

## Quadrupole Coupling – the Key to NMR Spectroscopy of Intermetallic Compounds

Frank Haarmann, Thorsten Goebel, Peter Jeglič<sup>1</sup>, Katrin Koch, Oliver Pecher, Helge Rosner, and Yuri Grin

### Introduction

In order to understand the chemical bonding of intermetallic compounds, the characterization of structural details is highly important. Since structural disorder is frequently observed in intermetallic compounds, strategies and tools have to be developed which compensate the restrictions of diffraction methods. Nuclear magnetic resonance (NMR) spectroscopy as a local probe has been shown to be highly suited for the investigation of disordered materials as electrically non-conducting glasses [1]. However, for samples showing metallic conductivity several NMR relevant couplings arise [2] and strategies, being suitable for glasses, can not be used without further modification. The di- and tetragallides of the alkaline earth metals and  $\text{NaGa}_4$  were chosen as model compounds to explore reliable quantities of NMR experiments of metallic materials. These compounds have simple crystal structures with one or two chemically non-equivalent sites and should not feature structural disorder. Hence, changes of the chemical bonding situation can be studied in two series of isotopic compounds.

### Model compounds: di- and tetragallides

The digallides of Sr and Ba crystallize in the  $\text{AlB}_2$  type of structure [3]. Planar honeycomb like nets are formed by three bonded atoms Ga(3b) (Fig. 1, left).  $\text{CaGa}_2$  crystallizes in the  $\text{CaIn}_2$  type of structure with puckered nets of Ga(3b+1b) atoms [4, 5]. The tetragallides  $M\text{Ga}_4$  with  $M = \text{Na}, \text{Sr},$  and Ba crystallize in the  $\text{BaAl}_4$  type of structure. The 3D framework is built by four- and five bonded atoms Ga(4b) and Ga(5b) (Fig. 1, right) [3,6].  $\text{CaGa}_4$  crystallizes in a monoclinic distorted variant of the  $\text{BaAl}_4$  type of structure [4].

<sup>69,71</sup>Ga NMR spectroscopy has been chosen for our systematic investigation of Ga in various environments with different cations. Both Ga isotopes possess a nuclear spin of  $I = 3/2$  and are therefore subject to magnetic dipole and electric quadrupole couplings. The magnetic dipole couplings result from the interaction of the nuclear magnetic dipole moment of the observed nuclei with the magnetic field caused by the environment. For the investigated compounds this results mainly in a shift of the NMR signal depending on the orientation of the crystallites with respect to the external mag-

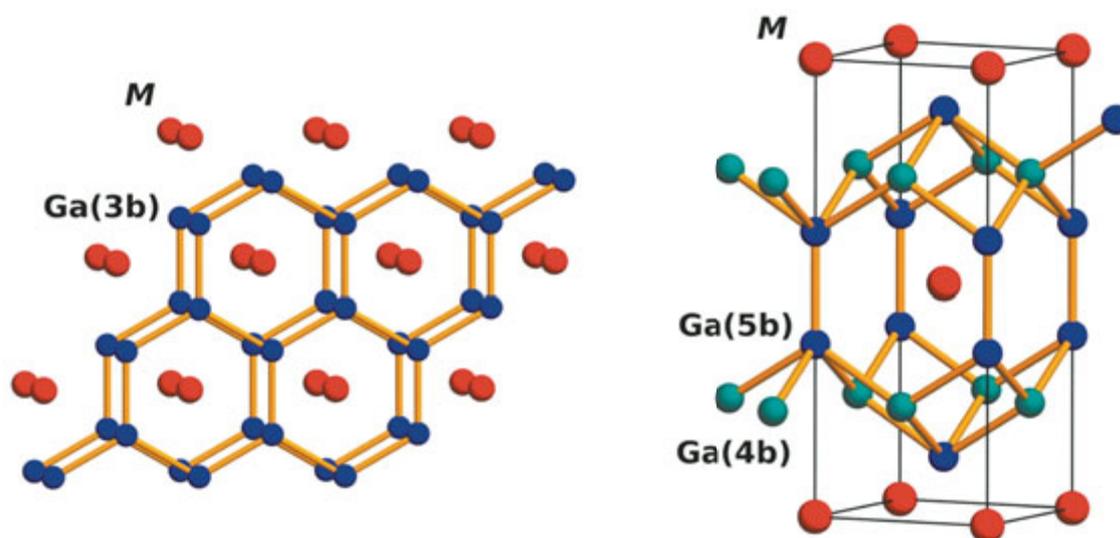


Fig. 1: The digallides  $M\text{Ga}_2$  with  $M = \text{Sr}$  and Ba crystallize in the  $\text{AlB}_2$  type of structure (left), the tetragallides  $M\text{Ga}_4$  with  $M = \text{Na}, \text{Sr},$  and Ba adopt a  $\text{BaAl}_4$  type of structure (right). Three-, four- and five-bonded Ga atoms are marked by Ga(3b), Ga(4b), and Ga(5b).

netic field used for the experiment. The electric quadrupole coupling results from the interaction of the nuclear quadrupole moment with the electric field gradient (EFG). It causes characteristic line shapes of the NMR signals for randomly oriented crystallites. For single crystals and oriented powders a variation of the resonance frequencies depending on the orientation of the EFG with respect to the external magnetic field is observed.

The  $^{71}\text{Ga}$  NMR signals of the main transition of the di- and tetragallides are presented in Fig. 2. The line shape of the signals proves clearly, that the signals are dominated by quadrupole coupling. Careful line shape analysis was used to determine the shift and quadrupole coupling parameters. For the digallides  $M\text{Ga}_2$  with  $M = \text{Ca}, \text{Sr},$  and  $\text{Ba}$  a single NMR signal is observed as expected for the one crystallographic Ga site in the crystal structure (Fig. 2, right). The two crystallographic non-equivalent sites of Ga(4b) and Ga(5b) are resolved for the investigated tetragallides. An assignment of the signals is complicated by the fact that the multiplicity of both sites is equal and therefore the signal intensity can not be used as a criterion. Furthermore, measurements of the relative signal intensities of nuclei with a quadrupole moment are

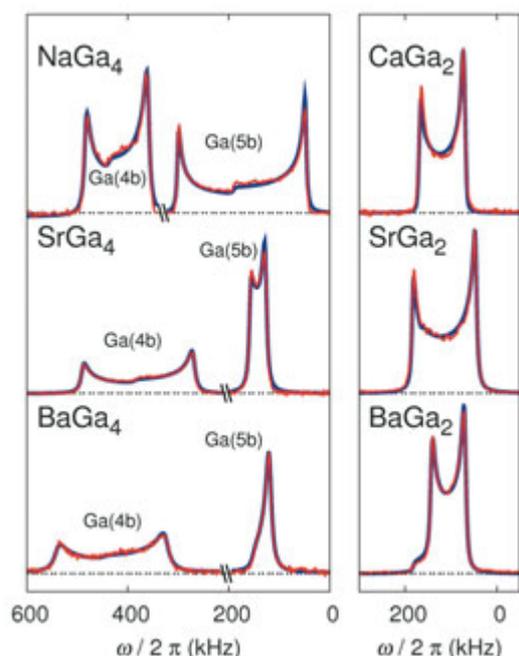


Fig. 2:  $^{71}\text{Ga}$  NMR signals of the di- and tetragallides of the alkaline earth metals and  $\text{NaGa}_4$  right and left, respectively. Assignment of the four and five bonded Ga(4b) and Ga(5b) atoms is indicated.

challenging especially if the signals cover a large frequency range [7]. Thus other criteria for signal assignment such as signal shift and / or quadrupole couplings have to be used.

The NMR signal shift of materials possessing metallic conductivity is realized by various mechanisms [2]. The nuclear magnetic moment can interact with the magnetic field at the nuclear site caused by electron motion and electron spin. The former is the so-called chemical shielding and the latter the Knight shift. In non-magnetic metallic compounds the NMR signal shift is often dominated by the Knight shift being in first approximation proportional to the density of states of the  $s$ -like conduction electrons ( $s\text{-DOS}(E_F)$ ). An assignment of the signals based on the  $s\text{-DOS}(E_F)$  of the Ga atoms of the tetragallides is shown in Fig. 2. The NMR signal shift as a function of the  $s\text{-DOS}(E_F)$  is depicted in Fig. 3. An almost linear relation as expected from theory is observed [2]. The deviation of the data points from the dotted line indicates the contributions of chemical shielding. At present stage no quantum mechanical programs are available to handle the NMR signal shift for metallic conductors. The signals of Ga(3b), Ga(3b+1b) and Ga(5b) overlap and are at low frequencies, while the signals of Ga(4b) are at high frequencies. Due to the overlap of the frequency ranges an assignment on the basis of the shift in-

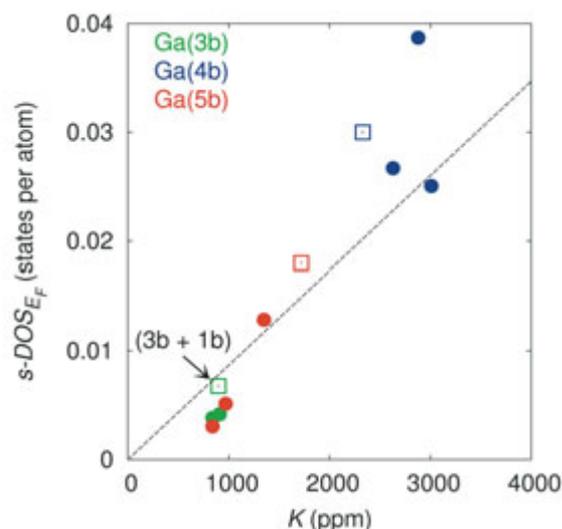


Fig. 3: NMR signal shift as a function of the  $s$ -like conduction electron density of states  $s\text{-DOS}(E_F)$  for di- and tetragallides. Squares refer to  $\text{CaGa}_2$  (green) and  $\text{CaGa}_4$  (red and blue). The dashed line represents the linear behaviour predicted by theory [2].

formation seems to be ambiguous. Nevertheless, the relative shifts of two signals within a single compound can be estimated using the  $s$ -DOS( $E_F$ ).

In contrast to the signal shift, quadrupole coupling is a well established quantity being accessible with quantum mechanical programs like FPLO and WIEN2k [8, 9]. A comparison of experimental results and quantum mechanically calculated values is depicted in Fig. 4. The agreement of the results is remarkable allowing an unambiguous assignment of the signals for the tetragallides. This assignment is in agreement with that based on the  $s$ -DOS( $E_F$ ) contributions of the Ga atoms. The deviation of the EFG obtained from NMR experiments and quantum mechanical calculations for SrGa<sub>2</sub> is beyond the confidence interval of  $\pm 15\%$ . This challenges the model of the crystal structure of SrGa<sub>2</sub>.

An analysis of the contributions to the EFG shows that it is dominated by the local electrons of the observed atom. Contributions of other atoms are negligible. Further analysis of the orbital characters of the local electrons causing the EFG proves that for the Ga compounds the  $p$ -like electrons dominate the anisotropy of the charge distribution. The so-called anisotropy function ( $\Delta n(p)$ ) which correlates the occupation of the different  $m_l$ -states of the  $p$ -like electrons with the main contribution of the electric field gradient ( $V_{ZZ}$ ) is shown in Fig. 5. A linear dependence of  $\Delta n(p)$  with  $V_{ZZ}$  indicates the direct correlation between these quantities. Deviations from the linear dependency point out contributions of electrons with different orbital character. The positive sign of the anisotropy

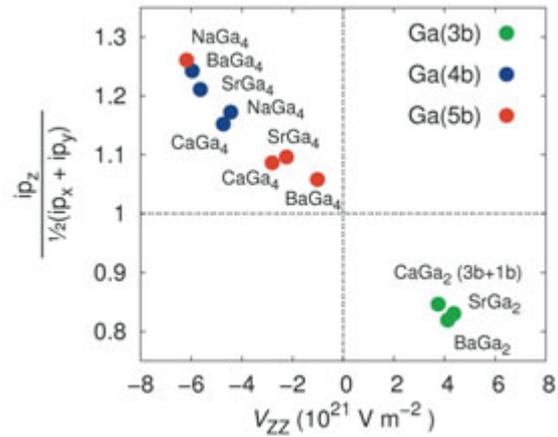


Fig. 4: Anisotropy function vs. the main component of the electric field gradient  $V_{ZZ}$  for di- and tetragallides.

function corresponds to an oblate-like electron density distribution. This is in agreement with the expected charge distribution of the digallides. The negative sign of  $V_{ZZ}$  for the tetragallides indicates a cigar-like electron density distribution of the Ga atoms.

#### Details for SrGa<sub>2</sub> and BaGa<sub>2</sub>

The deviation of  $V_{ZZ}$  of SrGa<sub>2</sub> determined by quantum mechanical calculations and NMR experiments challenges the structure model [5]. Single crystal X-ray diffraction experiments also indicate an unresolved structural feature of unusual anisotropic displacement of the Ga atoms [5,10]. Quantum mechanical calculations using the CaIn<sub>2</sub> type of structure prove that a puckering of the Ga layers by  $\pm 0.125 \text{ \AA}$  is energetically favourable compared to plane layers in the AlB<sub>2</sub> type of structure (Fig. 6). Considering such a shift of the Ga atoms for the quantum mechanical calculation of the EFG, good agreement with the values of the NMR experiment is obtained (Fig. 6, inset). Interestingly, a similar shift of the Ga atoms does not significantly change the value of  $V_{ZZ}$  for BaGa<sub>2</sub> (Fig. 6, inset). Nevertheless, also in BaGa<sub>2</sub> a puckering of the Ga layers is expected for energetic reasons. This is supported by the results of the X-ray diffraction data.

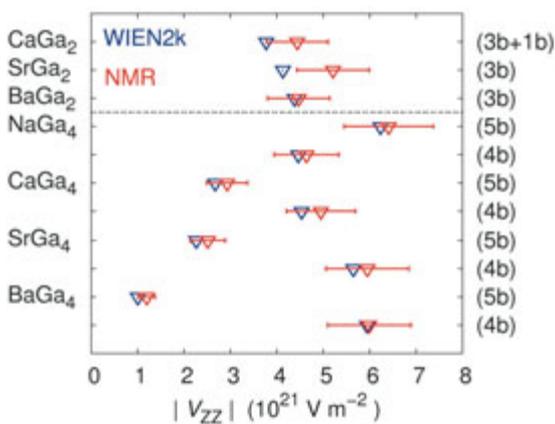


Fig. 5: Absolute values of the main component  $V_{ZZ}$  of the EFG of di- and tetragallides obtained by quantum mechanical calculations and NMR experiments.

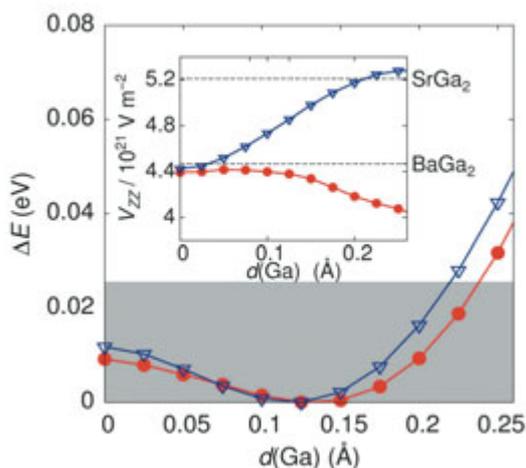


Fig. 7: Energy change as a function of the Ga atom shift in the  $Caln_2$  type of structure for  $SrGa_2$  (blue) and  $BaGa_2$  (red). The gray shaded area indicates the thermal energy at ambient temperature. The inset depicts the corresponding change of  $V_{zz}$ . Horizontal lines indicate the experimentally determined values at ambient temperature.

#### Substitution of cations: $Ca_xSr_{1-x}Ga_4$

To study the influence of the cations on the local bonding situation of the Ga atoms, a solid solution  $Ca_xSr_{1-x}Ga_4$  with  $0 \leq x \leq 1$  was investigated.

A systematic change of the  $^{69,71}Ga$  NMR signal line shape of regular powder with randomly oriented crystallites proves the influence of the cations on the bonding situations of the Ga atoms. To enhance the resolution of the NMR experiment the crystallites were aligned in the magnetic field. Especially for small amounts of Sr substitution by Ca additional signal contributions become visible (Fig. 7). The dependence of the line shape on the magnetic field and the isotope evidences that the additional signal is due to a change of the quadrupole coupling. The substitution of Sr by Ca results in a decrease for Ga(4b) and in an increase of the anisotropy of the charge distribution for Ga(5b). The same tendency is obtained by quantum mechanical calculations of the EFG. With increasing number of Ca atoms in the environment of the Ga atoms a larger change of the EFG is observed in these calculations.

#### Conclusion

The investigation of the di- and tetragallides clearly shows that quadrupole coupling represents the reliable information about the nature of inter-

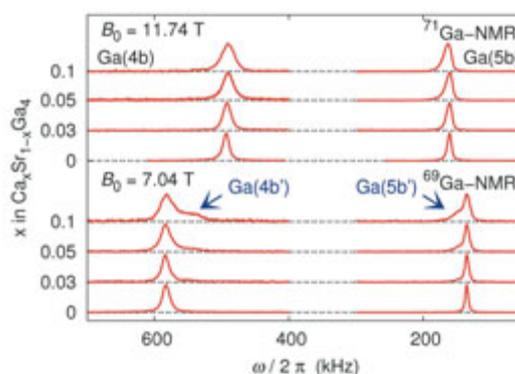


Fig. 6:  $^{69,71}Ga$  NMR signals of  $Ca_xSr_{1-x}Ga_4$  measured in different magnetic fields. The blue arrows mark additional signals contributions.

metallic compounds. The combination of NMR spectroscopy and quantum mechanical calculations provides insights in the local atomic arrangement and the chemical bonding. Thus, for  $SrGa_2$  and  $BaGa_2$  a puckering of the Ga layers was identified. In addition, a gradual modification of the anisotropy of the electron density distribution of the Ga atoms is revealed by a change of the quadrupole coupling of the tetragallides  $MGa_4$  with  $M = Na, Ca, Sr,$  and  $Ba$ .

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<sup>1</sup> Present address: Jožef Stefan Institute, Jamova 39, Ljubljana 1000, Slovenia