Hyperfine Interact
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Hyperfine interactions in intermetallic rare earth-gallium compounds studied by ^{111}Cd PAC

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Abstract Magnetic and electric hyperfine interaction of the nuclear probe ^{111}In/^{111}Cd in intermetallic compounds of the rare earth-gallium system have been investigated by perturbed angular correlation (PAC) spectroscopy. The PAC measurements, supported by X-ray diffraction, provide evidence for a marked phase preference of ^{111}In for hexagonal RGa$_2$ over orthorhombic RGa and of RGa$_3$ with the L12 structure over RGa$_2$. In the case of SmGa$_2$, the magnetic hyperfine field B_{hf}, the electric quadrupole interaction and the angle β between B_{hf} and the symmetry axis of the electric field gradient have been determined as a function of temperature. The angle $\beta = 0$ is consistent with the results of previous magnetization studies. Up to $T \leq 17$ K the magnetic hyperfine field has a constant value of $B_{hf} = 3.0(2)$ T. The rapid decrease at higher T gives the impression of a first-order transition with an order temperature of $T_N = 19.5$ K. In the RKKY model of indirect 4f interaction the

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ratio $T_C/B_{hf}(0)$ is a measure of the coupling constant. For ^{111}Cd:$SmGa_2$ ($T_C/B_{hf}(0) \sim$ 6.5 K/T) this ratio is significantly smaller than for the same probe in other R intermetallics ($SmAl_2 \sim 9.5$ K/T, $Sm_2In \sim 13.5$ K/T).

Keywords Magnetic hyperfine interaction · Rare earth gallium intermetallic compounds · Perturbed angular correlations

1 Introduction

The phase diagrams of gallium with the rare earth (R) metals $R =$ Ce, Pr, ..., Gd, Tb, ..., Er, Tm contain up to 6 intermetallic compounds [1, 2]. All R constituents form the phases RGa_6, RGa_2, RGa, and R_5Ga_3. The phases RGa_3 and R_3Ga_5 are found only for the heavy rare earth $R =$ Tb, Dy, ..., Tm, R_3Ga only for the light $R =$ Ce, Pr, Nd and Sm. At low temperatures long-range RKKY exchange coupling mediated by the conduction electrons leads to spontaneous magnetic order of the localized $4f$-moments in most of these intermetallics [3–6]. The spin polarization of the conduction electrons produces a Fermi contact hyperfine field B_{hf} at nuclear sites. Measurements of B_{hf} are therefore a valuable source of information on the exchange interaction and are also a useful tool for the investigation of phase transitions.

In the case of rare earth-gallium intermetallics hyperfine field measurements have reported up to now mainly for equiatomic RGa. Delyagin and Krylov [7] and Delyagin et al. [8] have used ^{119}Sn Mössbauer spectroscopy to study the spin dependence of the magnetic hyperfine field and the spin reorientation transitions of these ferromagnetic compounds.

We have initiated a systematic investigation of magnetic and electric hyperfine interactions in rare earth-gallium alloys using perturbed angular correlation (PAC) spectroscopy with the radioisotope ^{111}In→^{111}Cd as probe nucleus. In this contribution we report first results of this study. We present evidence for a marked preference of ^{111}In for hexagonal RGa_2 over orthorhombic RGa for $R =$ Sm, Nd, Pr and of RGa_3 over RGa_2 for $R =$ Ho, Er. Furthermore the magnetic hyperfine field of ^{111}Cd in $SmGa_2$ and its temperature dependence have been determined.

2 Experimental procedure

Intermetallic R-Ga alloys were synthesized by arc-melting of metallic constituents in the stoichiometry ratios 1:1 and 1:2 in Ar atmosphere. In some of the 1:2 samples a slight (1–2 %) R excess was used. For homogeneity, the samples were turned over and remelted several times. Weight losses by arc-melting usually were of the order of 1–2 %. The molten ingots were characterized by X-ray diffraction (XRD). Samples with the stoichiometry ratio 1:1 and heavy R constituents were found to be single phase (RGa). 1:1 samples with the light $R =$ Pr, Nd, Sm usually contained 2 phases, RGa and a contribution of RGa_2 of about 10 %. Samples with the stoichiometry ratio 1:2 were single phase RGa_2.

The samples were doped with the probe nucleus ^{111}In →^{111}Cd by diffusion in vacuum at 800 °C for 12 h. The PAC measurements were carried out with a standard

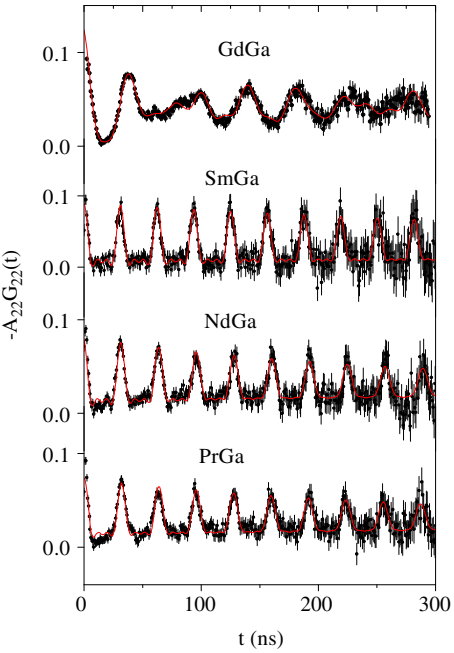

Fig. 1 Room temperature PAC spectra of ^{111}Cd in binary R-Ga compounds (R = Gd, Nd, Pr, Sm) synthesized in the stoichiometric ratio 1:1. In the case of R = Sm, Nd and Pr the QI parameters ν_q and η deduced from these spectra are identical to those reported for ^{111}Cd in the compounds RGa_2

4-BaF_2-detector set-up. Temperatures 8 K $\leq T <$ 300 K were reached with closed-cycle He refrigerator.

3 Results

Figure 1 show examples of room temperature PAC spectra of ^{111}Cd in some binary R-Ga compounds R = Gd, Nd, Pr, Sm which were synthesized with the stoichiometric ratio 1:1. The non-periodic pattern of the Gd-Ga sample indicates a perturbation by an axially asymmetric QI consistent with the orthorhombic CrB type structure (Cmcm space group) of RGa. Two sites of nearly equal intensity are required to reproduce the experimental data of GdGa: $\nu_q(1) = eQV_{zz}/h = 107.6$ MHz, $\eta(1) = (V_{xx} - V_{yy})/V_{zz} = 0.66$ and $\nu_q(2) = 84.1$ MHz, $\eta(2) = 0.96$.

According to the XRD analysis the heavy R-samples of stoichiometry 1:1 were single-phase RGa compounds. Since the QI at both the R-site and the Ga-site of the RGa structure is axially asymmetric, the observation of two axially asymmetric fractions suggests that the ^{111}In/^{111}Cd probe occupies both sites with equal probability. For a test of this hypothesis ab-initio calculations of the electric field gradient at both sites are underway.

In contrast to GdGa, the room temperature spectra of the 1:1 R-Ga samples with the light rare earth constituents R = Pr, Nd, Sm (Fig. 1) show a periodic time modulation of the anisotropy, indicating an axially asymmetric ($\eta = 0$) QI with quadrupole frequencies of ν_q = 207.4(3), 208.6(3), 211.2(3) MHz, for R = Nd, Pr and Sm, respectively. These QI parameters are identical to those reported by Mishra et al. [9] for hexagonal RGa_2.

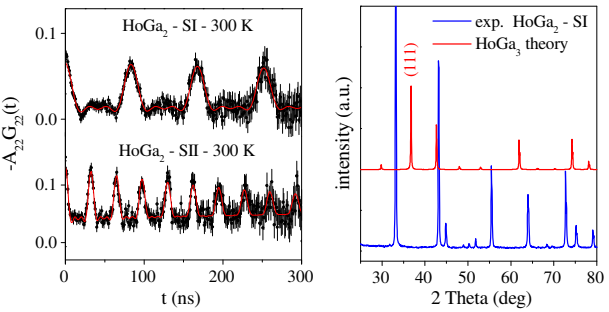

Fig. 2 PAC spectra (left) of ^{111}Cd in two nominally equal Ho-Ga (samples SI, SII) synthesized in the stoichiometry ratio 1:2. The right-hand section compares the experimental XRD spectrum of $HoGa_2$ (SI) (blue) to the theoretical pattern of $HoGa_3$ (red)

The XRD analysis had established that the 1:1-compounds of light R constituents are 2-phase samples, consisting predominantly of RGa and a 10 % contribution of RGa_2. The observation that PAC spectra of the light R are entirely dominated by the RGa_2 pattern then implies a pronounced preference of diffusing ^{111}In for the phase RGa_2.

An example of an even stronger phase preference is illustrated in Fig. 2 which shows two nominally identical samples (SI, SII) of the Ho-Ga system synthesized by arc melting in the stoichiometry ratio 1:2. SI and SII show quite different axially symmetric quadrupole perturbations: The frequency $\nu_q = 79.1(2)$ MHz of SI is practically identical to that reported for ^{111}Cd in $ErGa_3$ ($\nu_q = 78.9(1)$ MHz) [10]. This allows to identify sample SI as predominantly phase $HoGa_3$; sample SII with frequency $\nu_q = 204.7(2)$ MHz corresponds to the phase $HoGa_2$.

In the right-hand section of Fig. 2 the experimental XRD spectrum of a non-doped part of sample SI of $HoGa_2$ is compared to the theoretical XRD pattern of $HoGa_3$. The comparison of the two spectra at 2 theta = 36.73°—the position of the strongest $HoGa_3$ reflection (111)—clearly shows that the contamination of $HoGa_2$ by $HoGa_3$ is below the limit of XRD detection. Even so, the PAC pattern SI of nominal $HoGa_2$ is identical to that reported for synthesized $ErGa_3$, indicating that diffusing ^{111}In preferentially migrates to $HoGa_3$, even if the sample contains this phase only in miniscule amounts.

For a discussion of these phase preferences we refer to the work of Zacate and Collins [11]. In a thermodynamic model based on experimental data, these authors have shown that slight variations of the composition near stoichiometry may strongly affect the site/phase occupied by impurities in intermetallic compounds. For more insight in the present case, we intend to perform measurements over a finite range of compositions near the nominal stoichiometries of the R-Ga compounds.

Figure 3 illustrates the onset of magnetic order in $SmGa_2$ at $T < 20$ K. The complex non-periodic PAC pattern depends on the quadrupole frequency $\nu_q = eQV_{zz}/h$, the magnetic interaction frequency $\nu_M = g\mu_N B_{hf}/h$ and the angle β between the direction of the magnetic hyperfine field B_{hf} and of the maximum EFG component V_{zz} [12]. The values of these parameters at 8 K, obtained by a least-squares analysis of the measured spectrum, are $\nu_M = 7.0(3)$ MHz, $\nu_q = 222$ MHz, $\beta = 0°$. The temperature dependence of the magnetic hyperfine frequency of ^{111}Cd in $SmGa_2$ is shown in Fig. 4.

The magnetic frequency $\nu_M(8\ K) = 7.0(3)$ MHz corresponds a saturation value of the magnetic hyperfine field of $B_{hf} = 3.0(2)$ Tesla. Up to T = 17 K this frequency

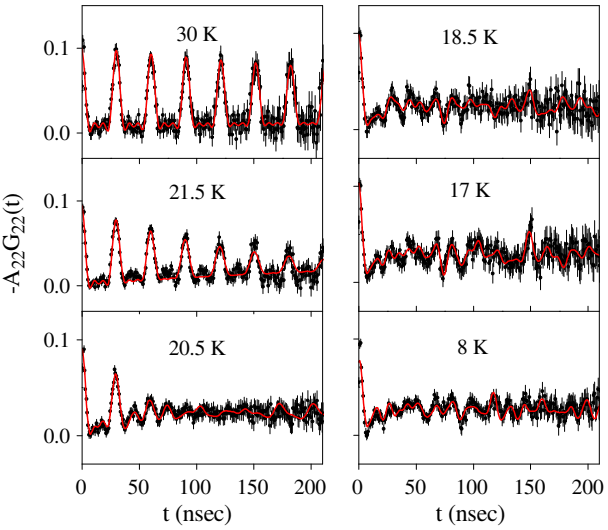

Fig. 3 PAC spectra of ^{111}Cd in $SmGa_2$ at different temperatures

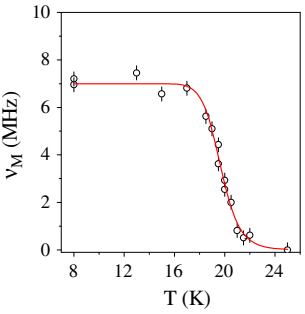

Fig. 4 The temperature dependence of the magnetic interaction frequency ν_M of ^{111}Cd in $SmGa_2$

remains constant and then decreases rapidly towards zero within an interval of $\Delta T = 3$ K, giving the impression of a first-order phase transition with an order temperature of $T_N = 19.5$ K. This value is in agreement with previous studies of the magnetic properties $SmGa_2$ [13, 14].

The finite width of the transition region possibly reflects a distribution of the order temperature, as observed in other intermetallic compounds [15]. The value of the angle β is consistent with the c-axis as axis of easy magnetization.

In the RKKY model of indirect $4f$ interaction the ratio $T_C/B_{hf}(0)$ is a measure of the coupling constant. For ^{111}Cd:$SmGa_2$ ($T_C/B_{hf}(0) \sim 6.5$ K/T) this ratio is significantly smaller than for the same probe in other R intermetallics (e.g. $SmAl_2 \sim 9.5$ K/T, $Sm_2In \sim 13.5$ K/T).

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