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Magnetic interaction in NdScGe: a local investigation by perturbed angular correlation spectroscopy

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Abstract

The magnetic and electric hyperfine interactions for the ^{111}Cd probe nucleus in the equi-atomic ferromagnetic compound NdScGe ($T_c \sim 200$ K) have been investigated by the time differential perturbed angular correlation (TDPAC) technique. The Cd probe occupying the Sc site experiences a large magnetic hyperfine field with saturation value $B_{hf}(0) = -8.5$ T. By comparing the results with the hyperfine field data in Nd metal and estimates made with the RKKY interaction, we find an indication for sizeable spin polarization of the conduction electrons in NdScGe. In addition, we find evidence of lattice softening near the Curie temperature reflected by an abrupt decrease in the quadrupole interaction frequency $\nu_Q(T)$.

1. Introduction

The magnetic behaviour of equi-atomic rare-earth intermetallic compounds RTX, where R is a rare earth, T is a transition 3d-element and X belongs to the p-group of elements, has been the subject of intensive investigations in recent years [1]. In particular, alloys with T = Ti and Sc and X = Si and Ge have attracted considerable interest. The compounds crystallize in either a tetragonal CeScSi-type ordered variant of the La_2Sb type or the related tetragonal CeFeSi-type structure and exhibit ferromagnetic or antiferromagnetic ordering with unusually high transition temperatures. For instance, CeScSi and CeScGe show antiferromagnetic ordering with $T_N = 26$ and 46 K respectively [2], while, SmScSi and SmScGe have been found to be ferromagnetic with Curie temperature $T_c = 270$ K [3]. For GdScGe and GdTiGe, T_c values of 350 and 374 K, respectively have been reported [4, 5]. The compound PrScGe exhibits multiple magnetic transitions below 140 K [3]. Considering that the magnetism in these alloys arises mainly due to the RKKY interaction between the moments on the rare-earth atoms, which are separated by a large R–R distance $d \sim 3.85$ Å (Ce–Ce distance in CeScSi), it is surprising that the compounds show such high magnetic ordering temperatures. In view of the intriguing and multi-faceted magnetic behaviour of these compounds, microscopic investigations using nuclear techniques namely NMR, Mössbauer and/or γ-ray perturbed angular correlation (PAC) are desirable. Such measurements can provide an insight into the magnetic interactions as well

as the spin dynamics over short length and timescales. In this paper we present a study of the ^{111}Cd hyperfine fields in the ferromagnetic NdScGe obtained from TDPAC measurements.

2. Experimental details

A polycrystalline alloy of NdScGe was prepared by melting stoichiometric amounts of high purity constituent elements in an argon arc furnace under a partial pressure of pure argon gas. The alloy button was flipped over and re-melted four times to ensure proper homogenization and annealed at 1050 °C for ten days. The sample was characterized by the room temperature powder x-ray diffraction measurement. It was also examined by optical and electron microscopy (SEM) to verify its homogeneity. The sample was found to be homogeneous and single phase, having CeScSi-type tetragonal structure (space group $I4/mmm$) with lattice parameters $a = 4.313(1)$ Å and $c = 15.821(2)$ Å. The magnetization studies were made as a function of temperature and applied field using a SQUID (Quantum Design) magnetometer.

Complementary to the bulk measurements, microscopic studies were performed by measuring the hyperfine fields using a time differential perturbed angular correlation (TDPAC) technique. The basic principle of the PAC technique lies in the directional correlation of γ-radiation emitted by nuclei with a preferred spin orientation and its modification caused by the hyperfine interaction between the nucleus and the electromagnetic fields produced by the surrounding atomic environment. Experimentally, a trace quantity of the radioactive impurity is introduced into the sample under investigation and one measures the hyperfine fields acting on the daughter nuclei as a function of physical variables such as temperature, pressure, concentration etc. For the present investigation, we have used a probe ^{111}Cd produced via the electron capture (EC) decay of ^{111}In. The 247 keV, $I^{\pi} = 5/2^{+}$ state in ^{111}Cd with a half-life $T_{1/2} = 84$ ns, nuclear quadrupole moment $Q = 0.8b$ and a magnetic moment $\mu_{\mathrm{I}} = -0.7656\ \mu_{\mathrm{N}}$ [6] serves as a sensitive probe for the detection of electric and magnetic hyperfine fields, which in turn provide the microscopic information on the magnetic interactions as well as the electronic charge distribution in the sample under investigation. The experimental information is expressed by the quadrupole interaction frequency ν_{Q} related to the principal component of the electric-field gradient (EFG), V_{zz}, and the Larmor frequency ω_{L} proportional to the magnetic hyperfine field B_{hf}. Further details on the PAC technique can be found elsewhere [7].

For the present measurements, a small piece of an NdScGe sample was doped with ^{111}Cd by diffusing the parent isotope ^{111}In. A tiny drop of commercially available $^{111}InCl_3$ solution was put on the sample and dried under an infrared lamp. The sample sealed in a quartz tube under high vacuum was heated at 950° for 24 h followed by rapid cooling to room temperature. It is important to mention that the typical concentration of Cd in the sample remains at $\leqslant$1 ppm and thus does not alter the bulk properties of the alloy. The hyperfine interaction parameters were extracted from the lifetime spectra of the 247 keV, 84 ns nuclear level in ^{111}Cd, recorded in 90°/180° geometry using a setup consisting of four BaF_2 detectors and a standard slow–fast coincidence circuit with time resolution better than 700 ps. The perturbation factor $A_{22}G_{22}(t)$ in the angular correlation function $W(\theta, t) = \sum_{kk} A_{kk}G_{kk}(t)P_k(\cos\theta)$ was obtained by constructing the appropriate ratio function, called the PAC time spectrum,

$$R(t) = \frac{2[W(180^\circ, t) - W(90^\circ, t)]}{[W(180^\circ, t) + 2W(90^\circ, t)]}$$

where $W(\theta, t)$ are the background subtracted normalized coincidence counts of the detectors placed at 180° and 90°. Measurements were carried out as a function of temperature in the range 25–300 K using a close cycle He refrigerator.

3. Results and discussion

Figure 1 shows the bulk magnetization data for NdScGe measured as a function of temperature and applied magnetic field. The isothermal magnetization data recorded at 10 K as a function of the applied field (M versus H) show hysteresis loops characteristic of a ferromagnet with saturation moment $\mu_S = 2.0\ \mu_B$/Nd which is significantly lower than the free ion value of 3.27 μ_B. This reduction in μ_S has been attributed to the strong crystalline electric field (CEF) in the tetragonal symmetry of the NdScGe lattice structure [3]. From zero-field-cooled M versus T data measured in a field of 5 kOe, the Curie temperature T_c was determined to be 197 K. The bulk magnetic properties of the sample used here are consistent with the data reported earlier [3]. The down turn in M versus T data below 50 K most likely arises due to the strong magnetic anisotropy as mentioned in [3].

Figure 2 displays some typical PAC spectra at different temperatures. All the spectra show single frequency with almost full anisotropy, indicating that the probe ^{111}Cd atoms occupy a unique lattice site, most likely substitutional. The spectra recorded above 200 K exhibit pure quadrupole interactions with $\nu_Q \sim 105.4(5)$ MHz and could be simulated with a unique randomly oriented electric field gradient $V_{zz} \sim 5.4 \times 10^{17}$ V cm^{-2} and a small asymmetry parameter $\eta = 0.15$. From a comparison of the chemical behaviour and ionic radius of the mother isotope ^{111}In and the atomic species of the sample under investigation, it is easy to exclude a substitutional Ge-site, but one cannot readily discriminate between Sc and Nd sites. However, since the ionic radius of In^{3+} is much closer to the value of Sc^{3+} rather than Nd^{3+}, the ^{111}In probe is likely to substitute preferably at the Sc site. Further, from a point charge calculation using atomic positions of CeScGe taken from [2] and the Sternheimer anti-shielding factor $\gamma_\infty = -31$ [8], the electric field gradient at the Sc site was estimated to be $V_{zz} = 4.56 \times 10^{17}$ V cm^{-2} with an asymmetry of $\eta = 0.135$. The values agree quite well with our experimental results. Although this surprisingly good agreement might be accidental, it supports the lattice site assignment discussed above.

In the ferromagnetic phase, the ^{111}Cd probe nuclei experience the combined influence of magnetic dipole and electric quadrupole interactions. As such, the spectra below 200 K were fitted for the combined interaction in which the magnetic hyperfine field B_{hf} and the electric field gradient with a relative angle β were treated as randomly oriented in space with respect to the detector plane. In the fitting procedure adopted here, the relative strengths of the magnetic hyperfine field and the electric quadrupole interaction defined by the ratio $y = \omega_L/\omega_Q$ and β were varied and the numerical simulation of the PAC spectra were performed for a range of y and β with fixed $\eta = 0.15$ for all temperatures. The best fit to the experimentally observed spectrum was determined from the minimization of χ^2. The extracted hyperfine field parameters are listed in table 1.

Figure 3 displays the temperature variation of B_{hf} and the quadrupole interaction frequency ν_Q. At 25 K the magnetic hyperfine field B_{hf} was found to be 8.25(15) T. The extrapolated zero temperature hyperfine field $B_{hf}(0)$ come out to be 8.5(1) T. To determine the sign of B_{hf}, a measurement was carried out at 25 K in $\pm 135°$ geometry and a transverse applied magnetic field of 7.5 kOe. In this geometry, the rotation direction of the PAC spectrum is sensitive to the sign of the magnetic hyperfine field [9]. The measured spectrum is shown in figure 2(b) together with the theoretical curves simulated for both positive and negative signs of B_{hf}. From the data, it can be easily seen that B_{hf} of Cd in NdScGe is negative. B_{hf} smoothly decreased with increasing temperature and vanished at $T_c \sim 195$ K, which compares well with the ordering temperature obtained from the bulk magnetization data. The onset of magnetic ordering is also visible from the damping (λ) of the PAC spectra which becomes quite strong below 190 K (see table 1). It is interesting to note that the quadrupole interaction frequency ν_Q decreases

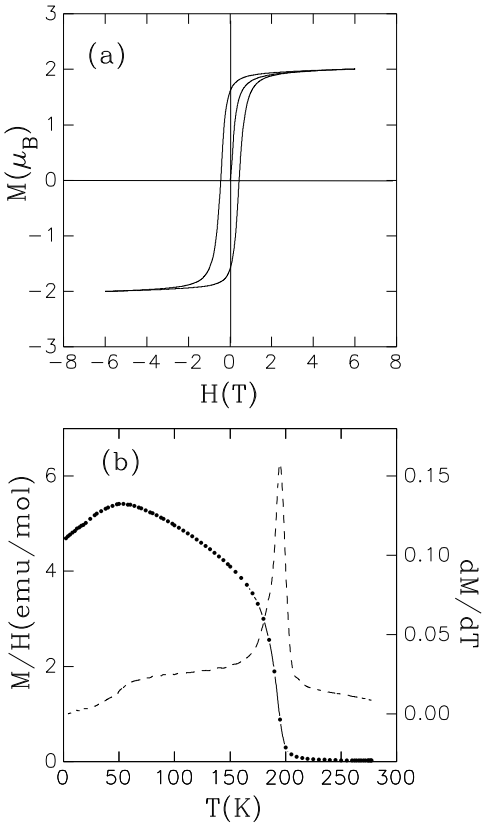

Figure 1. Magnetization data for NdScGe. (a) M versus H at 10 K and (b) M versus T in an applied field of 5 kOe. The dashed curve shows the plot of $\mathrm{d}M/\mathrm{d}T$.

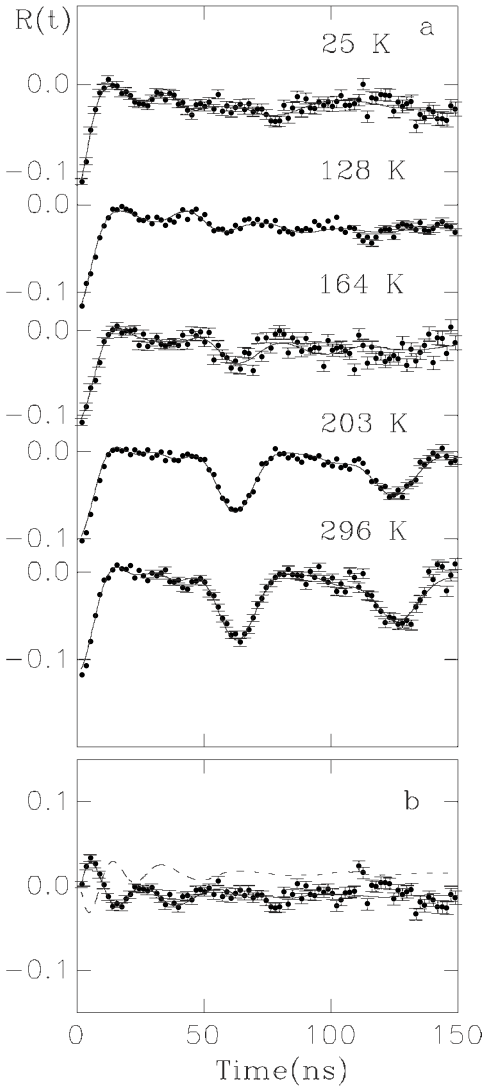

Figure 2. (a) Typical PAC spectra $R(t)$ for ^{111}Cd in NdScGe at different temperatures. (b) PAC spectrum recorded in $\pm 135°$ geometry at $T = 25$ K and a transverse magnetic field of 0.75 T. The solid and dashed curves represent theoretical curves simulated respectively with negative and positive signs of B_{hf}.

sharply near T_{c} followed by a smooth increase with decreasing temperature in the magnetically ordered state. This peculiar thermal variation of ν_{Q} data suggests a possible lattice instability near the ferromagnetic transition. Secondly, the relative angle between the magnetic hyperfine field and the electric field gradient, β turned out to be close to 45° at 25 K. With increasing T, the angle β was found to decrease, attaining a value of $\sim$30° near T_{c}. Taking the c-axis to be the principal symmetry direction for the electric field gradient and considering that the magnetic hyperfine field is anti-parallel to the spin direction (negative B_{hf}), the measured β can provide a rough idea about the spin arrangement in the sample. The data presented here

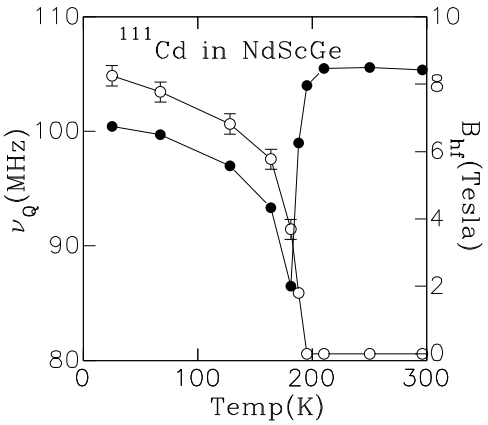

Figure 3. Temperature variation of the magnetic hyperfine field B_{hf} (open circles) and the quadrupole interaction frequency ν_Q (filled circles) for ^{111}Cd in NdScGe.

Table 1. Summary of the hyperfine interaction parameters for the ^{111}Cd nucleus in NdScGe.

Temperature (K)	Quadrupole frequency ν_Q (MHz)	Magnetic hyperfine field B_{hf} (T)	β (deg)	λ (MHz)
25	100.4(6)	8.25(10)	45(3)	10.3(10)
67	99.7(6)	7.77(10)	45(3)	10.8(11)
128	97.0(6)	6.83(10)	45(3)	9.9(10)
164	93.3(6)	5.78(10)	43(5)	10.4(10)
181	86.5(6)	3.7(10)	35(5)	8.8(9)
188	103.2(6)	1.8(10)	30(5)	6.9(7)
195	104.0(6)	0	—	5.1(5)
210	105.5(6)	0	—	4.6(5)
250	105.6(6)	0	—	4.3(4)
296	105.4(6)	0	—	4.0(4)

suggest a spin arrangement for NdScGe such that the Nd moments are inclined to both the c-axis and the ab-plane by $\sim$45°.

It is worthwhile comparing the magnetic hyperfine field of ^{111}Cd in NdScGe with those observed in other magnetic systems, in particular, Nd metal. For ^{111}Cd in Nd metal, B_{hf} has been measured to be 7.6 T at 15 K [10]. Considering the RKKY interaction as the main mechanism for the magnetic interaction in the rare-earth metals and compounds, the transferred magnetic hyperfine field at ^{111}Cd is expected to scale with the ratio of $(N\mu_{Nd})/r^3$, where N is the number of Nd atoms surrounding the Cd probe and r is the interatomic distance. Such a scaling of B_{hf} has been found to hold for ^{111}Cd in many Gd compounds [9–12]. From the above relation, using $\mu_{Nd} = 2.0\ \mu_B$ found from the bulk magnetization measurement and $r = 3.524$ Å for the Nd–Sc distance obtained from the x-ray data, the magnetic hyperfine field of ^{111}Cd in NdScGe is calculated to be $\sim$3.5 T which is much smaller than the measured value $B_{hf} = 8.5$ T. It should be mentioned that this discrepancy cannot be accounted for by the dipolar magnetic field from the Nd moments, which is $\leqslant$1 T at the ^{111}Cd site. We therefore feel that the large B_{hf} (^{111}Cd) observed in NdScGe presumably arises from the spin polarization of the conduction electrons. Analogous to the dilute PdFe/PdCo alloys, the conduction electron spin polarization suggested above might also be the reason for the observation of the high magnetic ordering temperatures in spite of the large R–R separation. Skorek *et al* [5] arrived

at a similar conclusion from their electronic structure calculations on GdTiGe and GdTiSi. Using the TB-LMTO method, they found a strong hybridization between the d states of Gd and Ti and a significant polarization of the Ti 3d electrons, resulting in an enhanced indirect exchange between the Gd ions. In GdTiSi which crystallizes in the related tetragonal CeFeSi-type structure with a T_c of 294 K, an anti-parallel polarization of the Ti-d states was also inferred.

In summary, the magnetic and electric hyperfine interactions of the ^{111}Cd probe nucleus in the ferromagnetic compound NdScGe ($T_c = 197$ K) have been investigated by perturbed angular correlation spectroscopy. We found a large decrease in the quadrupole interaction frequency ν_Q as T_c was approached from the paramagnetic side, indicating a lattice instability due to the onset of magnetic ordering. In addition, the observed large transferred magnetic hyperfine field of ^{111}Cd ($B_{hf} = -8.25$ T at 25 K) in NdScGe, compared to the corresponding value in Nd metal, suggests a large spin polarization of conduction electrons which might be responsible for the high magnetic ordering temperature of NdScGe.

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