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Magnetic hyperfine field at highly diluted Ce impurities in the antiferromagnetic compound $GdRh_2Si_2$ studied by perturbed gamma–gamma angular correlation spectroscopy

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ABSTRACT

The magnetic properties of $GdRh_2Si_2$ compound were investigated by hyperfine interactions and magnetization measurements. The temperature dependence of the magnetic hyperfine field (mhf) at highly diluted ^{140}La–^{140}Ce probe nuclei in the $GdRh_2Si_2$ compound was measured using perturbed gamma–gamma angular correlation spectroscopy. A well-defined magnetic interaction is observed at ^{140}Ce substituting Gd atoms in the compound below the Néel temperature (T_N). However, the temperature dependence of mhf shows a deviation from the expected Brillouin-like behavior and a sharp increase of mhf values is observed for temperatures below approximately half of T_N. This behavior has been associated with an additional magnetic interaction which is ascribed to the polarization of Ce spin moment induced by the magnetic field coming from Gd ions. A model based on the molecular-field theory is used to fit the temperature dependence of the mhf. The mhf contributions from the probe atom itself and from the magnetic Gd ions of the host matrix are determined. The results are compared to previous measurements of mhf at ^{140}Ce in Gd and GdAg compound. The contribution from the host to the mhf is discussed in terms of the f–s and f–d interactions.

1. Introduction

In order to study the origin and understand a wide variety of interesting magnetic phenomena associated with rare-earth intermetallic compounds it is useful to investigate the magnetic field from an atomic scale in an attempt to identify the origin of such phenomena. For instance, in a fundamental aspect, the way 4f spins of rare-earth elements couple each other in many intermetallic compounds is not well determined yet. Among the most powerful tools used to study electric and magnetic fields on an atomic scale are the hyperfine interactions (hfi), which are the interactions between the nuclear moments and magnetic fields or electric field gradients due to the electronic charge outside the nucleus. Experimental measurement of magnetic hyperfine interactions at a rare-earth site requires probe nuclei occupying the rare-earth positions. These probe nuclei can be the rare-earth ions themselves present in the studied compounds when resonance techniques such as Mössbauer spectroscopy or nuclear magnetic resonance (NMR) are used, or some different nuclei which can probe hyperfine interactions. Perturbed gamma–gamma angular correlation (PAC) spectroscopy is a hyperfine interaction technique which uses radioactive probe nuclei introduced in the samples substituting specific atoms in the crystal lattice. PAC spectroscopy therefore allows the use of the same probe nucleus to investigate magnetic hyperfine interactions in a family of compounds with different rare-earth elements.

A quite convenient probe nucleus for PAC measurements in rare-earth compounds is ^{140}Ce which can be used to investigate the local magnetism in the compounds where it substitutes rare-earth ions. Among the rare-earth elements, cerium atoms are responsible for interesting physical phenomena, such as superconductivity, Kondo effect, striking magnetic behavior and intermediate valence state, which are solely due to its single 4f electron with energy very close to the Fermi level that makes the Ce ion very sensitive to the chemical environment. Ce ions can exist in two valence states, one of them is Ce^{3+} where only one 4f electron remains and consequently a localized spin moment is found in such ions. These ions also create a contribution from the probe itself to the magnetic hyperfine field (mhf). The other valence state is Ce^{4+} with the electronic configuration of xenon and therefore no 4f electron is present, and as a consequence no contribution from the probe electrons to the mhf exists. Ce is also known to present intermediate valence configuration in many compounds [1,2]. The 4f spin in the Ce^{3+} configuration or in the intermediate valence configuration of Ce ions of ^{140}Ce probe nuclei can, therefore contribute to the mhf and interfere with

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the measurements of the mhf from the magnetic host atoms. The magnetic hyperfine field at the probe nuclei of magnetic rare-earth ions diluted in magnetic intermetallic compounds is however, in itself a very interesting and yet not well understood subject mainly because the exchange interaction between the localized magnetic moment on the probe atom and the magnetic host ions is not well described. It is noteworthy however, that the localized moment on diluted magnetic ions in magnetic matrices can only be measured by local techniques such as hfi techniques.

The problem of localized moments formation at impurities in metals was intensively studied in the past, particularly for magnetic transition metal impurities in non-magnetic metals [3], chiefly after the discovery of the Kondo effect [4], which describes the scattering of conduction electrons in a metal due to magnetic impurities in order to explain the temperature dependence of electrical resistivity. However, when the metal host is magnetic, an interaction between the host ions and the magnetic impurities appears and the situation is more complex and not unambiguously described yet. There are several measurements of mhf at 3d impurity probes in magnetic transition elements or compounds (see, for instance, references [5–7]), however very few studies on mhf measurements at rare-earth probes in rare-earth elements or compounds have been reported [8–10].

In the present work we have measured the temperature dependence of the mhf at ^{140}Ce in the intermetallic compound $GdRh_2Si_2$. Using a model based on molecular field theory [11] with some modifications [12], we have calculated the two contributions to the mhf: from the probe ions themselves and that from the magnetic Gd ions of the host matrix. The results are compared to those obtained from the fit to the temperature dependence of mhf at diluted ^{140}Ce probes in pure Gd with $T_C = 293$ K [8] and GdAg with $T_N = 132$ K [13] reported previously. These results along with the results from magnetization measurements were used to investigate the coupling between the 4f spins of Gd ions in terms of f–s and f–d interactions.

$GdRh_2Si_2$ belongs to the family of compounds RRh_2Si_2, where R is a rare-earth element, which have been extensively studied in the past since the discovery of superconductivity in $CeCu_2Si_2$ by Steglich et al. [14]. RRh_2Si_2 compounds have attracted special interest due to its several physical properties such as, for instance, long range magnetic ordering, antiferromagnetism, superconductivity, and Kondo effect [15]. Differently from the rest of the family, $GdRh_2Si_2$ has a relatively high Néel temperature ($T_N = 106$ K) ascribed to the strong exchange interaction between Gd ions whose localized magnetic moments ($\mu = 8.22\mu_B$)are oriented in the *a*–*b* plane, as revealed by Mössbauer measurements [16].

$GdRh_2Si_2$ crystallizes in the $ThCr_2Si_2$ prototype structure which belongs to the spatial group I4/*mmm* [17]. In this structure rare-earth atoms form a body-centered tetragonal sub-lattice. In such structure, rare-earth atoms occupy the crystallographic position (2a):(0,0,0), Si atoms occupy positions (4e):(0,0,z);(0,0,$\bar{z}$) while Rh atoms occupy the position (4d):(0,1/2,1/4).

2. Experimental

The samples of $GdRh_2Si_2$ were prepared by repeatedly melting the stoichiometric quantities of pure elements (Gd 99.9%, Rh 99.99% and Si 99.9999%) under argon atmosphere purified with a hot titanium getterer in an arc furnace. Subsequently, the samples were sealed under vacuum and annealed for one week at 900 °C. Afterwards, the samples were cut into slices and a part was used for the structural characterization with X-ray diffraction (XRD) technique using Cu K_α X-rays. The resulting XRD data were analyzed using the Rietveld refinement method. After assuring the correct crystalline phase, the remaining part of sample was again arc-melted but this time with radioactive ^{140}La nuclei, obtained by neutron irradiation of lanthanum metal, to substitute about 0.1% of Gd atoms. Radioactive ^{140}La ($t_{1/2} = 40.2$ h) β^- decays to the excited states of ^{140}Ce and a known gamma cascade in this decay is used for the PAC measurement.

An interesting feature of ^{140}Ce probe nuclei is that the intermediate state of the gamma cascade used in the PAC measurements has a relatively small electric quadrupole moment ($Q = 0.35$ b [18]), and a short half-life of only 3.5 ns which, limits the time window for the observation of hyperfine interactions. This implies that only quadrupole interactions with frequencies much higher than those usually found in most materials would be observed as a consequence, only magnetic dipole interactions might be observed with ^{140}Ce probe nuclei.

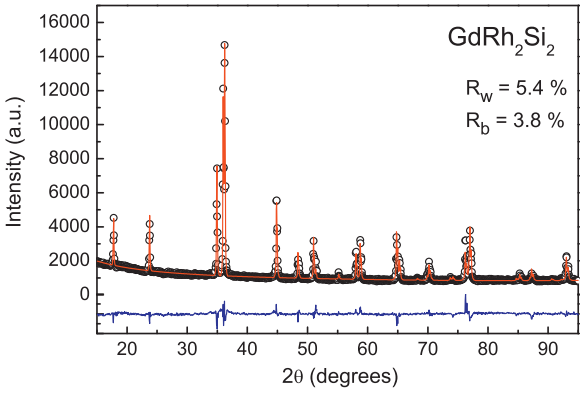

Fig. 1. X-ray diffraction pattern of $GdRh_2Si_2$ sample doped with approximately 0.1% of La. The solid line represents the calculated pattern obtained from the Rietveld refinement method. The residuals are shown in the lower part of each curve.

Samples used for PAC measurements with diluted radioactive ^{140}La were annealed under vacuum for 72 h at 950 °C, and subsequently measured in a conventional fast–slow coincidence set-up with four conical BaF_2 detectors. The PAC measurements were carried out in the temperature range of 10–295 K by using a closed-cycle helium cryogenic device. The gamma cascade of 329–487 keV populated from the decay of ^{140}La with an intermediate level with spin $I = 4^+$ at 2083 keV ($T_{1/2} = 3.45$ ns) in ^{140}Ce was used to measure the magnetic hyperfine field at Gd sites. The time resolution of the system was about 0.6 ns for the ^{140}Ce gamma cascade.

The PAC method is based on the observation of hyperfine interaction of nuclear moments with extra-nuclear magnetic field or electric field gradient. A detailed description of the method can be found elsewhere[19,20]. For an unpolarized ferromagnetic sample consisting of randomly oriented domains, the perturbation factor $G_{22}(t)$ of the correlation function, which contains detailed information about the hyperfine interaction, can be written (neglecting the A_{44} terms) as:

$$R(t) = A_{22}G_{22}(t) = A_{22}[0.2 + 0.4\cos(\omega_L t) + 0.4\cos 2(\omega_L t)] \quad (1)$$

Measurement of $G_{22}(t)$ allows the determination of Larmor frequency $\omega_L = \mu_N g B_{hf}/\hbar$ and since the *g*-factor of the intermediate level is well known it is possible to determine the magnetic hyperfine field B_{hf}. The experimental data at temperatures below T_N were analyzed with a pure magnetic dipole interaction.

The magnetization measurements of the ^{140}La-doped sample were performed after the radioactive isotope had mostly decayed. Those measurements were carried out with a commercial vibrating sample magnetometer (VSM), in the temperature range of 4.2–300 K with an externally applied magnetic field of 0.5 T.

3. Results and discussion

The results of XRD measurements indicated the formation of a single phase with tetragonal crystalline structure of $ThCr_2Si_2$-type which belongs to the I4/*mmm* space group. Within the resolution of XRD, no secondary phases were observed as can be seen in Fig. 1. The lattice parameters obtained from the analysis were $a = 4.041$ Åand $c = 9.981$ Å.

In Fig. 2 is shown the DC magnetic susceptibility as a function of the temperature. The features observed in the figure suggest that the sample shows an antiferromagnetic order with a Néel temperature of $T_N = (106 \pm 1)$ K. Below T_N the susceptibility shows an almost constant behavior with a slight tendency to increase as the temperature decreases to 4.2 K. Above the transition temperature, the susceptibility shows the characteristic Curie–Weiss behavior of the paramagnetic state as the temperature is increased. The fitting of the Curie–Weiss law to the experimental data yielded an effective magnetic moment $\mu_{eff} = 8.44(2)\mu_B$ per Gd ion. This value is somewhat higher than the calculated value considering the spin $S = 7/2$ ($7.94\mu_B$). This difference according to Czjzek et al. [16] is due to an additional magnetic moment induced at the 5d-electrons level by the 4f–5d exchange interaction which is added to the magnetic