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Magnetic hyperfine field at Nd sites in NdAg studied by perturbed angular correlation spectroscopy and ab-initio calculations

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ABSTRACT

The magnetic hyperfine field (B_{hf}) at Nd sites in NdAg was investigated experimentally by perturbed gamma–gamma angular correlation technique using ^{140}La–^{140}Ce probe nuclei and by first-principles electronic structure calculations. The temperature dependence of the observed B_{hf} shows a sharp deviation from an expected Brillouin-like behavior. This behavior is believed to result from an additional magnetic interaction from the polarization of Ce spin moments induced by an exchange interaction between Ce and Nd ions. The experimental results for the temperature dependence of B_{hf} have been fitted by using a model based on the molecular field theory. The results are discussed in terms of a competition between the RKKY interaction and the 5d–5d interaction for the indirect magnetic coupling between the magnetic Nd ions.

1. Introduction

The compounds in the family RAg (R = rare-earth element) when R ranges from Nd to Tm order anti-ferromagnetically whereas CeAg and PrAg show ferromagnetic ordering [1,2]. The chemical structure of these compounds is cubic of CsCl type and the anti-ferromagnetic order of some compounds in the family, namely NdAg [3], GdAg [4], TbAg [5] and DyAg [6], is characterized by adjacent ferromagnetic planes (1 1 0) having oppositely directed spins in the [0 0 1] direction [4–6]. RAg compounds where R elements are Ho and Er are known to present the same anti-ferromagnetic order but their magnetic moments are also subjected to an incommensurate sinusoidal modulation along the [1 0 0] direction and are tilted against the [0 0 1] direction [7,8]. As Nd is the next to Pr in the lanthanide series and NdAg is the first compound in the RAg family that presents anti-ferromagnetic order [1,3] and has been little investigated so far, a microscopic investigation would help to understand the change in the magnetic ordering at the side of light rare-earth compounds in that family.

A local experimental as well as theoretical investigation of the magnetism in this compound can also be very useful to better describe the coupling mechanism between the rare-earth magnetic ions. In this work, perturbed gamma–gamma angular correlation (PAC) technique was used to measure the magnetic hyperfine field B_{hf} in the compound NdAg using the ^{140}La–^{140}Ce nuclear probe at the Nd sites. However, the use of rare-earth probe nuclei in hyperfine interaction techniques introduces a contribution from the probe itself to the measured magnetic field, $B^i_{hf} = B_{4f} + B_{core}$, where B_{4f} is the magnetic field from the 4f moment and B_{core} is the contact field from the s-electrons in the core polarized by the 4f moment. As Ce ion has only one 4f electron in the Ce^{3+} state, and none in the Ce^{4+} state it can sometimes display a mixed valence state.

2. Experimental

The samples of NdAg were prepared by repeatedly melting the constituent elements, with radioactive ^{140}La produced by neutron irradiation of pure lanthanum metal for a few hours in a flux of 10^{13} ncm^{-2} s^{-1} in the IEA-R1 reactor, substituting about 0.2% of Nd atoms, in an arc furnace under argon atmosphere purified with a hot titanium getterer followed by an annealing at 700 °C in vacuum for 24 h. X-ray diffraction measurement indicated a single phase and the cubic CsCl-type structure with the Pm$\bar{3}$m space group for the samples. Magnetization measurements were carried out in the temperature range 4.2–200 K using a superconductor quantum interference device (SQUID) with an applied field of 0.01 T, and the results are shown in Fig. 1. The results show that the sample orders ferromagnetically below 25(2) K.

^{140}Ce nuclei populated from the beta decay of ^{140}La were used to measure the magnetic hyperfine field (B_{hf}) at Nd sites in a PAC spectrometer. The samples were measured in the temperature range of 10–295 K using a closed-cycle helium cryogenic device. A

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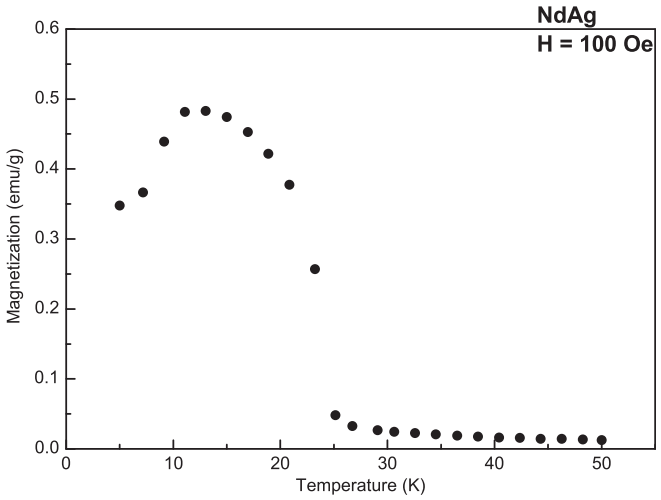

Fig. 1. Temperature dependence of the NdAg magnetization for a 100 Oe magnetic field.

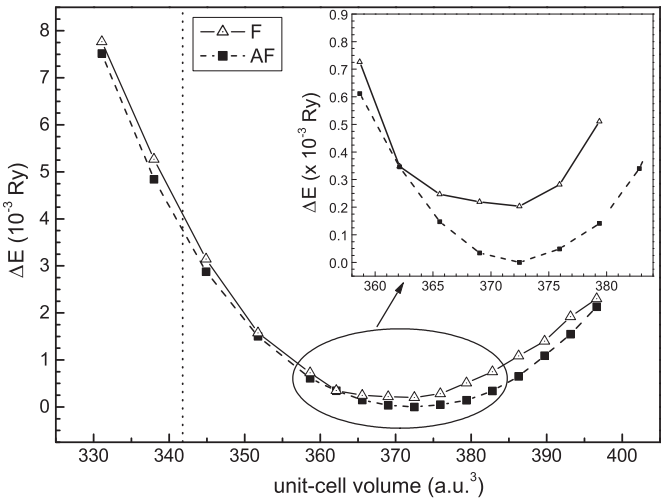

Fig. 2. Relative total energy as a function of the unit cell volume for ferromagnetic and anti-ferromagnetic NdAg. The vertical bar represents the experimental volume.

detailed description of the PAC method as well as the experimental procedure can be found elsewhere [9,10]. The experimental data for temperatures below T_N were analyzed for a pure magnetic dipole interaction because the quadrupole moment of the 2083 keV 4^+ state of ^{140}Ce is known to be very small and as a consequence quadrupole interactions are not expected to be observed.

3. First-principles calculations

Pure NdAg was reported to order anti-ferromagnetically [1,3]. Nevertheless, it was found in the present work that NdAg samples prepared with a small substitution of Nd, with only 0.2 atom percent of La, turns the compound to a ferromagnetic state, suggesting that NdAg lies near a magnetic instability like that observed for PrAg. In order to have a deeper insight into such instability, ab-initio electronic structure calculations on NdAg were performed in both the ferro and anti-ferromagnetic states of NdAg.

Previous detailed electronic structure calculations of NdAg compound in the ferromagnetic phase showed a hybridization of the localized Nd-f states with the extended conduction band states [11] and also some optical properties of the compound [12]. Here, the aim is to determine theoretically the difference between the energies of the ferromagnetic and the anti-ferromagnetic phases of the NdAg compound.

The self-consistent band-structure calculations were performed within the framework of the density functional theory (DFT) embodied in the WIEN2k computer code [13]. We have chosen for the muffin-tin spheres radii $R_{MT} = 2.9$ and 2.2 a.u. respectively for the rare-earth and Ag. The number of plane-waves was limited by the cut-off $K_{max} = 8/R_{MT}^{min}$, and the charge density was Fourier expanded up to $G_{max} = 14$. For the Brillouin zone integration, a mesh of 3400 K points was used within the whole zone. Exchange and correlation effects were treated with generalized gradient corrections (PBE-GGA) [14]. The valence states were treated within the scalar-relativistic approach taking into account the spin–orbit interaction and the core states are relaxed in a fully relativistic manner. A $2 \times 2 \times 1$ supercell and a regular $1 \times 1 \times 1$ cell were utilized for the anti-ferromagnetic and ferromagnetic cases, respectively. Only the number of vectors within the Brillouin zone and the total energy was scaled exactly according to the cell volume and all the remaining parameters were kept equal between these two calculations.

Table 1
Contributions to the total magnetic hyperfine field B_{hf} at Ce impurity in NdAg compounds obtained from electronic structure calculations considering different values for m_l.

m_l	B_c	B_{orb}	B_{dip}	B_{hf}
−3	30.60	−158.28	20.27	−107.41
−2	30.55	−106.51	−0.35	−76.31
−1	30.69	−53.66	−12.75	−35.72
0	30.11	−0.60	−16.33	−13.18

(All values of mhf are given in Teslas).

The total energy as a function of the unit cell volume for the ferromagnetic and anti-ferromagnetic couplings is shown in Fig. 2. As can be seen in the figure, the minimum of the energy curves occurs at cell volumes around 8% larger than the experimental volumes, which is a well-known effect produced by the limitations of the local density approximation, even with its improved version employed here, the generalized gradient approximation (GGA). Apart from this effect, it can be clearly seen in Fig. 2 that the difference in energy between the ferromagnetic and the anti-ferromagnetic cases of NdAg is very small, of the order of 10^{-4} Ry at the minimum of the curves.

It can be then concluded that NdAg compound order anti-ferromagnetically and that the $(\pi, \pi, 0)$ magnetic structure is not very stable. Possibly, this is a general trend as one moves down the rare-earth series in RAg compounds where, at the end, the CeAg presents a ferromagnetic order. The magnetic hyperfine field at Ce impurity in NdAg has also been calculated considering a supercell $(2 \times 2 \times 2)$ where Ce replaces Nd. The calculations have been performed for different m_l, the magnetic projection of L. The results are shown in Table 1, where B_c is the contact field, which contains the conduction electron field, B_{orb} is the 4f contribution from Ce ions and B_{dip} is the dipolar contribution.

4. Results and discussion

The PAC results show well-defined magnetic dipole interaction below the magnetic transition temperature. The observed magnetic interaction corresponds to the magnetic ordering of the Nd moments. Fig. 3 shows the temperature dependence of the experimental hyperfine field B_{hf} measured at ^{140}Ce substituting

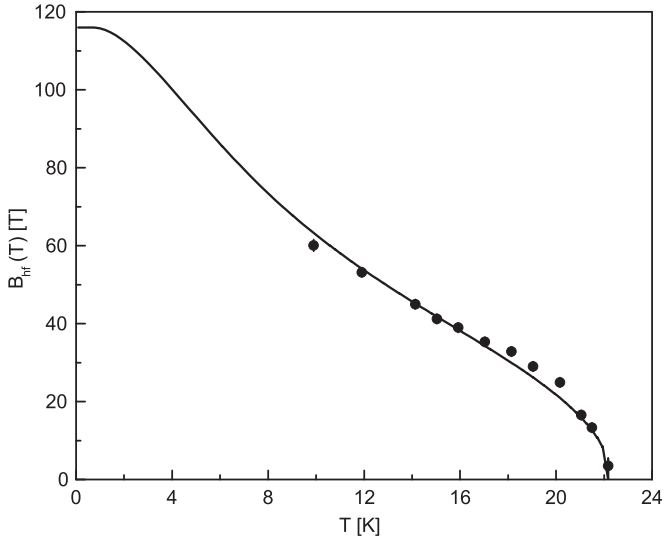

Fig. 3. Temperature dependence of the magnetic hyperfine field at Nd sites in NdAg for ^{140}Ce probe. The solid line represents the fitting to a molecular field model described in the text.

for Nd in NdAg compound. The measurements below ~22 K, however, show a sharp deviation from the expected normal behavior for a simple magnetic ordering. For example, the measured hyperfine field at 15 K is 41(1) T while at 10 K it is 60(2) T.

In order to explain the temperature dependence of B_{hf} a molecular field calculation was used which is based on a model proposed by Jaccarino et al. [15] and adapted to ^{140}Ce diluted in magnetic rare-earth hosts [16,17]. In this model the effective hyperfine field, B_{hf}, at the probe site is given by the sum of the contributions from the probe ion itself, B^i_{hf} and from the conduction electron polarization, B_{ce}, which scales with the host reduced magnetization $\sigma(T)$. B^i_{hf} is proportional to the thermal average of the impurity moment $\langle J^i \rangle$, which is localized and independent of temperature. The thermal average is taken over its levels in the exchange field of the host B^i_{exc}:

$$B_{hf}(T) = \frac{\langle J^i_z \rangle}{J^i} B^i_{hf}(0) \times B_{J^i}(y) + B_{ce}(0)\sigma(T) \quad (1)$$

where the argument of the Brillouin function $B_{J^i}(y)$ is given by $y = -\langle J^i_z \rangle g_{J^i} \mu_B \xi B^i_{exc} + \Delta/kT$, with the Landé factor $g_{J^i} = 6/7$, total angular momentum $J^i = 5/2$ for Ce^{3+}, and

$$B^i_{exc} = \frac{3kT_C}{(2g_J - 1)(J+1)\mu_B} \times \sigma(T) \quad (2)$$

B^i_{exc} splits the $\frac{5}{2}$ state of $4f^1$ Ce^{3+}, and Δ gives the energy difference of this state relative to the non-magnetic $4f^0$ Ce^{4+} state energy. ξ is a parameter that takes into account the fact that the host–impurity exchange may be different from the host–host exchange. For Nd^{3+} ions, $J = 9/2$ and $g_J = 8/11$.

The Néel temperature for NdAg found in the fitting of the model to experimental data is 22.3 K, which agree with the values of 22 K [1,3] found in the literature and with the value of 25(2) K obtained from magnetization measurements in the present work.

The issue of the magnetic interaction between a magnetic impurity ion diluted in a magnetic host is not well understood yet. Particularly, the host–impurity exchange interaction is not well described. The parameter ξ gives the strength of the impurity–host exchange interaction relative to the host–host exchange interaction. Therefore, $\xi = 1$ means that both interactions are equal. The results of the fitting show that this interaction ($\xi = 0.21$) is much weaker than that previously reported for DyAg ($\xi = 0.78$) [18]. One direct explanation would be that this magnetic interaction is directly proportional to the localized magnetic moment at the magnetic ion of the host, $\mu = 9.7\mu_B$ [19] for DyAg and $\mu = 2.19\mu_B$ [3] for NdAg.

The magnetic coupling between rare-earth moments can occur by indirect 4f–4f exchange, which, according to the RKKY theory, is mediated by a spin-polarization of the s-conduction electrons induced by the localized 4f-spins. The observed sinusoidal modulation of the magnetic moments on HoAg and ErAg [7,8] indicates that the RKKY mechanism, due to its oscillatory nature, is acting within these compounds. There is another possibility where the coupling is provided by intra-atomic 4f–5d exchange and direct 5d–5d interaction between the spin polarized 5d-electrons of neighboring rare-earth ions [20]. One example of a detailed theoretical analysis of such a mechanism can be seen for the $Gd_xLa_{1-x}Ni_5$ system [21]. According to the RKKY theory of indirect coupling the ratio between the conduction electron spin polarization (CEP) and the magnetic ordering temperature is expected to be proportional to $[J_{sf}(g_J - 1)(J+1)]^{-1}$, where J_{sf} is the s–f coupling constant. Considering that J_{sf} values do not appreciably change for DyAg [18] and NdAg compounds one expects that the $B_{ce}(0)$ value for DyAg be higher than the value for NdAg. The fitting results to the experimental data show that $B_{ce}(0) = 23$ T for NdAg whereas $B_{ce}(0) = 5.4$ T for DyAg [18], suggesting that RKKY prediction fails for NdAg.

By observing the changes in the rare-earth magnetic moments and the electronic populations of its 4f and 5d shells for NdAg when compared with previous results from ab-initio calculations for HoAg [22], one can see that a large change occurs for the 5d electrons. For the heavier HoAg case, the 5d polarization is small, 0.03, but it increases by the significant factor of three for the lighter compound, NdAg. This strongly suggests that the overlap between 5d shells increases even with the increase of the atomic distances on the lighter side of the series.

Thus, a situation of competition between the RKKY itinerant coupling and a direct d–d interaction is likely to be established. The direct d–d coupling is known to favor the ferromagnetic alignment between rare-earth ions [20]. The change from an antiferromagnetic to ferromagnetic order on the RAg series when R is a light rare-earth element can then be driven by a change in the magnitude of the RKKY interaction and, at the same time, be enforced by a direct d–d interaction.

As La impurities are introduced within the NdAg lattice an additional decrease of the RKKY is expected due to a decrease in the local magnetic moment and by the effect of de-phasing the RKKY interaction, but the direct d–d interaction would not decrease because of the existence of 5d electrons in La. If, in this case, the direct d–d interaction surpass the RKKY, the NdAg compound would order ferromagnetically, as observed experimentally.

The results of the fitting also show that the value for $|B_{hf}(0)| = 116$ T, $|B^i_{hf}(0)| = 93$ T and $|B_{ce}(0)| = 23$ T for $m_l = -3$, which reasonably agree with the values obtained in the calculations, considering that B^i_{hf} contains all other contribution and, therefore must have an opposite sign to B_{ce} as expected for $g_J < 1$. The explanation for the B^i_{hf} contribution to the magnetic interaction is the same as given for the temperature dependence of the B_{hf} at ^{140}Ce in $CeMn_2Ge_2$ [23]. In this compound ^{140}Ce probe nuclei are not an impurity and no local magnetic moment was observed at Ce sites. The local field is believed to result from the polarization of Ce spin moments induced by the magnetic field from Mn moments. In the case of NdAg compound, the magnetic interaction from the impurity is believed to result from the polarization of Ce f-spin moments induced by the magnetic field from Nd moments. As $B^i_{hf}(0)$ is much smaller than the magnetic

hyperfine field of 183 T for the free Ce^{3+} ion [24], one believes that the ground state of Ce ions in NdAg is greatly influenced by crystal field effects.

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