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STUDY OF THE MAGNETIC HYPERFINE FIELD ACTING ON ^{140}Ce PROBES IN NdAg BY TDPAC SPECTROSCOY AND AB-*INITIO* ELECTRONIC STRUCTURE CALCULATIONS

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ABSTRACT

The magnetic hyperfine field (MHF) acting on Ce nuclei inserted as probes within the NdAg inter-metallic compound was studied by perturbed angular correlation spectroscopy complemented with first-principles electronic structure calculations. It is found that the main contribution to the Ce MHF at low temperatures is due to the own Ce *4f* shell.

1. INTRODUCTION

In a previous work [1], measurements of magnetic hyperfine field (MHF) with the ^{140}Ce isotope inserted as probes in the NdAg compound were performed by means of perturbed angular correlation spectroscopy (PAC). It was observed that the MHF present a non expected behavior that departs from a normal Brillouin curve. Instead of being saturated at low temperatures, the MHF exhibits an increase at around half of the magnetic transition temperature of NdAg.

It was proposed in [1] that the orbital moment of the Ce *4f* aligns independently of the alignment of the electronic Nd spins. This way, the orbital component of the MHF of Ce could increase as the temperature decreases.
In order to study this effect we determine in this work the MHF by means of first-principles electronic structure calculations.

The MHF in an ion is represented by the following expression [2]:

$$\vec{B} = \vec{B}_c + \vec{B}_{orb} + \vec{B}_{dip} + \vec{B}_{cristal}\,, \tag{1}$$

where the terms on the right side are respectively the contact field (produced by *s* electrons spin polarization at the nucleus), the orbital field (arising from the electron current due to an electron orbit), the spin dipolar field (due to the distribution of spins around the nucleus) and

the crystal field that arises due to the magnetization of the sample and also due to spin distributions on other atoms except the probe.

The NdAg compound presents an anti-ferromagnetic order of the type (π π 0) [3], the same as observed for almost all RAg compounds excluding CeAg and PrAg. Magnetization measurements on NdAg doped with 0.1 atom percent with La turns the material to a ferromagnetic state [1], an effect that was studied in [4]. Due to this result our simulations were performed for the ferromagnetic state of this compound.
There are similar studies of the behavior of MHF on Ce in GdAg [5.6] and a good description on characteristics and properties of RAg compounds can be found in [7].

2. EXPERIMENT

The NdAg sample was prepared by arc melting the constituent elements under argon atmosphere along with neutron irradiated La substituting for 0.1 atom percent of Nd [1]. X-ray diffraction analysis after the decay of the radiation was performed and confirmed that the NdAg sample was constituted by a single CsCl type of crystalline structure, as expected. On the other hand, magnetization measurements showed that the sample presents a ferro-magnetic behavior, contrary to an anti-ferromagnetic (π π 0) type of structure, as expected from data collected on the literature. New samples were prepared and it was confirmed that systematically NdAg samples doped with a small amount as 0.1 atom percent with La present a ferromagnetic arrangement whereas those non doped samples exhibit the expected anti-ferromagnetic order.

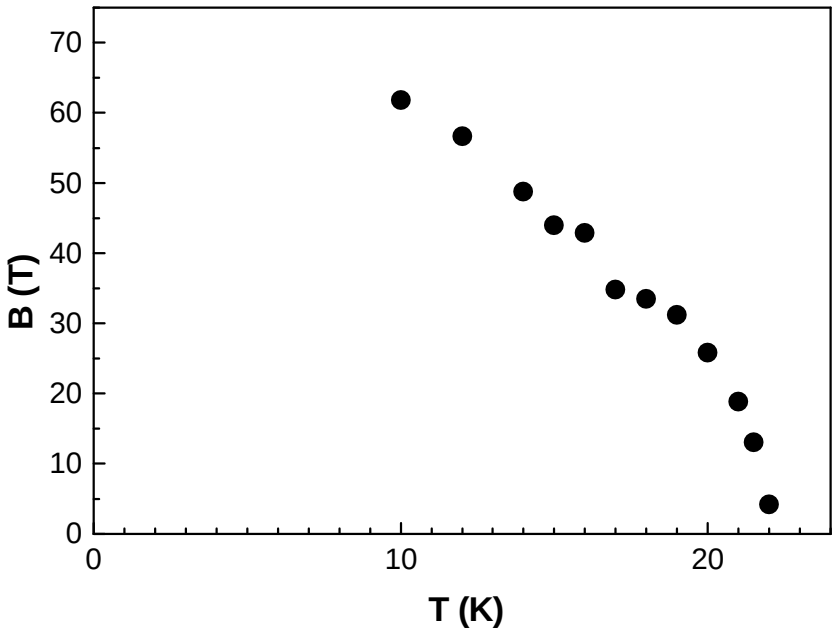

Figure 1. Magnetic hyperfine field on ^{140}Ce probes in NdAg as a function of temperature [1].

The time differential perturbed angular correlation measurements (TDPAC) were performed with a standard four BaF_2 detectors set-up of planar 90° - 180° geometry that generates 12 delayed coincidence spectra simultaneously. The combined time resolution of the detector and electronic system was 0.6 ns. The 329-487 keV γ-γ cascade of ^{140}Ce populated from the β decay of ^{140}La was utilized for the measurement of the hyperfine interaction on the nuclear level at 2083 keV with the 4^+ spin state. Since the quadrupole moment of this state is known to be very small, only magnetic interactions are supposed to be observed. More details of TDPAC technique is given in reference [8].

The measurements were taken as a function of temperature in the 8 -22 K range [1] with means of a closed cycle helium refrigerator. The temperature was controlled to better than 0.1 K. In figure 1, the result of these measurements is shown as a plot of the magnetic hyperfine field acting on ^{140}Ce nuclei as a function of the temperature of the NdAg sample [1]. The lower limit of the temperature range, 8 K, is defined by the closed-cycle-refrigerator. Above 22 K the sample is known to be on the paramagnetic state, resulting that the magnetic hyperfine field is zero above 22 K.

3. ELECTRONIC STRUCTURE CALCULATIONS

The calculations were performed within the scheme of the density functional theory (DFT) which is a very efficient method for solving the many body problem in solid state. In this formalism [9], all the observables are given as a functional of the electronic density (in our case, the spin densities). In particular, the total energy of the system is given by:

$$E_{tot}(\rho\uparrow,\rho\downarrow) = T_S(\rho\uparrow,\rho\downarrow) + E_{ee}(\rho\uparrow,\rho\downarrow) + E_{Ne}(\rho\uparrow,\rho\downarrow) + E_{xc}(\rho\uparrow,\rho\downarrow) + E_{NN}(\rho\uparrow,\rho\downarrow)$$

Here, $\rho\uparrow$ and $\rho\downarrow$ are the spin densities, T_s the single particle kinetic energy, E_{ee} the Hartree component of the electron-electron interactions, E_{Ne} the nuclei-electron Coulomb interaction, E_{xc} the exchange and correlation energy and E_{NN} the Coulomb nuclei-nuclei interaction energy. The aim in these calculations is to find the spin densities which minimize the energy or, equivalently, to solve the one particle Kohn-Sham equation in a self-consistent way [9]. The method employed here utilizes a basis set consisting of augmented plane waves plus local orbitals (APW+lo) as embodied in the WIEN2k [10] computer package. At each atomic position a sphere is defined within which the Kohn-Sham orbitals are described by orbitals that are the solution of the energy dependent radial Schrödinger equation times spherical harmonics whereas at the interstitial space the basis functions are plane waves constrained with special matching conditions at the sphere boundary. With this methodology, a good description of the charge density around the nucleus is achieved allowing to determine microscopic properties such as the hyperfine fields.

The main limitation of this method lies in the description of the exchange and correlation energy E_{xc}. The usual approach is the local spin density approximation (LSDA) or the improvements with the generalized gradient approximation (GGA), but both suffer for the improper description of the correlation energy and then especially fails to describe the open *d* or *f* electronic shells. The measurement and calculation of hyperfine fields are in this sense

very useful for testing these approximations as they are very sensitive to details of the charge distribution around an atomic nucleus.

The calculations were performed with the experimental value for the NdAg cell parameter, namely a = 3.712 Å and by choosing the muffin-tin radius R_{MT} = 2.9 and 2.2 a.u. respectively for Nd and Ag. The number of plane waves was limited to k_{max} = 8/R_{MT} *(Nd)*, the charge density was Fourier expanded up to G_{max} = 14 and, for the Brillouin zone integrations, a tetrahedral mesh of 3400 *k* points was utilized. Exchange and correlations effects were treated with generalized gradient corrections [11]. The $5s^2 5p^6 4f^1 5d^1 6s^2$ for Ce were treated as valence states, within the scalar-relativistic approach, taking into account the spin-orbit coupling, while the core states were relaxed in a fully relativistic manner. The calculation of the magnetic hyperfine field, also implemented into the WIEN2k code, was performed following the formulas due to Blügel et.al. [12], which include relativistic corrections. In order to simulate the impurity atom in the compound a super-cell containing 16 atoms (one impurity, seven Nd and 8 Ag) was employed.

In order to improve for the important correlation effects on the *4f* Ce states, we employed the GGA+U methodology [13]. In this method, external Hubbard parameters are needed in order to take into effect the intra-shell Coulomb interaction, and the method loses its first-principles character. To overcome the difficulty, we perform several calculations where several of the *4f* Ce states, with distinct values of the angular momentum L_Z, are tested individually.

3. RESULTS AND DISCUSSION

The results of the calculations are shown in table 1.

Table 1. Contributions and total values of Ce MHF substituting for Nd in NdAg for several of its sub-states.

	L_z	*Electronic shell*	B_c *(T)*	B_{orb} *(T)*	B_{dip} *(T)*	*Component sum (T)*	B_{total} [b,c] *(T)*
NdAg	-3	4f	30.60	-157.90	17.52	-109.78	-107.41
		oe[a]	----------	-0.38	2.75	2.37	
	-2	4f	30.55	-105.98	0.01	-75.42	-76.31
		oe	----------	-0.53	-0.36	-0.89	
	-1	4f	30.69	-53.00	-10.57	-32.88	-35.72
		oe	----------	-0.66	-2.18	-2.84	
	0	4f	30.11	0.00	-14.03	16.08	13.18
		oe	----------	-0,60	-2.30	-2.90	

a – summed contributions for the MHF from other electrons (oe) coming from the *s, p* and *d* shells

b – B_{total} was obtained by summing the two components *f* and (oe).

c – The experimental MHF is ~ 62 T à 10 K. [1]

From the values seen in this table, one can observe that the orbital component of the MHF is proportional to L_Z. Bellow the ordering temperature of NdAg, the orbital contribution is the main contribution for the MHF when m_l is equal to -3 or -2. The dipolar contribution presents a change in sign as function of L_Z. Its magnitude is relatively more significant when the orbital component has smaller values, e.g., for m_l equal -1 or 0. The Fermi contact contribution presents always the same direction, its magnitude is relatively constant as a function of L_Z and its magnitude is relatively significant whenever L_Z is small. Both, B_c and B_{dip} subtract themselves for the majority of the sub-states.

As the experimental MHF (~ 62 T) was measured at 10 K [1] and the calculations are valid to 0 K, is possible that measurements performed below the lowest attained temperature, 8 K, would show larger MHF than the value obtained at 10 K, since it can be seen in figure 1 that the curve did not attained a saturation at this temperature. Moreover, if one compare the calculated values seen in table 1 with the one resulted from the experiment, one can conclude the the more probable *4f* Ce state is m_l equal -2 or -1.

4. CONCLUSIONS

Experiments performed with the PAC technique with the aid of electronic structure calculations were shown to be worth to the study of the MHF acting on Ce probes substituting for Nd in NdAg compound. It was shown that the MHF is actually mainly due to the own Ce electronic structure, contrary to the usual case observed with In or Ta probes where the MHF is of transferred nature and resembles the magnetic properties of the compound itself.

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