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**“Origin of NMR chemical shieldings in solids
by analysis of occupied and unoccupied
states”**

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Abstract

NMR-Spectroscopy is a widely used method to investigate and determine the structure of molecules and solids. This thesis is focused on solid state NMR (SSNMR).

The results of experimental NMR chemical shifts can be compared to theoretical calculated chemical shieldings (CS) which is the main focus in the present thesis. Density-functional theory (DFT) calculations are used to calculate the CS in several inorganic compounds. There are several exchange-correlations functionals and here we applied the Perdew-Burke-Ernzerhof (PBE) and Becke Johnson (BJ) (only for metal sulfides and disulfides) potentials, to calculate the magnetic shielding in solid materials.

Once the CS are calculated, they can be correlated with the experimental measured chemical shifts by checking the slope of the linear fit, which should be ideally 1.0. Band wise analysis and character analysis of the occupied (ground state wavefunction and its 1st order perturbation) and unoccupied states give informations about the major contribution of the CS and its origin.

DOS-analysis showed that the energy separation between the s and p-bands among each other decreases from light to heavy metal compounds. It was found out that the major contributions of the CS comes from the S-p band in the sulfides, Si-p band in the silicides and Sn-p band in the stannides. Further investigations of these bands show that the contribution of the chemical shielding for the empty metal-d states decreases dramatically within the series.

Finally one can state that the negative increasing of the shieldings is due to two facts:

First, the decreasing energy separation between the s and p-bands throughout the series, which leads to larger hybridisation between the states. Secondly, the stronger coupling between the empty metal-d states and occupied S-p states in sulfides, Si-p states in silicides and Sn-p states in stannides within the series.

Zusammenfassung

NMR Spektroskopie ist eine oft verwendete Methode, um Strukturen von Molekülen und Festkörpern zu untersuchen und zu bestimmen.

In dieser Masterarbeit wird der Fokus auf Festkörper-NMR Spektroskopie gelegt.

Die Resultate der experimentellen chemischen Verschiebungen mit den theoretisch berechneten chemischen Abschirmungen sind das Hauptaugenmerk in dieser Abschlussarbeit. Dichtefunktionaltheorie (DFT)- Berechnungen werden genutzt, um magnetische Abschirmungen in verschiedenen anorganischen Materialien zu berechnen. Es gibt verschiedene Austausch- Korrelations-Potenziale aber in dieser Abschlussarbeit werden nur das Perdew-Burke-Ernzerhof (PBE) und das Becke Johnson (BJ) (nur fuer Metallsulfide und disulfide) Potential verwendet. Nachdem die CS (chemical shielding) berechnet wurden, koennen sie mit den experimentell gemessenen Werte korreliert werden, indem man die Steigung des linearen Fit ueberprueft, der idealerweise 1.0 betraegt. Band-Analysen und Charakter-Analysen der besetzten (Grundzustands-Wellenfunktion und ihre nach der 1. Ordnung gestoerten Wellenfunktion des selbigen Charakters) und unbesetzten Zustaenden geben Aufschluss ueber die Beitraege der CS und ihres Ursprungs.

DOS-Analysen zeigten, dass der Energie-Abstand zwischen s und p Zustaenden untereinander von Leicht zu Schwermetall Verbindungen sinkt. Es wurde herausgefunden, dass die hauptsaechliche chemische Verschiebung von den S-p Baendern in den Sulfiden, Si-p Baendern in den Siliziden und Sn-p Baendern in den Stanniden verursacht wird. Weitere Untersuchungen dieser Baender zeigten, dass der Anteil der chemischen Verschiebung fuer die leeren Metall-d Zustaende innerhalb der Serie stark sanken.

Schlussendlich kommt man zu der Annahme, dass die steigende negative Verschiebung aufgrund zweier Faktoren zustande kommt:

Erstens, aufgrund des sinkenden Energie-Abstandes zwischen den s und p-Zustaenden innerhalb der Serien, welcher zu einer staerkeren Hybridisierung fuehrt. Zweitens, durch die staerkere Kopplung der leeren Metall-d Zustaenden und besetzten S-p Zustaenden in den Sulfiden, Si-p Zustaenden in den Siliziden und Sn-p Zustaenden in den Stanniden binnen der Serien.

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Glossary

BJ

becke-johnson potential

CS

chemical shielding

DFT

density functional theory

GGA

generalized gradient approximation

LAPW

linear augmented plane wave method

LDA

local density approximation

NMR

nuclear magnetic resonance

PBE

Perdew Burke Ernzerdorf

R_{MT}

Muffin-Tin Radius

SCF

self consistent field

SSNMR

solid state NMR

1 Introduction

1.1 Theory of the Electronic structure

1.1.1 Quantum mechanics of many body theorem

In condensed matter physics one can use computational tools to calculate properties of materials. One can imagine that the nucleus (at a fixed position for a crystal) and the electrons which compose materials strongly interact with each other. This fact leads to the so called “Many body problem”, which makes a direct solution of Schroedinger’s equation (Eq. 1.1) very difficult. To solve this problem, an approximation has to be provided (3). The time evolution of the wavefunction is defined by the time-dependent Schroedinger equation, which describes the dynamic electronic states of a many body system:

$$\underbrace{\left[\frac{\hbar^2}{2m} \nabla^2 + V \right]}_{\hat{H}} \psi(r, t) = i\hbar \frac{\partial \psi}{\partial t}(r, t) \quad (1.1)$$

The wavefunction ψ is an eigenfunction of the Hamilton operator $\hat{H}$.

$\frac{\hbar^2}{2m} \nabla^2$ is the kinetic and V the potential energy of the electrons.

The time-independent and non relativistic Schroedinger equation is used to describe static electronic states of a system, which consists of N (e) electrons (mass m_i at position r_i) and M (n) nuclei (mass M_i and position R_i):

$$\underbrace{\left[\frac{\hbar^2}{2m} \nabla^2 + V \right]}_{\hat{H}} \psi(r_1, r_2, \dots, r_N, R_1, R_2, \dots, R_M) = E \psi(r_1, r_2, \dots, r_N, R_1, R_2, \dots, R_M) \quad (1.2)$$

where E is the energy, which is an eigenvalue of the Hamilton operator $\hat{H}$. This Hamiltonian $\hat{H}$ consists of five terms:

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn}. \quad (1.3)$$

$\hat{T}_e$ is the kinetic-energy operator of the electrons:

$$\hat{T}_e = - \sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2, \quad (1.4)$$

$\hat{T}_n$ is the kinetic-energy operator of the nuclei:

$$\hat{T}_n = - \sum_{i=1}^M \frac{\hbar^2}{2M_i} \nabla_i^2, \quad (1.5)$$

$\hat{V}_{ee}$ is the electron-electron repulsion:

$$\hat{V}_{ee} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{e^2}{4\pi\epsilon_0} \frac{1}{|r_i - r_j|}, \quad (1.6)$$

$\hat{V}_{en}$ is the electron-nucleus repulsion:

$$\hat{V}_{en} = - \sum_{i=1}^N \sum_{j=1}^M \frac{e^2}{4\pi\epsilon_0} \frac{Z_i}{|r_i - R_j|}, \quad (1.7)$$

$\hat{V}_{nn}$ is the nucleus-nucleus repulsion:

$$\hat{V}_{nn} = \sum_{i=1}^{M-1} \sum_{j=i+1}^M \frac{e^2}{4\pi\epsilon_0} \frac{Z_i Z_j}{|R_i - R_j|}, \quad (1.8)$$

Born and Oppenheimer assume that the mass of the nucleus is 2000 times bigger than the electron and thus the nuclei motion can be neglected. This leads to the so called “Born Oppenheimer approximation” where the kinetic energy operator $\hat{T}_e$ cancels out and the nucleus-nucleus repulsion $\hat{V}_{nn}$ in Eq. 1.3 can be assigned as constant (4). Heitler and London first applied this approximation to the hydrogen molecule (5).

1.1.2 Theory of DFT

To overcome the “Many body Problem”, which is described in the previous chapter, one can use now the electron density ρ instead of the electron wavefunction ψ . The principles of the Density functional theory (DFT) are based on the Hohenberg and Kohn- theorem ((1),(6)). It states that the total energy, E , can be given exactly as a functional of the ground state electronic density, ρ

$$E = E[\rho] \quad (1.9)$$

The theorem provides no guidance as to the form of $E[\rho]$, that means that the applicability of DFT depends on the discovery of accurate approximations. So $E[\rho]$ is written as follow:

$$E[\rho] = T_s[\rho] + E_{ei}[\rho] + E_H[\rho] + E_{xc}[\rho] \quad (1.10)$$

where $T_s[\rho]$ is the single particle kinetic energy, $E_{ei}[\rho]$ is the Coulomb interaction energy between the electrons and the nuclei and $E_H[\rho]$ is the Hartree component of the electron-electron energy and $E_{xc}[\rho]$ is the **exchange-correlation functional**.

$$E_H[\rho] = \frac{e^2}{2} \int d^3r d^3r' \frac{\rho(r)\rho(r')}{|r - r'|}. \quad (1.11)$$

where e is the elementary charge. The exchange correlation function $E_{xc}[\rho]$ is an unknown functional which must be approximated. Several useful functions are known:

1.LDA

In the so called local density approximation (LDA), $E_{xc}[\rho]$ is written as

$$E_{xc}[\rho] = \int d^3r \rho(r) \epsilon_{xc}(\rho(r)) \quad (1.12)$$

ϵ_{xc} is the exchange-correlation energy- density of the free electron gas and a local function of the density. In this approximation, the general inhomogenous electronic system is seen as locally homogenous and then the exchange correlation hole corresponding to the homogeneous electron gas is used, which is known with an excellent accuracy (6). The idea behind this approximation was already described in the Thomas-Fermi-Dirac-theory (7) It is used for systems where the electronic density is uniform such as bulk metals and for less uniform systems such as molecules, semiconductors and ionic crystals. The disadvantages of this method are for example that it fails to cancel the self-interaction for core regions in atoms and oververbinding.

2. GGA

Another method is the generalized gradient approximation (GGA), where the local density as well as its gradient are used to describe the exchange correlation function $E_{xc}[\rho]$. Here an expansion of the density in terms of the gradient and higher order derivatives is needed (6) (8). Comparison of different GGA functionals can be seen in (9). The exchange correlation energy can be written in the following form:

$$E_{xc}[\rho] = \int \rho(r) \epsilon_{XC}[\rho(r)] F_{XC}[\rho(r), \nabla \rho(r), \nabla^2 \rho(r), \dots] dr \quad (1.13)$$

where the function F_{XC} is an enhancement factor. In our case the BJ (Becke-Johnson, for metal sulfides and disulfides) and the PBE (Perdew, Burke

Ernzerhof) exchange functional were used:

PBE

Perdew, Burke and Ernzerhof introduced in 1996 a functional which is a analytic fit to the numerical GGA. This functional satisfies several exact conditions, which are described in (10). It is one of the most used functionals nowadays. The enhancement factor F_{XC} over the local exchange depends on the local density ρ , and the dimensionless density gradient $s=|\nabla\rho(r)|/(2k_F\rho)$. The chosen expression is

$$F_X(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2 / \kappa}, \quad (1.14)$$

where $\mu = \beta(\pi^2/3) = 0.21951$ and $\beta = 0.066725$. PBE choose the largest allowed values of $\kappa=0.804$.

BJ-potential and LDA- correlation

The Becke-Johnson exchange potential + LDA-correlation is often applied to calculate band gaps with an accuracy similar to very expensive GW calculations (11), (12). It is a semilocal approximation to an atomic "exact-exchange" potential and a screening term. One has to consider that this is just a XC-potential, not a XC-energy functional, which leads to the fact that E_{xc} is taken from LSDA. The Becke-Johnson exchange potential can be written as follow:

$$v_x^{BJ}(\mathbf{r}) = v_x^{BR}(\mathbf{r}) + \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{2t(\mathbf{r})}{\rho(\mathbf{r})}}, \quad (1.15)$$

where ρ is the electron density given in Eq. 1.21 and t is the KS kinetic-energy density,

$$t(r) = \frac{1}{2} \sum_{i=1}^N \nabla \varphi_i^*(r) \nabla \varphi_i(r) \quad (1.16)$$

and v_x^{BR} is the Becke-Roussel exchange potential,

$$v_x^{BR}(\mathbf{r}) = -\frac{1}{b(\mathbf{r})} (1 - e^{-x(\mathbf{r})} - \frac{1}{2} x(\mathbf{r}) e^{-x(\mathbf{r})}) \quad (1.17)$$

In Eq. 1.17, x is determined from a nonlinear equation involving ρ , $\nabla\rho$, $\nabla^2\rho$ and t and then b is calculated using this formula

$$b = \sqrt[3]{\frac{x^3 e^{-x}}{8\pi\rho}} \quad (1.18)$$

1.1.3 Solution of the Single Particle Kohn-Sham Equations (1)

Following equation describes the KS (Kohn Sham) orbitals:

$$\psi(\mathbf{r})_i = \sum_{\alpha} c_{i\alpha} \phi_{\alpha}(r), \quad (1.19)$$

where $\phi_{\alpha}(\mathbf{r})$ are the basis functions and the $c_{i\alpha}$ are the expansion coefficients. The density depends only on the KS orbitals and the coefficients are the only variables in the problem. One has to determine the $c_{i\alpha}$ for the occupied orbitals that minimize the total energy (self consistency).

$$T + V_{ei}(r) + V_H(r) + V_{xc}(r)\psi(r) = \epsilon_i(r)\psi(r), \quad (1.20)$$

The electron density can be written as a sum of single particle densities with the density given by a sum over the occupied orbitals,

$$\rho(\mathbf{r}) = \sum_{occ} \psi_i^*(r) \psi_i(r), \quad (1.21)$$

V_H and v_{xc} depend on ρ .

$$V_H(r) = e^2 \int d^3r' \frac{\rho(r')}{|r - r'|}, \quad (1.22)$$

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \quad (1.23)$$

The energy is rewritten using the single particle eigenvalues to eliminate the unknown functional, $T_s[\rho]$.

$$E[\rho] = E_{ii}[\rho] + \sum_{occ} \epsilon_i + E_{xc}[\rho] - \int d^3r \rho(r) (V_{xc}(r) + \frac{1}{2} V_H(r)) \quad (1.24)$$

where the sum runs over the occupied orbitals. In Fig. 1.1 one can see that the solutions for the density and $c_{i\alpha}$ are done stepwise. $c_{i\alpha}$ is determined in an iterative process, which finally solves the single particle equation Eq. 1.20 for a given density.

1.1.4 Self Consistency in DFT

As shown in Eq. 1.20, the potential $V(r)$ depends on the electron density $\rho(r)$, but $\rho(r)$ is obtained later from $\psi(r)$.

The solution of this problem is to refine the density iteratively by solving Eq. 1.20 and Eq. 1.21. Bendt and Zunger defined the direct minimization of the total energy with respect to the coefficient $c_{i\alpha}$ in Eq. 1.19 (13).

1.step

The coulomb and exchange potentials from Eq. 1.20 are generated from an input density $\rho_{in}(r)$, which is generated by superposition of free atomic densities:

$$\nabla V_C = -8\pi\rho_{in} \quad (1.25)$$

$$V = V_C + V_{ex} \quad (1.26)$$

2.step

The eigenvalues and eigenvectors are calculated by solving the KS-orbitals using the potentials from Eq. 1.26.

$$[-\nabla^2 + V] \psi_i(r) = \epsilon_i(\mathbf{r}) - \psi_i(\mathbf{r}) \quad (1.27)$$

3.step

After the creation of an output charge density (from the eigenvectors using Eq. 1.21), this density is mixed then with the input to get a refined input for the next iteration.

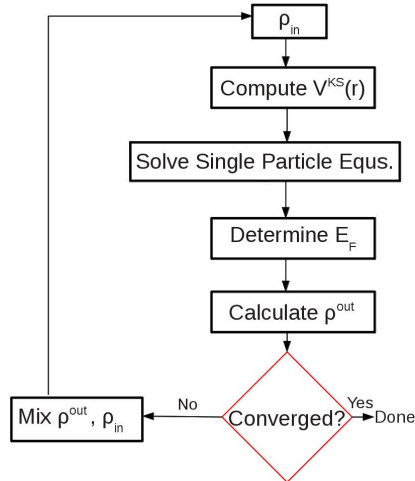


Figure 1.1: SCF-cycle.

1.1.5 Bloch's theorem and periodic boundary conditions (2)

Crystalline solids are made of a huge number of atoms (Avogadro's number (6×10^{23})). They can be seen as infinite and a small number of atoms (the basis of a unit cell) is replicated along the x, y and z directions in space.

Bloch's Theorem

The wavefunction of an electron in an external periodic potential $v(\mathbf{r}) = v(\mathbf{r} + \mathbf{a}_i)$ can be written as the product of an function with the same periodicity as the potential and a complex phase factor arising from the translational symmetry, i.e

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \quad (1.28)$$

$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{a}_i)$, a_i is the unit cell vector and $\mathbf{k}$ is a wavevector (2). In many pseudopotential codes $u_i(\mathbf{r})$ is expanded in terms of a Fourier series:

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{G}}^n e^{i(\mathbf{G} \cdot \mathbf{r})} \quad (1.29)$$

$\mathbf{G}$ are reciprocal lattice vectors, $\mathbf{R}$ is a real space lattice vector, $C_{\mathbf{G}}^n$ are plane wave expansion coefficients and n is the band index. Linear combination of plane waves are used now to describe the electron wave functions:

$$\Psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{k}+\mathbf{G}} C_{\mathbf{G}}^n e^{i(\mathbf{G}+\mathbf{k}) \cdot \mathbf{r}} \quad (1.30)$$

1.1.6 Density of states

The density of states (DOS) of a system describes the number of such states (classified with $\mathbf{k}$ and band indices n). Bloechl et al. 94 introduced the modified tetrahedron method (14), which was used in this thesis to calculate the DOS.

1.1.7 Methods for calculating the NMR chemical shifts

LCAO-MO methods

Quantum chemical calculations can be used to determine the NMR spectra of molecules and solid state systems and was early proposed by J.A.Pople in 1962 (15). The idea is to model the local environment by applying finite clusters of atoms (16). Other methods which have been used for calculating NMR shifts in solids are shown below:

LAPW (Linear Augmented Planewave method (17))

The LAPW method is a modification of the original augmented plane wave

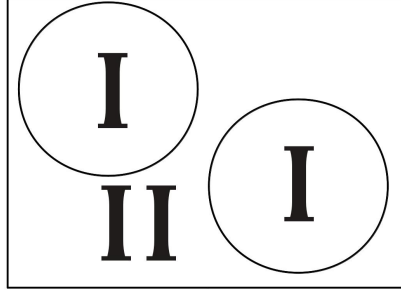


Figure 1.2: The unit cell is partitioned into atomic spheres(I) and an interstitial region(II).

method of Slater. The potential and wavefunctions can be divided into two regions, namely near an atomic nucleus, where they are nearly spherical and in the interstitial space between the atoms where they are smoother (Fig. 1.2). So the unit cell is partitioned into non-overlapping atomic spheres and an interstitial region. In the two types of regions different basis sets are used:

1. In the **interstitial** region a plane wave expansion is used

$$\phi_{\mathbf{k},\mathbf{G}}^{LAPW}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} \quad (1.31)$$

where $k_n = k + G$; G are the reciprocal lattice vectors and $\mathbf{k}$ is the wave vector inside the first brillouin zone. Each plane wave is augmented by an atomic-like function in every atomic sphere.

2. Inside the **atomic sphere** α , of radius R_α , a linear combination of radial functions times spherical harmonics $\mathbf{Y}_{\mathbf{LM}}(\mathbf{r})$ is used

$$\phi_{\mathbf{k},\mathbf{G}}^{LAPW}(\mathbf{r}) = \sum_{l,m} \left[A_{l,m}^{\alpha,\mathbf{k}+\mathbf{G}} u_l^\alpha(r, E_l) + B_{l,m}^{\alpha,\mathbf{k}+\mathbf{G}} \dot{u}_l^\alpha(r, E_l) \right] Y_{l,m}(\hat{r}) \quad (1.32)$$

where $u_l^\alpha(r, E_l)$ is the regular solution of the radial Schroedinger equation for energy E_l and the spherical part of the potential inside sphere α ; $\dot{u}_l^\alpha(r, E_l)$ is the energy derivative of $u_l^\alpha(r, E_l)$ evaluated at E_l ; the coefficients $A_{l,m}$ and $B_{l,m}$ are functions of $k + G$ and fixed by the requirement to be continuous in value and slope with the corresponding plane wave at the sphere boundary. u_l and $\dot{u}_l$ are obtained by numerical integration of the radial Schroedinger equation (18) (19).

The wave functions can now be constructed as a Fourier series in the interstitial region and as a (l, m) series inside the spheres:

$$\Psi_{n,\mathbf{k}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} C_{\mathbf{G}}^n e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}, & \mathbf{r} \in I \\ \sum_{l,m} W_{l,m}^{n,\alpha,\mathbf{k}}(r) Y_{l,m}(\hat{r}), & \mathbf{r} \in S_\alpha \end{cases} \quad (1.33)$$

$W_{l,m}^{n,\alpha,\mathbf{k}}(r)$ can be defined as follow:

$$\begin{aligned} W_{l,m}^{n,\alpha,\mathbf{k}}(r) = & \sum_{\mathbf{G},i} C_{\mathbf{G},i} [A_{l,m}^{\alpha,\mathbf{k},\mathbf{G},i} u_l^\alpha(r, E_l) \\ & + B_{l,m}^{\alpha,\mathbf{k},\mathbf{G},i} \dot{u}_l^\alpha(r, E_l) \\ & + C_{l,m}^{i,\alpha,\mathbf{k}} u_l^{\alpha,i}(r, E_l^i)] Y_{l,m}(\hat{r}) \end{aligned} \quad (1.34)$$

One has to add additional basis functions to make a consistent treatment of semicore and valence states, which are the so called “local orbitals (LO)”. The local orbitals can be seen as a combination of 2 radial functions at two different energies (E_1, E_2). One has to determine $A_{l,m}^{\alpha,\mathbf{k}}, B_{l,m}^{\alpha,\mathbf{k}}$ and $C_{l,m}^{\alpha,\mathbf{k}}$ from normalization.

$$\phi_{l,m,\mathbf{k}}^{LO,\alpha,i}(\mathbf{r}) = \begin{cases} 0, & \mathbf{r} \in I \\ [A_{l,m}^{i,\alpha,\mathbf{k}} u_l^\alpha(r, E_{1,l}) + B_{l,m}^{i,\alpha,\mathbf{k}} \dot{u}_l^\alpha(r, E_{1,l}) \\ + C_{l,m}^{i,\alpha,\mathbf{k}} u_l^{\alpha,i}(r, E_{2,l})] Y_{l,m}(\hat{r}), & \mathbf{r} \in S_\alpha \end{cases} \quad (1.35)$$

The solution of the Kohn-Sham equations are expanded in this combined basis set of LAPW's according to Eq. 1.19. $R_{MT}K_{max}$ is a cutoff parameter, which is usually 6-9 and controls the basis set, where R_{MT} is the smallest atomic sphere radius in the unit cell and K_{max} is the magnitude of the largest $\mathbf{G}$ vector in equation Eq. 1.31.

Other methods are the GAPW (Gaussian augmented-plane-wave method (20) and the GIPAW (Gauge-including projector augmented-wave method (21).

1.2 SSNMR-Spectroscopy

1.2.1 Basic concepts

Nuclear magnetic resonance (NMR) is a spectroscopic method that gives information about the atomic and electronic structure of materials. It is used in many disciplines like chemistry, biology, physics, material science and geology (20). NMR experiments measure the sum of an external field and the corresponding induced field at the nucleus by measuring the **transition energies** related to the reorientation of the nuclear magnetic moment. An external magnetic field $\mathbf{B}$ induces an electric current $\mathbf{j}_{\text{ind}}$ in the sample and this current is the source of an induced magnetic field $\mathbf{B}_{\text{ind}}$. The measured induced field depends strongly on the atomic and electronic structure of the material and thus NMR spectra give informations about these properties (22).

NMR measurements can be applied to both molecules and solids. For molecules one can state that there is an set of empirical rules which displays the relation between the NMR spectra and the atomic structure (23). Contrary to this, empirical rules for solid states are very difficult to employ (24) and thus so called “Ab initio calculations” can be applied to assign chemical shifts to specific sites. Theory behind ab initio quantum chemical calculations of NMR chemical shifts and parameters of molecules can be found in (25) and (26). In (20), (27),(28) and (29) the theory behind ab initio quantum chemical calculations in solids which electronic structure is solved by using the density functional theory (DFT) is described.

1.2.2 Theoretical approach

Induced current in DFT perturbation theory

A external magnetic field $\mathbf{B}_{\text{ext}}$, applied to a sample induces an electronic current density $\mathbf{j}_{\text{ind}}(\mathbf{r})$. This current produces an induced magnetic field $\mathbf{B}_{\text{ind}}$ at the nucleus (Fig. 1.3). A linear response theory can be used as follow (20)

$$\mathbf{B}_{\text{ind}}(\mathbf{R}) = -\overleftrightarrow{\sigma}(R)\mathbf{B}, \quad (1.36)$$

$\overleftrightarrow{\sigma}(r)$ is the chemical shielding tensor. The isotropic shielding $\sigma(\mathbf{R})$ can be calculated now from this equation

$$\sigma(\mathbf{R}) = \text{Tr}[\overleftrightarrow{\sigma}(\mathbf{R})] \quad (1.37)$$

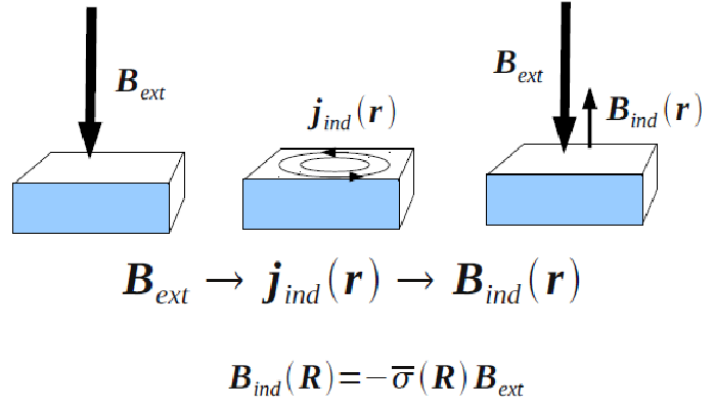


Figure 1.3: Influence of the external magnetic field B_{ext} on the sample.

The experimentally measured chemical shift δ can be get only with respect to some **reference compound**

$$\delta(\mathbf{R}) = \sigma_{ref} - \sigma(\mathbf{R}) \quad (1.38)$$

The Biot-Savart law is now applied to integrate the induced current $\mathbf{j}_{ind}(\mathbf{r})$ to finally get the induced field

$$\mathbf{B}_{ind}(\mathbf{R}) = \frac{1}{c} \int d^3r \, \mathbf{j}_{ind}(\mathbf{r}) \times \frac{\mathbf{R} - \mathbf{r}}{|\mathbf{r} - \mathbf{R}|^3}, \quad (1.39)$$

The single particle Hamiltonian can be written as follow:

$$H = \frac{1}{2} \left(\mathbf{p} + \frac{1}{c} \mathbf{A}(\mathbf{r}) \right)^2 + V(\mathbf{r}), \quad (1.40)$$

$\mathbf{p}$ is the momentum operator, $V(\mathbf{r})$ is the effective single particle potential, and $\mathbf{A}(\mathbf{r})$ is the vector potential.

In the symmetric gauge $\mathbf{A}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times \mathbf{r}$ and the Hamiltonian becomes:

$$H = \frac{1}{2} \mathbf{p}^2 + V(\mathbf{r}) + \frac{1}{2c} \mathbf{r} \times \mathbf{p} \cdot \mathbf{B} + \frac{1}{8c^2} (\mathbf{B} \times \mathbf{r})^2 \quad (1.41)$$

where the first two terms belong to the unperturbed Hamiltonian, while the third term is the first order perturbation ($H^{(1)}$) with respect to the external field $\mathbf{B}$:

$$H^{(1)} = \frac{1}{2c} \mathbf{r} \times \mathbf{p} \cdot \mathbf{B}. \quad (1.42)$$

The current operator in the presence of the magnetic field is defined as follow:

$$\mathbf{J}(\mathbf{r}') = \mathbf{J}^p(\mathbf{r}') + \mathbf{J}^d(\mathbf{r}') \quad (1.43)$$

$$\mathbf{J}^p(\mathbf{r}') = -\frac{\mathbf{p}|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|\mathbf{p}}{2} \quad (1.44)$$

$$\mathbf{J}^d(\mathbf{r}') = -\frac{\mathbf{B} \times \mathbf{r}'}{2c} |\mathbf{r}'\rangle\langle\mathbf{r}'|, \quad (1.45)$$

$\mathbf{J}^p$ and $\mathbf{J}^d$ are the paramagnetic and diamagnetic current operators.

The total current density can be calculated as a sum of the expectation values of the current operator applied to the occupied Kohn-Sham states.

One only needs the first order terms with respect to the external field $\mathbf{B}$ to calculate the induced current:

$$\begin{aligned} \mathbf{j}_{ind}(\mathbf{r}') = & \sum_o \left[\langle \Psi_o^{(1)} | \mathbf{J}^{(0)}(\mathbf{r}') | \Psi_o^{(0)} \rangle + \langle \Psi_o^{(0)} | \mathbf{J}^{(0)}(\mathbf{r}') | \Psi_o^{(1)} \rangle \right. \\ & \left. + \langle \Psi_o^{(0)} | \mathbf{J}^{(1)}(\mathbf{r}') | \Psi_o^{(0)} \rangle \right], \end{aligned} \quad (1.46)$$

$\psi^{(0)}$ is an occupied orbital of the unperturbed Hamiltonian, $J^0(\mathbf{r}')$ the unperturbed part of the current operator, $J^1(\mathbf{r}')$ the first order perturbation of the current operator and $\psi^{(1)}$ the first-order perturbation of $\psi^{(0)}$, projected on the subspace of the unoccupied states. Following standard perturbation theory formula is used:

$$|\Psi_n^{(1)}\rangle = \mathcal{G}(\epsilon_n) H^{(1)} |\Psi_n^{(0)}\rangle, \quad (1.47)$$

where $\mathcal{G}$ is the Green function operator:

$$\mathcal{G}(\epsilon) = \sum_e \frac{|\Psi_e^{(0)}\rangle\langle\Psi_e^{(0)}|}{\epsilon - \epsilon_e}, \quad (1.48)$$

and the sum is running over the unoccupied Kohn-Sham orbitals. If one apply expressions for $J^0(\mathbf{r}')$, $J^1(\mathbf{r}')$ and $\Psi_o^{(1)}$ into Eq. 1.62 one can write the following:

$$\begin{aligned} \mathbf{j}_{ind}(\mathbf{r}') = & \sum_o Re \left[\langle \Psi_o^{(0)} | \mathbf{J}^p(\mathbf{r}') \mathcal{G}(\epsilon_o) H^{(1)} | \Psi_o^{(0)} \rangle \right] \\ & - \frac{1}{2c} \rho(\mathbf{r}') \mathbf{B} \times \mathbf{r}' \end{aligned} \quad (1.49)$$

where the first term is the paramagnetic current and second term the diamagnetic current contribution to the total induced current. Following problem occurs now (22):

“These terms depend on the gauge origin, on the choice of the origin of the unit cell and they may become large and opposite in sign. As the diamagnetic component is related to the ground state charge density, it will converge faster with respect to the basis set than the paramagnetic contribution which contains a sum over the unoccupied states. This is the so-called **"gauge origin problem"** which leads to a dependence of the chemical shift on a change in the gauge origin. This represents a problem for practical calculations where finite basis sets are used for computing the unperturbed wave functions. In order to avoid such convergence problems, it is convenient to rewrite the diamagnetic contribution using a **commutator**”:

$$\rho(\mathbf{r}')\mathbf{B} \times \mathbf{r}' = - \sum_o \langle \Psi_o^{(0)} | \frac{1}{i} [\mathbf{B} \times \mathbf{r}' \cdot \mathbf{r}, \mathbf{J}^p(\mathbf{r}')] | \Psi_o^{(0)} \rangle \quad (1.50)$$

f sum rule (20)

The generalized f-sum rule is employed which holds for any pair of Hermitian operators $\mathcal{O}$ and $\mathcal{E}$, where $\mathcal{O}$ and $\mathcal{E}$ are, odd and even on time reversal;

$$\langle \phi | \mathcal{O} | \phi' \rangle = - \langle \phi' | \mathcal{O} | \phi \rangle \quad (1.51)$$

and

$$\langle \phi | \mathcal{E} | \phi' \rangle = \langle \phi' | \mathcal{E} | \phi \rangle \quad (1.52)$$

for any $|\phi\rangle$ and $|\phi'\rangle$ such that $\langle \mathbf{r} | \phi \rangle$ $\langle \mathbf{r} | \phi' \rangle$ are real.
From this expression the **f sum rule** takes this form:

$$2 \sum_o = \left\langle \psi_0^{(0)} \left| \frac{1}{i} [\mathcal{E}, \mathcal{O}] \right| \psi_0^{(0)} \right\rangle \quad (1.53)$$

$$\begin{aligned} & - 2 \sum_{o,o'} \frac{1}{i} \langle \psi_0^{(0)} | \mathcal{O} | \psi_0^{(0)} \rangle \langle \psi_0^{(0)} | \mathcal{E}, \mathcal{S}^{(0)} | \psi_0^{(0)} \rangle \\ & = -4 \sum_o \text{Re} \left[\left\langle \psi_0^{(0)} \left| \mathcal{O} \mathcal{G}(\epsilon_o^{(0)}) \frac{1}{i} [\mathcal{E}, H^{(0)} - \epsilon_o^{(0)} S^{(0)}] \right| \psi_0^{(0)} \right\rangle \right] \end{aligned} \quad (1.54)$$

The **diamagnetic** current can now be written as follow:

$$\begin{aligned} \mathbf{j}_{ind}(\mathbf{r}') &= 2 \sum_o \text{Re} \left[\langle \Psi_o^{(0)} | \mathbf{J}^p(\mathbf{r}') \mathcal{G}(\epsilon_o) H^{(1)} | \Psi_o^{(0)} \rangle \right. \\ & \quad \left. - \langle \Psi_o^{(0)} | \mathbf{J}^p(\mathbf{r}') \mathcal{G}(\epsilon_o) \frac{\mathbf{B} \times \mathbf{r}'}{2c} \cdot \mathbf{v} | \Psi_o^{(0)} \rangle \right] \end{aligned} \quad (1.55)$$

where $v = \frac{1}{i}[r, H^{(0)}]$.

The induced current takes now this form:

$$\mathbf{j}_{ind}(\mathbf{r}') = \frac{1}{c} \sum_o Re \left[\langle \Psi_o^{(0)} | \mathbf{J}^p(\mathbf{r}') \mathcal{G}(\epsilon_o) \right. \\ \left. ((\mathbf{r} - \mathbf{r}') \times \mathbf{p} \cdot \mathbf{B}) | \Psi_o^{(0)} \rangle \right] \quad (1.56)$$

The position operator, which is not well defined in an extended system, is replaced with the limit (27):

$$(\mathbf{r} - \mathbf{r}') \cdot \hat{\mathbf{u}}_i = \lim_{q \rightarrow 0} \frac{1}{2q} \left(e^{iq\hat{\mathbf{u}}_i \cdot (\mathbf{r} - \mathbf{r}')} - e^{-iq\hat{\mathbf{u}}_i \cdot (\mathbf{r} - \mathbf{r}')} \right), \quad (1.57)$$

where $\hat{\mathbf{u}}_i$ is the unit vector of the Cartesian frame of reference, and q is the modulation wave vector. To calculate the $\mathbf{j}_{ind}$, one has to take the limit and finally one can write the induced current as follow:

$$\mathbf{S}(\mathbf{r}', q) = \frac{1}{c} \sum_{x,y,z} \sum_o Re \left[\frac{1}{i} \langle \Psi_o^{(0)} | \mathbf{J}^p(\mathbf{r}') \mathcal{G}(\epsilon_o) \right. \\ \left. \mathbf{B} \times \hat{\mathbf{u}}_i \cdot e^{iq\hat{\mathbf{u}}_i \cdot (\mathbf{r} - \mathbf{r}')} \mathbf{p} | \Psi_o^{(0)} \rangle \right]. \quad (1.58)$$

A k -dependet Green-function is used:

$$\mathcal{G}_{\mathbf{k}}(\epsilon) = \sum_e \frac{|u_{e,\mathbf{k}}^{(0)}\rangle \langle u_{e,\mathbf{k}}^{(0)}|}{\epsilon - \epsilon_{e,\mathbf{k}}}, \quad (1.59)$$

The paramagnetic current operator is now represented as follow:

$$\mathbf{J}_{\mathbf{k},\mathbf{k}'}^p(\mathbf{r}') = - \frac{(-i\nabla + \mathbf{k})|\mathbf{r}'\rangle \langle \mathbf{r}'| + |\mathbf{r}'\rangle \langle \mathbf{r}'| (-i\nabla + \mathbf{k})}{2}, \quad (1.60)$$

The paramagnetic augmentation term $\mathbf{S}(\mathbf{r}', q)$ can now be written as follow:

$$\mathbf{S}(\mathbf{r}', q) = \frac{1}{cN_{\mathbf{k}}} \sum_{\alpha=x,y,z} \sum_{o,\mathbf{k}} Re \left[\frac{1}{i} \langle u_{o,\mathbf{k}}^{(0)} | \mathbf{J}_{\mathbf{k},\mathbf{k}+\mathbf{q}_{\alpha}}^p(\mathbf{r}') \right. \\ \left. \mathcal{G}_{\mathbf{k}+\mathbf{q}_{\alpha}}(\epsilon_o) \mathbf{B} \times \hat{\mathbf{u}}_i \cdot \mathbf{v}_{\mathbf{k},\mathbf{k}+\mathbf{q}_{\alpha}} | u_{o,\mathbf{k}}^{(0)} \rangle \right] \quad (1.61)$$

where $v_{k,k'} = -i\nabla + k'$.

These expression for $S(\mathbf{r}', \mathbf{q})$ allow the evaluation of the all **electron current** $\mathbf{j}_{\text{ind}}(\mathbf{r}')$ response through Eq. 1.46 (27).

Induced current in LAPW

The concepts of LAPW were discussed in Chapter 1.1.7. The induced current density can be described as a Fourier series in the interstitial and a spherical harmonics expansion inside the spheres(17) :

$$\mathbf{j}_{\text{ind}}(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} \mathbf{j}_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}, & \mathbf{r} \in I \\ \sum_{l,m} \mathbf{j}_{l,m}^{\alpha}(r) Y_{l,m}(\hat{r}). & \mathbf{r} \in S_{\alpha}, \end{cases} \quad (1.62)$$

where $\mathbf{j}_{\mathbf{G}}$ are the Fourier coefficients and $\mathbf{j}_{l,m}^{\alpha}(r)$ are radial functions which depend on the distance from the nucleus α .

$\mathbf{j}_{l,m}^{\alpha}(r)$ is written as finite derivatives

$$\mathbf{j}_{\mathbf{G}} = \lim_{q \rightarrow 0} \frac{1}{2q} [\mathbf{S}_{\mathbf{G}}(q) - \mathbf{S}_{\mathbf{G}}(-q)], \quad (1.63)$$

$$\mathbf{j}_{l,m}^{\alpha}(r) = \lim_{q \rightarrow 0} \frac{1}{2q} [\mathbf{S}_{l,m}(r, q) - \mathbf{S}_{l,m}(r, -q)]. \quad (1.64)$$

$S(\mathbf{r}, q)$ from Eq. 1.61 can be expressed as follow:

$$\mathbf{S}(\mathbf{r}, q) = \frac{1}{cN_{\mathbf{k}}} \sum_{\alpha=x,y,z} \sum_{\mathbf{k}} \sum_{o,e} \frac{1}{(\epsilon_{e,\mathbf{k}+\mathbf{q}_{\alpha}} - \epsilon_{o,\mathbf{k}})} \text{Re} \left[\frac{1}{i} \left(\mathbf{A}_{\mathbf{k},\mathbf{q}_{\alpha}}^{o,e}(\mathbf{r}) + \mathbf{B}_{\mathbf{k},\mathbf{q}_{\alpha}}^{o,e}(\mathbf{r}) \right) C_{\mathbf{k},\mathbf{q}_{\alpha}}^{o,e} \right],$$

where $\mathbf{A}_{\mathbf{k},\mathbf{q}_{\alpha}}^{o,e}(\mathbf{r})$, $\mathbf{B}_{\mathbf{k},\mathbf{q}_{\alpha}}^{o,e}(\mathbf{r})$, $C_{\mathbf{k},\mathbf{q}_{\alpha}}^{o,e}$ are

$$\mathbf{A}_{\mathbf{k},\mathbf{q}_{\alpha}}^{o,e}(\mathbf{r}') = \langle u_{o,\mathbf{k}} | (\mathbf{p} + \mathbf{k}) | \mathbf{r}' \rangle \langle \mathbf{r}' | u_{e,\mathbf{k}+\mathbf{q}_{\alpha}} \rangle \quad (1.65)$$

$$\mathbf{B}_{\mathbf{k},\mathbf{q}_{\alpha}}^{o,e}(\mathbf{r}') = \langle u_{o,\mathbf{k}} | \mathbf{r}' \rangle \langle \mathbf{r}' | (\mathbf{p} + \mathbf{k} + \mathbf{q}_{\alpha}) | u_{e,\mathbf{k}+\mathbf{q}_{\alpha}} \rangle \quad (1.66)$$

$$C_{\mathbf{k},\mathbf{q}_{\alpha}}^{o,e} = (\mathbf{B} \times \hat{\alpha}) \cdot \langle u_{e,\mathbf{k}+\mathbf{q}_{\alpha}} | (\mathbf{p} + \mathbf{k}) | u_{o,\mathbf{k}} \rangle, \quad (1.67)$$

$\mathbf{A}_{\mathbf{k},\mathbf{q}_{\alpha}}^{o,e}(\mathbf{r}')$ and $\mathbf{B}_{\mathbf{k},\mathbf{q}_{\alpha}}^{o,e}(\mathbf{r}')$ are the vector fields expanded using plane waves and spherical harmonics in the interstitial and inside spheres.

Fig. 1.4 shows the induced current density for ZrS_2 .

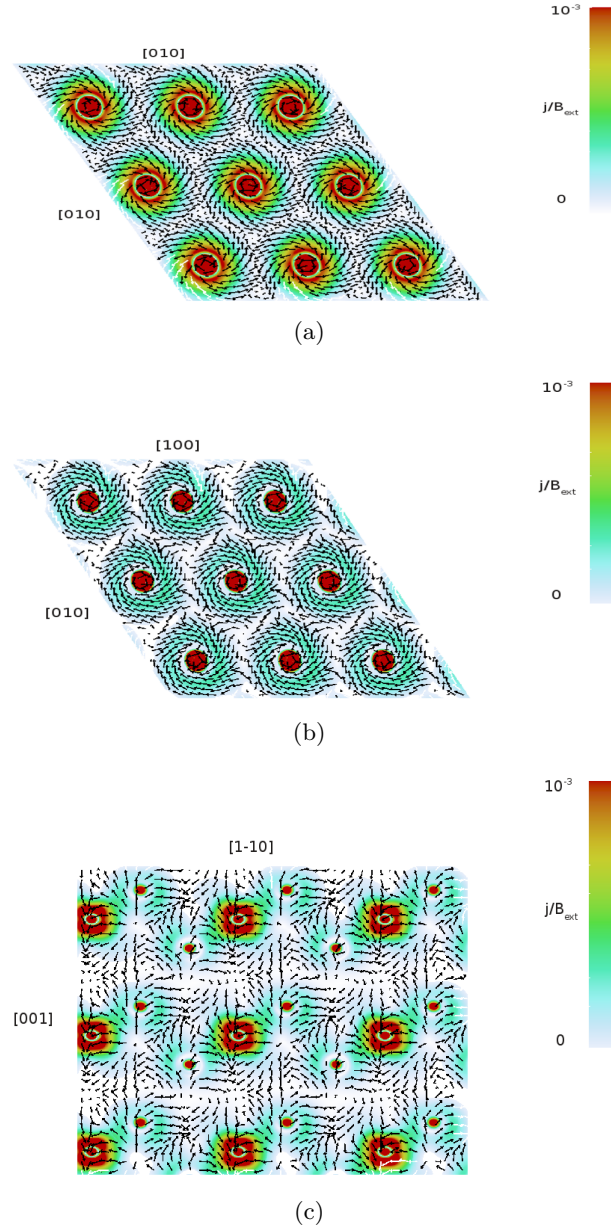


Figure 1.4: Fig.(a) shows the induced current density for ZrS_2 plotted along the $[001]$ plane for Zr and S atoms, Fig.(b) the induced current density plotted again along the $[001]$ plane (directions are indicated) through the S atoms and Fig (c) along the $[110]$ plane containing both, Zr and S atoms. The external magnetic field is applied in the z-direction of the elementary cell.

1.2.3 SSNMR in WIEN2k

To calculate the chemical shielding in a solid, one has to do several steps:

1st step: Generating a struct- file

Creating a new case directory:

If one opens Wien2Web (the fully web enabled interface to Wien2k), one can create a new directory using the “Create” button.

Creating the case.struct file:

To create a struct.file, one has to start the struct-file generator using “Execution StructGen”. After that, w2web creates an empty structure template, in which one can specify structural data.

2nd step: Initialization of the calculation

This step is done by running the script “init_lapw” from the command line. Initializing the calculation will run several steps automatically, where **x** is the script to start WIEN2k programs. These several steps are run automatically:

x nn: calculates the nearest neighbours up to specified distance and determines the atomic sphere radii. The distance is specified by giving it a distance factor.

x sgrouop: calculates the point and spacegroups for the given structure.

x symmetry: generates the space group symmetry operations, determines the point group of the individual atomic sites, generates the LM expansion for the lattice harmonics (in case.in2_st) and local rotation matrices (incase.struct_st)

instgen_lapw: one can define the spin-polarization of each atom. This is very important for spin-polarized calculations and in particular for anti-ferromagnetic cases

x lstart: generates atomic densities and determines how the orbitals are treated in the band structure calculations. One has to specify the exchange correlation potential and an energy that separates valence from core state.

x kgen: generates a k-mesh in the Brillouin zone (BZ). One has to specify the number of k-points in the whole BZ.

x dstart: generates a starting density for the SCF cycle by superposition of atomic densities.

3rd step: The SCF cycle

This step is done by running the script “run_lapw” from the command line. Then following steps are done:

LAPW0: generates potential from density, which was calculated using the command **x dstart** (see above).

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

4th step: Calculations of chemical shielding (CS)

After the SCF- cycle was done, one has to add extra local orbitals (LO) at high energies:

`x_nmr -mode in1:` generates `case.in1_nmr` with 10 extra LO's at high energies.

`x_nmr -p:` runs the following modes:

`klist:` generating k points

`lapw1:` calculation of eigenvalues and eigenvectors

`lapw2:` calculation of valence densities from eigenvectors

`core:` calculation of the core densities from eigenvectors

`current:` calculation of the induced current

`integ:` integration of the induced current

One has to enter a number of the k-mesh. It creates the corresponding mesh in the full-BZ as well as the shifted k-meshes.

The final shifts can be found in `case.outputnmr_integ`.

Bandwise analysis:

The CS contribution for the specific bands are calculated by using following command:

`x_nmr -mode -current -emin e1 -emax e2 -p:`

where e1 represents the energy minimum and e2 the energy maximum.

Character analysis:

The CS contribution for the characters of the states are calculated using this commands:

`x_nmr -mode -current-emin e1 -emax e2 -filt_curr_o atom l -p:`

filter in current density (`make_current_sp`) of **occupied states** according Eq. 1.46. Leaves only nonzero $A_{l,m}$ for iat (atom) and l (quantum number).

`x_nmr -mode -current -emin e1 -emax e2 -filt_curr_o atom l1
-filt_curr_fop atom l2 -p:`

filter in current density (`make_current_sp`) of the **1st order perturbation** of the occupied wave-function according Eq. 1.46. Leaves only nonzero $A_{l,m}$ for iat and l

`x_nmr -mode -current -emin e1 -emax e2 -filt_curr_o atom l1`

`-filt_curr_fop atom l2 -filt_cxyz_q atom2 l3:`

filter in coupling matrix elements (in `make_cxyz`) for the **empty states** according Eq. 1.47 (green only). Leaves only nonzero $A_{l,m}$ for l and l .

Plotting the current density in the elementary cell:

`x_nmr -mode plot:` this creates following files

`current_x.dx`
`current_y.dx`
`current_z.dx`
`current_mode.dx`
`current.dx`
`current_1d.dx`

After that one has to run the script “current2dx-1”. This makes automatically a current density plot (Eq. 1.46) in the program **Data Explorer**.

2 Calculations of NMR chemical shifts in nonmetallic systems

The orbital motion of the electrons causes the chemical shielding in nonmetallic systems (30).

2.1 Chemical shifts of metal sulfides and disulfides

Sulfur is found as a pure element, as sulfid and sulfate minerals and in amino acids. Sulfur state NMR (SSNMR) can be applied for direct characterization of S-containing materials. This method provides informations on S local coordination and electronic environment. ^{33}S isotope can be detected by NMR, which has a gyromagnetic ratio (1/13 of ^1H) and a low natural abundance (0.76%), which leads to the problem of the most difficult nuclei to study by NMR. ^{33}S is a quadrupolar nucleus with a nuclear spin $I=3/2$ and has a relative large quadrupole moment ($Q = -6.4 \times 10^{-28} \text{m}^2$). This large quadrupole moment leads to rapid T_2 relaxation which causes extremely broad lines in solid states. Nevertheless there are some reasons why ^{33}S NMR is used:

1. Significant chemical structure information can be obtained, by directly observing ^{33}S .
2. Its chemical shift range exceeds 800 ppm, which is four times that of ^{13}C and nearly 16 times that of ^1H .
3. Its NMR properties are more sensitive than the NMR properties of ^{13}C and ^1H nuclei (31).

In this thesis, the focus is kept on alkaline-, earth alkaline metal sulfides and transition metal disulfides. Metal sulfides show some interesting features like high melting points, semi-metallic character or good water solubility which make them important in the use of ceramics, photocells and in the pulp and paper industry (kraft process). Some of them can also be used as lubricants for optical and sensitive instruments because of their low friction coefficients. Transition metal disulfides exhibit layered structures which is shown in Fig. 2.2. Due to this peculiar structure, they are needed in applications such as catalysis, ceramics, semiconductors, energy storage electronics and optical devices (32).

2.1.1 Structural parameters

Alkali M_2S (Li,Na)-, earth alkaline metal sulfides MS ($M=Mg, Ca, Sr, Ba$) and Group 4-6 transition metal disulfides MS_2 ($M=Zr, W, Mo, Ti$) and sulfide (ZnS) were used for the investigations between the theoretical calculated chemical shieldings (CS) and the experimental chemical shifts. The structural parameters of metal sulfides and disulfides are presented in Table 2.1. One can declare that all sulfides show cubic symmetry except for ZnS (hexagonal symmetry). BaS has the largest elementary cell, while all transition metal disulfides show hexagonal symmetry, where WS_2 has the largest elementary cell. Table 2.2 shows the atomic coordinates, the RMT (Muffin-Tin Radius: atomic sphere radius) and the space group in the unit cell. A RK_{MAX} of 7 was used for the calculations.

Table 2.1: Lattice parameters and angles in the unit cell of metal sulfides and disulfides.

	a / Å	b / Å	c / Å	$\alpha / ^\circ$	$\beta / ^\circ$	$\gamma / ^\circ$
sulfides						
Li_2S [(33)]	5.76	5.76	5.76	90	90	90
Na_2S [(34)]	6.54	6.54	6.54	90	90	90
MgS [(35)]	5.20	5.20	5.20	90	90	90
CaS [(35)]	5.71	5.71	5.71	90	90	90
ZnS [(36)]	3.84	3.84	6.28	90	90	120
SrS [(37)]	6.02	6.02	6.02	90	90	90
BaS [(38)]	6.37	6.37	6.37	90	90	90
disulfides						
WS_2 [(39)]	3.15	3.15	12.36	90	90	120
MoS_2 [(40)]	3.16	3.16	12.29	90	90	120
ZrS_2 [(41)]	3.65	3.65	5.82	90	90	120
TiS_2 [(42)]	3.40	3.40	5.70	90	90	120

It is obvious from Table 2.2 that all metal sulfides have the same space group ($Fm-3m$) except from ZnS ($P63mc$). If one compares the space groups of the transition metal disulfides with each other, one can obtain that MoS_2 and WS_2 have the same one ($P63/mmc$), while ZrS_2 and TiS_2 have the space group of $P-3m1$. Fig. 2.1 presents the NaCl structure of SrS on the left picture and the Zinc-Blende-Structure of ZnS on the right one, while Fig. 2.2 shows the CdI_2 structure of ZrS_2 and MoS_2 structure of WS_2 . Each sheet of W atoms is “sandwiched” by two sheets of S atoms (44).

Table 2.2: Atomic coordinates, RMT and space group of metal sulfides and disulfides. *geo.opt.= geometry-optimized structure ((43)) for WS₂

	Atom	x	y	z	RMT	Space group
sulfides						
Li ₂ S [(33)]	Li	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	2.06	<i>Fm-3m</i>
	S	0.00	0.00	0.00	2.39	
Na ₂ S [(34)]	Na	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	2.50	<i>Fm-3m</i>
	S	0.00	0.00	0.00	2.47	
MgS [(35)]	Mg	0.00	0.00	0.00	2.38	<i>Fm-3m</i>
	S	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	2.26	
CaS [(35)]	Ca	0.00	0.00	0.00	2.50	<i>Fm-3m</i>
	S	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	2.48	
ZnS [(36)]	Zn	$\frac{1}{3}$	$\frac{2}{3}$	0.00	2.37	<i>P63mc</i>
	S	$\frac{1}{3}$	$\frac{2}{3}$	0.375	1.94	
SrS [(37)]	Sr	0.00	0.00	0.00	2.50	<i>Fm-3m</i>
	S	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	2.50	
BaS [(38)]	Ba	0.00	0.00	0.00	2.50	<i>Fm-3m</i>
	S	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	2.50	
disulfides						
*WS ₂ [(39)]	W	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	2.33	<i>P63/mmc</i>
	S	$\frac{1}{3}$	$\frac{2}{3}$	0.634	1.91	
MoS ₂ [(40)]	Mo	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	2.39	<i>P63/mmc</i>
	S	$\frac{1}{3}$	$\frac{2}{3}$	0.621	2.05	
ZrS ₂ [(41)]	Zr	0.00	0.00	0.00	2.46	<i>P-3m1</i>
	S	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	2.12	
TiS ₂ [(42)]	Ti	0.00	0.00	0.00	2.33	<i>P-3m1</i>
	S	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	2.01	

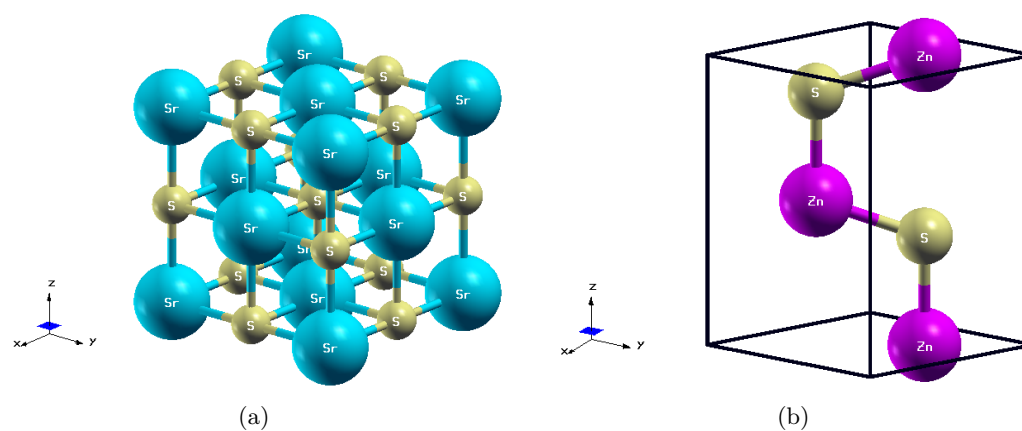


Figure 2.1: NaCl-Structure of SrS (a) and Zinc-Blende-Structure of ZnS (b)

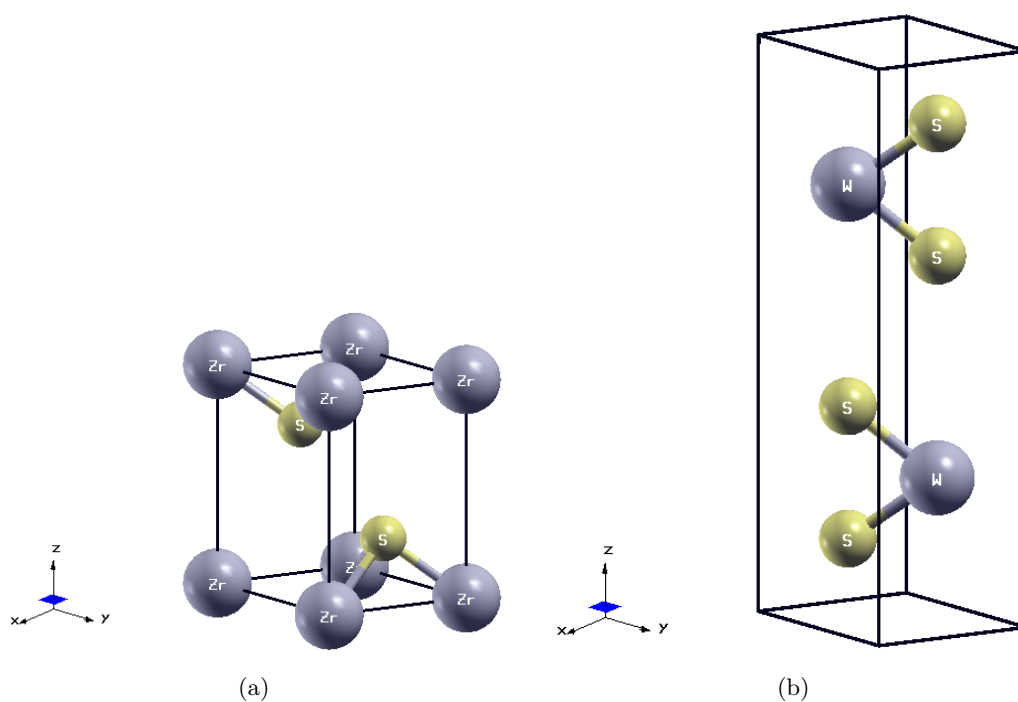


Figure 2.2: CdI₂-Structure of ZrS₂ (a) and MoS₂-Structure of WS₂ (b)

2.1.2 Calculations of the chemical shieldings

In 1951 the authors Dharmatti and Weaver (45) determined the magnetic moment of ^{33}S in CS_2 by using a nuclear induction spectrometer (46). Several papers can be found on ^{33}S NMR spectroscopy, from measuring NMR chemical shifts of biological relevant molecules like taurin to solid states like metal sulphates in the cement chemistry, which is used to distinguish between the sulphates present in a cement paste ((47), (48), (49), (50)). Experimental measurements of the NMR chemical shift of alkali M_2S (Li,Na)- and earth alkaline metal sulfides MS ($\text{M}=\text{Mg},\text{Ca},\text{Sr},\text{Ba}$) were carried out by Rinaldi and Youngs (31). Andre Sutrisno, Victor V. Tersikh and Yining Huang showed in (44) that measurements of NMR chemical shifts, quadrupole constants (C_Q) and electric field gradients (EFG) can be performed on Group 4-6 transition metal disulfides MS_2 ($\text{M}=\text{Zr},\text{W},\text{Mo},\text{Ti}$).

The comparison of the measured NMR shifts with the NMR chemical shieldings calculated with the PBE and BJ exchange correlation functional for ^{33}S nuclei in metal sulfides and disulfides are presented in Table 2.3, Fig. 2.3 and Fig. 2.4. All calculations which are presented in this work have been carried out using the WIEN2K code that is described in (51). This code uses the augmented plane wave plus the local orbital (APW+LO) which is explained in Chapter 1.1.7 and Density functional theory to perform electronic structure calculations Chapter 1.1.2. A k mesh of $6\times 6\times 6$ was used for the calculations. The measured and calculated values correlate quite well and the slope of the linear fit is nearly the same as the correct value of 1.0.

Table 2.3: The isotropic shielding σ_{iso}^{LAPW} computed with PBE and BJ exchange correlation potential ^{33}S in metal sulfides and disulfides. The experimental shifts $\delta_{iso}^{expt.}$ are given with reference to Cs_2SO_4 at 333ppm from CS_2 for sulfides and CS_2 for disulfides. The theoretical shifts δ_{iso}^{LAPW} are given with a reference taken from the linear fit equations included in Fig. 2.3. exp.= experimental, *geo.opt.= geometry-optimized structure for WS_2 . All values in ppm.

	$\sigma_{iso}^{LAPW,PBE}$	$\sigma_{iso}^{LAPW,BJ}$	$\delta_{iso}^{LAPW,PBE}$	$\delta_{iso}^{LAPW,BJ}$	$\delta_{iso}^{expt.}$	structure
sulfides						
Li_2S	797.2	847.8	-373.9	-379.5	-347.0 [(31)]	exp.
Na_2S	786.9	846.7	-364.9	-379.8	-338.0 [(31)]	exp.
MgS	558.0	654.4	-165.4	-207.1	-174.9 [(31)]	exp.
CaS	347.7	381.3	43.0	48.5	-29.1 [(31)]	exp.
ZnS	692.8	705.3	-302.0	-250.6	-236.5 [(31)]	exp.
SrS	329.5	389.4	45.4	31.7	42.8 [(31)]	exp.
BaS	73.7	156.5	270.0	234.8	291.3 [(31)]	exp.
disulfides						
* WS_2	404.0	427.8	-13.1	9.3	-90.0 [(44)]	geo.opt.
MoS_2	167.9	148.3	187.7	254.0	200.0 [(44)]	exp..
ZrS_2	-73.9	-13.0	398.3	387.2	435.0 [(44)]	exp.
TiS_2	-524.0	-469.2	804.3	727.7	795.0 [(44)]	exp

It is obvious in Fig. 2.3 that the chemical shielding (CS) decreases for the alkali and earth alkaline metal sulfides with **increasing atomic number** of the metal atom. That means that the CS depends on the unit cell volume.

For the transition metal disulfides one can clearly state that the CS contribution increases from light to heavy transition metal compounds which is the reverse case of the metal sulfides. The decreasing of the energy separations could also lead to the negative increasing throughout the series. Comparing the calculated chemical shifts using PBE and BJ potential with the experimental chemical shifts, one can say that both methods show good agreement. The CS calculated with the PBE potential showed always a little bit larger value as the calculated CS within the BJ potential, except for CaS , MoS_2 and WS_2 . The CS decreases by **filling up the metal d states** in the metal atom for the series TiS_2 , ZrS_2 , MoS_2 and ZnS_2 (WS_2 has more electrons in the d-orbital than Mo but incongruously a smaller CS). This trend corresponds to the explanation for different CS within the series in Fig. 4.5. One has also to mention that TiS_2 is the only metallic compound here and its CS correlates perfectly with the other nonmetals.

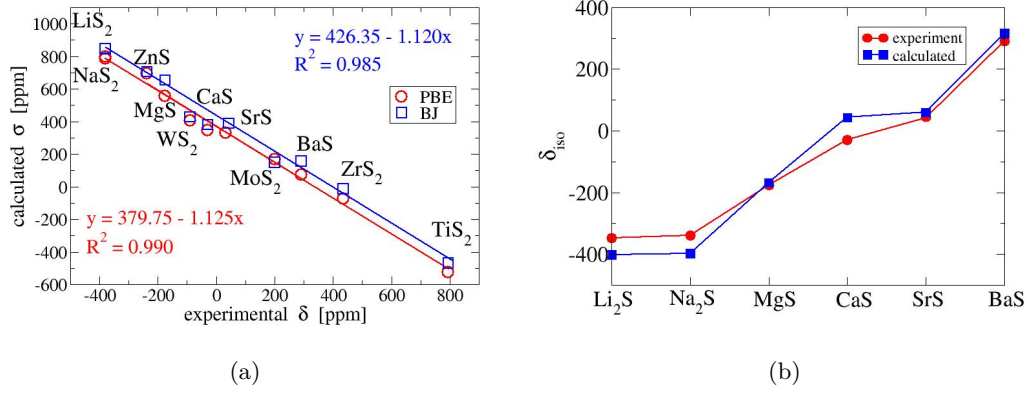


Figure 2.3: Fig. (a) presents the correlation between the measured chemical shifts $\delta_{\text{iso}}^{\text{expt.}}$ and the calculated chemical shieldings $\sigma_{\text{iso}}^{\text{LAPW,PB}}$ using the PBE exchange correlation functional (red) and $\sigma_{\text{iso}}^{\text{LAPW,BJ}}$, using of BJ exchange correlational functional (blue). The y-intercept of 379.9 corresponds to the reference value. Fig.(b) shows the correlation between the calculated chemical shifts using the PBE exchange correlational functional and the experimental chemical shifts from (31).

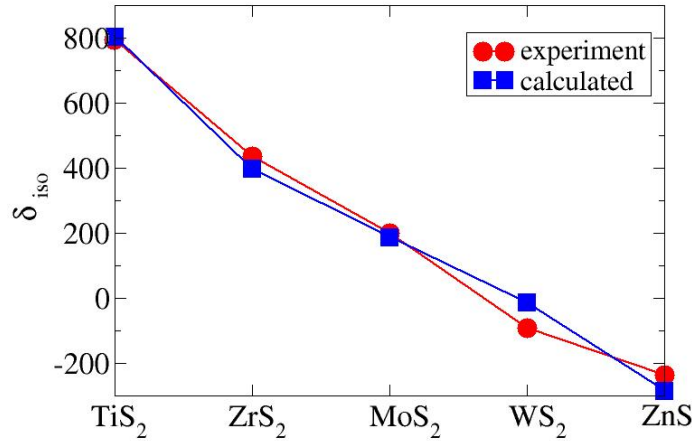


Figure 2.4: Correlation between the calculated chemical shifts using the PBE exchange correlational functional and the experimental chemical shifts of transition metal sulfide (ZnS) and disulfides from (31) and (44).

DOS and charges of states (QTL) in metal sulfides

Fig. 2.5 shows different density of states (DOS) of BaS and ZnS. It can be clearly seen that the S-3p band (red) has the highest energy range which is located near the Fermi Niveau (E_F) in both BaS and ZnS. ZnS shows obviously also a metal-d band (green). If one compares the energy difference between the metal and the sulfur states within the series, one can clearly state that the energy difference between **metal-p and S-p states** and the energy difference between the **S-s and metal-s states** becomes much smaller within the series. It is also obvious that the energies of these bands increase within the series;

Li₂S:

Li-1s states: -46.4 - -46.1 eV, S-3s states: -11 - -10 eV, S-3p states: -2.7 - 0 eV;

Na₂S:

Na-2s states: -52.3 - -51.9 eV, Na-2p states: -23.7 - -23.03 eV, S-3s states: -10.2 - -9.6 eV, S-3p states: -1.5 - 0 eV;

MgS:

Mg-2s states: -77.0 - -76.9 eV, Mg-2p states: -43.7 - -43.9 eV, S-3s states: -12.6 - -10.7 eV, S-3p states: -4.75 - 0 eV.

CaS:

Ca-3s states: -40 - -39 eV, Ca-3p states: -21 - -20.5 eV, S-3s states: -11.3 - -10.4 eV, S-3p states: -3 - 0 eV.

SrS:

Sr-4s states: -33.9 - -33.5 eV, Sr-4p states: -16.8 - -15.6 eV, S-3s states: -10.8 - -9.8 eV, S-3p states: -2.6 - 0 eV.

BaS:

Ba-5s states: -26.3 - -25.9 eV, Ba-5p states: -12.4 - -11.0 eV, S-3s states: -10.3 - -8.89 eV, S-3p states: -1.8 - 0 eV.

ZnS:

S-3s states: -12.9 - -11.8 eV, Zn-3d states: -6.4 - -5.4 eV S-3p states: -5.1 - 0 eV.

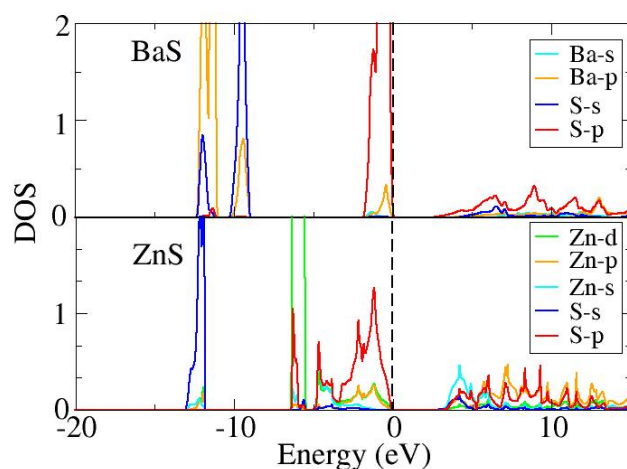


Figure 2.5: DOS of BaS and ZnS.

After analysing those energy values for the metal and sulfur states, one can state following: The smaller the energy difference between the Me-s and S-s states and between the Me-p and S-p states within the series the stronger the interaction of those states within the series. This finally leads to an negative increasing chemical shielding within the series.

Fig. 2.6(a) shows the CS of alkali and earth alkaline metal sulfides plotted against the metal-p charges in the S-p band. One can see that Li_2S , Na_2S and MgS show no trend, while the CS of CaS , SrS and BaS decreases with increasing metal-p charges (QTL) in the S-p band. This is especially true if one compares the value of the CS (-653.9 ppm) and metal-p charge (0.06) of CaS with the CS (-960.0 ppm) and metal-p charge (0.15) of BaS . Fig. 2.6(b) displays the CS of the metal sulfides plotted against the S-p charges in the metal-p band. Compared to Fig. 2.6(a) there is a clear dependence of the CS with the S-p charges within the series for all metal sulfides. Li has no p orbitals, that is why Li_2S is not mentioned in this picture. It is obvious that the CS increases (not decreases as for the metal-p charges in the S p band) with increasing S-p charges in the metal p band. From this figure one can obtain that Na_2S and MgS don't show a CS contribution from the metal p band which is also indicated in Table 2.4. If one looks at the range of the Density of states (DOS) for Na-2p and especially Mg-2p states one can clearly state that those states are lying at low energies which explains the nearly zero value for the S-p charges in the metal-p band. All in all one can say from Fig. 2.6(b) that the increasing S-p charges in the metal p band within the series results in the larger hybridisation between the states and finally contributes to a negative increasing of the chemical shielding from light to heavy metal compounds.

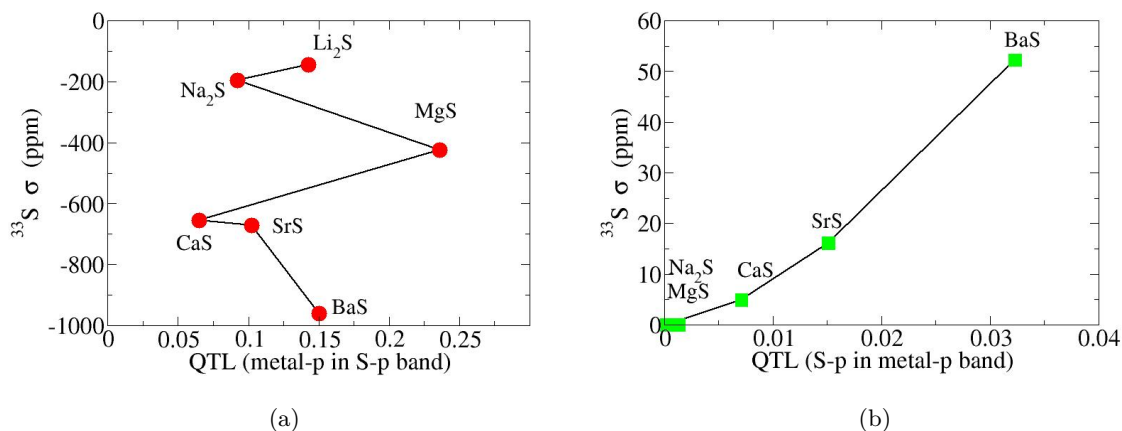


Figure 2.6: Fig.(a) presents the metal-p charges in the S-p band plotted against the CS contribution of the S-p band of metal sulfides. Fig.(b) shows the S-p charges in the metal-p band plotted against the CS contribution of the metal-p band of metal sulfides. QTL are the partial charges.

DOS and charges of states (QTL) in metal disulfides

Fig. 2.8 shows the DOS of MoS_2 and ZrS_2 and Fig. 2.7 the DOS of WS_2 . The DOS of MoS_2 and WS_2 clearly reveal a metal-d band, respectively, which starting point was taken at the energy minimum of the band (-1.58eV for MoS_2 and -3.3eV for WS_2). In contrast to the metal sulfides, the topmost valence band is dominated by the metal-d character for WS_2 and ZrS_2 . The S-3p band is the highest energy band for ZrS_2 . The different energy ranges for the metal and sulfur states ranges are presented below.

WS_2 :

W-5s states: -75 - -74.1 eV, W-5p states: -39.5 - -38.9 eV, W-4f states: -28.9 - -28.6 eV, S-3s states: -17.1 - -14 eV, S-3p states: -8.4 - -3.3 eV, W-5d states: -3.3 - 0eV.

MoS_2 :

Mo-4s states: -61.7 - -61.3 eV, Mo-4p states: -35.8 - -35.4 eV, S-3s states: -14.9 - -12.5 eV, S-3p states: -6.9 - -1.58 eV, Mo-4d states: -1.58 - 0eV.

ZrS_2 :

Zr- 4s states: -49.9 - -49.1 eV, Zr-4p states: -27.5 - -27.1 eV, S-3s states: -12.9 - -11.3 eV, S-3p states: -4.4 - 0 eV.

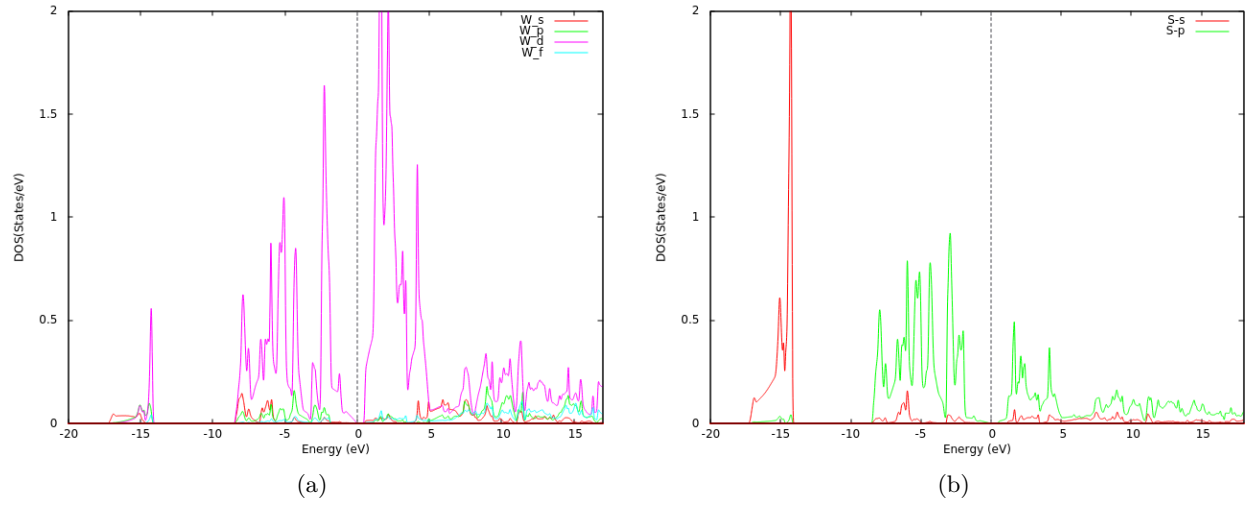


Figure 2.7: In Fig.(a) the DOS of W and in Fig.(b) the DOS of S in WS₂ is given.

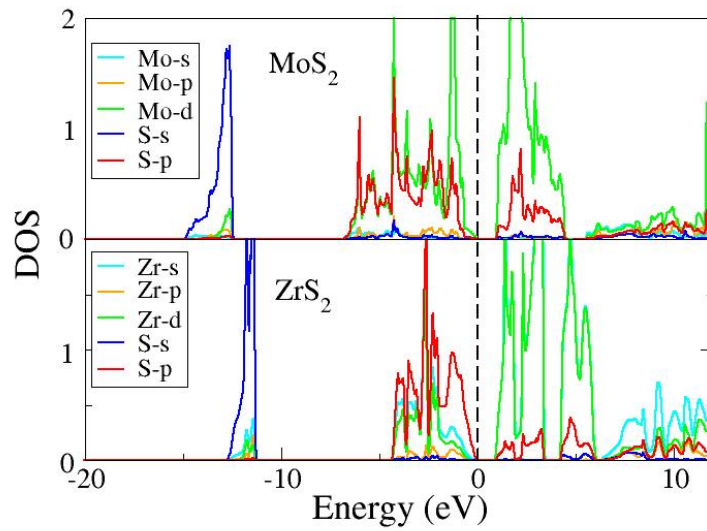


Figure 2.8: DOS of MoS₂ and ZrS₂.

The comparison of the energy difference between the **metal-p** and **S-p** states and the **S-s** and **metal-s** states leads to following results: The energy difference between the metal-p and S-p states and between S-s and metal-s states decreases in the following series: WS_2 , MoS_2 , ZrS_2 . From this analysis one can clarify that the hybridisation between those states becomes larger from heavy to light metal compounds, which is the reverse case of the metal sulfides. Fig. 2.9(a) shows the CS contribution only of the S-p band of transition metal sulfides plotted against the metal-p charges in the S-p band. The CS decreases with increasing metal p charges from ZrS_2 to WS_2 . Fig. 2.9(b) displays the relation between the CS contribution of the metal p band and the S-p charges in the corresponding band. An additional compound (ZnS) is added to the plot to make a better understanding of this trend. First of all one can clearly obtain that the CS increases with increasing S-p charges in the following series: ZnS , MoS_2 , WS_2 , ZrS_2 . This trend can be clarified by the electron configuration of the transition metal-d orbitals. The CS decreases by filling up the metal-d orbitals for metal disulfides and sulfide (ZnS). Fig. 2.10 presents the metal-d charges in the S-p band plotted against the CS of the corresponding band. It is evident that the CS decreases with increasing size of the metal atom in the compounds.

Analyzing Fig. 2.6, Fig. 2.9 and Fig. 2.10, shows that the CS contributions from the metal-p and S-p band have opposite signs which is due to the major bonding character of the orbitals in the metal-p band and major antibonding character of the orbitals in the S-p band (Fig. 4.1).

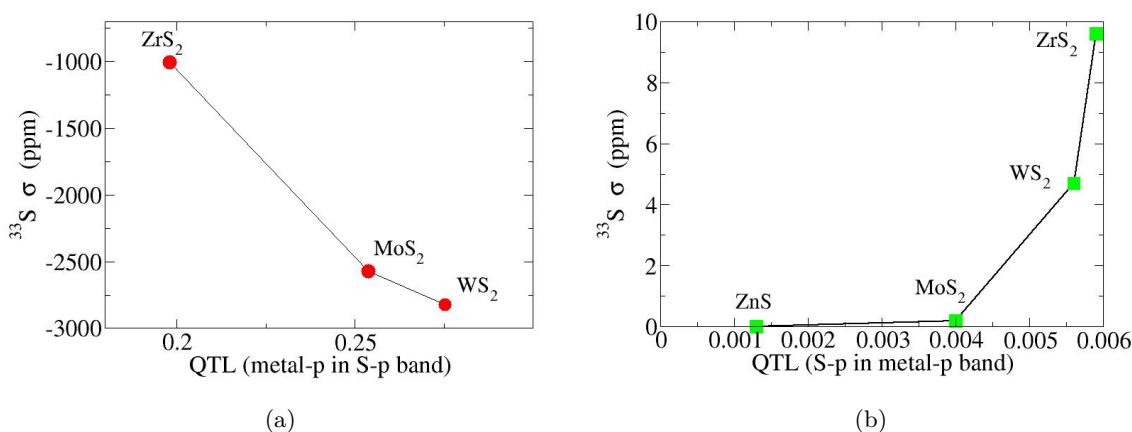


Figure 2.9: Fig.(a) presents the metal-p charges in the S-p band. Fig.(b) shows the S-p charges in the metal-p band plotted against the chemical shielding of corresponding bands.

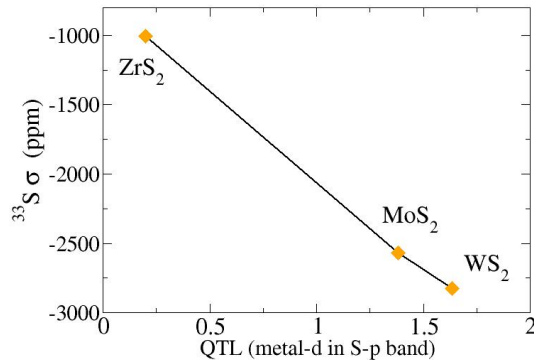


Figure 2.10: Metal-d charges in the S-p band plotted against the CS of the corresponding band.

Origin of NMR shielding in sulfides

The main goal in this thesis is to find out from which atoms and its orbitals the major contribution of the CS comes from. In order to analyse the values for the CS that are shown in Table 2.3, one has to make a stepwise analysis:

1. Bandwise analysis

This means that the energy ranges for the partial DOS has to be considered to get the CS that comes from the “bands”. An example is shown in Fig. 2.5 for BaS. In this case, one has to separate the energy range for Ba-5s (-28 - -26 eV), Ba-5p (-13 - -10 eV), S-3s (-10 - -9eV) and S-3p bands (-2 - 0 eV) to get the CS that are caused only in those “bands” (energy ranges).

2.a. Character analysis of the occupied states of the wavefunction

Once the CS for the “bands” are evaluated, the CS for the occupied wavefunctions $\psi_0^{(0)}$ and their first order perturbation $\psi_0^{(1)}$ are calculated using Eq. 1.46 and Eq. 1.47. This analysis is important because Eq. 1.41 shows that the external magnetic field is only present in the first order perturbation of the Hamiltonian. The Hamiltonian-operator in Eq. 1.42 is then used in Eq. 1.47 to get the CS for the 1st order perturbation of the characters of the wavefunctions.

2.b Character analysis of the **un**occupied states of the wavefunction

The last step in this analysis is to evaluate the CS that is caused by the empty (unoccupied) states of the wavefunction. In order to do this, Eq. 1.47 is decomposed to get the CS contribution that comes from the empty states of the

wavefunction $\psi_e^{(0)}$.

1. Bandwise analysis

Table 2.4 presents the CS that are calculated for the **total**, **sphere** (evaluated by integrating the induced current only in the atomic sphere) and **core** CS contribution (integrating of the induced current only in the core region of an atom). The last four columns in this table show the CS contribution that are caused in the so called “**bands**” with each of them presenting an high density of states in an limited energy range of an DOS-plot (Fig 2.11).

Table 2.4: Band-resolved contribution to ^{33}S isotropic shielding. Calculation of the band contribution of TiS_2 were not done (*nc = not calculated). All values in ppm.

	<i>total</i>	<i>sphere</i>	<i>core</i>	S-s band	metal-p band	S-p band	metal-d band
sulfides							
Li_2S	797.2	787.2	979.0	8.4	—	-145.2	—
Na_2S	786.9	777.8	979.0	4.2	0.1	-196.8	—
MgS	558.0	543.4	979.0	3.2	-0.9	-424.1	—
CaS	347.7	341.9	979.0	-0.4	4.9	-653.9	—
ZnS	692.8	675.9	979.0	3.9	0.2	-212.3	-66.2
SrS	329.5	324.5	979.0	5.0	16.1	-671.0	—
BaS	73.7	67.7	979.0	-0.6	52.1	-960.0	—
disulfides							
WS_2	404.0	383.0	979.0	-0.5	4.7	-2824.9	2259.9
MoS_2	167.9	148.0	979.0	-0.5	0.2	-2570.1	1772.6
ZrS_2	-73.9	-89.9	979.0	2.9	9.6	-1060.5	—
TiS_2	-524.0	-349.3	979.0	*n.c	n.c	n.c	n.c

Analyzing Table 2.4 and Fig. 2.11, one can state that the major contribution of the CS is caused by core region which stays constant within the series. The CS contribution of the sphere region is smaller than the CS of the core region but decreases from light to heavy metal atom compounds for metal sulfides. For this reason, one can state that the CS must be induced by the valence region, i.e band region. It is obvious that the major contribution for all metal sulfides comes from the **S-p band**. It shows a negative increasing by increasing the atomic number of the metal in the sulfide (Fig. 2.12). BaS is the only sulfide, in which the metal-p band contribution plays a role. ZnS reveals a significant contribution from the metal-d-band. Adding the CS contribution that is caused

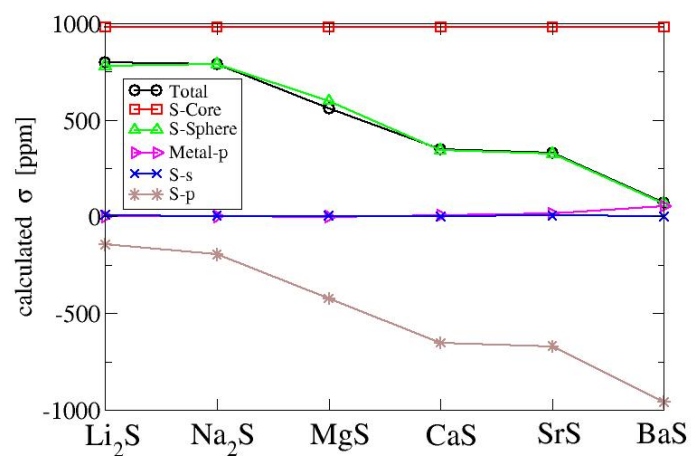


Figure 2.11: Band, total, core and sphere CS contribution are represented in this Figure.

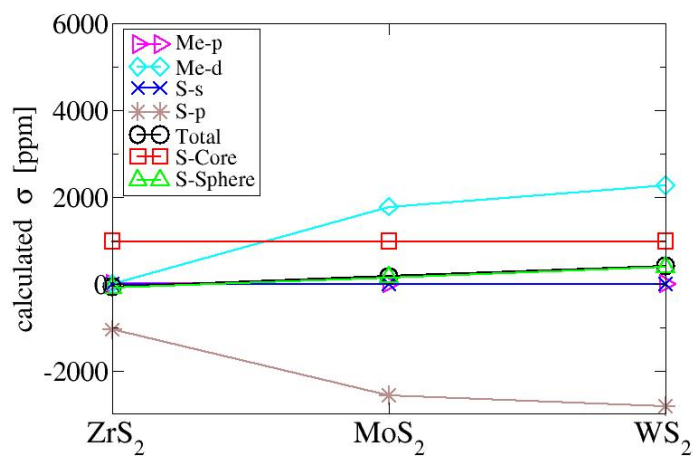


Figure 2.12: Band, total, core and sphere CS contribution of metal disulfides are represented in this Figure.

by the band region to the CS that comes from the core region leads to the CS contribution of the sphere region.

The CS contribution from the core region is also the largest for Group 4-6 transition metal disulfides and sulfide (ZnS) but stays constant within the series. Again, the only CS contribution which varies within the series, comes from the sphere region. In contrast to the bandwise of alkali and earth alkaline sulfides, the CS contribution of the S-p band is also negativ but decreases from light to heavy Group 4-6 transition metal compounds. One has also to mention that MoS₂ and WS₂ show a significant positive CS contribution from the **metal-d band**.

2.a Character analysis of *occupied* states of the wavefunction

The CS contribution for the first order pertubation of the wave function is presented in Table 2.5 and Fig. 2.13. Only the major contribution of the CS for the occupied ground state wavefunction ($\psi_0^{(0)}$) and its first order pertubation ($\psi_0^{(1)}$) were taken into account. This analysis leads to the conclusion, that only the Sulfur p and d characters of the wavefunction show significant contributions to the CS.

Table 2.5: Major contribution for the CS calculated for occupied ground state wavefunction ($\psi_0^{(0)}$) and its first order perturbation ($\psi_0^{(1)}$) (ppm). All values below 10 ppm are not quoted. All values in ppm.

metal <i>p</i> band										
	sulfides							disulfides		
	Li ₂ S	Na ₂ S	MgS	CaS	SrS	BaS	ZnS	MoS ₂	WS ₂	ZrS ₂
$\psi_0^{(0)} _{S,l=1}$					20.2	54.5				
$\psi_0^{(1)} _{S,l=1}$					20.2	54.5				

S <i>p</i> band								S <i>p</i> band + metal <i>d</i> band		
	sulfides							disulfides		
	Li ₂ S	Na ₂ S	MgS	CaS	SrS	BaS	ZnS	MoS ₂	WS ₂	ZrS ₂
$\psi_0^{(0)} _{S,l=1}$	-152.4	-204.8	-425.5	-661.4	-679.4	-970.0	-223.2	-797.5	-568.6	-1073.0
$\psi_0^{(1)} _{S,l=1}$	-219.4	-274.3	-485.9	-729.7	-749.6	-1040.1	-348.9	-848.1	-620.0	-1040.1
$\psi_0^{(1)} _{S,l=2}$	65.3	66.5	63.6	65.5	66.7	65.0	47.2	56.7	58.0	59.2
$\psi_0^{(0)} _{S,l=2}$	7.1	3.4	5.7	7.1	3.3	7.1	7.1	8.5	3.9	8.8

metal <i>d</i> band										
	sulfides							disulfides		
	Li ₂ S	Na ₂ S	MgS	CaS	SrS	BaS	ZnS	MoS ₂	WS ₂	ZrS ₂
$\psi_0^{(0)} _{S,l=1}$	—	—	—	—	—	—	-59.9	n.c	n.c	n.c
$\psi_0^{(1)} _{S,l=1}$	—	—	—	—	—	—	-61.6	n.c	n.c	n.c

Metal sulfides

Metal-*p* band

By looking at the CS that comes from the ground state wavefunction $\psi_0^{(0)}$ and its first order perturbation $\psi_0^{(1)}$ in the metal-*p* band of SrS and BaS, one can say that the CS are positive and caused by the **S-*p* states**. The CS contribution from $\psi_0^{(0)}|_{S,l=1}$ and $\psi_0^{(1)}|_{S,l=1}$ of BaS is more than twice larger than from SrS. According to Table 2.4, one can estimate that the CS contribution of the metal *p* bands of BaS and SrS have approximately the same magnitude as their CS contribution from the ground state wavefunction $\psi_0^{(0)}$ and its first order perturbation $\psi_0^{(1)}$. The same is valid for the metal-*d* band for ZnS.

S-*p* band

In the S-*p* band, the CS contribution for the ground state wavefunction $\psi_0^{(0)}$

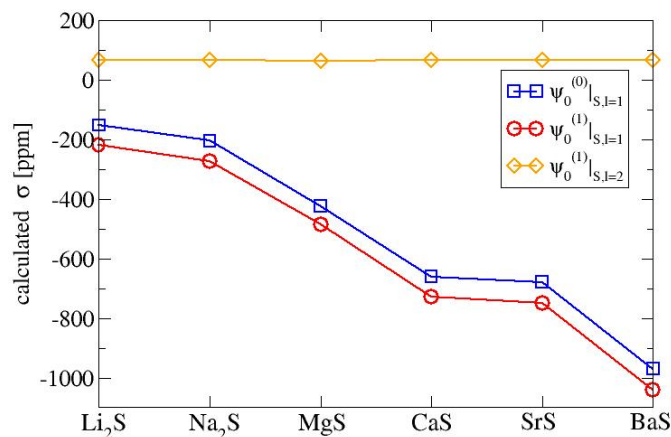


Figure 2.13: This Figure represents the different CS contribution of the occupied ground state wavefunction ($\psi_0^{(0)}$) and its first order perturbation ($\psi_0^{(1)}$) in the S-p band for different metal sulfides.

and its first order perturbation $\psi_0^{(1)}$ of the S-p states is the major one and decreases by increasing the atomic number of the metal atom in the sulfides. This CS contributions show a negative shielding in contrast to the CS contributions that were caused from the metal-p band. One also has to consider, that there is also a not a too small but constant contribution from the first order perturbation $\psi_0^{(1)}$ of the ground state wavefunction of the S-d state.

Transition metal sulfide and disulfides

S-p band

Fig. 2.14 shows that only the occupied S-p groundstate wave function and its 1st order perturbation increase within the series, while the 1st order perturbation of the wavefunction for the S-d states $\psi_0^{(1)}|_{S,l=2}$ stays constant throughout the series.

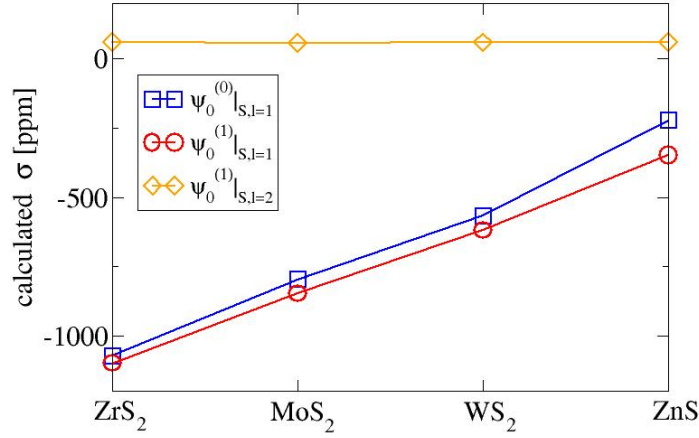


Figure 2.14: CS contribution of the occupied ground state wavefunction $\psi_0^{(0)}$ and its 1st order perturbation ($\psi_0^{(1)}$) in the S-p and Me-d band for different metal disulfides and metal sulfide (ZnS).

2.b.Character analysis of the *unoccupied* states of the wavefunction

The next step in this analysis is to find out how the empty states influence $\Psi_o^{(1)}$. For that purpose the integral $\langle \Psi_e^{(0)} | H^{(1)} | \Psi_o^{(0)} \rangle$ is decomposed entering the definition of the Eq. 1.48. The contribution of the chemical shieldings of the unoccupied states for a specific band and its first order perturbation of the wavefunction $\Psi_o^{(1)}$ are represented in Table 2.6.

2.1 Chemical shifts of metal sulfides and disulfides

Table 2.6: Major contribution for the CS calculated for the empty states of the wavefunctions and interstitial region. All values below 10 ppm are not quoted. All values in ppm.

metal p band, $\psi_0^{(1)} _{S,l=1}$										
sulfides								disulfides		
	Li ₂ S	Na ₂ S	MgS	CaS	SrS	BaS	ZnS	MoS ₂	WS ₂	ZrS ₂
$\psi_e^{(0)} _{S,l=0}$										
$\psi_e^{(0)} _{S,l=1}$										
$\psi_e^{(0)} _{metal,l=0}$										
$\psi_e^{(0)} _{metal,l=2}$					15.0	29.3				
<i>Interstitial</i>						28.4				

S p band								S p band + metal d band		
sulfides								disulfides		
	Li ₂ S	Na ₂ S	MgS	CaS	SrS	BaS	ZnS	MoS ₂	WS ₂	ZrS ₂
$\psi_e^{(0)} _{S,l=0}$	13.2	45.1	20.2	19.0	16.5	11.0	98.4	28.6	16.0	27.9
$\psi_e^{(0)} _{S,l=1}$	-794.5	-985.8	-835.5	-888.5	-921.8	-977.6		-1040.2	-889.7	-1046.9
$\psi_e^{(0)} _{S,l=2}$	-11.7	-35.7	-51.2	-15.0				40.1	39.4	69.4
$\psi_e^{(0)} _{metal,l=0}$	42.9	134.4	19.9	37.2	47.9	47.92	122.5	26.4	30.9	24.4
$\psi_e^{(0)} _{metal,l=1}$	45.0	62.0	73.8	-16.9		-80.8		-44.6	-29.1	
$\psi_e^{(0)} _{metal,l=2}$				-289.8	-309.4	-392.9	19.1	-165.4	-91.4	-585.3
<i>Interstitial</i>	462.1	530.1	283.9	401.9	453.3	349.6	19.1	225.0	230.8	375.1

metal d band, $\psi_0^{(1)} _{S,l=1}$										
sulfides								disulfides		
	Li ₂ S	Na ₂ S	MgS	CaS	SrS	BaS	ZnS	MoS ₂	WS ₂	ZrS ₂
$\psi_e^{(0)} _{S,l=0}$	—	—	—	—	—	—		n.c	n.c	n.c
$\psi_e^{(0)} _{S,l=1}$	—	—	—	—	—	—	-33.4	n.c	n.c	n.c
$\psi_e^{(0)} _{S,l=2}$	—	—	—	—	—	—		n.c	n.c	n.c
$\psi_e^{(0)} _{metal,l=0}$	—	—	—	—	—	—		n.c	n.c	n.c
$\psi_e^{(0)} _{metal,l=1}$	—	—	—	—	—	—	-27.4	n.c	n.c	n.c
$\psi_e^{(0)} _{metal,l=2}$	—	—	—	—	—	—		n.c	n.c	n.c
<i>Interstitial</i>	—	—	—	—	—	—		n.c	n.c	n.c

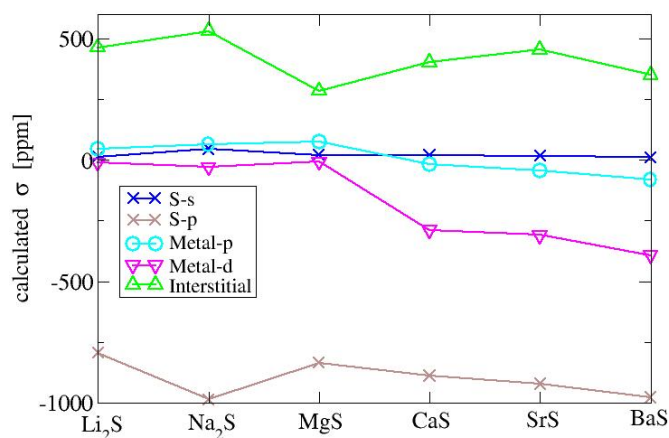


Figure 2.15: This Figure represents the different CS contribution of the unoccupied ground state wavefunction ($\psi_e^{(0)}$) of $\psi_0^{(1)}|_{S,l=1}$ in the S-p band for different metal sulfides.

Metal sulfides

Metal-p band

After decomposing integral $\langle \Psi_e^{(0)} | H^{(1)} | \Psi_o^{(0)} \rangle$ of the sulfur-p character to evaluate the CS contribution for the empty states, one can state that the major contribution in the metal-p band comes from the empty metal-d states $\psi_e^{(0)}|_{metal,l=2}$ and the interstitial only for region for BaS.

S-p band

The same was done for the S-p band in metal sulfides. The results for the **S-p band** indicate that there are many contributions from the empty states but only the contribution of the **empty metal-d states** decreases dramatically by increasing the atomic number of the metal atom in the compound. The major contributions come from the empty sulfur-p state and interstitial region but those stay nearly constant.

Transition metal sulfide and disulfides

S-p band

The major contribution for the empty states for $\psi_0^{(1)}$ of the S-p character are caused by the empty metal-d and S-p states.

The CS contribution for the **empty metal-d states** for $\psi_0^{(1)}$ of the S-p character increases from light to heavy metal atoms in the metal disulfides

(Fig. 2.16).

Metal d band

In the metal-d band of ZnS, the majority S-p character in $\psi_0^{(0)}$ only couples to the empty S-p and metal-p character in $\psi_e^{(0)}$.

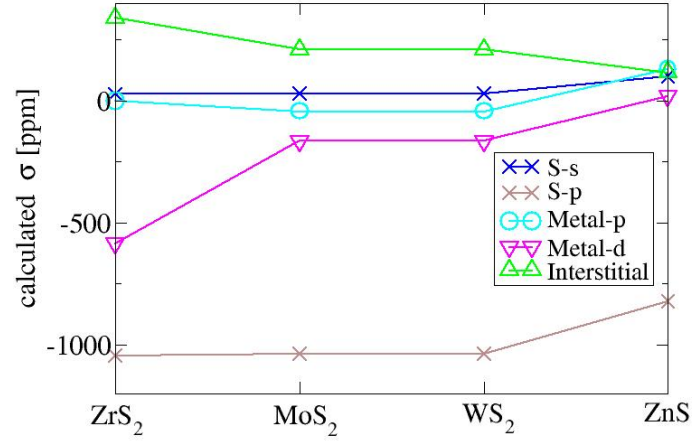


Figure 2.16: CS contribution of the unoccupied ground state wavefunction ($\psi_e^{(0)}$) of $\psi_0^{(1)}|_{S,l=1}$ in the S-p and metal-d band for different metal disulfides and metal sulfide (ZnS).

2.2 Chemical shifts of alkali metal silicides

Today materials, which are based on the element silicon, are often used in technological applications because of their chemical and physical properties. Therefore those materials are widely used as thermoelectric devices and in the microelectronic industry. While Si is mainly used in microelectronic devices, intermetallic silicides like the so called “Zintl phases” are often applied as high temperature furnace elements due to their oxidation resistance at elevated temperatures. Those “Zintl phases” are polar intermetallic phases and consist of covalent and ionic bonding. They are built of Si_4^{4-} units which can be seen in Fig 2.17. In this thesis, the Zintl phases of M_4Si_4 ($\text{M}=\text{K}, \text{Rb}, \text{Cs}$) and Ba_2Si_4 and Rb_7NaSi_8 were investigated. NMR-spectroscopy measurements of those compounds can be conducted on ^{29}Si with nuclear spin $I=1/2$ (52).

2.2.1 Structural parameters

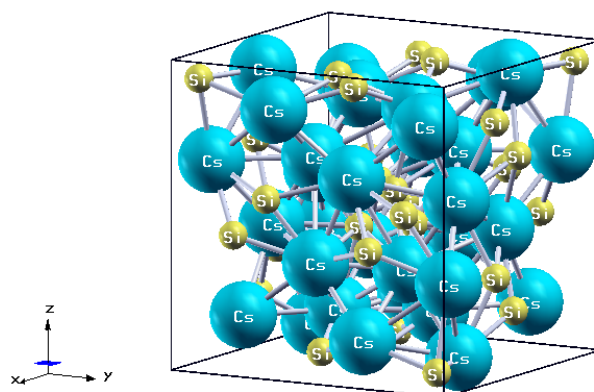
In Table 2.7 and Table 2.8 one can see the structural parameters, i.e. lattice parameters and angles, atomic coordinates RMT, space group and calculated structure of metal silicides which were used for the NMR calculations. A RK_{MAX} of 7 was taken again for the calculations. It is obvious that all compounds except Ba_2Si_4 (orthorombic symmetry) show cubic symmetry. In contrast to the structure of metal sulfides and disulfides, which were discussed in the chapter above, one can clearly see that all compounds have two silicon atoms at a different crystallographic site, whereas Ba_2Si_4 shows even three different silicon atoms in the unit cell.

Table 2.7: Lattice parameters and angles in the unit cell of metal silicides.

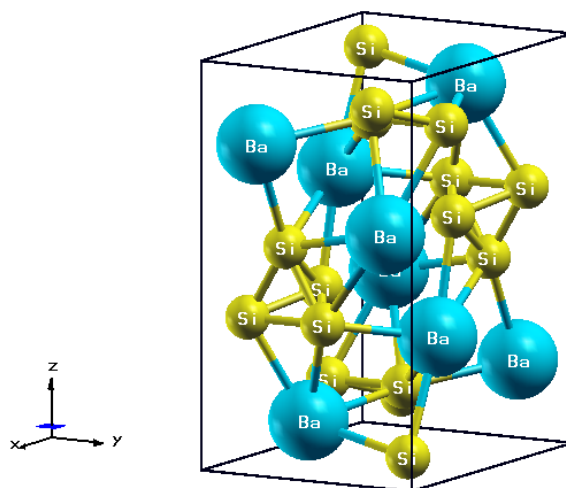
	a / Å	b / Å	c / Å	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$
K_4Si_4 [(53)]	12.62	12.62	12.62	90	90	90
Rb_4Si_4 [(54)]	13.04	13.04	13.04	90	90	90
Cs_4Si_4 [(55)]	13.51	13.51	13.51	90	90	90
Ba_2Si_4 [(56)]	8.92	6.75	11.53	90	90	90
Rb_7NaSi_8 [(57)]	13.04	13.04	13.04	90	90	90

Table 2.8: Atomic coordinates, RMT and space group and calculated structure of metal silicides.

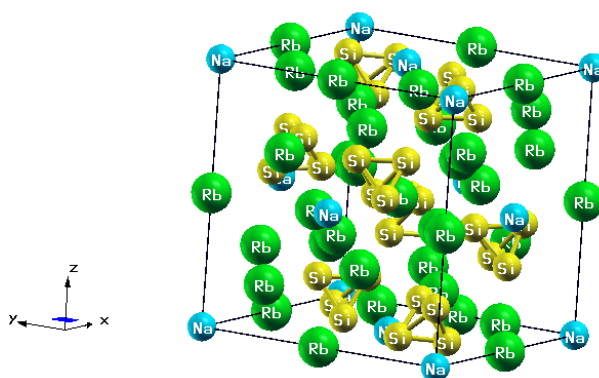
	Atom	x	y	z	RMT	Space group	structure
K ₄ Si ₄ [(53)]	K	$\frac{1}{6}$	0.833	$\frac{1}{6}$	2.50	<i>P</i> -43 <i>n</i>	geo.opt
	K	0.433	0.639	$\frac{1}{6}$	2.50		
	Si	0.431	0.568	0.431	2.21		
	Si	0.074	0.817	0.437	2.21		
Rb ₄ Si ₄ [(53)]	Rb	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	2.50	<i>P</i> -43 <i>n</i>	geo.opt
	Rb	0.934	0.140	$\frac{2}{3}$	2.50		
	Si	0.934	0.065	0.934	2.21		
	Si	0.571	0.315	0.939	2.21		
Cs ₄ Si ₄ [(53)]	Cs	$\frac{2}{3}$	0.832	$\frac{1}{6}$	2.20	<i>P</i> -43 <i>n</i>	geo.opt
	Cs	0.434	0.641	$\frac{1}{6}$	2.20		
	Si	0.436	0.563	0.436	2.20		
	Si	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	2.20		
Ba ₂ Si ₄ [(54)]	Ba	0.985	$\frac{1}{4}$	0.807	2.50	<i>Pnma</i>	geo.opt
	Ba	$\frac{1}{6}$	$\frac{1}{4}$	0.405	2.50		
	Si	0.803	$\frac{1}{4}$	0.535	2.19		
	Si	0.582	$\frac{1}{4}$	0.409	2.19		
	Si	0.806	0.428	0.354	2.19		
Rb ₇ NaSi ₈ [(55)]	Rb	0.225	0.686	0.458	2.50	<i>Pa</i> -3	geo.opt
	Rb	0.00	0.00	$\frac{1}{2}$	2.50		
	Na	$\frac{1}{2}$	$\frac{1}{2}$	0.00	2.50		
	Si	0.300	0.699	0.199	2.20		
	Si	0.423	0.561	0.202	2.20		



(a)



(b)



(c)

Figure 2.17: KGe_4 -structure of Cs_4Si_4 (a) $\text{BaSi}_2(\text{oP}_{24})$ -structure of Ba_2Si_4 (b) and Rb_7NaGe_8 -structure of Rb_7NaSi_8 (c).

2.2.2 Calculations of the chemical shieldings

Experimental measurements of NMR chemical shifts of ^{29}Si atom for different metal silicides are presented in (58) and (59). Haarmann and Poecher already investigated the calculated chemical shielding and experimental chemical shift of the metal silicides M_4Si_4 ($\text{M}=\text{K}, \text{Rb}, \text{Cs}$) and Ba_2Si_4 in (52). They performed electronic calculations using the all-electron, full-potential local orbital (FPLO) minimum basis method and the CASTEP (60) method (ultrasoft pseudopotentials, using GIPAW method) (both methods were applied using the PBE exchange correlation functional). After analyzing the charge transfer in the compounds using the electron localization function (ELF), which can be seen as a bonding indicator, they came to the conclusion, that the crucial reason for the varities within the series is the different charge transfer, which decreases from light to heavy metal compounds for M_4Si_4 ($\text{M}=\text{K}, \text{Rb}, \text{Cs}$) and finally contributes to a decreasing in the chemical shielding.

NMR chemical shieldings were calculated using the PBE exchange correlational functional. Table 2.9 presents the calculated CS, the chemical shifts, which were also calculated using a reference that is taken from the linear fit equations included in Fig. 2.18, and the experimental chemical shifts. A k-mesh of $2 \times 2 \times 2$ was used. It is apparent, that the calculated CS is positive for all metal silicides for both Si1 and Si2 atoms and decreases from light to heavy metal compounds. The calculated chemical shielding of Rb_7NaSi_8 shows an significant and interesting fact: It has the largest value, which leads to the assumption, that by following the trend of the CS from light to heavy metal compounds, only the Na-atom is influencing the CS. In Fig. 2.18(a) one can obtain the calculated CS for Si1, Si2 and Si3 plotted against the experimental chemical shifts while Fig. 2.18(b) shows the correlation of the calculated and experimental chemical shifts. In the left picture, one can state a linear value slope of approximately one, while the right one shows that the calculated and experimental chemical shifts are in good agreement.

Table 2.9: The isotropic shielding σ_{iso}^{LAPW} computed with PBE exchange-correlation potentials for ^{29}Si in metal silicides. The experimental shifts $\delta_{iso}^{expt.}$ are given with reference to $(\text{CH}_3)_4\text{Si}$. The theoretical shifts δ_{iso}^{LAPW} are given with a reference taken from the linear fit equations included in Fig. 2.18. All values in ppm.

	Si1			Si2			Si3		
	σ_{iso}^{LAPW}	$\delta_{iso}^{expt.}$	δ_{iso}^{LAPW}	σ_{iso}^{LAPW}	$\delta_{iso}^{expt.}$	δ_{iso}^{LAPW}	σ_{iso}^{LAPW}	$\delta_{iso}^{expt.}$	δ_{iso}^{LAPW}
K_4Si_4	650.7	-346.2 [(52)]	-336.7	625.7	-322.6[(52)]	-313.3	—	—	—
Rb_4Si_4	617.0	-304.3 [(52)]	-306.5	602.9	-292.0 [(52)]	-292.3	—	—	—
Cs_4Si_4	505.6	-188.8 [(52)]	-202.6	505.6	-188.8 [(52)]	-202.6	—	—	—
Ba_2Si_4	368.4	-99.9 [(52)]	-112.7	334.1	-50.2 [(52)]	-40.4	368.8	-84.3 [(52)]	-72.6
Rb_7NaSi_8	664.0	-348.9 [(53)]	-350.6	633.0	-319.4 [(52)]	-321.5	—	—	—

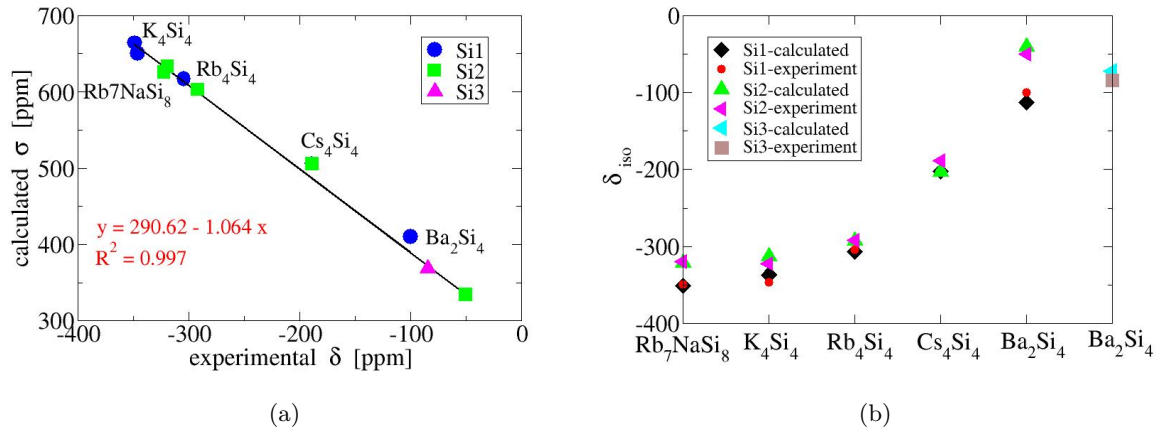


Figure 2.18: Fig.(a) presents the correlation between the measured chemical shifts $\delta_{\text{iso}}^{\text{expt.}}$ and the calculated chemical shieldings $\sigma_{\text{iso}}^{\text{LAPW,PBE}}$ using the PBE exchange correlation functional. Fig.(b) shows the correlation between the calculated chemical shifts applying the PBE functional and the experimental chemical shifts from (52) (53).

DOS and charges of states (QTL) in metal silicides

Since the calculated CS for Si1, Si2 and Si3-atoms for metal silicides, which are shown Table 2.9 do not show much difference, further investigations of the calculated CS were only performed on Si1. Fig. 2.19 shows different density of states (DOS) of Cs_4Si_4 and Ba_2Si_4 , and Fig. 2.20 the DOS of Rb_7NaSi_8 . One can obtain two Si-s bands at different energy ranges, respectively and the Si-p band (red) is the highest energetic one, which is located near the Fermi Niveau. Another fact is, that the band gap for Ba_2Si_4 is much smaller than for Cs_4Si_4 , whereby the shielding of the Si atom is much affected (Chapter 4.1). If one compare the energy difference between the metal-s states and the Si-s states within the series, one can clearly see that the energy difference between **metal-p and Si-p states** and the energy difference between the **Si-s and metal-s states** again becomes much smaller within the series. It is also obvious that the energies of these bands increase within the series;

K_4Si_4 :

K-3s states: -30.9 - -30.4 eV, K-3p states: -14.7 - -14.0 eV, Si-3s states: -10.4 - -10.1 eV, Si-3s states: -5.7 - -5.5 eV, Si-3p states: -2.9 - 0 eV.

Rb_4Si_4 :

Rb-4s states: -27.7 - -27.2 eV, Rb-4p states: -12.3 - -11.3 eV, Si-3s states: -10.3 - -9.8 eV, Si-3s states: -5.6 - -4.8 eV, Si-3p states -2.7 - 0 eV.

Cs_4Si_4 :

Cs-5s states: -22.6 - -22.0 eV, Cs-5p states: -9.8 - -8.5 eV, Si-3s states: -10.5 -

-10.0 eV, Si-3s states: -5.2 - -4.8 eV, Si-3p states: -2.2 - 0 eV.

Ba₂Si₄:

Ba-5s states: -27.6 - -27.0 eV, Ba-5p states: -13.2 - -12.4 eV, Si-3s states: -10.8 - -10.3 eV, Si-3s states: -6.3 - -5.1 eV, Si-3p states: -3.4 - 0 eV.

Rb₇NaSi₈:

Na-2s states: -48.9 eV, Rb-4s states: -25.3 - -24.6 eV, Na-2p states: -20.8 eV, Rb-4p states: -11.7 - -10.7 eV, Si-3s states: -10.0 - -9.6 eV, Si-3s states: -5.2 - -4.7 eV, Si-3p states: -2.4 - 0 eV.

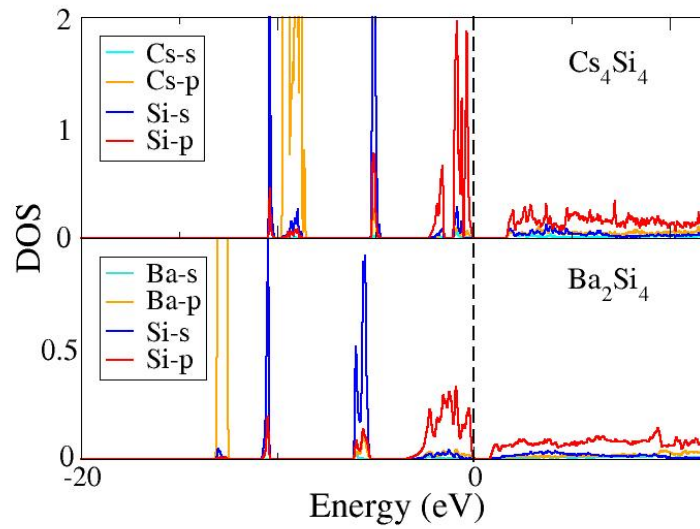


Figure 2.19: DOS of Cs₄Si₄ and Ba₂Si₄.

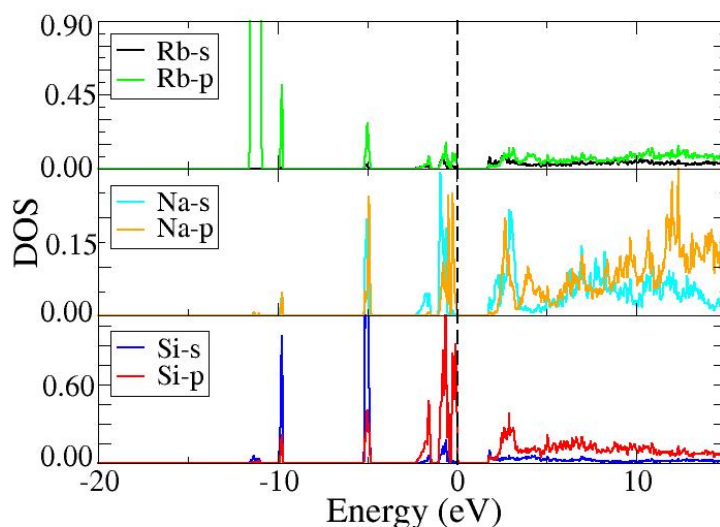


Figure 2.20: DOS of Rb_7NaSi_8 .

The analysis of the DOS and charges of states (QTL) leads to similar results as for the metal sulfides and disulfides which were discussed in Chapter 2.1.2. The smaller the energy difference between the **Me-s** and **Si-s** states and between the **Me-p** and **Si-p** states within the series indicates that the interaction of those states gets stronger within the series which finally leads to a negative increasing of the chemical shielding within the series.

The CS contribution of the Si-p band plotted against the metal-p charges in the corresponding band is presented in Fig. 2.21(a). It is clearly shown that the CS decreases with increasing metal-p charges in the corresponding band within the series. While the range of the metal-p charges of K_4Si_4 , Rb_4Si_4 and Cs_4Si_4 reaches from 0.035 to 0.056, the metal-p charge of Ba_2Si_4 shows a very large value of 0.124. This may be due to the different crystal system (orthorhombic) of this compound. Fig. 2.21(b) displays the relation between the Si-p charges of the metal-p band and the CS contribution of the corresponding band. The CS increases in contrary to Fig. 2.21(a) with increasing Si-p charges within the series. The second difference is that Cs_4Si_4 shows the largest Si-p charges within the series and a large CS contribution of the metal-p band in distinction from the other metal silicides. Looking at the CS contribution, which comes from the metal-p band, one can state that K_4Si_4 and Rb_4Si_4 do not show any contribution which is caused by the low energy range of the metal-p states which were shown before. In summary it can be said, therefore, that the CS contribution for the metal-p band increases with increasing Si-p charges in the corresponding band, a larger hybridisation between the states is present and

finally contributes to a negative increasing of the CS from light to heavy metal compounds..

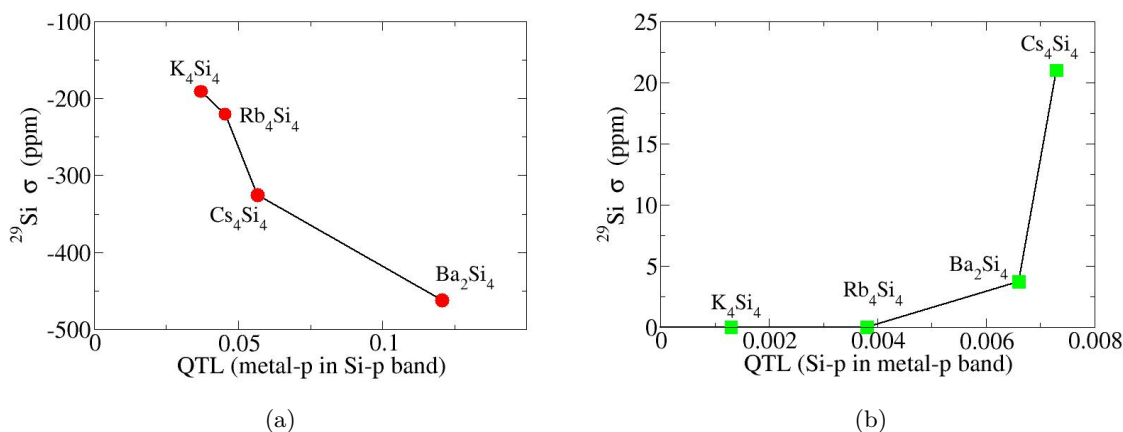


Figure 2.21: Fig. (a) presents the metal-p charges in the Si-p band. Fig.(b) shows the Si-p charges in the metal-p band.

Origin of NMR shielding in silicides

In order to get informations about the origin of NMR shielding in those compounds, the same procedure that was done for the sulfides described in Chapter 2.1.2, is used for the silicides. That means a stepwise analysis was conducted, i.e bandwise and character analysis of the wavefunctions. The Si-s bands refer to the higher energetic bands.

1. Bandwise analysis

Again, we start with the so called “Band wise analysis”, which means that investigations were conducted on the shieldings that are induced in the specific energy ranges for silicon and metal states which are described above. In Table 2.10 and Fig. 2.22 one can see the calculated CS contribution for total, sphere, core and band regions for different metal silicides. As expected, the core region shows the major CS contribution but stays constant throughout the series. Only the CS contribution of the sphere region decreases within the series. This leads to the fact, that the CS must be caused by the valence region, i.e band region. The major CS contribution comes from the **Si-p band** which shows negative shielding and decreases by increasing the atomic number of the metal silicides. There is also a small positive metal-p CS contribution from the metal-p band of Cs_4Si_4 . Apparently, the Si-s bands reveal small negative shielding and do not vary much throughout the series. Summing up the CS contribution that is caused by the core region to the CS that comes from the band (valence) region, gives the CS contribution of the sphere region.

Table 2.10: Band-resolved contribution to ^{29}Si isotropic shielding. All values in ppm.

	<i>total</i>	<i>sphere</i>	<i>core</i>	Si-s band	Si-p band	metal-p band
K_4Si_4	625.7	604.2	837.7	-22.4	-191.1	5.4
Rb_4Si_4	602.9	581.1	837.7	-22.4	-220.8	-0.4
Cs_4Si_4	505.6	485.7	837.7	-23.7	-325.3	21.0
Ba_2Si_4	368.3	347.2	837.7	-18.7	-461.9	3.7
Rb_7NaSi_8	633.0	609.5	837.7	-21.8	-190.0	2.3

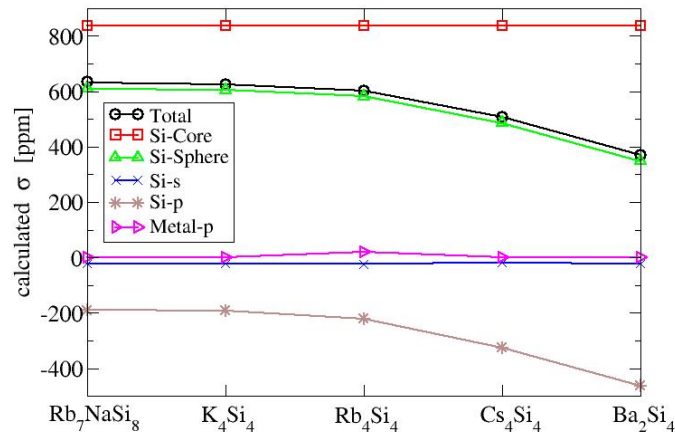


Figure 2.22: The CS contribution of total, core, sphere and bands regions.

2.a Character analysis of *occupied* states of the the wavefunction

Table 2.11 lists the CS contributions for the occupied states of the wavefunction $\psi_0^{(0)}$ at its first order perturbation $\psi_0^{(1)}$. Again, only those CS contribution were considered, which are crucial ingredients, affecting its amount.

Table 2.11: Major contribution for the CS calculated for occupied ground state wavefunction ($\psi_0^{(0)}$) and its 1st order perturbation ($\psi_0^{(1)}$). All values below 10 ppm are not quoted. All values in ppm.

metal <i>p</i> band					
	K ₄ Si ₄	Rb ₄ Si ₄	Cs ₄ Si ₄	Ba ₂ Si ₄	Rb ₇ NaSi ₈
$\psi_0^{(0)} _{Si,l=1}$			26.1		
$\psi_0^{(1)} _{Si,l=1}$			26.1		
Si <i>s</i> band					
	K ₄ Si ₄	Rb ₄ Si ₄	Cs ₄ Si ₄	Ba ₂ Si ₄	Rb ₇ NaSi ₈
$\psi_0^{(0)} _{Si,l=1}$	-23.4	-23.4	-24.7	-18.9	-22.6
$\psi_0^{(1)} _{Si,l=1}$	-23.6	-24.3	-25.7	-19.4	-23.4
Si <i>p</i> band					
	K ₄ Si ₄	Rb ₄ Si ₄	Cs ₄ Si ₄	Ba ₂ Si ₄	Rb ₇ NaSi ₈
$\psi_0^{(0)} _{Si,l=1}$	-206.2	-236.7	-341.3	-476.0	-208.1
$\psi_0^{(1)} _{Si,l=1}$	-209.0	-257.5	-361.9	-495.8	-228.2
$\psi_0^{(1)} _{Si,l=2}$	23.0	23.5	22.6	22.5	22.9

Metal-p band

It is quite interesting that the CS contribution in the metal-p band of Cs₄Si₄ comes only from the **Si-p character**, although most of the charge is localised at the metal atom.

Si-s band

Analyzing the CS contributions in the Si-s band leads to follow results: Again, only the Si-p character contributes to the shielding, which is presented by the calculated values of $\psi_0^{(0)}|_{Si,l=1}$ and $\psi_0^{(1)}|_{Si,l=1}$. It is shown, that those shieldings are negative and stay nearly constant within the series.

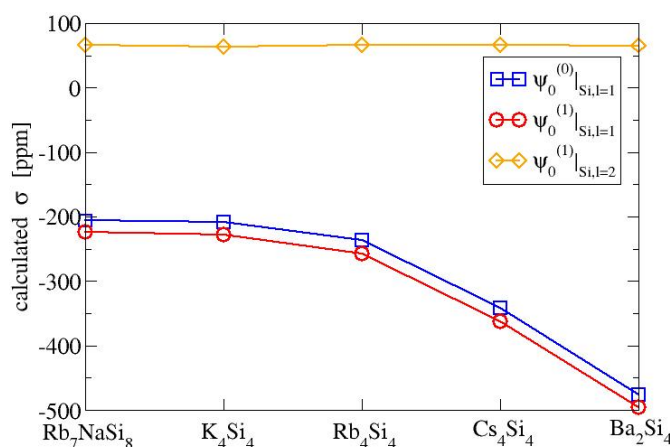


Figure 2.23: Different CS contribution of $\psi_0^{(0)}|_{Si,l=1}$, and its 1st order perturbation of its p and d-characters $\psi_0^{(1)}|_{Si,l=1}$ $\psi_0^{(1)}|_{Si,l=2}$.

Si-p band

It is obvious from table Table 2.11 and Fig. 2.23 that the major CS contribution in the **Si-p band** comes from the ground state wavefunction $\psi_0^{(0)}$ and its first order perturbation $\psi_0^{(1)}$ of the **Si-p character**. One can notice, that the shieldings are negative and decrease throughout the series. Quite the contrary displays the behaviour of the 1st order perturbation of the empty Si-d character ($\psi_0^{(1)}|_{Si,l=2}$) for the occupied Si-p state. Its CS is positive and stays constant within the series.

2.b.Character analysis of the *unoccupied* states of the wavefunction

The next step in this analysis is to find out how the **empty** states influence $\Psi_o^{(1)}$. In order to do this, the same process, that was carried out for the metal sulfides, i.e. decomposing the integral $\langle \Psi_e^{(0)} | H^{(1)} | \Psi_o^{(0)} \rangle$ entering the definition of Eq. 1.48, to receive the contribution of the chemical shieldings for the unoccupied states for a specific band and its first order perturbation $\Psi_o^{(1)}$, was also performed for the metal silicides. All “important” values, i.e significant contribution to the shielding, are represented in Table 2.12 and Fig. 2.24.

Table 2.12: Major contribution for the CS calculated for the empty states of the wavefunctions and interstitial region. All values below 10 ppm are not quoted. All values in ppm.

metal <i>p</i> band, $\psi_0^{(1)} _{Si,l=1}$					
	K ₄ Si ₄	Rb ₄ Si ₄	Cs ₄ Si ₄	Ba ₂ Si ₄	Rb ₇ NaSi ₈
<i>Interstitial</i>			19.7		
Si <i>s</i> band, $\psi_0^{(1)} _{Si,l=1}$					
	K ₄ Si ₄	Rb ₄ Si ₄	Cs ₄ Si ₄	Ba ₂ Si ₄	Rb ₇ NaSi ₈
$\psi_e^{(0)} _{Si,l=0}$	18.7	18.3	17.5	17.0	12.0
$\psi_e^{(0)} _{Si,l=1}$	-24.3	-23.9	-22.7	-20.5	-25.4
<i>Interstitial</i>	-17.2	-17.9	- 23.9	-16.5	-17.2
Si <i>p</i> band, $\psi_0^{(1)} _{Si,l=1}$					
	K ₄ Si ₄	Rb ₄ Si ₄	Cs ₄ Si ₄	Ba ₂ Si ₄	Rb ₇ NaSi ₈
$\psi_e^{(0)} _{Si,l=0}$	28.3		26.1		
$\psi_e^{(0)} _{Si,l=1}$	-344.0	-345.4	-343.2	-378.8	-356.8
$\psi_e^{(0)} _{Si,l=2}$					
$\psi_e^{(0)} _{metal,l=0}$					25.8
$\psi_e^{(0)} _{metal,l=2}$				-62.3	
<i>Interstitial</i>	121.8	109.1	17.2	-30.5	123.1

Metal-p band

Only the **interstitial region**, which is positive, is responsible for the chemical shielding for the 1st order perturbation of Si-p character ($\psi_0^{(1)}|_{Si,l=1}$) of Cs₄Si₄.

Si-s band

The CS contribution of the empty Si-s states are positive and stay nearly constant within the series, while the CS contribution of the Si-p states and

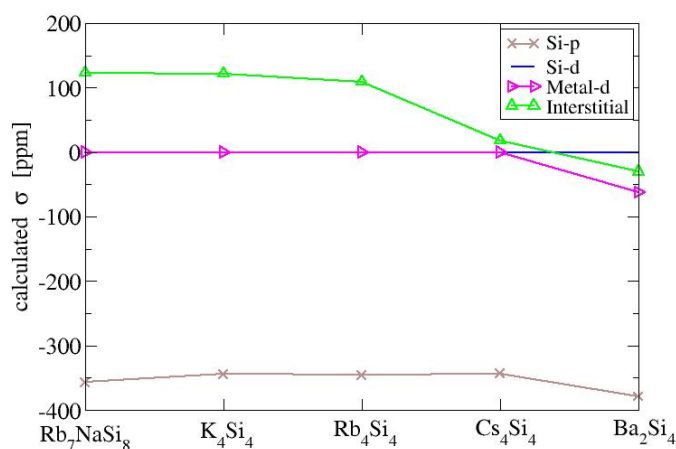


Figure 2.24: Changing of the CS for the unoccupied states of the wavefunctions of $\psi_0^{(1)}|_{Si,l=1}$ in the Si-p band and interstitial region within the series.

interstitial region are negative but also stay nearly constant throughout the series.

Si-p band

One can clearly see in Table 2.12 that the empty Si-p states show the largest negative contribution but only the CS contribution for the **empty metal-d states** and **interstitial** region changes within the series: Obviously, only Ba₂Si₄ displays a contribution to the shielding from the empty metal-d states ($\psi_e^{(0)}|_{metal,l=2}$), which is negative and quite large, compared to the missing significant CS contributions for the empty metal-d states of the other compounds.

2.3 Chemical shifts of alkali metal stannides

Tin alloys and intermetallic tin compounds show interesting electrical, mechanical and magnetic properties. Because of this fact, they are used as pewterware, bronzes, solders, fusible alloys, superconductors, capsules for wine bottles or tinplate packaging. The last investigations of the chemical shielding of nonmetals were performed on the alkali metal tetra-stannides M_4Sn_4 ($M = Na, K, Rb, Cs$). Haarmann and Grüner (61) already described the synthesis, structure and measured and calculated CS of those compounds. This group can also be assigned to the so called “Zintl phases” described in Chapter 2.2. They consist of 2D Sn nets and tetrahedral Sn_4 anions and belong to the group of semiconductors. Haarmann and Grüner carried out calculations of the CS, using the local density approximation within density functional theory (DFT).

2.3.1 Structural parameters

The structural parameters, i.e lattice parameters, angles, atomic coordinates, RMT and space group of metal stannides are given in Table 2.13 and Table 2.14. A RK_{MAX} of 7 was used for the calculations. All compounds show a tetragonal crystal system where the lattice parameters increase with increasing size of the alkali metal atom. It is evident that all of those compounds show the same space group of $I41/acd$.

Table 2.13: Lattice parameters and angles in the unit cell of metal stannides.

	a / Å	b / Å	c / Å	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$
Na_4Sn_4 [(56)]	10.46	10.46	17.39	90	90	90
K_4Sn_4 [(57)]	11.40	11.40	18.64	90	90	90
Rb_4Sn_4 [(62)]	11.75	11.75	19.21	90	90	90
Cs_4Sn_4 [(62)]	12.12	12.12	19.82	90	90	90

Table 2.14: Atomic coordinates, RMT and space group of metal stannides.

	Atom	x	y	z	RMT	Space group
Na ₄ Sn ₄ [(56)]	Na	$\frac{3}{4}$	0.874	0.00	2.50	<i>I41/acd</i>
	Na	$\frac{1}{4}$	0.375	0.125	2.50	
	Sn	0.126	0.179	0.813	2.20	
K ₄ Sn ₄ [(57)]	K	$\frac{1}{4}$	0.383	0.00	2.50	<i>I41/acd</i>
	K	0.624	0.874	0.125	2.50	
	Sn	0.115	0.186	0.318	2.21	
Rb ₄ Sn ₄ [(62)]	Rb	$\frac{1}{4}$	0.391	0.00	2.50	<i>I41/acd</i>
	Rb	0.620	0.870	0.125	2.50	
	Sn	0.110	0.185	0.319	2.50	
Cs ₄ Sn ₄ [(62)]	Cs	$\frac{1}{4}$	0.392	0.00	2.50	<i>I41/acd</i>
	Cs	0.618	0.868	0.125	2.50	
	Sn	0.106	0.188	0.321	2.50	

2.3.2 Calculations of the chemical shieldings

Tin NMR spectroscopy can be provided on ¹¹⁵Sn, ¹¹⁷Sn and ¹¹⁹Sn atom, while ¹¹⁹Sn spectroscopy is the most sensitive method (63), (Fig. 2.25).

As given in (61), Haarmann and Grüner interpreted the large shieldings for the metal stannide compounds again as the consequence of the peculiarities of bonding interaction between the cations and anions and within the anions. After analysing the charge transfer in the compounds using the electron localization function (ELF), they came to following result:

The decrease of the CS with increasing size of the cation was a result due to the charge distribution of the Sn atoms. The Sn atom acts as an ELF attractor, which means that a charge (electron) transfer occurs from the cation (M) to the anion (Sn) in the tetra stannides and thus influences the shielding of the Sn nuclei. This leads to an observable trend, in which the electron count for the Sn atoms decreases going from the lightest metal atom M=Na to M=Cs, that finally causes a decreasing of the CS within the series.

As for metal silicides, only the PBE exchange correlation functional was used to calculate the CS of the metal stannides. Table 2.15 shows the results for all calculations of $\sigma_{iso}^{LAPW,PBE}$. A k-mesh of 2x2x2 was used for the calculations. What we see here, is that all shieldings are positive and quite large, compared to the shieldings of metal sulfides and silicides, which are described in the previous chapters. The same behaviour of the CS, that was observed for the metal sulfides and silicides, i.e decreasing of the CS from light to heavy metal compounds, is also valid for the metal stannides. This is of course reflected in the positive increasing chemical shift within the series. The change between Na₄Sn₄ and K₄Sn₄ is rather small, however a big jump appears between Rb₄Sn₄ and Cs₄Sn₄. For all compounds a geometry optimized structure (geo.opt.) was

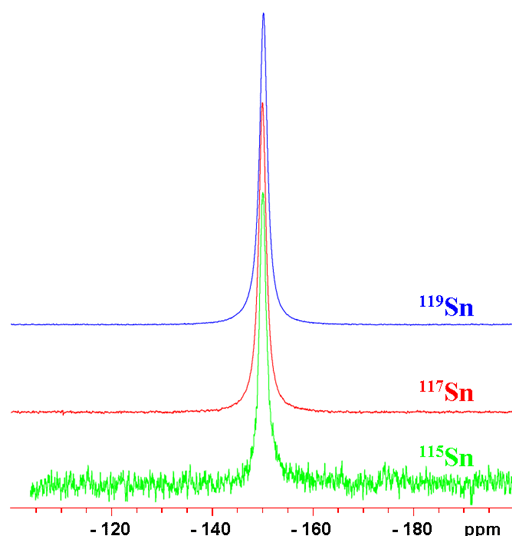


Figure 2.25: Different sensitivities of ^{115}Sn , ^{117}Sn and ^{119}Sn spectroscopy.

used. In Fig. 2.26(a) the correlation between the calculated chemical shielding and the experimental measured chemical shift is presented. It is obvious from the coefficient of determination of 0.999 that the CS and chemical shifts show an observable trend and a good correlation. The slope of the linear fit is equal to 1.199, which is a bad value, because it should be ideally 1.0. The intercept of 2129.5 was used in Fig. 2.26(b) as the reference value for the calculated chemical shifts. One can immediately realize from Fig. 2.26(b) that the calculated chemical shifts and the experimental measured chemical shifts are in an almost perfect agreement.

Table 2.15: Calculations of the CS σ_{iso} using the PBE exchange correlational functional. The experimental shifts $\delta_{iso}^{expt.}$ are given with reference to $(\text{CH}_3)_4\text{Sn}$. The theoretical shifts δ_{iso}^{LAPW} are given with a reference taken from Fig. 2.26(a). All values in ppm.

	$\sigma_{iso}^{LAPW,PBE}$	$\delta_{iso}^{LAPW,PBE}$	$\delta_{iso}^{expt.}$	structure
Na_4Sn_4 [(56)]	3780.0	-1380.3	-1371.0	geo.opt
K_4Sn_4 [(57)]	3728.2	-1328.2	-1343.0	geo.opt
Rb_4Sn_4 [(62)]	3562.4	-1162.6	-1189.0	geo.opt
Cs_4Sn_4 [(62)]	3068.1	-768.4	-784.0	geo.opt

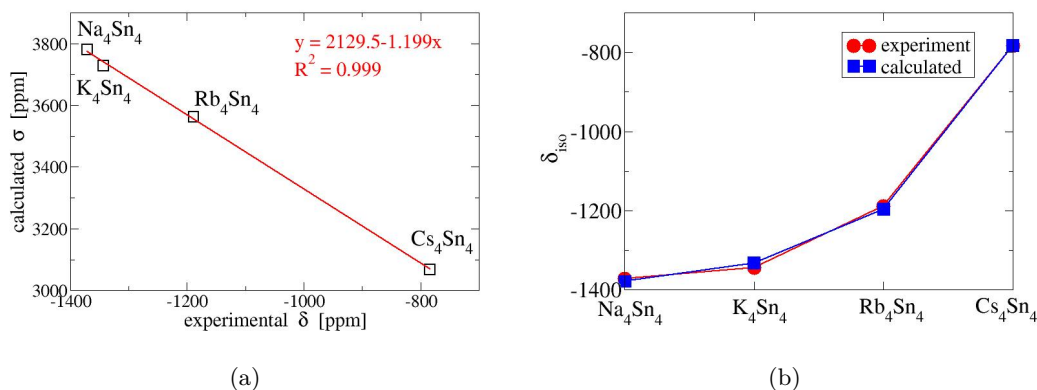


Figure 2.26: The left Figure shows the experimental chemical shifts from (61) plotted against the calculated CS for M₄Sn₄ (M=Na,K,Rb,Cs) using the PBE exchange functional. The right picture shows both experimental and calculated chemical shifts for the metal stannides.

DOS and charges of states (QTL) in metal stannides

In Fig. 2.27 the DOS of K₄Sn₄ is represented. One can again obtain two different Sn-s bands (blue) at two different energy ranges and the Sn-p band is the topmost valence band. The energy ranges of the states of the alkali metal stannides are shown below. It is obvious that the energy difference between **metal-p** and **Sn-p** states and the energy difference between the **Sn-s** and **metal-s** states again becomes much smaller within the series. The energies of these bands increase within the series;

Na₄Sn₄:

Na-2s states: -52.7 - -52.5 eV, Na-2p states: -24.7 - -24.3, Sn-3d states: -21.1 - -20.5 eV, Sn-5s states: -9.4 - -8.8 eV and -6.7 - -5.3 eV, Sn-5p states: -3.1 - 0 eV.

K₄Sn₄:

K-3s states: -30.9 - -30.6 eV, Sn-3d states: -20.6 - -20.0 eV, K-3p states: -14.8 - -14.0 eV, Sn-5s states: -8.8 - -8.4 eV and -5.8 - -5.1 eV, Sn-5p states -2.2 - 0 eV.

Rb₄Sn₄:

Rb-4s states: -27.8 - -27.5 eV, Sn-3d states: -20.8 - -20.1 eV, Rb-4p states: -12.4 - -11.6 eV, Sn-5s states: -8.9 - -8.4 eV and -5.8 - -5.2 eV, Sn-5p states: -2.3 - 0 eV.

Cs₄Sn₄:

Cs-5s states: -22.6 - -22.4 eV, Sn-3d states: -20.7 - -20.1 eV, Cs-5p states: -10.2 - -9.0 eV, Sn-5s states: -8.7 - -8.2 eV and -5.6 - -5.1 eV, Sn-5p states: -2.2 - 0 eV.

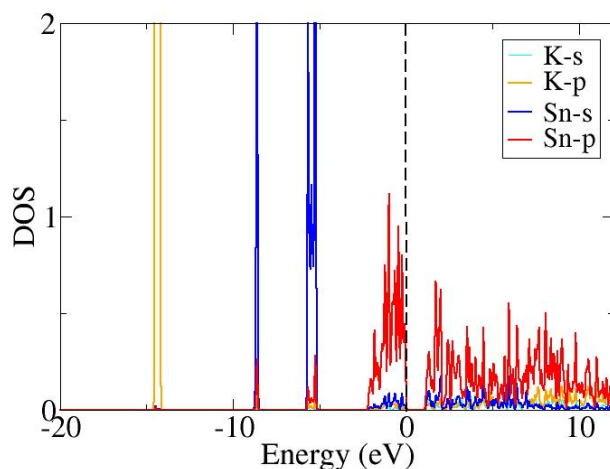


Figure 2.27: DOS of K_4Sn_4 .

This analysis shows again that the same trend which holds for the metal sulfides and silicides holds also for the metal stannides, i.e. that the smaller the energy difference between the **Me-s** and **Sn-s** states and between the **Me-p** and **Sn-p** states within the series the larger the interaction of those states within the series. This leads to a negative increasing of the chemical shielding from light to heavy metal compounds.

The metal-p charges in the Sn-p band and the CS of the corresponding band is given in Fig. 2.28(a) while the Sn-p charges in the metal-p band plotted vs the CS of the corresponding band is presented Fig. 2.28(b). The metal-p charges in the Sn-p band increase with decreasing CS of the corresponding band within the series except for Na_4Sn_4 . Fig. 2.28(b) shows the increasing CS contribution for the metal-p band with increasing Sn-p charges of the corresponding band within the series but now for all metal stannides. This plot certifies again that the compounds containing the alkali metals with low atomic number like Na_4Sn_4 and K_4Sn_4 nearly do not show CS contribution from the metal-p band which is due to the very low energy range of its states. Finally one can state again that the increasing of the Sn-p charges for the metal p band and the increasing of the metal-p charges for the Sn-p band within the series causes the larger hybridisation between the states and finally contributes to a negative increasing of the CS throughout the series.

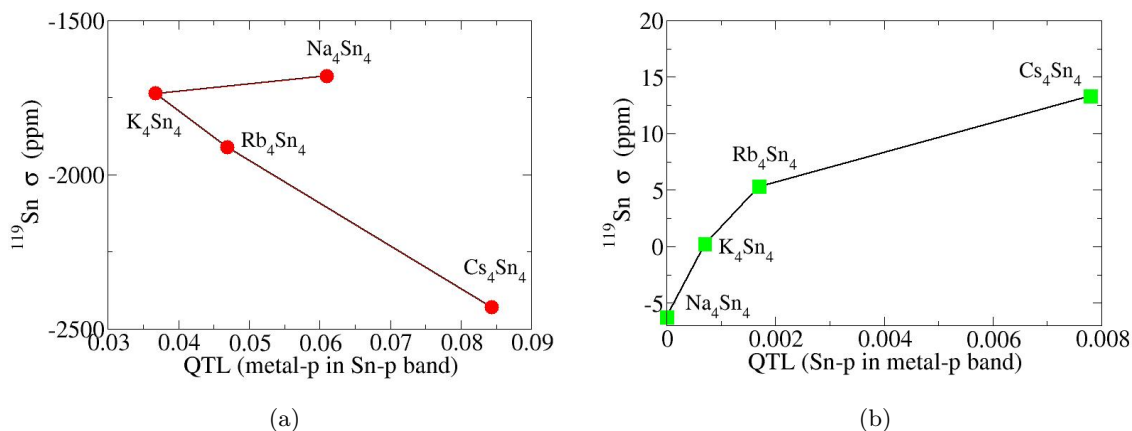


Figure 2.28: Fig.(a) presents the metal-p charges in the Sn-p band. Fig.(b) shows the Sn-p charges in the metal-p band for metal stannides.

Origin of NMR shielding in stannides

After the calculations of the shieldings in the metal stannides, the main focus was again the analysis of the CS caused by the occupied and unoccupied states in those compounds to achieve informations about the origin of the NMR shielding in those compounds. For that reason, the same procedure, which was done for the metal sulfides-, disulfides and silicides, was also carried out for the metal stannides, i.e a bandwise and character analysis of the wavefunctions.

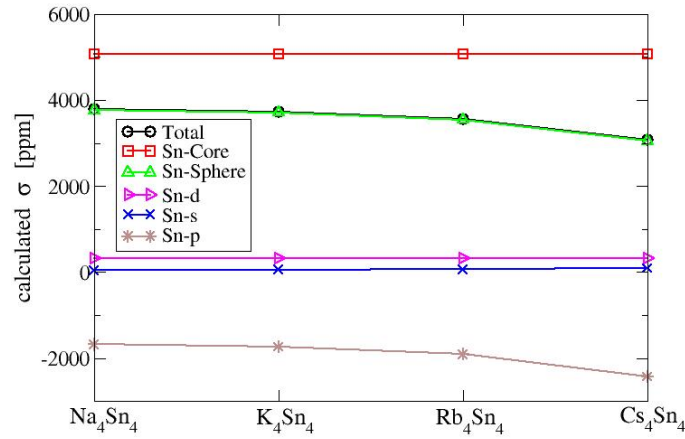
1. Bandwise analysis

As for all metal compounds in the previous chapters, the starting point of such an analysis, is again the so called “Band wise analysis”. In this analysis, the CS contribution that is caused by tin and metal states, which energy ranges are assigned in the previous chapter, were investigated. Table 2.16 and Fig 2.29 show that the major contribution of the CS originates from the core region. However, this contribution is positive and does not change throughout the series. In contrast to this, the CS that comes from the sphere region decreases from light to heavy metal compounds. That means that the CS must be generated by the valence region, i.e band region.

Looking at the shieldings that are caused in the band regions, one can finally state that only the CS of the Sn-p band is negative and responsible for the variation of the CS within the series. It is also obvious that a moderate positive Sn-p and a small Sn-s band contribution is present, however those contributions stay nearly constant throughout the series. The values for the CS of the metal-p bands are positive and tiny, thus they can be neglected. Finally, adding the CS contribution that is caused by the band region to the CS that is originating from the core region results in the CS contribution of the sphere region.

Table 2.16: Band-resolved contribution to ^{119}Sn isotropic shielding. All values in ppm.

	<i>total</i>	<i>sphere</i>	<i>core</i>	Sn-d band	Sn-s band	Sn-p band	metal-p band
Na_4Sn_4	3780.1	3762.4	5075.8	317.1	45.6	-1680.6	1.2
K_4Sn_4	3728.3	3710.2	5075.8	320.4	57.9	-1737.0	2.4
Rb_4Sn_4	3562.1	3545.5	5075.8	319.5	62.3	-1911.3	5.3
Cs_4Sn_4	3068.8	3053.8	5075.8	318.0	79.6	-2430.4	13.3

**Figure 2.29:** The CS contribution of total,core,sphere and bands regions.

2.a Character analysis of *occupied* states of the the wavefunction

In Table 2.17 one can obtain the major CS contribution for the metal-d, Sn-s and Sn-p bands decomposed according to s, p and d characters of $\psi_0^{(0)}$ and $\psi_0^{(1)}$.

Metal-d band

Only the **Sn-d character** of the ground state wave function ($\psi_0^{(0)}|_{Sn,l=2}$) contributes to the shielding in the **metal-d band**. Analyzing its first order perturbation $\psi_0^{(1)}$ shows an interesting fact. There is a small CS contribution from the Sn-p character, a larger contribution from the Sn-d character and the largest contribution is caused by the **Sn-f character** of the wavefunction. All three contributions from the the first order perturbation of $\psi_0^{(0)}$ stay fairly constant within the series.

Sn-s band

The contribution of the CS in the Sn-s band is due to the Sn-p character of $\psi_0^{(0)}$. First order perturbation of orbital characters of $\psi_0^{(0)}$ shows that the whole CS comes from the **Sn-p character**. The CS contribution slightly increases

Table 2.17: Major contribution for the CS calculated for the occupied ground state wavefunction ($\psi_0^{(0)}$) and its first order perturbation ($\psi_0^{(1)}$). Values below 10 ppm were not quoted. All values in ppm.

metal <i>d</i> band				
	Na ₄ Sn ₄	K ₄ Sn ₄	Rb ₄ Sn ₄	Cs ₄ Sn ₄
$\psi_0^{(0)} _{Sn,l=2}$	320.2	325.5	324.8	323.4
$\psi_0^{(1)} _{Sn,l=1}$	12.0	13.9	14	13.9
$\psi_0^{(1)} _{Sn,l=2}$	-63.9	-58.9	-59.8	-61.4
$\psi_0^{(1)} _{Sn,l=3}$	370.7	369.5	369.8	370.2

Sn <i>s</i> band				
	Na ₄ Sn ₄	K ₄ Sn ₄	Rb ₄ Sn ₄	Cs ₄ Sn ₄
$\psi_0^{(0)} _{Sn,l=1}$	46.1	63.7	63.1	93.2
$\psi_0^{(1)} _{Sn,l=1}$	46.2	63.7	63.7	92.1

Sn <i>p</i> band				
	Na ₄ Sn ₄	K ₄ Sn ₄	Rb ₄ Sn ₄	Cs ₄ Sn ₄
$\psi_0^{(0)} _{Sn,l=1}$	-1546.1	-1658.5	-1846.2	-2384.7
$\psi_0^{(1)} _{Sn,l=1}$	-1558.4	-1679.5	-1867.4	-2406.7
$\psi_0^{(1)} _{Sn,l=2}$	23.2	27.0	24.9	23.9
$\psi_0^{(1)} _{Sn,l=3}$	10.7	11.38		7.9
$\psi_0^{(0)} _{Sn,l=2}$	-140.1	-80.4	-69.5	-51.8
$\psi_0^{(1)} _{Sn,l=2}$	-141.9	-82.6	-71.7	-54.2

within the series.

Sn-p band

Investigations of the Sn-p band show that the CS contribution caused by $\psi_0^{(0)}|_{Sn,l=1}$ and $\psi_0^{(1)}|_{Sn,l=1}$ are negative and decreases dramatically within the series. There is also a smaller contribution from the $\psi_0^{(0)}|_{Sn,l=2}$ and its first order perturbation $\psi_0^{(1)}|_{Sn,l=2}$ which stays fairly constant within the series.

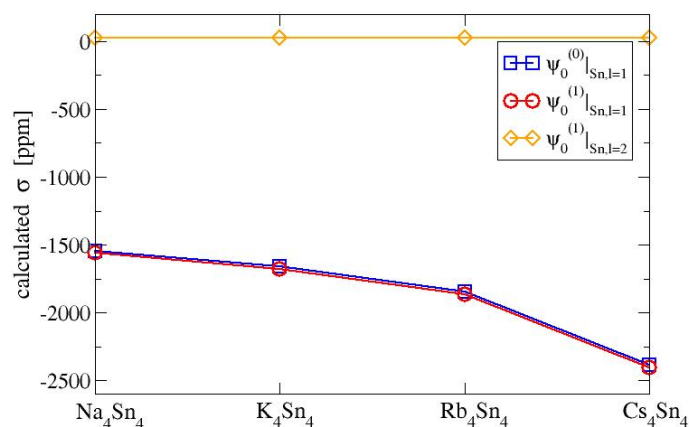


Figure 2.30: Decreasing of the CS contribution for $\psi_0^{(0)}|_{Sn,l=1}$ and its 1st order perturbation of its p and d-characters $\psi_0^{(1)}|_{Sn,l=1}$ $\psi_0^{(1)}|_{Sn,l=2}$.

2.b.Character analysis of the *unoccupied* states of the wavefunction

The main question is again now, how the empty states influence $\Psi_o^{(1)}$. The contribution of the chemical shieldings of the **unoccupied states** for a specific band and first order perturbation of the wavefunction $\Psi_o^{(1)}$ for a selected angular momentum (l) are represented in Table 2.18.

Metal-d band

The only significant empty ground state wavefunctions causing the CS in $\psi_0^{(1)}|_{Sn,l=2}$ in the metal-d band are that of Sn-d, Sn-f character and interstitial region. Those values stay constant within the series. Analyzing the CS of the empty states in $\psi_0^{(1)}|_{Sn,l=3}$ in the same band, one can notice that the CS is positive and the entire contribution is produced by the empty f character of Sn.

Sn-s band

The interstitial region is responsible for the CS caused in $\psi_0^{(1)}|_{Sn,l=1}$ in the Sn-s band. There is also a very small CS contribution from the empty Sn-s characters for $\psi_0^{(1)}|_{Sn,l=1}$ of Cs_4Sn_4 in the same band.

Sn-p band

The major negative but nearly constant contribution of the CS of $\psi_0^{(1)}|_{Sn,l=1}$ in the Sn-p band is due to the **Sn-p character** of the empty state wavefunction $\psi_e^{(0)}|_{Sn,l=1}$. The only significant changes of the CS within the series are presented in the **metal-d character** of the empty state of the wavefunction $\psi_e^{(0)}|_{metal,l=2}$ and the interstitial region in which both the CS increases negatively throughout the series. Analyzing the shielding which originates from the Sn-d character of the occupied wave function $\psi_0^{(0)}|_{Sn,l=2}$ from the Sn-p band

shows that the empty Sn-d states, which have a negative fairly constant contribution to the shielding and the interstitial region, which is also negative but reveals a positive increasing of the CS from light to heavy metal compounds.

Table 2.18: Major contribution for the CS calculated for the empty states of the wavefunctions and interstitial region. Values below 10 ppm were not quoted. All values in ppm.

metal <i>d</i> band, $\psi_0^{(1)} _{Sn,l=2}$				
	Na ₄ Sn ₄	K ₄ Sn ₄	Rb ₄ Sn ₄	Cs ₄ Sn ₄
$\psi_e^{(0)} _{Sn,l=2}$	-556.5	-304.1	-304.6	-304.6
$\psi_e^{(0)} _{Sn,l=3}$	-61.8	-55.5	-55.6	-56.1
<i>Interstitial</i>	557.5	307.4	307.34	307.0
metal <i>d</i> band, $\psi_0^{(1)} _{Sn,l=3}$				
$\psi_e^{(0)} _{Sn,l=3}$	364.7	367.9	367.9	367.7
Sn <i>s</i> band, $\psi_0^{(1)} _{Sn,l=1}$				
	Na ₄ Sn ₄	K ₄ Sn ₄	Rb ₄ Sn ₄	Cs ₄ Sn ₄
$\psi_e^{(0)} _{Sn,l=0}$				28.7
<i>Interstitial</i>	39.8	46.5	47.5	55.4
Sn <i>p</i> band, $\psi_0^{(1)} _{Sn,l=1}$				
	Na ₄ Sn ₄	K ₄ Sn ₄	Rb ₄ Sn ₄	Cs ₄ Sn ₄
$\psi_e^{(0)} _{Sn,l=0}$	168.3	181.6	184.3	161.3
$\psi_e^{(0)} _{Sn,l=1}$	-1545.3	-1555.5	-1579.9	-1605.1
$\psi_e^{(0)} _{Sn,l=2}$	73.7	88.4	78.7	75.9
$\psi_e^{(0)} _{Sn,l=3}$	15.6	14.7	14.7	15.6
$\psi_e^{(0)} _{metal,l=0}$	107.2	77.4	79.1	77.2
$\psi_e^{(0)} _{metal,l=1}$	19.9			-22.3
$\psi_e^{(0)} _{metal,l=2}$	-23.3	-124.0	-150.6	-204.1
<i>Interstitial</i>	-250.5	-307.0	-425.7	-810.2
Sn <i>p</i> band, $\psi_0^{(1)} _{Sn,l=2}$				
$\psi_e^{(0)} _{Sn,l=1}$				-12.0
$\psi_e^{(0)} _{Sn,l=2}$	-28.4	-30.9	-28.9	-29.7
<i>Interstitial</i>	-105.9	-57.3	-46.6	-31.7

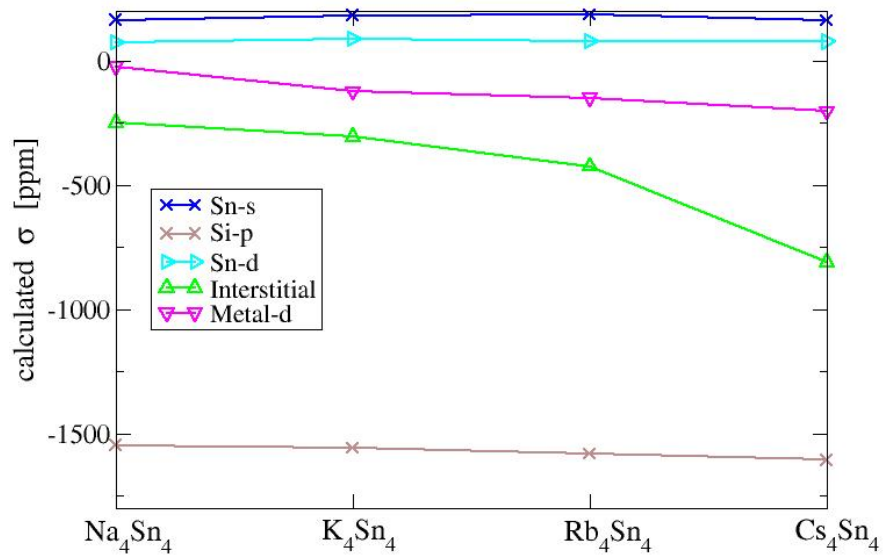


Figure 2.31: Changing of the CS for the unoccupied states of the wavefunctions of $\psi_0^{(1)}|_{Sn,l=1}$ in the Sn-p band and interstitial region within the series.

3 Calculations of NMR chemical shifts in metallic systems

The CS contribution of metals are different from nonmetals (64):

”The shielding in metallic systems arises from two mechanisms. The familiar orbital response of the electrons, the so called ”Shielding in a periodic system” and the Knight shift, which arises from a **spin polarization** induced by the external field”.

3.1 Chemical shifts of alkali and earth alkaline metal gallides

Gallides also belong to the Zintl phases which are described in Chapter 2.2. They form intermetallic phases with attractive Ga-Ga interactions. In this thesis, NMR quantum chemical calculations were performed at tetragallides MGa_4 ($\text{M}=\text{Na}, \text{Sr}, \text{Ba}$). In this case, $^{69,71}\text{Ga}$ with a nuclear spin of $I=3/2$ are the NMR active isotopes (65). The metal gallides belong to the group of metals in contrast to the previous compounds (metal sulfides-, disulfides and silicides) which is proven by the DOS given in Fig. 3.1, i.e a small but non-negligible DOS at the Fermi Energy (0 eV) is present.

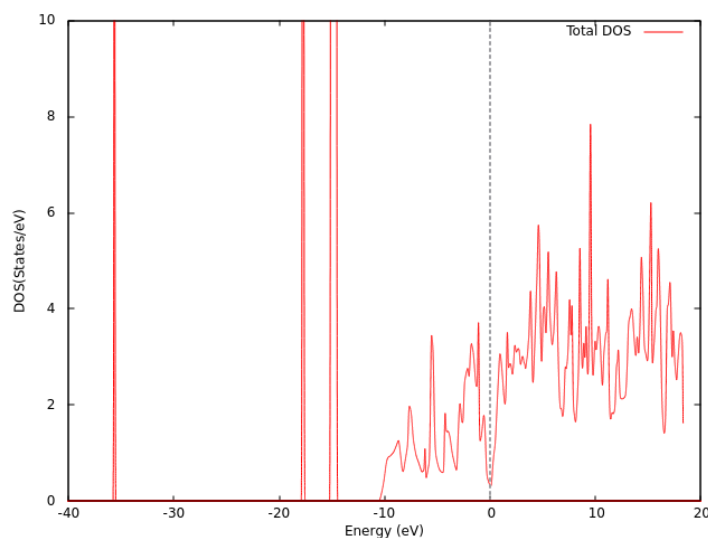


Figure 3.1: Total DOS of SrGa_4 .

3.1.1 Structural parameters

Table 3.1 presents lattice parameters and angles of all calculated gallides MGa_4 ($\text{M}=\text{Na}, \text{Sr}, \text{Ba}$). Table 3.2 lists atomic coordinates, RMT and space group of tetragallides. A RK_{MAX} of 7 was again applied for the calculations. It is evident from Table 3.1 that all metal gallides exhibit a tetragonal crystal system. In this case, the parameters increase from light to heavy metal compounds, except for the c parameter. All tetragallides have the space group $I4/mmm$ and show two different Ga-atoms within the unit cell. A geometry optimized structure calculation was conducted for all compounds (Table 3.2). Fig. 3.2 displays the structure of BaGa_4 .

Table 3.1: Lattice parameters and angles of different alkali and earth alkaline metal gallides.

	a / Å	b / Å	c / Å	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$
NaGa_4 [(66)]	4.23	4.23	11.27	90	90	90
SrGa_4 [(67)]	4.44	4.44	10.70	90	90	90
BaGa_4 [(68)]	4.56	4.56	10.77	90	90	90

Table 3.2: Atomic coordinates, RMT, RK_{MAX} and Space group of tetragallides.
* geo.opt= geometry optimized structure

	Atom	x	y	z	RMT	Space group
* NaGa_4 [(66)]	Na	0.00	0.00	0.00	2.50	$I4/mmm$
	Ga	$\frac{1}{2}$	0.00	$\frac{3}{4}$	2.30	
	Ga	0.00	0.00	0.609	2.30	
* SrGa_4 [(67)]	Sr	0.00	0.00	0.00	2.50	$I4/mmm$
	Ga	$\frac{1}{2}$	0.00	$\frac{3}{4}$	2.39	
	Ga	0.00	0.00	0.618	2.39	
* BaGa_4 [(68)]	Ba	0.00	0.00	0.00	2.50	$I4/mmm$
	Ga	$\frac{1}{2}$	0.00	$\frac{3}{4}$	2.40	
	Ga	0.00	0.00	0.620	2.40	

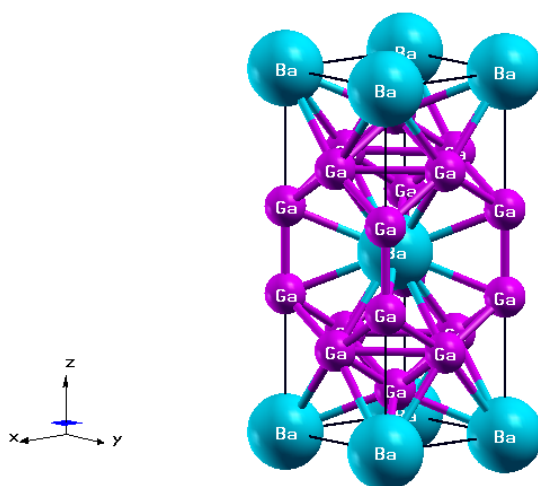


Figure 3.2: ThCr₂Si₂-Structure of BaGa₄.

3.1.2 Calculations of the chemical shieldings

The two isotopes of Gallium, ⁶⁹Ga and ⁷¹Ga are stable and can be found naturally, whereby both of these isotopes exhibit a nuclear spin of $I=3/2$, natural abundance of 60.4% and 39.6%, a quadrupole moment of $0.178 \cdot 10^{-28} \text{m}^2$ and $0.122 \cdot 10^{-28} \text{m}^2$, respectively (69).

Due to the quadrupole broadening, which is caused by the interaction of the nuclear quadrupolar momentum with the electric field gradient (EFG) tensor at the nucleus position, the NMR line-shapes are very broad. In (69) and (70) NMR chemical shifts of solid state Ga-compounds were already measured. NMR chemical shieldings of metal tetragallides MGa₄ (M=Na,Ca,Ba) were calculated using the PBE exchange correlational functional. Those results were compared with experimental NMR chemical shifts from (65).

Haarmann and Koch (65) made calculations of NMR chemical shieldings for metal stannides by applying the PBE functional within the DFT. They also used the full-potential augmented plane wave plus local orbitals (APW+lo) code WIEN2k to calculate the density of states (DOS).

As mentioned before, the shielding of metals originates from both orbital motion of the electrons and the spin polarization induced by the external field. In Table 3.3 the results for the calculated CS for both orbital contribution (OC) and spin contribution (SC) and experimental chemical shifts from (65) are shown. It is obvious from Fig. 3.3(a) that the calculated shieldings and even the experimental shifts are quite large and positive, which is in contrast to the metal silicides. Due to the small coefficient of determination of 0.699, one can say that the shieldings do not show an observable trend like for the nonmetal compounds in the previous chapters. The slope is positive and far from the ideal value of 1.0, in contrast to the metal sulfides-,silicides-, and stannides. The positive chemical shifts can be explained due to the reinforcement of the magnetic field caused by the conduction electrons of the metals. Fig. 3.3(b) shows the correlation between the experimental chemical shifts and the calculated chemical shifts. One can notice, that there is a bad correlation

between those shifts, especially for the Ga(5b) atoms.

Differences between CS calculations of metals and nonmetals

If one compares the analysis of the CS of metals with the CS of nonmetals from previous chapters, one can notice some considerable differences between them: First, the k-mesh for metals (metal gallides in our case) is very large, compared to that of nonmetals. This is due to the different electronic structure of metals, for which lots of k-points are required to describe the unoccupied states and to convergence the k-points within the brillouin zone (Fig. 3.4). These empty states are also pertubated at the Fermi Energy due to the applied magnetic field. As a result of this, a k-mesh of 43x43x43 was used for the metal gallides (Fig. 3.4). Secondly, the calculated and experimental CS for metal gallides increases arbitrary with increasing size of the alkali and earth alkaline metal, respectively. Because of this fact, further investigations on the origin of these shieldings were not done.

Table 3.3: Calculations of the σ_{iso} , $\sigma_{iso,OC}^{LAPW}$ (Orbital Contribution) and $\sigma_{iso,SC}^{LAPW}$ (Spin Contribution) for **Ga(4b)** using the PBE exchange correlational functional. The experimental shifts $\delta_{iso}^{expt.}$ are given with reference to Ga(NO₃)₄. The theoretical shifts δ_{iso}^{LAPW} are given with a reference taken from Fig 3.3. All values in ppm.

	σ_{iso}^{LAPW}	δ_{iso}^{LAPW}	$\delta_{iso}^{expt.}$	$\sigma_{iso,OC}^{LAPW}$	$\sigma_{iso,SC}^{LAPW}$	structure
NaGa ₄	3051.6	2762.9	2880.1 [(65)]	2010.3	1041.3	geo.opt.
SrGa ₄	2384.8	3060.0	2630.0 [(65)]	1445.0	739.3	geo.opt.
BaGa ₄	3082.4	2923.6	3010.1 [(65)]	2041.8	1039.4	geo.opt.

Table 3.4: Calculations of the σ_{iso} , $\sigma_{iso,OC}^{LAPW}$ (Orbital Contribution) and $\sigma_{iso,SC}^{LAPW}$ (Spin Contribution) for **Ga(5b)** using the PBE exchange correlational functional. The experimental shifts $\delta_{iso}^{expt.}$ are given with reference to Ga(NO₃)₄. The theoretical shifts δ_{iso}^{LAPW} are given with a reference taken from Fig. 3.3. All values in ppm.

	σ_{iso}^{LAPW}	δ_{iso}^{LAPW}	$\delta_{iso}^{expt.}$	$\sigma_{iso,OC}^{LAPW}$	$\sigma_{iso,SC}^{LAPW}$
NaGa ₄	3082.3	464.6	1350 [(65)]	2070.6	1015.2
SrGa ₄	1478.1	1509.2	970.1 [(65)]	876.1	602.0
BaGa ₄	1860.0	934.8	840.0 [(65)]	1230.1	630.3

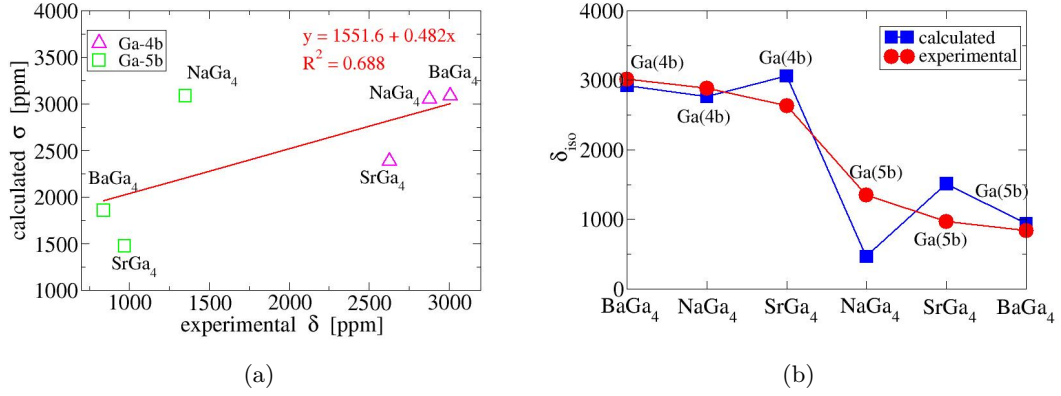


Figure 3.3: Fig.(a) shows the correlation between the calculated σ_{iso} and experimental δ_{iso} from (65) and Fig.(b) the correlation between the calculated δ_{iso} and experimental $\delta_{iso}^{expt.}$.

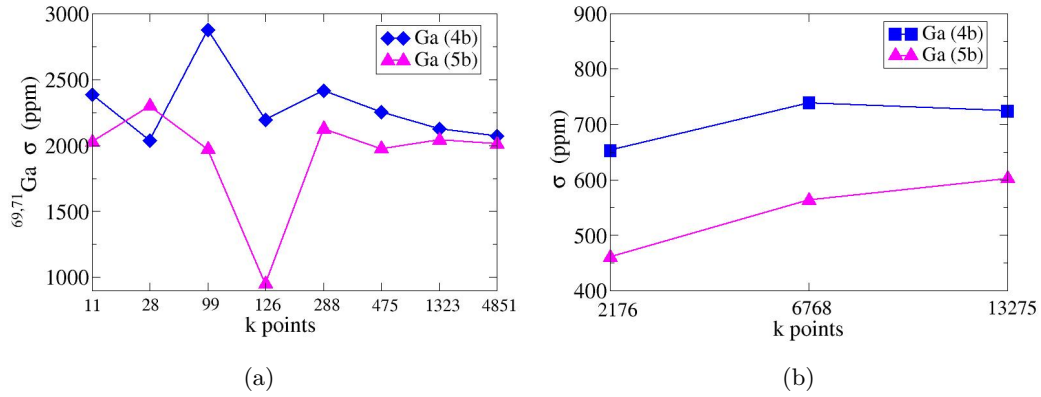


Figure 3.4: Fig.(a) represents the convergence of the k-mesh for the calculated CS for the Orbital-Contribution of NaGa₄ and Fig.(b) the same, but for the Spin-Contribution of SrGa₄.

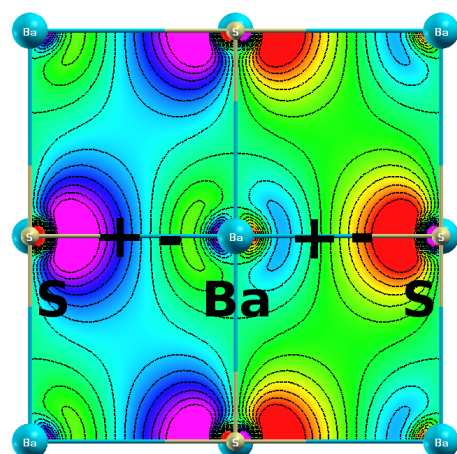
4 Explanation for the different chemical shieldings and sign

4.1 Bonding and antibonding interactions of X-p and Me-p states

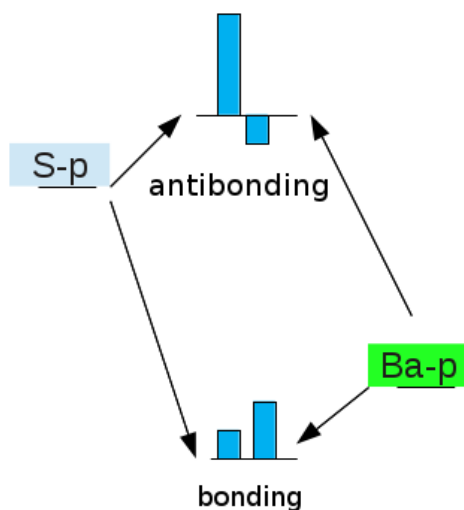
If one compares the CS contribution of $\psi_0^{(1)}|_{X,l=1}$ (X=S, Si, Sn) from the **metal-p band** and the $\psi_0^{(0)}|_{X,l=1}$ from the **X-p band** in metal sulfides and silicides, one can see a big difference in the chemical shift, i.e for example the value for $\psi_0^{(0)}|_{X,l=1}$ in the X-p band of BaS is **20 times bigger** than $\psi_0^{(0)}|_{X,l=1}$ for the metal-p band and has the opposite sign. This can be explained due to the covalent interaction between metal-p states in the X-p band and X-p states in the metal-p band which is illustrated in Fig. 4.1.

4.2 Coupling to the metal-d states

After analyzing the CS contribution of the characters of the unoccupied states $\psi_e^{(0)}$ in metal-, sulfides, silicides and stannides from the X-p band, one can clearly see that the CS of the **metal-d character** is changing within the series. This leads to the assumption that the increasing of the CS within the series does not only come from the stronger covalent interaction which was explained before, it is also due to the **lowering of the metal-d states throughout the series** (Fig. 4.2- 4.4) which finally allows a stronger coupling of the X-band (hybridized with metal-p) in the valence band with the metal-d band in the conduction band. This can be described by Eq. 1.48, which points out that the CS for $\psi_0^{(1)}$ increases by decreasing the energy in the denominator within the series.



(a)



(b)

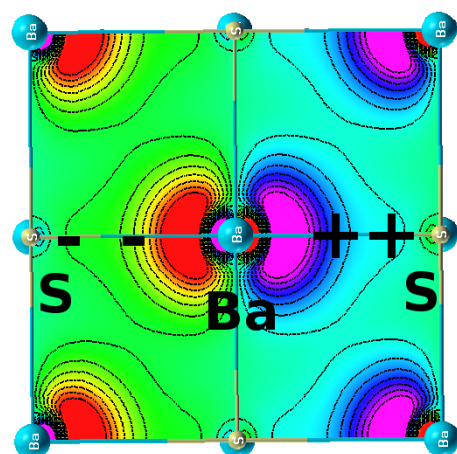


Figure 4.1: Fig.(a) states that the **antibonding** character of the metal-p and S-p orbitals is responsible for the large negative CS from the S-p band (-952 ppm) in BaS because the antibonding character is much more localised at the S-p state. Fig.(b) shows that the **bonding** character of the metal-p and S-p orbitals is responsible for midsize positive CS originating from the metal-p band (52 ppm).

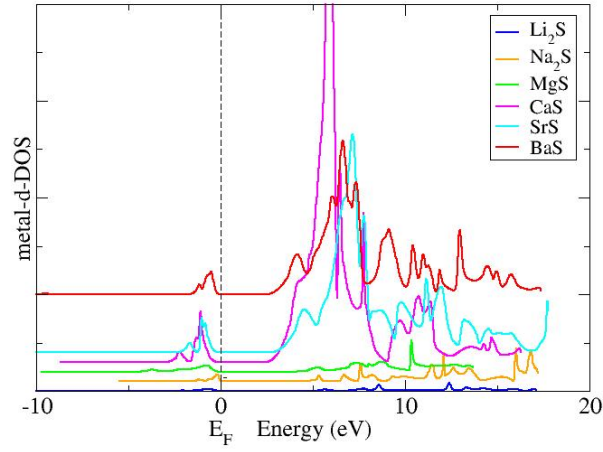


Figure 4.2: Lowering of the metal-d DOS of metal sulfides within the series.

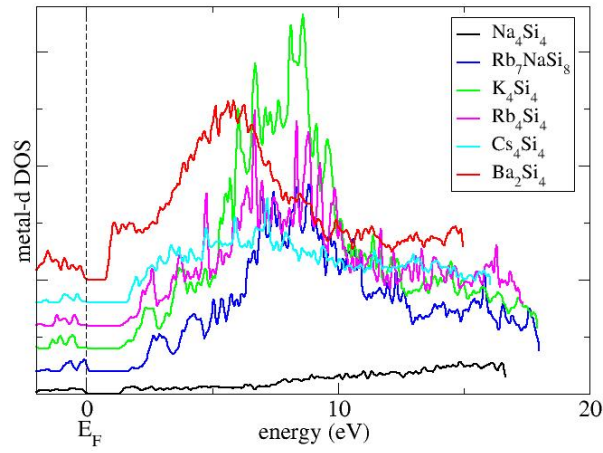


Figure 4.3: Lowering of the metal-d DOS of metal silicides within the series.

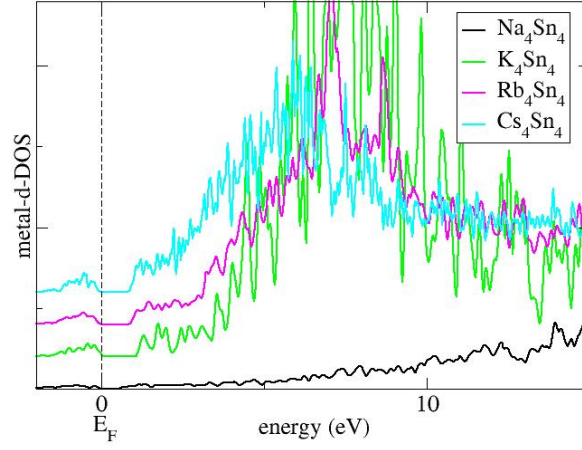


Figure 4.4: Lowering of the metal-d DOS of metal stannides within the series.

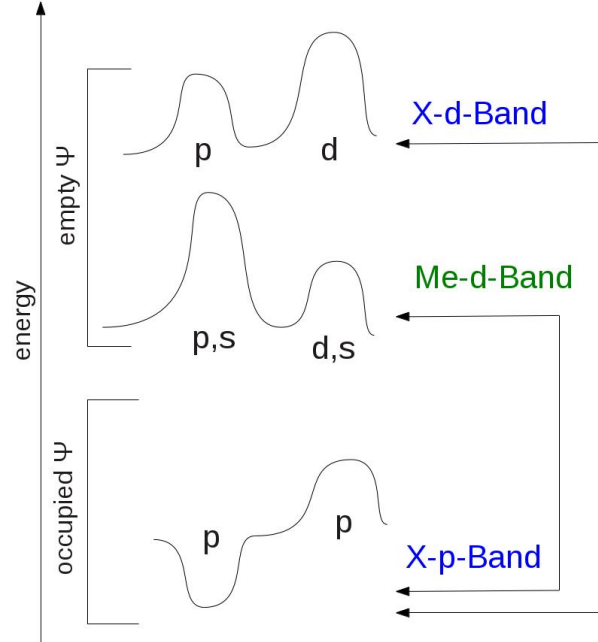


Figure 4.5: Coupling of the occupied p-states in the X (=S,Si,Sn)-band with the empty states in the Me-d band and X-d band.

5 Conclusions

The major two questions in this thesis were: From which atoms and its orbitals does the contribution of the chemical shielding come from and what is the explanation for the different chemical shieldings and their sign in the calculated solids for nonmetals. It was found out that the chemical shielding increases negatively within the series, that means the CS decreases by increasing the atomic number of the metal atom, except for transition metal disulfides. The bandwise analysis shows that the major CS contribution comes from the X (S,Si,Sn)- band and increases negatively from light to heavy metal compounds. For the transition metal disulfides one can state that the positive increasing of the CS within the series is due to the positive contribution originating from the metal-d band. The character analysis of the occupied wavefunctions shows that only its X-p character changes within the series for the X-p band. By analyzing the unoccupied wavefunctions of this band, one can clearly see that the CS stays nearly constant for every empty state except for the Me-d states. This observation leads to the assumption, that the reason for a decreasing of the CS for the metal sulfides-, silicides and stannides is due to lowering of the energy of the Me-d states, that means decreasing band gap and finally stronger interaction of the occupied states in the X-p band with the empty Me-d states. The energy separation between the metal-p and X-p states is also decreasing from light to heavy metal compounds, which results in larger hybridisation between the states and finally contributes to a negative increasing within the series. The calculations of the gallides (MGa_4) show a complete different behaviour, i.e the CS increases arbitrary from light to heavy metal compounds.

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Curriculum Vitae

Education

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German	fluent
English	fluent
Latin	basic

January 22, 2014