the neighborhood of the impurity. Hence, a very accurate electronic-structure calculation is required;
- the introduction of an impurity atom in the elementary cell reduces the symmetry and increases the computational time drastically;
- normally, in order to mimic the real structure, a supercell has to be created;
- an atomic relaxation of the nearest neighbors of the introduced impurity might be necessary.

In most of the spinel compounds only ¹¹¹In(¹¹¹Cd) probes happened to occupy the B-site, where the quadrupole interaction at ¹¹¹Cd was measured. Thus the efg of a Cd-impurity at the B-site constitutes the main computational task. The normal spinel structure has three nonequivalent atoms, a center of symmetry and contains 14 atoms in the primitive cell (see Table 4.8). For the impurity-case configuration a basis of at least 56 atoms ($A_8B_{15}CdC_{32}$) should be used, which consists of four primitive cells of the "normal" structure, where one of the B-atoms is replaced by Cd. Despite the fact that such a new structure has a much lower symmetry (11 nonequivalent atoms) it still has a center of inversion. It is worth noting that inversion symmetry leads to a real symmetric instead of a complex hermitian eigenvalue problem, and this reduces the required computer memory by a factor of two.

Property	Normal case	Impurity case
Number of the nonequivalent atoms	3	11
Number of the symmetry operations	48	12
Center of symmetry (inversion)	yes	yes
Number of atoms for all positions of the point group	56	224
Atoms to calculate	14	56
Time of a calculation on Pentium III 700 MHz, 256 MB	1-2 days	9-12 days

Table 4.8. Comparison of some properties between normal (host) and impurity-case calculations in the case of the spinel structure.

Since the computational time scales with the third power of the number of atoms per cell, the size of the supercells that can be treated within an acceptable time is very limited. In the case of the spinel structure the creation of the real supercell would lead to more than 100 atoms per cell. Therefore instead of the real supercell, the conventional spinel unit cell was used, but now with the basis of 56 atoms instead of 14. Under these circumstances even the conventional spinel unit cell, which contains 56 atoms, can be considered with high reliability as a quasi-supercell, but with dimension of the normal unit cell.

In Table 4.8 one can see that the computational time significantly increases in the impurity-case calculation. Therefore a reasonable compromise between the required accuracy and the time of a calculation should be found, especially if one intends to carry out a relaxation. For normal (host) calculations the following parameters for the spinel structure were used: GGA-approach, $R_{mt}K_{max} = 8.0$, 20 k-points in the IBZ, GMAX = 14, LMAX = 12. But from section 4.2.4 it is known that the reasonable convergence could also be reached for $R_{mt}K_{max} = 7.5$ and 4 k-points in the IBZ. Therefore, the following four types of calculations were carried out:

- 1. host compound: 20 k-points in the IBZ, $R_{mt}K_{max} = 8$;
- 2. host compound: 4 k-points in the IBZ, $R_{mt}K_{max} = 7.5$;
- 3. quasi-impurity system an artificial supercell, where the host atom is used instead of the impurity-atom: 6 k-points in the IBZ, $R_{mt}K_{max} = 7.5$;
- 4. real impurity-case: 6 k-points in the IBZ, $R_{mt}K_{max} = 7.5$.

In Table 4.9 the results of such calculations for $ZnAl_2S_4$ are collected. In principle, the results for a single unit cell and the supercell without impurity should be the same, but due to different basis sets and k-meshes small differences occurred, indicating the accuracy limits of such calculations.

Atom Nor	Normal c 20k-points	alculation s, RKM=8	Normal calculation 4k-points, RKM=7.5		Nr Atom	Quasi-impurity Al _{Al} 6k-points, RKM=7.5			
	F , mRy/a.u.	$V_{zz},$ 10^{21} V/m^2	F , mRy/a.u.	V_{zz} , V_{zz} , 10^{21} V/m^2		F , mRy/a.u.	$V_{zz}, 10^{21} V/m^2$	η	
Zn	0	0	0	0	1	Zn	0.008	0	0
ZII	0	0	0	0	2	Zn	0.028	0	0.002
					3	Al	0.037	-0.189	0.002
Al	0	-0.195	0	-0.188	4	Al	0	-0.190	0.002
					5	Al	0.009	-0.189	0.002
					6	S	1.809	2.987	0
					7	S	1.771	2.987	0.000
S	1.767	2.965	1.797	2.957	8	S	1.815	2.987	0.000
					9	S	1.788	2.986	0.000
					10	S	1.757	2.986	0.000
Al	0	-0.195	0	-0.188	11	Al	0	-0.190	0

Table 4.9. Comparison between normal (host) and quasi-impurity calculations for $ZnAl_2S_4$. The atom 11 is the quasi-impurity in this structure. Here RKM $\equiv R_{ml}K_{max}$.

Daramatar	ZnA	1_2S_4	CdI	n_2S_4	HgIn ₂ S ₄		
1 al alletel	Normal	Impurity	Normal	Impurity	Normal	Impurity	
V_{zz} , $10^{21} V/m^2$	-0.195	-0.772	-2.160	-1.194	-2.573	-1.328	
F , mRy/a.u.	1.767	78.244	0.723	10.215	0.164	9.209	

Table 4.10. Results of the impurity-case calculations for Cd at the B-site in $ZnAl_2S_4$, $CdIn_2S_4$ and $HgIn_2S_4$ compared with the normal (host) calculations. $|\mathbf{F}|$ is the absolute value of the forces at the nearest neighbors of the impurity Cd-atom.

It is interesting to note that forces, V_{zz} and η values at the inequivalent lattice sites in the artificial supercell - which, however, are of course equivalent in the unit cell - turned out to be identical within the quoted accuracy that encouraged us to go on with real impurity-case calculations. For other spinels (e.g., CdIn₂S₄, HgIn₂S₄) the situation is similar.

The results of the impurity-case calculations (see Table 4.10) revealed that the efg at the impurity atom for $CdIn_2S_4$ and $HgIn_2S_4$ changes by a factor of two, whereas for $ZnAl_2S_4$ it changes even by a factor of four as compared to the host atom. For the In-spinels the forces at

the nearest neighbors of the impurity are not so large, because of the similar size of the In- and Cd-atoms. However, in the case of $ZnAl_2S_4$ large forces (78.2 mRy/a.u.) emerge that certainly require subsequent relaxation at least in the nearest environment of a Cd-atom in order to obtain realistic efg.

For relaxations of the atoms in the spinelsupercell the program "mini", which is included in the WIEN97-package, was used. This program performs movements of the atomic positions according to the calculated forces on the nuclei. It automatically determines the equilibrium position of all individual atoms obeying the symmetry constrains of a given space group. In this work a damped Newton dynamics method was utilized. This method performs geometry optimization according to $\mathbf{R}_{i}^{l+l} = \mathbf{R}_{i}^{l} + \delta_{i} \mathbf{F}_{i}^{l} + \eta_{i} (\mathbf{R}_{i}^{l} - \mathbf{R}_{i}^{l-l}),$ where \boldsymbol{R}_{i}^{l} and \boldsymbol{F}_{i}^{l} are the coordinate and force at the time step *l*, respectively (see Fig. 4.15). When the force has changed its direction from the last to the present time step (or it is within the tolerance), η_i will be set to $1 - \eta_i$. For every step of the geometry relaxation a complete calculation



Fig. 4.15: Flow-chart of the mini-program.

with given internal parameters is required. In order to achieve a reasonable convergence of the relaxation altogether 7-14 or even more steps are necessary. Therefore such a relaxation procedure takes a rather long time. Moreover, in order to increase the efficiency of the relaxation process, good initial values, such as delta δ_i and damping parameters η_i , which determine the speed of motion, should be found for each individual system. And last but not least, the number of atoms, involved in the relaxation process, also plays a crucial role in terms of the speed of convergence. Therefore, at first, the relaxation of only the nearest environment of the impurity atom has been carried out, i.e. the relaxation of six S-atoms surrounding a Cd-atom.

In Table A.3 (Appendix) the summary of the impurity-case calculations for $ZnAl_2S_4$ without and with relaxation are presented, and in Fig. 4.16 the calculated total energy, the force on the atoms being relaxed, the distance impurity-nearest shell (six S-atoms) and the efg at the impurity atom during the relaxation process are shown. An analysis of the table and diagrams revealed that after the relaxation of the nearest environment of the Cd-impurity the distance from the impurity atom (Cd) to the nearest neighbors (S-atoms) increased by 7 % (0.163 Å) that resulted in an increase of the efg at the Cd-site by 54 %.

It is interesting to note that shifting of the S-atoms surrounding the Cd-impurity is not radial, but along the body diagonals (i.e., along <111> direction) away from the impurity atom towards the A-cations so that the symmetry of the structure remains the same (see Fig. 4.17). This means that the octahedron becomes less distorted. For the normal spinel structure it would imply a decrease of the anion parameter u and a diminution of the



Fig. 4.16: Calculated total energy (a), force on the atoms being relaxed (b), distance impurity-nearest shell (c), and efg at the Cd-impurity (d) during the relaxation process for $ZnAl_2S_4$.



Fig. 4.17: Part of the spinel supercell showing the directions of relaxation for the first nearest environment of a Cd-impurity (six S-atoms).

tetrahedrons. In this context it is interesting to analyze $CdIn_2S_4$. In the first approximation the very local environment of the impurity Cd-atom can be considered as a part of the inverse spinel, where a host Cd-atom occupies the B-site. In this case according to the calculations the anion parameter changes from u = 0.25918 for the normal spinel structure to u = 0.25609 for the "inverse" spinel structure. This fact is consistent with the assumption described in section 4.4 that the anion parameter u = 0.2572 is a theoretical minimum for spinels with a normal structure.

Taking into account the relatively large change of the efg due to the relaxation of the first atomic shell of the impurity atom, it is reasonable to check the influence of the second and third atomic shells too. Since the force on the given atom is calculated as superposition of all acting forces of the surrounding environment, the rigid second and third atomic shell could impede further movement of the atoms being relaxed that otherwise would result in longer distance $R_{Cd-Atom10}$ and another efg. As expected, the relaxation of all three atomic shells caused an increase of the distance $R_{Cd-Atom10}$ by 0.01 Å, but it has not changed the efg at the impurity-site significantly (see Table A.3, Appendix) so that its change is in the order of the basis set effects (less than 5 %). Therefore one can conclude that within the quoted accuracy it is sufficient to carry out the relaxation only with the first atomic shell around the impurity atom. For other spinels similar results were obtained.

In Table 4.11 the calculated values of the efg at the B-site for $CdIn_2S_4$, $HgIn_2S_4$ and $ZnAl_2S_4$ are compared with the experimental ones. The agreement between theory (host calculation) and experimental NMR-data³ for $ZnAl_2S_4$ is perfect. In the PAC-experiments with ¹¹¹In(¹¹¹Cd) probes, as discussed in section 3.4, a strong temperature dependence of the efg at the B-site was observed that was found to be not connected with the thermal expansion.

³ The NMR measurement was kindly carried out by Dr. E. Brendler and Prof. B. Thomas, TU Bergakademie Freiberg, Chemical Department.

Therefore, in order to exclude thermal effects, the extrapolated values of the efg at 0 K were taken. In section 4.3 it was shown that in spinel compounds a variation of the lattice constants (e.g., due to thermal expansion or uncertainties of experimental values) result in very small changes of the efg, provided that for every lattice constant the anion parameter is optimized. That is why in the performed calculations the lattice constants at 300 K were taken.

		V _{zz} , WIE	Vzz, Experiment (this work)			
Substance	Host	Impurity without relaxation	Impurity with relaxation	corrected to Cd (Sternheimer)	NMR ²⁷ Al (300 K)	PAC ¹¹¹ Cd (0 K)
CdIn ₂ S ₄	-2.16	-1.19	-1.31	2.4		1.3
HgIn ₂ S ₄	-2.57	-1.33	-1.40	2.9	_	1.4
ZnAl ₂ S ₄	-0.20	-0.77	-1.18	1.3	0.22(1)	1.6

Table 4.11. Calculated and experimental values of V_{zz} (in 10^{21} V·m⁻²) at the B-site for some spinel compounds.

For comparison, the theoretical values corrected to the Cd-probe, using the Sternheimer antishielding factors ($\gamma_{\infty}^{Cd} = -24.4$, $\gamma_{\infty}^{In} = -21.9$, $\gamma_{\infty}^{Al} = -2.76$ [Gus95]), are also included in Table 4.11. In spite of the fact that this correction for ZnAl₂S₄ was satisfactory, for CdIn₂S₄ and HgIn₂S₄, in contrast, it predicted quite wrong results, namely, even an increase of the efg instead of a decrease. The possible explanation of this phenomenon is given in section 4.4. The experimental results at ¹¹¹Cd are lower by a factor of roughly two for CdIn₂S₄, HgIn₂S₄ and higher by a factor of eight for ZnAl₂S₄ as compared to the host B-site. This has also been shown by the impurity-case calculations. Hence, the electronic charge distribution around the impurity is very different from that of a regular B-site. These facts prove that such corrections widely-used in the past are not always appropriate for estimations of the measured efg.



Fig. 4.18: Chart showing the influence of the impurity atom in $CdIn_2S_4$ on the efg (left axis) and forces (right axis) with respect to the distance $R_{Cd-atom}$ from the impurity atom (Cd) to a given atom. Here NC = Normal Calculation, i.e. the calculation without impurity, and IC = Impurity Calculation without relaxation. Missing bars mean zero for corresponding values.

Calculations and experimental results for other materials [Sch98] also support these findings. Therefore in these cases only *ab initio* calculations of efg including impurity specific effects can yield realistic results.

Nevertheless, under these circumstances a question arises about physical correctness of such an impurity model, since the ratio between impurity and host atoms is larger compared to the experimental case. However, in the chosen supercell the impurity atom has the same five atomic shells of the nearest neighbors (26 atoms) as in the ideal situation of a highly diluted impurity system. The influence of the impurity on the other atoms in the supercell is confined within these five atomic shells as illustrated in Fig. 4.18. From the analysis of the efg and forces for all atoms of the supercell one can conclude that indeed atoms, which are located further than the fifth atomic shell ($R_{Cd-atom} > 4.76$ Å), are practically not affected by the introduction of the impurity.

An additional argument can be presented on the basis of similar impurity-case calculations successfully carried out by other groups for various compounds and impurities even with less number of atoms in the supercell than in this work (see Table 4.12). All these facts suggest that within the required accuracy and actual computer performance the model chosen in this work is appropriate and realistic, and the calculated efg are reliable.

Compound	Number of atoms in SC	SC formula	Impurity	Relaxation	Reference
TiO ₂	12	Ti ₃ CdO ₈	Cd	yes	[Err00]
CdTe	32	$Cd_{16}Te_{15}A_{Te}$	N, P, As, Sb	yes	[Lan00]
WC	16	W ₇ ReC ₈		yes	[Sch98]
WS ₂	24	W7ReS16	Po	no	
WSe ₂	24	W7ReSe16	Ke	no	
WSi ₂	24	W7ReSi16		no	
Fe	16	Fe ₁₅ X	RbXe	yes	[Cot01]
CdIn ₂ S ₄	56		Cd	yes	this work
HgIn ₂ S ₄	56	$A_8B_{15}CdC_{32}$			
ZnAl ₂ S ₄	56				

Table 4.12. Review of some impurity-case calculations carried out for various compounds and impurities. Note that in the case of Fe spin-polarized calculations were performed and the magnetic hyperfine fields were determined, respectively. Here SC = supercell.

4.7 Technical details

As mentioned in section 4.2, the WIEN97 program performs self-consistent calculations, i.e. several iterations should be carried out until the specified convergence criterion is met. For spinels this range amounts to 11-18 iterations. Since in spinel compounds the anion parameters have to be determined (see section 4.3), at least four calculations with different u parameters should be accomplished, in order to obtain a proper energy curve, plus one final test calculation with the determined u. Besides, several test calculations should be carried out in advance (see section 4.2.4) in order to find the optimal initialization parameters such as the number of k-points, $R_{mt}K_{max}$ and others. That is why before 2000 even ordinary (host) calculations for spinel compounds were time consuming due to limited PC performance and impurity-case calculations were not possible at all (see Table 4.13).

Property		Normal c	Impurity-case			
	Pentium II, 350 MHz, 512 MB RAM		Athlon 1400 MHz, 512 MB RAM		Athlon 1400 MHz, 512 MB RAM	
	RKM=8 20k-points	RKM=7.5 4k-points	RKM=8 20k-points	RKM=7.5 4k-points	RKM=8 20k-points	RKM=7.5 6k-points
Matrix Size	1639	1397	1639	1397	6660	5517
required memory	65 MB	57 MB	65 MB	57 MB	422 MB	300 MB
one iteration	1h 50m	18m	30m	6m	42h 20m	7h 20m
number of iteration	10-15	10-15	10-15	10-15	10-15	10-15
one step	1d	4h	7h	1.5h	17.6-26.5d	3-4.6d
number of steps	5	5	5	5	10-15	10-15
total time	5d	20h	1.5d	7.5h	176-397d	30-69d

Table 4.13. Comparison of average timing between non-spinpolarized normal (host) and impurity-case calculations for $CdIn_2S_4$ using PCs with different performance. Here RKM $\equiv R_{mt}K_{max}$.

But with the development of new powerful PCs and compilers with high performance, impurity-case calculations and even relaxations have become feasible. However, even in this situation the measures described below had to be taken in order to minimize the computational efforts.

- 1. A reasonable compromise between accuracy and duration of a calculation by means of minimization of such parameters as $R_{mt}K_{max}$ and the number of k-points was found.
- 2. **k-point parallelization**. Within the distribution of WIEN97 it is possible to execute numerically the most intensive parts of the code in parallel. Parallelization is achieved on the k-point level by distributing subsets of the k-mesh to different processors and subsequent summation of the results of these subsets. The implemented strategy can be



Fig. 4.19: Time gain for a calculation with respect to number of PCs in the cluster. Here τ^N is normalized time of calculation.

used both on a multiprocessor architecture and on a heterogeneous (even multiplatform) network. The requirements, setup and configuration of the k-point parallelization are described in detail in the WIEN97 User's Guide [Bla99]. In Fig. 4.19 the efficiency of this approach with respect to the number of PCs in the cluster is presented. With increase of the number of PCs in the cluster the time gain becomes smaller. Therefore it is more reasonable to construct, e.g., instead of one cluster with ten PCs, two clusters with five PCs for calculations of two different tasks. For the calculations described in this chapter a cluster of four PCs (two Athlon 900MHz, 512MB RAM, 1 GB swap and two Athlon 1400MHz, 512MB RAM, 1 GB swap) was formed. *Alone this procedure has sped up the calculations by a factor of roughly four*.

- 3. Iterative diagonalization. The LAPW1-routine sets up the Hamiltonian and finds by diagonalization eigenvalues and eigenvectors. Since diagonalization is usually the most time consuming part of the calculations, in WIEN97 a special approach called "iterative diagonalization" was implemented. This scheme starts from an old eigenvector (previous scf-iteration) and produces only approximate eigenvalues/vectors, but can be significantly faster than "full diagonalization", in particular, if the ratio of matrix size to number of relevant (e.g. occupied) eigenvalues is large. However, this procedure needs additional memory.
- 4. The reasonable accuracy of the convergence was selected in order to eliminate additional iterations, which lead to small changes versus long computational time.
- 5. The usage of a high performance compiler for a given architecture and operating system and successive compilation of the code with optimized parameters can substantially decrease the computational time. Therefore, the commercial pgf77-compiler (Portland Group High Performance Fortran) [www.pgroup.com] for Linux was set up. The WIEN97 code compiled with pgf77 turned out to be faster by a factor of 1.5-3.5 than that compiled with the freeware g77-compiler.

6. And last but not least, RAM (Random-Access Memory) on every PC connected in the cluster was increased up to 512 MB (originally 256 MB) in order to minimize the usage of "swap" (virtual memory on the hard disk), which is certainly slow as compared to DRAM.

Thus, the calculations carried out in this work have shown that nowadays, in principle, there is no need to buy an expensive workstation, and even such complicated and time consuming calculations as impurity-cases with relaxations can be performed on a cluster of PCs within a reasonable time, provided that the measures mentioned above have been taken.
Summary

The ferromagnetic spinels (FMS) CdCr₂Se₄, CdCr₂S₄, HgCr₂Se₄ and CuCr₂Se₄ have acquired scientific interest and importance since the 60-ties due to their outstanding properties like giant magnetoresistance, photoferromagnetic effects, red shift of the optical absorption edge, giant Faraday rotation and others that provides the basis for the design of devices with various applications. Moreover, the FMS have particular perspectives in spintronics because of the coexistence of semiconducting and ferromagnetic properties, and relatively high Curie temperatures in comparison with other ferromagnetic semiconductors. It should be emphasized that properties of FMS can be changed by aimed doping in a wide range using e.g. Ag, In, Ga and Br as impurities or by solid solutions made from the various combinations of the FMS. Furthermore, in some cases even new anomalous effects can be obtained that do not take place in host materials.

Numerous experiments carried out on FMS with various methods have clarified many questions from the crystal growth conditions to electrical, optical and magnetic properties. However, at the same time, new problems appeared that were beyond the scope of the methods utilized for the characterization of the FMS. Taking into account the drastic influence of the doping impurities on the properties of the FMS, the lattice site occupation of the doping atoms and their behavior under various thermal conditions and treatments is of utmost importance. However, the knowledge concerning the site occupations was based on indirect information like electrical or magnetic properties obtained by classical macroscopic methods. For instance, the most important dopants Ag and In have been supposed to occupy solely the A-site until now.

In contrast, by the perturbed angular correlations (PAC) technique it is possible to obtain information on the position and behavior of the corresponding doping atoms in the substances investigated on an atomic scale. Moreover, in the arsenal of the PAC method the following probe nuclei ^{111m}Cd(¹¹¹Cd), ¹¹¹In(¹¹¹Cd), ¹¹¹Ag(¹¹¹Cd), ⁷⁷Br(⁷⁷Se), ¹¹⁷Cd(¹¹⁷In), ^{199m}Hg(¹⁹⁹Hg) and ¹⁰⁰Pd(¹⁰⁰Rh) are available and represent either the doping impurities mentioned above or constituents of the FMS used in solid solutions.

In this work, as method of introduction of radioactive probes, ion implantation (mainly at the ISOLDE-implanter/CERN) was utilized exclusively. Thereby the extent and annealing behavior of implantation damages could be studied *in situ*. The experiments in the paramagnetic state indicated that the damaged environments of the implanted probes, which manifest themselves via a frequency distribution of the quadrupole interaction, are not described by a statistical arrangement of atoms, but they are correlated with the symmetry of the undisturbed lattice. Moreover, measurements in the ferromagnetic state surprisingly showed a defined magnetic dipole interaction for as-implanted samples. These facts suggest that the spin ordering is not influenced to such an extent by implantation defects as the lattice ordering.

As mentioned above, the site occupation and behavior of implanted probes was one of the main subjects of the investigations in this thesis. The site occupation in the FMS can not be explained by the valency of impurity atoms or their ionic radii only, since it depends on many

factors. In terms of the PAC-study the FMS have an advantage versus non-magnetic substances, since they can be examined in two states: in the paramagnetic and in the ferromagnetic state. That is why by combination of results of the electric quadrupole and magnetic dipole interactions one can unambiguously determine the site occupation and the behavior of implanted probes. Additionally, one can utilize the beneficial property of the PAC-probes ^{111m}Cd(¹¹¹Cd), ¹¹¹In(¹¹¹Cd) and ¹¹¹Ag(¹¹¹Cd), which decay via the same exited level and have the same daughter nucleus ¹¹¹Cd. Hence, the final experimental results can be compared directly.

In the FMS ^{111m}Cd(¹¹¹Cd), ¹¹¹Ag(¹¹¹Cd), ¹¹⁷Cd(¹¹⁷In) and ^{199m}Hg(¹⁹⁹Hg) probes were found to occupy the A-site and ⁷⁷Br(⁷⁷Se) the C-site exclusively. However, for ^{199m}Hg in CuCr₂Se₄ evidence of both the A- and B-site occupations was observed. As to ¹¹¹In(¹¹¹Cd) probes, the investigations unambiguously showed that in CdCr₂Se₄, CdCr₂S₄ and HgCr₂Se₄ they substitute both the A-site and the B-site with a certain ratio depending on the thermal treatment. Thus, in these materials the A-site substitution after "normal" annealing amounts to 11(3) % in CdCr₂Se₄, 30(4) % in CdCr₂S₄ and 62(3) % in HgCr₂Se₄. This behavior can be understood considering the ratio of the octahedral and tetrahedral bond lengths R^O/R^T of the host compounds decreasing from CdCr₂Se₄ to HgCr₂Se₄.

The PAC-experiments carried out for $CuCr_2Se_4$ with ^{111m}Cd, ¹¹¹Ag(¹¹¹Cd) and ⁷⁷Br(⁷⁷Se) probes at different temperatures have revealed the presence of the asymmetric splitting in the Fourier spectrum, which manifests itself by an additional peak with a lower frequency and amplitude compared to the main peak. This effect has not been observed in the other FMS. According to the Lotgering-based model of the electronic structure for CuCr₂Se₄ [Lot64, Lot68] this phenomenon can be explained by the presence of Cr³⁺ and Cr⁴⁺ cations.

¹¹¹In(¹¹¹Cd) probes behave in CuCr₂Se₄ anomalously. First, they exclusively substitute the A-site contrary to results for the other FMS and the ratio R^{O}/R^{T} , which preferably suggests the B-site occupation. Second, for ¹¹¹In(¹¹¹Cd) probes only a single line in the Fourier spectrum was observed and no asymmetric splitting was found. According to the mechanisms of conductivity in CdCr₂Se₄, CdCr₂Se₄, and HgCr₂Se₄, where doping with In leads to the reduction of the Cr valency, ¹¹¹In probes in CuCr₂Se₄ can cause the transition Cr⁴⁺ \rightarrow Cr³⁺ in the very nearest surrounding of the probes, thereby the spectra look similar to those of the other FMS, i.e., with only one peak in the Fourier spectrum.

In the arsenal of the PAC method there is a detector configuration, which allows the sign determination of internal magnetic fields. In this work several configurations intended for sign-sensitive measurements with four detectors and eight start-stop detector combinations were suggested and tested. Among them the optimal arrangement was discovered and argued for. Good agreement between experiments with 135°- and 180°/90°-geometry proves that this approach is a reliable and valuable tool in PAC, which can and should be used in the areas of solid state physics, where the sign determination of internal magnetic fields plays a crucial role. For all probes substituted at the A-site a positive magnetic hyperfine field was found that is consistent with NMR results. However, the internal magnetic field at the B-site for HgCr₂Se₄ (and most likely for CdCr₂Se₄ and CdCr₂S₄) measured with ¹¹¹In(¹¹¹Cd) probes turned out to be positive in contrast to the negative value measured with ⁵³Cr by NMR.

Measurements of the quadrupole coupling constant with ¹¹¹In(¹¹¹Cd) at the B-site for various spinels including even non-magnetic compounds CdIn₂S₄, HgIn₂S₄, ZnAl₂S₄ revealed a surprisingly strong temperature dependence of the efg, which increases linearly with rising temperature. In order to check the influence of the thermal lattice expansion on the efg in spinels, *ab initio* calculations with different lattice constants corresponding to different temperatures have been performed. The results of the calculations clearly indicated that the temperature dependence of the efg due to the variation of lattice parameters is much too small and moreover is even wrong in sign in order to explain the phenomenon observed. The variety of results obtained for the temperature dependence of the efg in non-metals suggests that it is really a complex scientific question. However, in spinels it can be attributed not only to the properties of host materials, but also (and maybe to a larger extent) to the properties of ¹¹¹In(¹¹¹Cd) probes themselves.

Electric and magnetic hyperfine fields measured in this work are valuable quantities, which can help to test a theoretical charge and spin density distribution determined by *ab initio* calculations. In this work the FLAPW method within density functional theory embodied in the WIEN97 program was used. With the help of WIEN97 it was feasible to determine the theoretical anion parameters u on the basis of the experimental lattice constants a using two different numerical approaches, namely, from the minimum of the total energy and directly using the forces at the nuclei, with excellent agreement between these two approaches. It turned out that the efg at the B- and C-sites strongly depend on the u parameter. Besides, it was revealed that the efg remain practically the same for a wide range of changes of the lattice constants for a given spinel compound, provided that for every lattice constant the anion parameter is optimized. Thus, the small deviations in the experimental lattice constants (less than 2 %) play an insignificant role in comparison with well-performed optimizations of the anion parameters.

After determination of the anion parameters, the efg at the B- and C-sites (the efg at the Asite is zero) for a number of spinel compounds including non-magnetic ones were calculated. The theoretical efg showed a linear dependence on the anion parameter and could be divided into two groups. An analysis of this dependence revealed some interesting peculiarities:

- Compounds with the ratio of tetrahedral R^T and octahedral R^O cation-anion distances $R^O/R^T > 1$ correspond to the first group (except ZnAl₂S₄) and compounds with $R^O/R^T < 1$ to the second group.
- Comparison with the experimental PAC results using the Sternheimer corrections revealed good agreement with theory for the second group and quite wrong results for the first group (In-spinels).
- According to band structure calculations using WIEN97, all spinels belonging to the first group are indirect semiconductors (except Cu-compounds which exhibit metallic behavior) and those belonging to the second group are direct semiconductors.
- Electron density calculations carried out for each compound in the vicinity of the B-site indicated a quite different bonding character for the substances from different groups. In the first group there is a trend to have more covalent contribution around the B-site, whereas in the second one more ionic bond character is observed. This may explain the

disagreement with the Sternheimer corrections for the first group mentioned above, since the Sternheimer corrections are known to work well only for compounds with ionic bond characters.

• The value of u = 0.2572 obtained as an intersection of the lines from the two groups in the $V_{zz}(u)$ dependence can be considered as a theoretical minimum for spinels with a normal structure determined from first principles.

The spin-polarized calculations carried out for the FMS revealed that for the cubic A-site the theoretical magnetic hyperfine fields are of the same order of magnitude as compared to the experimental results, whereas at the B- and C-site they are significantly smaller than the experimental ones. However, the signs of the magnetic fields and magnetic moments were determined correctly. The Fixed Spin Moment (FSM) procedure, which normally simplifies the study of magnetic materials particularly those with ferromagnetic phases, could not help to overcome the problem either. It suggests that such a complicated magnetic system requires a more sophisticated treatment for the correct determination of magnetic hyperfine fields.

Most of the PAC-probes represent impurities in the substances investigated, e.g. in most of the spinel compounds ¹¹¹In(¹¹¹Cd) probes occupy the B-site, where the quadrupole interaction at ¹¹¹Cd was measured. Thereby one has to carry out the so-called "impurity-case" calculation, i.e. the efg at the B-site occupied by a Cd-impurity should be the main computational task. For the impurity-case configuration a basis of 56 atoms ($A_8B_{15}CdC_{32}$) was used that consists of four primitive cells of the normal structure, where one of the Batoms is replaced by Cd. Since impurity-case calculations are in general very time consuming, in this thesis only the non-magnetic spinels CdIn₂S₄, HgIn₂S₄, and ZnAl₂S₄ were considered. The results of the impurity-case calculations revealed that the efg at the impurity atom in CdIn₂S₄ and HgIn₂S₄ changes by a factor of two, whereas in ZnAl₂S₄ it changes even by a factor of four as compared to the host atom. However, in order to obtain reliable efg, subsequent relaxation at least in the nearest environment of a Cd-atom was required due to non-zero forces at the nearest neighbors of the impurity (especially for ZnAl₂S₄ with |F| = 78.2 mRy/a.u.). For relaxations of the atoms in the spinel-supercell an approach, based on movements of the atomic positions according to the calculated forces on the nuclei, was used. From the analysis of the efg and forces for all atoms of the supercell one can draw the important conclusion that atoms located further than the fifth atomic shell are practically not affected by the introduction of the impurity. Moreover, comparison of results of the relaxation with the first atomic shell of the impurity atom and that with the second and third atomic shells revealed that within the required accuracy (in the order of the basis set effects) it is sufficient to carry out relaxation only with the first atomic shell. The agreement between the final theoretical and experimental PAC results is excellent. And last but not least, the successful ab initio calculations carried out in this work including impurity specific effects and relaxations have evidenced that nowadays such complicated problems can be solved on a cluster of high performance PCs.

Table A.1. Theorused for calculatBergakademie Fre	retical and experi- ions are presente eiberg, Institut für	mental anion pai ed as well. For r Metallkunde) u	rameters for vari all available sp ising X-ray analy	ious spinel comj vinel compound ysis. For other n	pounds. Muffin- ls the lattice co laterials marked	-tin radii (R_{mt}), norstants were defined with ^{*)} the lattic	natrix sizes and stermined by D	effective <i>R</i> _{mt} <i>K</i> _{ma} iplPhys. G. Sc e taken from [La	x parameters hreiber (TU m70].
Compound	a, Å	u ^{Exp} [Lan70]	u ^{Energy}	u ^F orce	R _{mt} at A-site	R _{mt} at B-site	R _{mt} at C-site	Matrix Size	R _{mt} K _{max} effective
CdCr ₂ Se ₄	10.75	0.265	0.26521	0.26521	2.4	2.3	2.25	1639	8.00
CdCr ₂ S ₄	10.244	0.265	0.26578	0.26581	2.25	2.15	2.18	1591	7.99
HgCr ₂ Se ₄	10.753	0.265	0.26611	0.26610	2.4	2.2	2.35	1687	7.93
CuCr ₂ Se ₄	10.337	0.25756	0.25778	0.25754	2.1	2.1	2.1	1807	7.99
CdIn ₂ S ₄	10.8434	0.261	0.25918	0.25914	2.25	2.35	2.35	1639	7.93
HgIn ₂ S ₄	10.812	0.263	0.25960	0.25964	2.3	2.35	2.3	1459	7.84
ZnAl ₂ S ₄	10.009	0.25963	0.25950	0.25945	2.1	2.1	2.1	1591	7.98
CuCr ₂ S ₄	9.822*)	0.259	0.25809	0.25793	2.0	2.0	2.0	1759	7.98
CuCr ₂ Te ₄	$11.137^{*)}$	0.256	0.25708	0.25696	2.2	2.3	2.3	1987	7.99
HgCr ₂ S ₄	$10.273^{*)}$	0.265	0.26675	0.26671	2.3	2.14	2.2	1639	7.96
MgAl ₂ O ₄	$8.0836^{*)}$	0.262	0.26308	0.26319	1.7	1.85	1.75	1471	7.91
CdIn ₂ O ₄	$9.166^{*)}$	0.261	0.26198	0.26227	2.15	2.35	1.75	2085	7.90
ZnAl ₂ O ₄	8.0813*)	0.264	0.26413	0.26405	2.05	1.85	1.6	1913	7.98

Appendix

Table A.2. Calculated m	lagnetic momen	ts (in μ_B) for a 1	number of magn	etic spinels.						
Connormo?	A-v	site	B-s	ite	C-s	ite	Interst	titial	Magnetic per mo	moment olecule
Compound	Spin-Up Spin-Down	Magnetic moment	Spin-Up Spin-Down	Magnetic moment	Spin-Up Spin-Down	Magnetic moment	Spin-Up Spin-Down	Magnetic moment	without interstitial	with interstitial
CdCr ₂ Se ₄	23.1283345 23.1122479	0.016087	12.6675926 9.7562007	2.911392	16.0159041 16.0968036	-0.0809	12.9458082 11.9761915	0.969617	5.515271	6.00008
CdCr ₂ S ₄	22.9535184 22.9344487	0.01907	12.4284936 9.6588258	2.769668	7.2380584 7.2943377	-0.05628	12.4744908 11.1411283	1.333363	5.333286	5.999968
HgCr ₂ Se ₄	38.9884577 38.9754937	0.012964	12.5207022 9.6758777	2.844825	16.1671736 16.2473813	-0.08021	12.6027815 11.3665569	1.236225	5.381774	5.999887
$\mathrm{HgCr}_2\mathrm{S}_4$	38.8339809 38.8146059	0.019375	12.4093357 9.6479420	2.761394	7.2608624 7.3175328	-0.05667	12.6074325 11.2391220	1.368311	5.315483	5.999639
CuCr ₂ Se ₄	13.7519931 13.8728890	-0.1209	12.3193414 9.6675495	2.651792	15.7292275 15.8727147	-0.14349	15.4781090 14.5090242	0.969085	4.608724	5.093267
CuCr ₂ S ₄	13.6310100 13.7646174	-0.13361	12.1258085 9.6248052	2.501003	6.9042639 7.0303349	-0.12607	15.0234311 13.7060690	1.317362	4.364116	5.022797
CuCr ₂ Te ₄	13.8711238 13.9472248	-0.0761	12.6450097 9.8067131	2.838297	24.4574117 24.5920798	-0.13467	16.3316913 15.8287886	0.502903	5.061814	5.313266
ZnCr ₂ Se ₄	14.2208667 14.2030200	0.017847	12.6643653 9.7795338	2.884832	16.1085245 16.1769662	-0.06844	12.0328245 11.0598799	0.972945	5.513751	6.000224

110

Table A.3. Summary of the impurity-case calculations for $ZnAl_2S_4$ without relaxation, with relaxation of the nearest environments of the impurity atom only (Atom 10) and with relaxation of the three nearest atomic shells (Atoms 2, 5 and 10). Here $R_{Cd-atom}$ – distance from the impurity atom (Cd) to a given atom; |F| - absolute value of the force on a given atom. Marked with shading are:

Atom 11 – impurity Cd-atom

Atom 10 -the first nearest shell to the impurity

Atom 5 - the second nearest shell to the impurity

Atom 2 - the third nearest shell to the impurity

				-									
	× + ~	C	d _{Al} without	relaxation		Cd _{Al} wi	th relaxation	t of the Atom	10	Cd _{Al} with re	elaxation of tl	he Atoms 2, 5	i and 10
IN	Atom	$R_{\rm Cd-atom,}~{\rm \AA}$	F , mRy∕a.u.	$\frac{\mathbf{V}_{\mathbf{zz}}}{10^{21}\mathrm{V/m}^2}$	μ	$\mathbf{R}_{Cd-atom}, \mathrm{\AA}$	F , mRy/a.u.	$\frac{\mathbf{V}_{\mathbf{zz}}}{10^{21}\mathrm{V/m}^2}$	۲	$R_{Cd-atom}$, Å	F , mRy/a.u.	$\frac{V_{zz}}{10^{21}V/m^2}$	ե
1	Zn	6.5010	0.580	-0.055	0	#	0.386	-0.049	0	#	0.715	-0.067	0
2	Zn	4.1495	3.717	-0.229	0.558	#	7.574	-1.148	0.100	4.1749	0.439	-0.617	0.773
3	AI	6.1292	0.496	-0.187	0.017		0.346	-0.187	0.331	#	0.190	-0.183	0.073
4	AI	7.0774	0	-0.183	0.211		0	-0.176	0.847	#	0	-0.173	0.873
5	Al	3.5387	4.080	-0.245	0.039	#	96.9	0.292	0.041	3.5489	0.379	0.313	0.005
9	S	4.1693	3.670	3.052	0		6.454	3.231	0	#	7.893	3.174	0
٢	S	5.5549	1.958	2.844	0.182		6.642	2.855	0.119	#	7.869	2.847	0.095
8	S	4.3917	1.659	3.076	0.105	#	3.591	3.310	0.081	#	1.923	3.321	0.137
6	S	7.3484	1.733	2.956	0.006		1.978	2.933	0.045	#	1.722	2.949	0.047
10	S	2.4109	78.244	2.968	0.371	2.5741	0.207	2.878	0.022	2.5806	0.330	2.855	0.040
11	Cd	10.009	0	-0.772	0	#	0	-1.183	0	#	0	-1.136	0

Table A.4. Summary of the impurity-case calculations for $CdIn_2S_4$ without relaxation and with relaxation of the nearest environments of the impurity atom (Atom 10) compared with normal (host) calculations. Here $RKM \equiv R_m K_{max}$, $R_{cd-atom}$ – distance from the impurity atom (Cd) to a given atom; |F| - absolute value of the force on a given atom. Marked with shading are:

Atom 11 – impurity Cd-atom

Atom 10 – the first nearest shell to the impurity

				for and a										
Atom	Normal 20k-poin	calculation ts, RKM=8	Normal c 4k-points,	alculation RKM=7.5	Nr	Atom		Cd _{In} withou	ıt relaxation		Cd _{in} wi	ith relaxatic	on of the Ato	m 10
	F , mRy/a.u.	$\mathop{\mathbf{V}_{{\bf z}{\bf z}}}_{10^{21}{\bf V}/m^2}$	F , mRy/a.u.	$\mathop{V_{zz}}_{10^{21}{\rm V/m}^2}$			$\mathbf{R}_{\mathrm{Cd-atom}},$	F , mRy/a.u.	$V_{zz}_{10^{21} V/m^2}$	ц	$\mathbf{R}_{\mathrm{Cd-atom}}, \ \hat{\mathbb{A}}$	 F , mRy/a.u.	V_{zz} 10 ²¹ V/m ²	μ
۲U	C	C	C	U	1	Cd	7.0430	0.963	-0.159	0		1.005	-0.176	0
	0	0	>	þ	2	Cd	4.4954	4.26	-0.733	0.176	#	1.749	-0.992	0.045
					3	In	6.6402	1.159	-2.168	090.0	#	1.331	-2.166	0.039
In	0	-2.160	0	-2.139	4	In	7.6674	0	-2.135	0.004	#	0	-2.125	0.026
					5	In	3.8337	6.818	-2.113	0.149		4.65	-2.021	0.410
					9	S	4.5229	3.105	2.502	0	#	3.702	2.560	0
					7	S	6.0194	0.933	2.126	0.528		1.595	2.135	0.534
\mathbf{S}	0.723	2.426	0.207	2.437	8	S	4.7556	1.562	2.611	0.164	#	1.497	2.680	0.153
					6	S	7.9668	0.42	2.412	0.024		0.322	2.420	0.010
					10	S	2.6151	10.215	1.949	0.407	2.6492	0.737	2.050	0.125
In	0	-2.160	0	-2.139	11	Cd	10.8434	0	-1.194	0	#	0	-1.306	0

d 10) con 1 a given	
1 1 3	
5 and ce oi	
oms 2, the for	
lls (Atc due of	
nic she dute va	
est aton - absc	
tom; F	
the thre given at	
tion of () to a g	
relaxat om (Cd	
nd with urity at	
ation aı he impı	
ut relax from t	
, withor istance	
HgIn ₂ S ₄ _{atom} – d	
ns for l _{ax} , R _{Cd} -	
lculatio ≡ <i>R</i> ™K ^m	
case ca RKM ₌	
purity- . Here	
the im tations :	
mary of st) calcu ding are	
5. Sumi nal (hos rith shae	
able A.: ith norn arked w	

Atom 11 – impurity Cd-atom

Atom 10 – the first nearest shell to the impurity

Atom 5 - the second nearest shell to the impurity

Atom 2 – the third nearest shell to the impurity

1													
	5 and 10	μ	0	0.076	0.007	0.046	0.301	0	0.207	0.044	0.001	0.093	0
	of Atoms 2, 5	$\mathrm{V}_{\mathbf{zz}}_{\mathrm{10}^{21}\mathrm{V/m}^2}$	-0.167	-3.610	-2.587	-2.556	-2.458	5.026	4.564	5.026	4.761	5.000	-1.402
	elaxation o	F , mRy/a.u.	0.845	0.486	0.352	0	0.628	2.297	0.911	2.419	0.088	0.398	0
	Cd _{In} with r	$R_{Cd-atom}, {\rm \AA}$	#	4.4699	#	#	3.8125	#	#	#	#	2.6253	#
		μ	0	0.135	0.040	0.022	0.174	0	0.202	0.076	600.0	0.039	0
	relaxation	V_{21} V_{V/m^2}	-0.371	-1.754	-2.593	-2.567	-2.531	4.987	4.562	5.035	4.748	4.815	-1.328
	'd _{In} without	F , mRy/a.u.	1.286	5.278	1.06	0	7.011	2.689	0.873	1.993	0.128	9.209	0
antry (C	$R_{Cd\text{-}atom}, \text{\AA}$	7.0226	4.4824	6.6210	7.6452	3.8226	4.5012	6.0000	4.7450	7.9354	2.6030	10.812
	Atom		Hg	Hg	In	In	In	S	s	S	S	S	Cd
	Nr		1		3	4	5	9	7	8	6	10	11
	calculation , RKM=7.5	$V_{zz}_{10^{21} V/m^2}$	0		-2.523			4.765					-2.523
	Normal c 4k-points,	F , mRy/a.u.	0		0			0.505					0
	alculation s, RKM=8	V_{zz} 10 ²¹ V/m ²	0			-2.573				4.798			-2.573
	Normal c 20k-point:	F , mRy/a.u.	0			0				0.164			0
	Atom		Hg			In				\mathbf{N}			In

Abbreviations

ADCAM	Analog to Digital Converter And Memory
at.%	atomic percent
CERN	European Organisation for Nuclear Research
CS	Combined Scheme
DFT	Density Functional Theory
EC	Electron Capture
efg	electric field gradient
EXP	Experiment
ext	external
fcc	face-centered cubic
FLAPW	Full-potential LAPW
FM	Ferromagnetic state
FMR	Ferromagnetic Resonance
FMS	Ferromagnetic Spinels
FSM	Fixed Spin Moment
GGA	Generalized Gradient Approximation
GPS	General Purpose Separator
HI	Hyperfine Interaction
HMI	Hahn-Meitner Institute
HRS	High Resolution Separator
IBZ	Irreducible wedge of the Brillouin Zone
IPAC	Integral Perturbed Angular Correlations
ISL	Ionen Strahl Labor
ISOLDE	Isotope Separator On-Line DEvice
IT	Isomeric Transition
KS	Kohn-Sham
LAPW	Linearized Augmented Plane Waves
LO	Local Orbitals
LSDA	Local Spin Density Approximation
ME	Mössbauer Effect
meas	measurement
NMR	Nuclear Magnetic Resonance
NN	Nearest Neighbor
NO	Nuclear Orientation
PAC	Perturbed Angular Correlations
PAD	Perturbed Angular Distribution
PC	Personal Computer

pgf	Portland Group high performance Fortran
PM	Paramagnetic state
PS	Proton-Synchrotron
RAM	Random-Access Memory
RPA	Random Phase Approximation
RT	Room Temperature
SC	Supercell
SCF	Self-Consistency cycle
TAC	Time-to-Amplitude Converter
theo	theory
VLSI	Very Large Scale Integration

References

- [Abe00] G.N. Abelyashev, V.N. Berzhansky, S.N. Polulyakh, N.A. Sergeev, Physica B 292 (2000) 323.
- [Abe86] G.N. Abelyashev, V.N. Berzhansky, Y.V. Fedotov, Solid State Phys. 28 N 8 (1986) 2548.
- [Ada94] J.M. Adams, G.L. Catchen, Phys. Rev. B 50 (1994) 1264.
- [Aka99] H. Akai, T. Kotani, Hyperfine Int. 120/121 (1999) 3.
- [Ant99] V.N. Antonov, V.P. Antropov, B.N. Harmon, A.N. Yaresko, A.Ya. Perlov, Phys. Rev. B 59 (1999) 14552.
- [Ara73] T. Arai, M. Wakaki, S. Onari, J. Phys. Soc. Japan. 34 (1973) 68.
- [Bab83] A.A. Babitsyna, S.M. Ryabchenko, Yu.V. Fedotov, Sov. Solid State Phys. 25 (1983) 2520.
- [Bai77] A.I. Bairamov, A.G. Gurevich, L.M. Emiryan, N.N. Parfenova, Phys. Lett. A 62 (1977) 242.
- [Bal65] P.K. Baltzer, H.W. Lehmann, M. Robbins, Phys. Rev. Lett. 15 (1965) 493.
- [Bal66] P.K. Baltzer, P.J. Wojtowicz, M. Robbins, E. Lopatin, Phys. Rev. 151 (1966) 367.
- [Bar64] R.G. Barnes, R.L. Mössbauer, E. Kankeleit, J.M. Poindexter, Phys. Rev. 136 (1964) 175.
- [Bar81] H. Barfuss, G. Böhnlein, P. Freunek, R. Hofmann, H. Hohenstein, W. Kreische, H. Niedrig, A. Reimer, W. Keppner, W. Körner, Hyp. Int. 9 (1981) 235.
- [Bar83] H. Barfuss, G. Böhnlein, F. Gubitz, W. Kreische, B. Röseler, Hyp. Int. 15/16 (1983) 815.
- [Bar84] H. Barfuss, Thesis, Erlangen (1984).
- [Ber02] H.H. Bertschat, K. Potzger, A. Weber, W.-D. Zeitz, Eur. Phys. J. A 13 (2002) 233.
- [Ber67] S. Berger, H. Pinch, J. Appl. Phys. 38 (1967) 949.
- [Ber68] S.B. Berger, J.I. Budnick, T.J. Burch, J. Appl. Phys. 39 (1968) 658.
- [Bla00] P. Blaha, K. Schwarz, W. Faber, J. Luitz, Hyperfine Int. 126 (2000) 389.
- [Bla83] P. Blaha, K. Schwarz, Int. J. Quantum Chem. XXIII (1983) 1535.
- [Bla99] P. Blaha, K. Schwarz, J. Luitz, "WIEN97", ISBN 3-9501031-0-4 (1999).
- [Bon68] P.F. Bongers, G. Zanmarchi, Sol. St. Comm. 6 (1968) 291.
- [Bro65] C.G. Broyden, Math. Comp. 19 (1965) 577.
- [Bur70] T.J. Burch, J.J. Murphy, J.I. Budnick, S. Skalski, J. Appl. Phys. 41 (1970) 1327.
- [But89a] T. Butz, Hyperfine Interactions 52 (1989) 189.
- [But89b] T. Butz, S. Saibene, Th. Fraenzke, M. Weber, Nucl. Instrum. Methods Phys. Res. A 284 (1989) 417.
- [But96] T. Butz, Z. Naturforsch. 51a (1996) 396.
- [Buz86] V.P. Buzhor, R.Yu. Lyalikova, S.I. Radautsan, Neorgan. Mater. 22 (1986) 403.
- [Chr76] J. Christiansen, P. Heubes, R. Keitel, W. Klinger, W. Loeffler, W. Sadner, W. Witthuhn, Z. Phys. B24 (1976) 177.
- [Chr83] J. Christiansen, "Hyperfine interactions of radioactive nuclei" (Topics in current physics 31), Springer-Verlag, Berlin (1983).
- [Col67] C. Colominas, Phys. Rev. 153 (1967) 558.
- [Con94] A. Continenza, T. Pascale, F. Meloni, M. Serra, Phys. Rev. B 49 (1994) 2503.
- [Cot01] S. Cottenier, H. Haas, Hyperfine Int. 133 (2001) 239.
- [Das01] S. Das Sarma, American Scientist 89 No. 6 Nov. (2001) 516.
- [Die00] M. Dietrich, A. Burchard, D. Degering, M. Deicher, J. Kortus, R. Magerle, A. Möller, V. Samokhvalov, S. Unterricker, R. Vianden, Z. Naturforsch. 55a (2000) 256.
- [Die01] M. Dietrich, J. Bartels, M. Deicher, K. Freitag, V. Samokhvalov, S. Unterricker, Mat. Res. Soc. Symp. Vol. 655 (2001) CC10.11.1.

- [Die98a] M. Dietrich, "Untersuchungen von Defektchalkopyrithalbleitern AB_2C_4 mit der Methode der gestörten γ - γ Winkelkorrelation (PAC)", Dissertation, TU Bergakademie Freiberg (1998).
- [Die98b] M. Dietrich, J. Kortus, W. Cordts, S. Unterricker, phys. stat. sol. (b) 207 (1998) 13.
- [Die99] M. Dietrich, D. Degering, J. Kortus, S. Unterricker, M. Deicher, A. Burchard, R. Magerle, the ISOLDE-Collaboration, Hyperfine Interactions 120/121 (1999) 359.
- [Err00] L.A. Errico, G. Fabricius, M. Rentería, Z. Naturforsch. 55a (2000) 267.
- [Fir96] R.B. Firestone, V.S. Shirley (Editor), "Table of Isotopes", 8th ed., Wiley CD-ROM Edition (1996).
- [Fle99] R. Flederling, M. Keim, G. Reuscher, W. Ossau, G. Schmidt, A. Waag, L.W. Molenkamp, Nature 402 (1999) 787.
- [For83] D. Forkel, W. Engel, M. Iwatschenko-Borho, R. Keitel, W. Witthuhn, Hyp. Int. 15/16 (1983) 821.
- [For99] D. Forkel-Wirth, Rep. Prog. Phys. 62 (1999) 527.
- [Gog86] M. Gogolovich, J. Kusz, J. Warczewski, S. Yuszczyk, J. Phys. C 19 (1986) 7121.
- [Goo67] J.B. Googenough, Solid State Commun. 5 (1967) 577.
- [Gri75] S.M. Grigorovich, A.V. Novoselova, Yu.M. Ukrainski, Neorgan. Mater. 11 (1975) 2125.
- [Gur74] A.G. Gurevich, Yu.M. Yakovlev, V.I. Karpovich, M.A. Vinnik, A.N. Ageev, E.V. Rubalskaya, B.L. Lapovok, Proceed. Int. Conf. on Magnetism Moscow Vol. 5 (1974) 469.
- [Gus95] A.A. Gusev, I.M. Reznik, V.A. Tsitrin, J. Phys.: Condens. Matter 7 (1995) 4855.
- [Haa67] C. Haas, A.M.J.G. van Run, P.F. Bongers, W. Albers, Solid State Commun. 5 (1967) 657.
- [Haa93] H. Haas, P. Blaha, S. Unterricker, D. Forkel-Wirth, G. Correia, Jahresbericht HMI GmbH Berlin, Bereich Schwerionenphysik (1993) 115.
- [Hah52] H. Hahn, K.F. Schroeder, Z. anorg. allg. Chem. 269 (1952) 132.
- [Hah96] T. Hahn, "International Tables for Crystallography", Volume A: Space-group symmetry, 4th ed., Kluwer Acad. Publ. (1996).
- [Har66] G. Harbeke, H. Pinch, Phys. Rev. Lett. 17 (1966) 1090.
- [Hel88] K.-H. Hellwege, "Einführung in die Festkörperphysik", Springer-Verlag, Berlin (1988).
- [Hof93] H.C. Hofsäss, "UNCPAC V5.24 Perturbed γ-γ Angular Correlations Program", Universität Konstanz (1993).
- [Hoh64] P. Hohenberg, W. Kohn, Phys. Rev. B 136 (1964) 864.
- [Hun74] H.J. Hunger, Dissertation, TU Bergakademie Freiberg (1974).
- [Jha87] S. Jha, M. Elfazani, S. Yehia, C. Mitros, S. Kumar, G.M. Julian, R.A. Dunlap, A. Vasques, F.G.M. DaCunha, S.M.M. Ramos, Hyp.Int. 34 (1987) 423.
- [Kan81] J. Kanamori, H.K. Yoshida, K. Terakura, Hyperfine Interactions 9 (1981) 363.
- [Kar95] E. Karlsson, "Solid state phenomena: as seen by muons, protons, and excited nuclei", ISBN 0-19-853778-6, Clarendon press Oxford (1995).
- [Kis82] P. Kistaiah, K. Satyanarayana Murthy, K.V. Krishna Rao, J. of materials science lett. 1 (1982) 285.
- [Kit96] C. Kittel, "Introduction to solid state physics", Wiley, New York (1996).
- [Kog80] N. Koguchi, K. Masumoto, Japan. J. Appl. Phys. 19-3 (1980) 273.
- [Koh65] W. Kohn, L.J. Sham, Phys. Rev. A 140 (1965) 1133.
- [Kri73] K. Krien, A.G. Bibiloni, K. Freitag, J.C. Soares, R. Vianden, Phys. Rev. B 8 (1973) 2248.
- [Kug00] E. Kugler, Hyperfine Interactions 129 (2000) 23.
- [Kun76] Z.E. Kun'kova, T.G. Aminov, L.L. Golik, Fiz. Tverd. Tela 18 (1976) 2083.
- [Lan00] S. Lany, P. Blaha, J. Hamann, V. Ostheimer, H. Wolf, T. Wichert, Phys. Rev. B 62 (2000) R2259.
- [Lan70] Landolt-Börnstein, "*Magnetic and other properties of oxides and related compounds*", New Series, ed. K.-H. Hellwege, Vol. III/4b, Springer (1970).
- [Lav00] A.A. Lavrentiev, N.Yu. Safontseva, V.A. Dubeiko, B.V. Gabrel'yan, I.Ya. Nikiforov, Solid state physics 42 (2000) 1992.

- [Lee71] T.H. Lee, T. Coburn, R. Gluck, Sol. St. Comm. 9 (1971) 1821.
- [Leh67] H.W. Lehmann, Phys. Rev. 163 N 2 (1967) 488.
- [Leh70] H.W. Lehmann, G. Harbeke, Phys. Rev. B 1 (1970) 319.
- [Ler87a] A. Lerf, T. Butz, Angew. Chem. 99 (1987) 113.
- [Ler87b] A. Lerf, T. Butz, Hyperfine Interactions 36 (1987) 275.
- [Lin86] B. Lindgren, Phys. Rev. B 34 (1986) 648.
- [Lin96] B. Lindgren, Hyp. Int. (C) 1 (1996) 613.
- [Los89] N.N. Loshkareva, Yu.P. Suhomkov, B.A. Ghizhevski, A.A. Samokhvalov, Jurn. Tehn. Fiz. (Pis'ma) 15 (1989) 83.
- [Lot64] F.K. Lotgering, Proc. Int. Conf. on Magnetism, Nottingham (1964) 533.
- [Lot65] P.K. Lotgering, Proc. Int. Conf. on Magnetism, London (1965) 533.
- [Lot68] F.K. Lotgering, R.P. van Stapele, J. Appl. Phys. 39 (1968) 417.
- [Mae97] H. Maekawa, S. Kato, K. Kawamura, T. Yokokawa, American Mineralogist 82 (1997) 1125.
- [Mav98] Ph. Mavropoulos, N. Stefanou, B. Nonas, R. Zeller, P.H. Dederichs, Phys.Rev.Lett. 81 (1998) 1505.
- [Mel70] F. Meloni, G. Mula, Phys. Rev. B 2 (1970) 392.
- [Men66] N. Menyuk, K. Dwight, R. Arnott, A. Wold, J. Appl. Phys. 37 (1966) 1387.
- [Men96] L. Mendoza-Zelis, A.F. Pasquevich, F.H. Sanchez, A. de Virgilis, Materials Science Forum 225-227 (1996) 401.
- [Mer81] A.I. Merkulov, S.I. Radautsan, W.E. Tezlevan, Solid State Physics 2S N 6 (1981) 1795.
- [Mer85] M.C. Mery, P. Veillet, K. Le Dang, Phys. Rev. B 31 N 5 (1985) 2656.
- [Met68] S. Methfessel, D. Mattis, "Magnetic Semiconductors", Handb. Phys. Bd. 18/1, Springer-Verlag, Berlin (1968).
- [Min71] K. Minematsu, K. Miyatani, T. Takahashi, J. Phys. Soc. Japan. 31 (1971) 123.
- [Mit96] D.W. Mitchell, T.P. Das, W. Potzel, W. Schiessl, H. Karzel, M. Steiner, M. Köfferlein, U. Hiller, G.M. Kalvius, A. Martin, W. Schäfer, G. Will, I. Halevy, J. Gal, Phys. Rev. B 53 (1996) 7684.
- [Miy71] K. Miyatani, K. Minematsu, Y. Wada, F. Okamoto, K. Kato, P.K. Baltzer, J. Phys. Chem. Solids 32 (1971) 1429.
- [Miy80] K. Miyatani, Japan. J. Appl. Phys. 19-3 (1980) 237.
- [Mo96] S.D. Mo, W.Y. Ching, Phys. Rev. B 54 (1996) 16555.
- [Moh88] M. Mohsen, F. Pleiter, Hyperfine Interactions 39 (1988) 123.
- [Mom00] N. Mommer, T. Lee, J.A. Gardner, W.E. Evenson, Phys. Rev. B 61 (2000) 162.
- [Mos71] F. Moser, P.K. Ahrenkiel, E. Carnall, J. AppL Phys. 42 (1971) 1449.
- [Nei83] H.St.C. O'Neill, A. Navrotsky, American Mineralogist 68 (1983) 181.
- [New82] R.C. Newman, Rep. Prog. Phys. 45 (1982) 1163.
- [Nik78] K.G. Nikiforov, S.I. Radautsan, V.E. Tezlevan, Doklady Akad. Nauk SSSR 239 (1978) 77.
- [Nik81] K.G. Nikiforov, S.I. Radautsan, W.E. Tezlevan, "Sulfochromit kadmiya", Izdatelistvo Stiintsa, Kishinev (1981).
- [Nik82] K.G. Nikiforov, A.G. Gurevich, S.I. Radautsan, L.M. Emiryan, V.E. Tezlevan, Phys. St. Sol. A 72 (1982) K37.
- [Nik99] K.G. Nikiforov, "Magnetically ordered multinary semiconductors", Progress in Crystal Growth and Characterization of Materials (1999).
- [Oga82] F. Ogata, T. Hamajima, T. Kambara, K. Gondara, J. Phys. C: Solid State Phys. 15 (1982) 3483.
- [Ogu81] T. Oguchi, T. Kambara, K.I. Gondaira, Phys. Rev. B 24 (1981) 3441.
- [Ohn00] H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl, Y. Ohno, K. Ohtani, Nature 408 (2000) 944.
- [Ohn02] H. Ohno, F. Matsukura, Y. Ohno, JSAP International 5 (January 2002) 4.

- [Ohn99] Y. Ohno, D.K. Young, B. Beschoten, F. Matsukura, H. Ohno, D.D. Awschalom, Nature 402 (1999) 790.
- [Oka74] F. Okamoto, K. Ametani, T. Oka, Japan. J. Appl. Phys. 13 (1974) 187.
- [Oka79] T. Okada, H. Sekizawa, T. Yamadaya, J. Physique Colloq. 40 (1979) C2-299.
- [Oko77] I. Okonska-Kozlowska, M. Jelonek, Z. Drzazga, Z.anorg.allg.Chem. 436 (1977) 265.
- [Oko94] I. Okonska-Kozlowska, I. Jendrzejewska, Journal of Alloys and Compounds 215 (1994) 157.
- [Osi98] V.V. Osipov, N.A. Viglin, A.A. Samokhvalov, Physics Letters A 247 (1998) 353.
- [Ovc79] S.G. Ovchinnikov, Solid State Physics 21 N 10 (1979) 2994.
- [Pal99] G. Pal, K.C. Sebastian, S.N. Chintalapudi, D.R.S. Somayajulu, Hyp. Int. 120/121 (1999) 409.
- [Par02] Y.D. Park, A.T. Hanbicki, J.E. Mattson, B.T. Jonker, Applied Physics Letters 81 N 8 (2002) 1471.
- [Par99] S.S.P. Parkin, K.P. Roche, M.G. Samant, P.M. Rice, R.B. Beyers, R.E. Scheuerlein, E.J. O'Sullivan, S.L. Brown, J. Bucchigano, D.W. Abraham, Y. Lu, M. Rooks, P.L. Trouilloud, R.A. Wanner, W.J. Gallagher, J. Appl. Phys. 85 (1999) 5828.
- [Pas31] L. Passerini, M. Baccaredda, Atti Accad. Lincei 14 (1931) 33.
- [Pea85] Pearson's Handbook of Crystallographic Data for Intermetallic Phases, ed. by P. Villars, L.D. Calvert, American Society for Metals (1985).
- [Per92] J.P. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244.
- [Per96] J.P. Perdew, S. Burke, M. Ernzerhof, Phys. Rev. Let. 77 (1996) 3865.
- [Phi71] H. v. Philipsborn, J. Crystal Growth 9 (1971) 296.
- [Pin68] H. Pinch, S. Berger, J. Phys. Chem. Sol. 29 (1968) 2091.
- [Ple78] V.G. Pleshchev, V.N. Konev, A.F. Gerasimov, Neorgan. Mater. 14 (1978) 223.
- [Pro74] V. Prosser, P. Hlidek, P. Hoschl, P. Polivka, M. Zvara, Czech. J. Phys. 524 (1974) 1168.
- [Pro92] V.K. Prokopenko, A.A. Shemyakov, T.G. Aminov, N.M. Kovtun, Neorgan. Mater. 28 (1992) 1622.
- [Pul69] P. Pulay, Mol. Phys. 17 (1969) 197.
- [Rad78] S.I. Radautsan, "*Magnitnye poluprovodnikovye spineli tipa CdCr₂Se₄*", Akademia Nauk Moldavskoi SSR, Izdatelistvo Stiintsa, Kishinev (1978).
- [Rad80] S.I. Radautsan, V.E. Tezlevan, K.G. Nikiforov, J. Cryst. Growth 49 (1980) 67.
- [Rag71] R.S. Raghavan, P. Raghavan, Nucl. Instrum. Methods 92 (1971) 435.
- [Rag73] R.S. Raghavan, P. Raghavan, E.N. Kaufmann, K. Krien, R.A. Naumann, Phys. Rev. B 7 (1973) 4132.
- [Rao75] G.N. Rao, "Hyperfine Fields", Atomic Data and Nuclear Data Tables Vol. 15 No. 6 (1975) 557.
- [Rod93] A.M. Rodriquez, H. Saitovich, P.R.J. Silva, J. Weberszpil, J.C. Fernandes, M.A. Continentino, Hyperfine Interactions 79 (1993) 937.
- [Sch92] K. Schwarz, P. Blaha, Z. Naturforsch. 47a (1992) 197.
- [Sch96] G. Schatz, A. Weidinger, "Nuclear Condensed Matter Physics", John Wiley & Sons, ISBN 0-471-95479-9, Chichester (1996).
- [Sch98] P. Schmidt, T. Soldner, W. Tröger, X. Ni, T. Butz, P. Blaha, Z.Naturforsch. 53a (1998) 323.
- [Shi98] J. Shitu, A.F. Pasquevich, A.G. Bibiloni, M. Renteria, F.G. Requejo, Modern Physics Letters B 12 (1998) 281.
- [Shm80] P.C. Schmidt, K.D. Sen, T.P. Das, A. Weiss, Phys. Rev. B 22 (1980) 4167.
- [Sie98] R. Sielemann, Nucl. Instrum. Methods Phys. Res. B 146 (1998) 329.
- [Sim95] J.L. Simmonds, Phys. Today 48(4) (1995) 26.
- [Sin91] D. Singh, Phys. Rev. B 43 (1991) 6388.
- [Sin94] D. Singh, "Planewaves, pseudopotentials and the LAPW method", Kluwer Academic Publishers, Boston (1994).
- [Sol98] T. Soldner, W. Tröger, T. Butz, P. Blaha, K. Schwarz, Z. Naturforsch. 53a (1998) 404.

- [Sta69] G.H. Stauss, Phys. Rev. 181 (1969) 636.
- [Ste50] R.M. Sternheimer, Phys. Rev. 80 (1950) 102.
- [Ste54] R.M. Sternheimer, Phys. Rev. 95 (1954) 736.
- [Ste68] M.B. Stearns, Phys. Rev. 168 (1968) 588.
- [Ste71] M.B. Stearns, Phys. Rev. B 17 (1971) 2809.
- [Tan94] J. Tang, L. Li, S.S. Saxena, A. Puri, A.U. Falster, W.B. Simmons, IEEE Transactions on magnetics 30 No. 6 (1994) 4972.
- [Tre72] Yu.D. Tretyakov, I.V. Gordeev, V.A. Alferov, Yu.G. Saksonov, Neorgan. Mater. 8 (1972) 2215.
- [Tsu87] V.V. Tsurkan, S.A. Ratseev, V.E. Tezlevan, V.M. Mytsu, All-Union Con. "Ternary Semiconductors and their Application", Abstracts Vol. 1, Kishinev (1987) 155.
- [Tsu97] V. Tsurkan, S. Radautsan, M. Baran, R. Szymczak, H. Szymczak, J. Phys. IV France 7 (1997) C1-271.
- [Unt80] S. Unterricker, P. Hlidek, M. Zvara, F. Schneider, phys.stat.sol. (b) 102 (1980) K 27.
- [Unt83] S. Unterricker, F. Schneider, M. Zvara, P. Hlidek, Hyperfine Interactions 15/16 (1983) 759.
- [Unt91] S. Unterricker, Isotopenpraxis 27 (1991) 69.
- [Unt96] S. Unterricker, M. Dietrich, A. Möller, R. Vianden, M. Deicher, R. Magerle, W. Pfeiffer, G. Böhm, L. Pasemann, the ISOLDE Collaboration, Cryst. Res. Technol. 31 (1996) 761.
- [Unt98] S. Unterricker, M. Dietrich, D. Degering, J. Kortus, M. Deicher, R. Magerle, A. Burchard, the ISOLDE-Collaboration, Inst. Phys. Conf. Ser. No 152 Section E (1998) 777.
- [Vai81] D. Vaiude, M. Elfazani, M. DeMarco, S. Jha, P. Sollten, J.W. Snider, G. Julian, J.W. Blue, Hyp. Int. 10 (1981) 873.
- [Vai94] B.K. Vainshtein, V.M. Fridkin, V.L. Indenborn, "Structure of Crystals", Springer-Verlag (1994).
- [Ves72] V.G. Veselago, E.S. Vigeleva, G.I. Vinogradova, V.T. Kalumikov, V.E. Mahotkin, Jurn. Eksp. Teor. Fiz. (Pis'ma) 15 (1972) 316.
- [Ves90] V.G. Veselago, G.I. Vinogradova, A.A. Garmonov, S.G. Rudov, E.G. Zhukov, I. Kurbankychev, V.A. Levshin, Jurn. Eksp. Teor. Fiz. 97 (1990) 559.
- [Vin76] G.I. Vinogradova, K.M. Golant, A.A. Minakov, A.V. Zachatskaya, All-Union Conference "Temary Semiconductors and their Application", Abstracts, Kishinev (1976) 127.
- [Vin83] G.I. Vinogradova, R.R. Gareev, All-Union Conf. "Ternary Semiconductors and their Application", Abstracts, Kishinev (1983) 90.
- [Wad71] Y. Wada, K. Ametani, Thermochim. Acta 2 (1971) 237.
- [Wei01] S.-H. Wei, S.B. Zhang, Phys. Rev. B 63 (2001) 045112
- [Wei81] M. Weinert, J. Math. Phys. 22 (1981) 2433.
- [Wet61] F.W. de Wette, Phys. Rev. 123 (1961) 103.
- [Wic86] Th. Wichert, E. Recknagel in "Microscopic Methods in Metals", Topics in Current Physics vol. 40, Springer Berlin (1986) 317.
- [Wil84] A.R. Williams, V. Moruzzi, J. Kubler, K. Schwarz, Bull. Am. Phys. Soc. 29 (1984) 278.
- [Wim81] E. Wimmer, H. Krakauer, M. Weinert, A.J. Freeman, Phys. Rev. B 24 (1981) 864.
- [Win96] A. Winiarski, I. Okonska-Kozlowska, J. Heimann, M. Neumann, Journal of Alloys and Compounds 232 (1996) 63.
- [Wit85] W. Witthuhn, Hyp. Int. 24-26 (1985) 547.
- [Yam79] O. Yamashita, Y. Yamaguchi, I. Nakatani, H. Watanabe, K. Masumoto, J. Phys. Soc. Jpn. 46 (1979) 1146.
- [Zar86] V.N. Zaritski, R.A. Sadykov, Fiz. Tverd. Tela 28 (1986) 3292.
- [Zie92] J.F. Ziegler (Edit.), "Handbook of ion implantation technology", Elsevier Science Publishers B.V., Amsterdam (1992).

Acknowledgements

It is a great pleasure for me to have now the opportunity to express my gratitude to all the people who gave me the possibility to complete this thesis.

The first person I would like to thank is my supervisor Prof. S. Unterricker. During my post-graduate study I have known him as a person of principles. His boundless enthusiasm, integral view on research, and directive for providing "only high-quality work and not less", have made a deep impression on me. I owe him lots of gratitude for having shown me this way of research. He provided a motivating, enthusiastic, and critical atmosphere during the many discussions we had. Besides of being an excellent supervisor, Prof. Unterricker was as close as a relative to me especially at the beginning of my research. I am really glad that I have had an opportunity to work in his group and to write my thesis under his supervision.

I am deeply indebted to my second supervisor Prof. I.M. Tiginyanu from the Technical University of Moldova, whose support, stimulating suggestions and encouragement helped me in all the time of research. His dynamic thoughts, his broad and profound knowledge, his warm smile and his constructive comments have given me a great backing. It was Prof. Tiginyanu, who together with Prof. V. Sontea (the dean of the faculty "Computers, Informatics and Microelectronics", Technical University of Moldova) selected and nominated me as a candidate for the DFG-Fellowship at the graduate college "Crystal Engineering and Crystallization" in Freiberg, encouraged me to go ahead with my thesis and thereby irrevocably changed my life. Without their kind support and belief in me who knows what would have happened to me ...

I would like to express my gratitude to Dr. Igor Burlakov for having shared the same office with me and for having been an excellent colleague and partner during the most time of my PhD work. Igor deserves my warmest thanks for thought-stimulating questions, many discussions, encouragement and good humor throughout the course of this research, for providing me with brotherly advice and tips that helped me a lot in staying on the right track and for his firm friendship I ever had.

I would like to thank Dr. Marc Dietrich who kept an eye on the progress of my work and always was available when I needed his advice. Especially the strict and extensive comments as well as many discussions and interactions with Marc had a direct impact on the final form and quality of this thesis. Without his permanent assistance during experiments and especially by implantations at ISOLDE my life would have been considerably harder. I am happy to have shared working conditions with him, since he imparted to me diverse bits of knowledge and wisdom during various stages of our communication. He could not even realize how much I have learned from him.

I feel especially indebted to Dr. Jens Kortus for his sincere interest, inspiring discussions, interpretations and helpful hints concerning FLAPW-calculations with the WIEN97 program. Jens has always taken time out of his busy schedule wherever he was so that I could ask him

lots of questions and break a deadlock. Besides, his insightful and detailed comments on the drafts of this thesis are greatly appreciated.

I am deeply bound to Dr. F. Schneider who gave a lot of his time, invaluable advice, spiritual support, encouragement and subtle direction of my efforts throughout the time it took me to achieve the end of this work. I also want to thank Dr. W. Cordts for all his assistance and tips especially related with the computer technique. I am grateful to all my colleagues, co-workers and other people at the Institute of Applied Physics who gave me the feeling of home atmosphere being at work. Special recognition is also deserved for the skilled assistance of Mr. D. Emmrich and Mrs. H. Püschel from the mechanical workshop as well as Mr. H. Zimmerman from the electrical workshop.

I wish to express my special gratitude to Dr. V.E. Tezlevan and Dr. V.V. Tsurkan from the Academy of Sciences of Moldova for growing high quality monocrystals, without which this work would be impossible, and Prof. I.M. Tiginyanu for organizing this process. I have furthermore to thank the ISOLDE-Collaboration for the possibility to carry out high quality implantations, Dr. M. Deicher from the University of Konstanz as well as Dr. W. Tröger and Prof. T. Butz from the University of Leipzig for the possibility to use their PAC spectrometers at ISOLDE and for their permanent readiness to help and support me during experiments at ISOLDE. I am also thankful to Dipl.-Phys. G. Schreiber (TU Bergakademie Freiberg, Institut für Metallkunde) for X-ray analysis of the crystals; to Dr. E. Brendler and Prof. B. Thomas (TU Bergakademie Freiberg, Chemical Department) for the NMR measurements; to Dr. W.D. Zeitz, Dr. H.E. Mahnke and Dipl.-Phys. V. Koteski for their kind support during the implantation and measurements with ¹⁰⁰Pd(¹⁰⁰Rh) at HMI; to Dr. R. Vianden from the University of Bonn for implantation of ¹¹¹In(¹¹¹Cd).

Especially I am obliged to Prof. W. Voigt and Dr. M. Bremer for accepting me as a member of the graduate college "Crystal Engineering and Crystallization" as well as for providing me an excellent work environment and their kind assistance. This research has financially been supported for the first three years by the Deutsche Forschungsgemeinschaft (DFG) and later on by the Bundesministerium für Bildung und Forschung (BMBF). I thank them all for their confidence in me.

Needless to say, I could not have survived even a year in Germany far away from my homeland without the understanding, love, care and support of my family. I feel a deep sense of gratitude to my mother, father and sister, who formed part of my vision and taught me the good things that really matter in life, who ceaselessly and tirelessly encouraged me. I must apologize to them for the various kinds of anxiety which must have been caused by my abrupt decision to study abroad. I wish that we will share the delight of this accomplishment soon.

Last but certainly not least, a special heartfelt thanks goes to all my friends, relatives and acquaintances, who have supported me in every possible way during this hard but important period of my life. Completing the chain of my gratitude I apologize that I could probably not list everyone that I am thankful to.