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Local investigation of magnetism at *R* and In sites in *R*NiIn (*R*=Gd, Tb, Dy, Ho) compounds

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The local magnetism at *R* and In sites in *R*NiIn (*R*=Gd, Tb, Dy, Ho) compounds was investigated by measuring hyperfine interactions via perturbed gamma-gamma angular correlation (PAC) technique using ^{140}La$-^{140}$Ce and ^{111}In$-^{111}$Cd probe nuclei. PAC measurements carried out below respective T_C for each compound showed a combined electric quadrupole plus magnetic dipole interaction for ^{111}Cd probe at In sites and a pure magnetic interaction for ^{140}Ce at *R* sites. The temperature dependence of the magnetic hyperfine field (B_{hf}) shows that, whereas the B_{hf} values at rare-earth sites measured with ^{140}Ce drop to zero at temperatures around the expected T_C for each compound, the respective fields at In sites measured with ^{111}Cd drop to zero at lower temperatures. The difference between the temperatures at which B_{hf} is zero for ^{140}Ce and ^{111}Cd probes when compared with T_C of each compound shows that this difference decreases with decreasing T_C values. The results are discussed in terms of the Ruderman-Kittel-Kasuya-Yosida model for magnetic interactions and the crystalline electric field. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2709421]

I. INTRODUCTION

An important group within the ternary series *RTX* (*R* =rare-earth metal, *T*=transition metal, *X*=*sp* element) is formed by intermetallic compounds that crystallize in the ZrNiAl-prototype hexagonal structure of space group $P\bar{6}2m$ and show interesting magnetic properties and a variety of magnetic structures.[1,2] This structure is formed by magnetic *R*-*T* layers alternated with nonmagnetic *T*-*X* layers. The magnetic *R* atoms occupy the positions x, 0, 1/2; 0, x, 1/2; and $\bar{x}$, $\bar{x}$, 1/2, and form a triangular structure, which is a deformed Kagomé lattice. In such of triangular arrangement of magnetic atoms a frustration of magnetic interactions occurs when an antiferromagnetic order is present. The *R*NiIn family of compounds, which also crystallize in the ZrNiAl-type structure, has been very little studied so far.[3,4] In this family, GdNiIn, TbNiIn, DyNiIn, and HoNiIn order ferromagnetically below 96, 70, 30, and 20 K, respectively.[5]

In the present work, it has been investigated the temperature dependence of the magnetic hyperfine field (mhf) on both *R* and In sites in *R*NiIn (*R*=Gd, Tb, Dy, Ho) compounds. Perturbed gamma-gamma angular correlation (PAC) technique was used to measure mhf in these compounds using the ^{111}In$-^{111}$Cd and ^{140}La$-^{140}$Ce probe nuclei at the In and *R* sites, respectively.

II. EXPERIMENTAL PROCEDURE

The polycrystalline samples of *R*NiIn were prepared by repeatedly melting the constituent elements (*R* 99.99%, Ni 99.998%, In 99.9999%) in an arc furnace under argon atmosphere purified with a hot titanium getterer. Carrier free ^{111}In nuclei were introduced into the sample by diffusion. A separate sample for each compound was prepared in a similar way but with radioactive ^{140}La nuclei, substituting about 0.1% of *R* atoms. For this purpose the radioactive ^{140}La obtained by neutron irradiation of lanthanum metal in the IEA-R1 reactor at IPEN was melted along with the constituent elements. All samples of each compound were annealed in vacuum for 48 h at 800 °C. The final samples were analyzed by x-ray diffraction measurements, which indicated a single phase and ZrNiAl-type structure with the $P\bar{6}2m$ space group for each compound.

The PAC measurements were carried out using a spectrometer consisting of four conical BaF$_2$ detectors with a conventional fast-slow coincidence electronic setup. The well known gamma cascade of 172–245 keV, populated from the decay of ^{111}In with an intermediate level with spin $I=5/2^+$ at 245 keV ($T_{1/2}=84.5$ ns) in ^{111}Cd, was used to investigate the hyperfine interactions at In sites. 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 (B_{hf}) at Ce. The samples were measured in the temperature range of 8–300 K by using a closed-cycle helium cryogenic device. The time resolution of the system was about 0.6 ns for both gamma cascades.

The PAC method is based on the observation of hyperfine interaction of nuclear moments with extra nuclear magnetic fields (B_{hf}) or an electric field gradient. The technique measures the time evolution of the γ-ray emission pattern caused by hyperfine interactions. A description of the method as well as details about the PAC measurements can be found else where.[6,7] The perturbation factor $G_{22}(t)$ of the correlation function contains detailed information about the hyperfine interaction. Measurement of $G_{22}(t)$ allows the determination of the Larmor frequency $\omega_L=\mu_N g B_{\mathrm{hf}}/\hbar$, the nuclear

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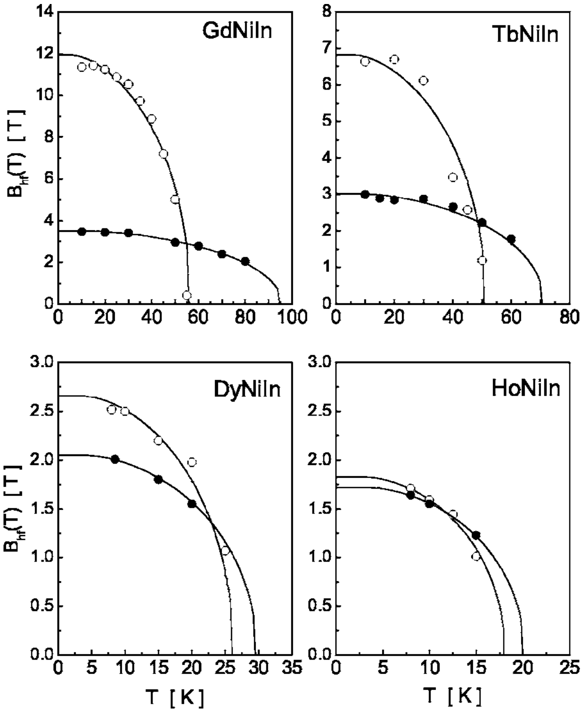

FIG. 1. Temperature dependence of magnetic hyperfine fields for ^{111}Cd (open circles) and ^{140}Ce (full circles) in *R*NiIn as a function of temperature. The lines correspond to the Brillouin function for the *S* spin of rare-earth elements of each compound.

quadrupole frequency $\nu_Q = eQV_{zz}/h$, as well as the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{xx}, V_{yy}, and V_{zz} are the components of the electric field gradient (efg) tensor in its principal axis system. Consequently, from the known *g* factor and quadrupole moment *Q* of the 245 keV state of ^{111}Cd and the 487 keV state of ^{140}Ce, the magnetic hyperfine field B_{hf} the major component V_{zz} of efg and its asymmetry parameter η can be determined.

III. RESULTS AND DISCUSSION

The quadrupole moment of the 2083 keV 4^+ state of ^{140}Ce is known to be very small, consequently one expects to observe an almost pure magnetic dipole interaction in the ferromagnetic phase of the samples using this probe. Below Curie temperature a unique magnetic interaction was observed for ^{140}Ce at rare-earth atom sites of the samples. The temperature dependence of B_{hf} is shown in Fig. 1.

The PAC spectra for ^{111}Cd measured above the magnetic transition temperature show a major fraction (62%–81%) with well defined quadrupole interaction for all studied compounds except GdNiIn for which a single frequency was observed. The additional minor interaction observed for the other three compounds is due to probe nuclei occupying some other site, probably the rare-earth sites, or trapped in vacancies. In TbNiIn, at room temperature, for instance, 81% of ^{111}Cd probes show an interaction with $\nu_Q = 80.8(1)$ MHz, $\delta = 2.4(1)\%$, and $\eta = 0.81(1)$, while 19% are associated with $\nu_Q = 88.1(1)$ MHz, $\delta = 0$, and $\eta = 1$. In GdNiIn also at room temperature, all probes feel an interaction with a quadrupole frequency $\nu_Q = 82.8(1)$ MHz, distribution $\delta = 1.1(1)\%$, and asymmetry parameter $\eta = 0.80(1)$.

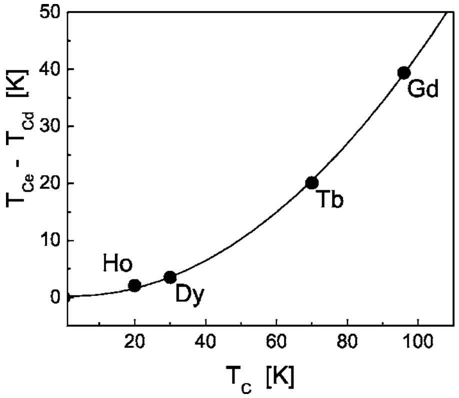

FIG. 2. Difference in the magnetic ordering temperatures measured with ^{140}Ce and ^{111}Cd (see text) as a function of the Curie temperature of each compound.

Below T_C at low temperatures, each compound shows a combined magnetic dipole plus electric quadrupole interaction. These spectra are characterized each by a major quadrupole frequency and a temperature dependent magnetic dipole interaction. The temperature dependence of the magnetic hyperfine field associated with the major interaction for each compound is shown in Fig. 1. A Brillouin function for *S* spin of the *R* element in each compound was fitted to the experimental B_{hf} values for both ^{140}Ce and ^{111}Cd in order to determine their saturation values at 0 K and the magnetic ordering temperatures.

A comparison of the temperature dependence of the B_{hf} shows a significant difference in the transition temperatures determined with ^{140}Ce and ^{111}Cd probes for each compound. For example, in the case of GdNiIn, the transition temperatures are $T_{\mathrm{Cd}} \sim 56$ K and $T_{\mathrm{Ce}} \sim 96$ K, respectively, for ^{111}Cd and ^{140}Ce probes. We have ruled out the possibility that this difference is sample dependent first because the same behavior was observed in three different GdNiIn samples measured with ^{111}Cd probes, and second because the minor fraction observed in TbNiIn, which was assigned to ^{111}Cd probes occupying Tb sites, shows a magnetic interaction with $T_C = 68.3$ K (while $T_{\mathrm{Cd}} = 51.2$ K for probes occupying In sites in the same sample), very close to the reported value of $T_C = 70$ K ($T_{\mathrm{Ce}} = 71.3$ K). Different magnetic phases could also explain the difference in the magnetic transition temperatures, but magnetization measurements[5] show secondary phases only for GdNiIn at $T_t = 79$ K and DyNiIn at $T_t = 12.5$ K, which are very different from the transition temperatures observed for ^{111}Cd probe. It was also observed that the difference in these temperatures $T_{\mathrm{Ce}} - T_{\mathrm{Cd}}$ is dependent on the value of T_C of each compound taken from Ref. 5. The difference is smaller for smaller T_C values. Furthermore, this correlation is well described by a polynomial function of second order, as shown in Fig. 2.

The saturation values of B_{hf} measured with ^{111}Cd are larger than the values measured with ^{140}Ce in all compounds. This observation can be ascribed to two reasons, one is related to the bond distance between the probe and the magnetic rare-earth ion (~3.2 Å for ^{111}Cd–Gd and ~3.9 Å for ^{140}Ce–Gd in GdNiIn). The other reason can be the polarization of the inner shells in the ^{140}Ce probe atom due to a spin

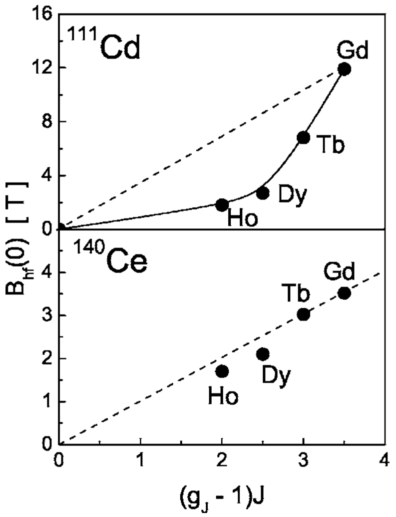

FIG. 3. The saturation fields $B_{hf}(0)$ for ^{111}Cd probes (top) and ^{140}Ce in *R*NiIn compounds as a function of the spin projection $(g-1)J$ of *R* elements. The lines are visual guides.

polarization of the 5*d* electrons. This core polarization gives rise to an opposite sign contribution to B_{hf} when compared to the transfer field from the neighboring magnetic rare-earth ions.

As in the case of the rare-earth metals, the magnetic order of rare-earth intermetallic compounds is sustained by indirect 4*f*-4*f* exchange, which according to the Ruderman-Kittel-Kasuya-Yosida (RKKY) theory, is mediated by a spin polarization of the *s*-conduction electrons induced by the localized *f* spins. Another model uses the concept of intra-atomic 4*f*-5*d* exchange coupling and 5*d*-5*d* interaction between the spin polarized 5*d* electrons of neighboring *R* atoms.[8] In both cases, a spin polarization arises which leads, via Fermi contact interaction, to a magnetic hyperfine field B_{hf} at the nucleus of a probe atom. As long as spin exchange is the dominant mechanism, one expects the hyperfine field to be proportional to $(g-1)J$, the spin projection of *S* along *J*. Therefore, in most rare-earth ferromagnets one finds that the relation B_{hf} vs $(g-1)J$ is, in fact, approximately linear.[9] The saturation values of B_{hf} for ^{140}Ce and ^{111}Cd as a function of the spin projection $(g-1)J$ are shown in Fig. 3. The $B_{hf}(0)$ values for ^{140}Ce to a good approximation seem to follow a linear behavior with $(g-1)J$ with a small deviation for DyNiIn and HoNiIn values that are slightly lower than the linear behavior. However, the values for ^{111}Cd show a completely different behavior with a sharp deviation from the expected linear relationship for TbNiIn, DyNiIn, and HoNiIn, showing a decrease in the $B_{hf}(0)$ values. A similar behavior was already observed[9] for the magnetic hyperfine field measured with ^{111}Cd at *R* sites in *R*Ni$_2$ compounds. The systematics behavior of B_{hf} for *R*Ni$_2$ was explained as a consequence of the crystalline electric field (CEF) that reduces the magnetic interactions in compounds where the rare-earth ion has larger orbital magnetic moments.

The saturation value of B_{hf} at ^{111}Cd sites in GdNiIn was compared to the Curie temperature,[10] and the result showed a ratio of $B_{hf}/T_C=0.12$ T/K that agrees very well with the value $B_{hf}/T_C=0.116$ T/K previously reported[11] for the comparison of the saturation value of B_{hf} at ^{111}Cd sites in some Gd compounds. The saturation value of B_{hf} at ^{140}Ce on Gd sites in GdNiIn was also compared to the respective transition temperature along with other Gd compounds and showed a linear behavior as well.[12] According to the RKKY theory of indirect coupling the ratio between the conduction electron spin polarization (CEP) and the ordering temperature is expected to be proportional to $[J_{sf}(g-1)(J+1)]^{-1}$, where J_{sf} is the *s*-*f* coupling constant, *g* the Landé factor, and *J* the total angular momentum. The linear relation between B_{hf} at ^{140}Ce and the magnetic transition temperature thus may imply that the main contribution to the B_{hf} comes from the CEP at the probe site via Fermi contact field from *s* electrons. In general, the magnetic hyperfine field at rare-earth nuclei comes predominantly from the orbital contribution of 4*f* electrons, yielding fields of the order of hundred of teslas. In free ion Ce^{3+} for instance, $B_{hf} \sim 185$ T.[13] Therefore, we conclude that the ^{140}Ce probes in this case behaves as closed shell nuclei like ^{111}Cd.

The difference in the temperatures at which B_{hf} is zero for ^{140}Ce probe at *R* sites and ^{111}Cd probe at In sites in each compound could be explained by the difference in the local neighborhood of each site. The crystal structure of *R*NiIn compounds is built out of two types of basal plane layers one with $(3R+\mathrm{Ni})$ for $z=0.5$ and without rare-earth atoms (3In +2Ni) for $z=0$. We believe that this structural property and the presence of the CEF would explain the observation.

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