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Citation: AIP Advances **6**, 056024 (2016); doi: 10.1063/1.4944654
View online: http://dx.doi.org/10.1063/1.4944654
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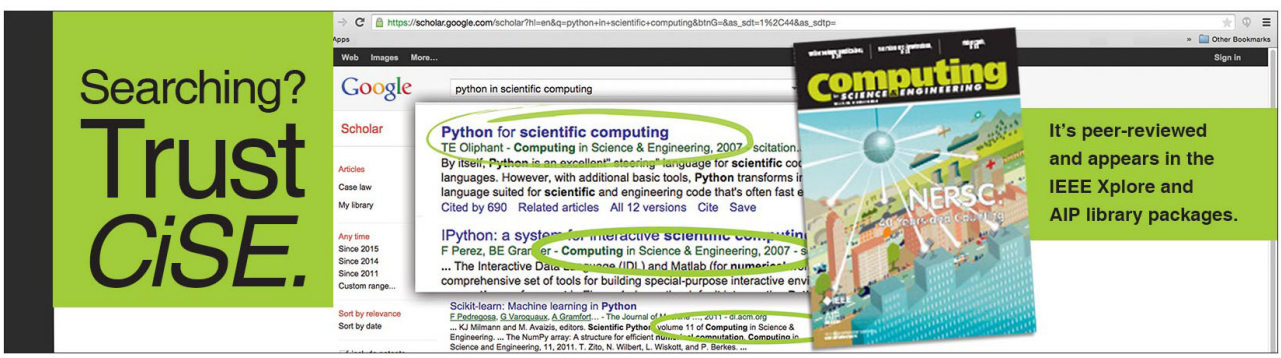

Mapping the magnetic hyperfine field in $GdCo_5$

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(Presented 12 January 2016; received 6 November 2015; accepted 11 February 2016; published online 17 March 2016)

The magnetic hyperfine field (B_{hf}) in ferrimagnetic $GdCo_5$ compound has been investigated as a function of temperature by Mössbauer effect (ME) spectroscopy and perturbed angular correlation (PAC) spectroscopy using ^{119}Sn and ^{111}Cd probe nuclei, respectively. Results show that the non-magnetic probe atoms ^{119}Sn and ^{111}Cd substitute all three non-equivalent positions in $GdCo_5$: Gd, Co_I, and Co_{II}. For ^{119}Sn and ^{111}Cd probes at Gd sites, the saturation magnetic hyperfine fields are very different with values of B_{hf1} = 57.0(1) T and B_{hf1}= 20.7(1) T, respectively. For ^{119}Sn and ^{111}Cd atoms localized at Co_I and Co_{II} sites the magnetic hyperfine fields are practically identical and, in saturation, reach the values of B_{hf2} = 11.6(1) T and B_{hf2} = 11.1(2) T, and B_{hf3} = 14.8(1) T and B_{hf3} = 14.4(2) T, respectively. [http://dx.doi.org/10.1063/1.4944654]

I. INTRODUCTION

Compounds of the series $RECo_5$ (where RE is a rare-earth metal) have a great potential for practical applications as permanent magnets with colossal coercivity.[1] These compounds crystallize in the hexagonal structure of $CaCu_5$ (space group P6/*mmm*, No. 047) in which Co atoms occupy two nonequivalent sites, the 2c and 3g sites, while the RE ions are located in the 1a position. The $RECo_5$ compounds are ferromagnetically ordered for the light RE metals (RE and Co magnetic moments are aligned), and present ferrimagnetic ordering for the heavy RE (RE and Co moments are unaligned). These compounds have high magnetic ordering temperatures reaching 1000 K due to intensive Co-Co magnetic exchange interaction. The magnetic moments of Co atoms are approximately the same for all $RECo_5$ compounds: $\mu_{Co} \approx 1.6\text{-}1.7\ \mu_B$ and are oriented oppositely to the spin moment of the RE ions over the entire range of magnetic ordering of the compounds. The magnetic moments of RE ions are close to the corresponding values for free +3 ions. Neutron diffraction study[2–4] and Mössbauer investigation using RE isotopes and ^{57}Fe impurity nuclei[5,6] allow to investigate the dependence of the magnetic moments of RE and Co sublattices of $RECo_5$ compounds with the increase of temperature or pressure.

In this paper, we report results of a comparative study of the magnetic hyperfine fields for non-magnetic ^{119}Sn and ^{111}Cd probes in the $GdCo_5$ compound measured, respectively, by Mössbauer spectroscopy (MS) and perturbed angular correlation (PAC) spectroscopy. Non-magnetic atoms do not have own magnetic moment, consequently the electronic polarization of their nuclei is formed from the surrounding magnetic atoms. Recently, huge positive magnetic hyperfine fields (HFs), up to B_{hf} = 57 T were found for impurity atoms ^{119}Sn on RE-sites of RE-T (RE = rare earth, T = Fe,Co) intermetallic compounds.[7] Since both Gd and Co magnetic sublattices are magnetic ordered below T_C = 1014 K,[1] it is expected that the magnetic hyperfine fields at the ^{119}Sn and ^{111}Cd

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nuclei are induced by Gd and Co magnetic sublattices, similar to the formation of HFs for ^{119}Sn and ^{111}Cd probes in $RECo_2$ compounds.[8,9]

II. EXPERIMENTAL PROCEDURE

Polycrystalline samples of $GdCo_5$ compound were prepared by arc melting stoichiometric amounts of high-purity metals under argon atmosphere and the resulting pellets were cut in pieces. One piece was re-melted with 0.5 at.% of tin enriched by the ^{119}Sn isotope to form the sample intended for Mössbauer measurements. ^{111}In carrier-free as $^{111}InCl_3$ solution was deposited on another part of the sample which was also re-melted in the arc furnace to prepare the sample for PAC spectroscopy measurements with ^{111}Cd. The resulting ingots containing the probes were turned over and re-melted three times. After melting, the samples were encapsulated in a quartz tube under helium atmosphere at low pressure and submitted to thermal annealing at 800 ^{o}C during 24 h. Finally, samples were characterized by X-ray diffraction (XRD) and the data were analyzed by Rietveld method. XRD showed the hexagonal $CaCu_5$-type structure without visible contamination by the other phase.

Mössbauer measurements were performed between 5-400 K using a constant acceleration spectrometer with 35 mCi $Ca^{119m}SnO_3$ source. In order to enhance the effect of resonance absorption and resolution in detecting the 23.9 keV γ-radiation, a resonance $CaSnO_3$-based detector was used. The quadrupole shift in the components of the hyperfine structure was small enough to be treated by perturbation theory. The ^{119}Sn MS spectra were fitted as set of magnetic sextets with different values of the magnetic hyperfine fields (HFs), isomer shifts (IS), and quadrupole shifts (ΔE_Q) of the resonance lines.

PAC measurements using ^{111}In(^{111}Cd) probe nuclei were carried out in the temperature range from 40 K to 1040 K using a closed loop helium cryogenic system (for temperatures below 300 K) and a small furnace in the six- or four-detector spectrometers both associated with conventional fast-slow electronic setup to measure the delayed gamma-gamma coincidences. ^{111}Cd probe nuclei have intermediate level of 245 keV (nuclear spin I = 5/2, half-life $T_{1/2}$ = 84.5 ns, and g-factor g = 0.306 ± 0.001) for ^{111}Cd. Six- or four-BaF_2 detector spectrometers were used in the measurements with ^{111}In(^{111}Cd) probe nuclei. A description of the method as well as details about the PAC measurements can be found elsewhere.[10,11] The spin rotation spectra ($R(t)$) obtained in the PAC measurements allows, in the dipole magnetic interaction, the determination of the Larmor frequency $\omega_L = \mu_N g B_{hf}/\hbar$, where μ_N is the nuclear magneton, and consequently the magnetic hyperfine field B_{hf} is obtained.

III. RESULTS AND DISCUSSION

A. ^{119}Sn in $GdCo_5$

The absorption Mössbauer spectrum at 78 K for ^{119}Sn probes (see Fig. 1) was fitted with three magnetic sextets corresponding to the three inequivalent sites of localization of tin atoms in the crystal lattice of the $GdCo_5$ compound: Gd, Co_I, and Co_{II} positions (1a, 2c, and 3g-sites of $CaCu_5$ structure, respectively). The ^{119}Sn probes localized at these sites have significant differences of their local environment on the nearest Gd and Co atoms, interatomic distances, and on a local symmetry of sites. For three positions of ^{119}Sn atoms occupation, the HF's magnitudes at 5K were found to be B_{1a} = 57.0(1) T, B_{2c} = 11.6(1) T, and B_{3g} = 14.8(1) T, respectively. The intensity ratio of subspectra is equal to $I_{1a} : I_{2c} : I_{3g}$ = 43:34:23 (in percents of summary spectrum intensity).

The intensities of subspectra do not correspond to the statistical distribution of probes in crystal sites. There is a preferential occupation of 1a and 2c sites by ^{119}Sn probes. The correspondence of each subspectrum to the sites of tin localization was determined from the analysis of all parameters of the hyperfine interaction. It was established earlier in Ref. 7, that the biggest HF corresponds to the ^{119}Sn atoms localized at Gd sites, and that B_1a is aligned with the Co magnetic moments. As the 1a and 2c sites have axial symmetry, the main components V_{zz} of the electric field gradient for both sites are also directed along the c axis. Since Gd and Co magnetic moments are aligned with the c

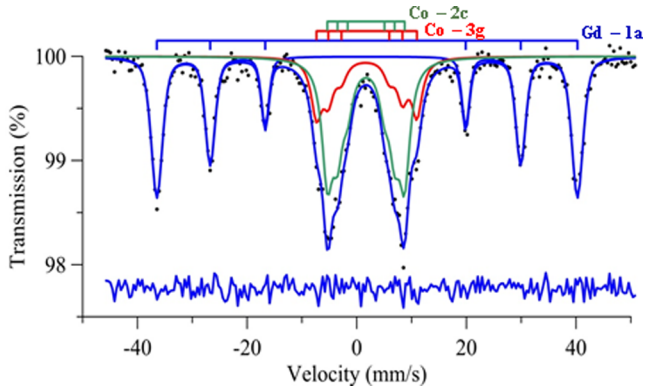

FIG. 1. The Mössbauer spectrum for ^{119}Sn probes at $GdCo_5$ compound at 78 K. Solid lines are the least squares fit of the theoretical functions to the experimental data.Three subspectra corresponding to the nonequivalent 1a, 2c, and 3g sites of tin occupation are shown.

axis, the HFs B_{1a} and B_{2c} are also directed along c-axis, and the azimuthal angle $\theta = 0^o$. From the fitting of ^{119}Sn spectra in $GdCo_5$ at the different temperatures, we have found a positive quadrupole shift for ^{119}Sn probes localized at 1a Gd-sites and have not found any quadrupole interaction for ^{119}Sn probes at 2c (Co_I) sites. At the same time, the subspectrum for ^{119}Sn probes localized at 3g (Co_{II}) sites with lower axial symmetry shows significant positive quadrupole shift of resonance lines.

To determine the contribution from Co magnetic sublattice to the HF, we have measured at 78 K and at 300 K the Mössbauer spectra for ^{119}Sn probes in YCo_5 compound with the same $CaCu_5$ crystal structure and $\mu_{Co} \sim 1.7\ \mu_B$.[12] For three positions of ^{119}Sn atoms occupation in YCo_5, the HF's magnitudes extrapolated to 5 K were found to be B_{1a} = 43.0(2) T, B_{2c} = 1.6(2) T, and B_{3g} = 2.2(2) T. The magnitudes of B_{2c} and B_{3g} for ^{119}Sn in YCo_5 are very similar to the value of the HF for ^{119}Sn probes in Co with hfc structure: B_{hf} = -2.3 T.[13] Since the magnetic moments of the Y atoms do not exceed 0.2 μ_B, the HFs for ^{119}Sn probes in YCo_5 are entirely due to the magnetic Co environment. The magnitude of B_{1a} for YCo_5 is almost the same as the HF for ^{119}Sn probes in Lu sites of $LuFe_2$ (B_{hf} = 45.0 T)[8] despite the fact that Y atom in YCo_5 has 18 Co atoms as the nearest neighbors (nn) and the Lu atom in $LuFe_2$ has only 12 nn Fe atoms. This fact may indicate that the 6 Co_I atoms (lying in the basal plane) do not give a significant contribution to B_{1a} field because it is formed by the Co_{II} magnetic moments arranged in hexagonal 3g layers and directed along the c axis.

Because the shortest Gd-Gd distances are about 4 Å along the c axis (2 nn Gd) and about 5 Å along the a-axis (6 nn Gd), the interaction between the moments of Gd is mediated through the Co atoms. The contribution from Gd magnetic sublattice to the HF for ^{119}Sn probes at Gd sites of $GdCo_5$ is equal to the difference between the values B_{1a} for $GdCo_5$ and YCo_5: (57 T - 43 T = 14 T). This value is almost twice as much as the contribution of Gd-Fe magnetic exchange interaction to the HF for ^{119}Sn probes in Gd sites of $GdFe_2$ (52.6 T - 45.0 T = 7.6 T).[8] At the same time, the Gd sites have only four Gd nn in $GdFe_2$, twice less than in $GdCo_5$. It follows from this that the contributions from Gd sublattice to the HFs for ^{119}Sn probes in $GdCo_5$ and $GdFe_2$ compounds are proportional to the number of the Gd magnetic moments in the nearest environment of tin probe atoms. The Gd magnetic moments located in the same (a-b) plane give the main contribution of Gd-sublattice to B_{1a}. The similar analysis for B_{2c} and B_{3g} has shown that HFs for ^{119}Sn in the three inequivalent sites of $GdCo_5$ are formed by both, Co and Gd magnetic sublattices. The contribution from Co sublattice to the HFs is positive relatively to Co magnetic moments,[7] but the contribution from Gd sublattice is negative relatively to Gd moments. As a result, the contributions from Gd and Co magnetic moments to the HFs at ^{119}Sn probe atoms in $GdCo_5$ are added.

The HFs for ^{119}Sn probes in all three sites of $GdCo_5$ are decreased by about 15-20% with the increase of the temperature from 5 K to 300 K. The temperature dependence of the HFs differs from the temperature dependence of summary magnetization of $GdCo_5$ and of sublattice's magnetic

moments. Isomer shifts (IS) for ^{119}Sn probes for all three sites of localization in $GdCo_5$ were found within the range from 1.78 mm/s to 1.75 mm/s at 5 K. These magnitudes are intermediate values between IS for ^{119}Sn probes in RE and 3d metals. This fact confirms the existence of the of 5d-3d electronic hybridization in $GdCo_5$.

B. ^{111}Cd in $GdCo_5$

Magnetic hyperfine interactions at ^{111}Cd nuclei in RE-3d compounds were investigated earlier in $RECo_2$[9,14] and in RE-Ni compounds[9,15] in which the atoms ^{111}Cd occupy only RE sites. In the present study, a technique of introducing (^{111}In)^{111}Cd probes to the $GdCo_5$ compound is different from that applied to references 14 and 15. Due to this method described above, ^{111}Cd probes are placed not only in Gd sites, but also occupy the Co sites. Perturbation functions for ^{111}In(^{111}Cd) probes in $GdCo_5$ measured at several temperatures are shown in Fig. 2. Analysis of the spectra showed that in $GdCo_5$ the ^{111}Cd atoms are placed in all three non-equivalent positions: one Gd 1a position (18% of all ^{111}Cd probe nuclei) and two Co positions: Co_{2c} (54% of ^{111}Cd nuclei) and Co_{3g} (28% of ^{111}Cd nuclei).

At 78 K, the magnetic frequency corresponding to ^{111}Cd probes at Gd-sites reaches 48.3(2) MHz (B_{1a} = 20.7 (1) T). This magnitude is slightly smaller to HF value for ^{111}Cd nuclei substituting Gd ions in $GdCo_2$ (B_{hf} = 21.18 T).[14] The values of the HFs for ^{111}Cd substituting Co_{2c} and Co_{3g} sites were found to be B_{2c} = 11.1 (2) T and B_{3g} = 14.4 (2) T, respectively.

It should be noted that the sign of the HFs for ^{111}Cd probes in RE-sites of $RECo_2$ compounds was not determined,[14] as in the present work, for ^{111}Cd in all three localization sites. However, by analogy with the results for ^{119}Sn we can confidently assume that the HFs on ^{111}Cd probes in $GdCo_5$

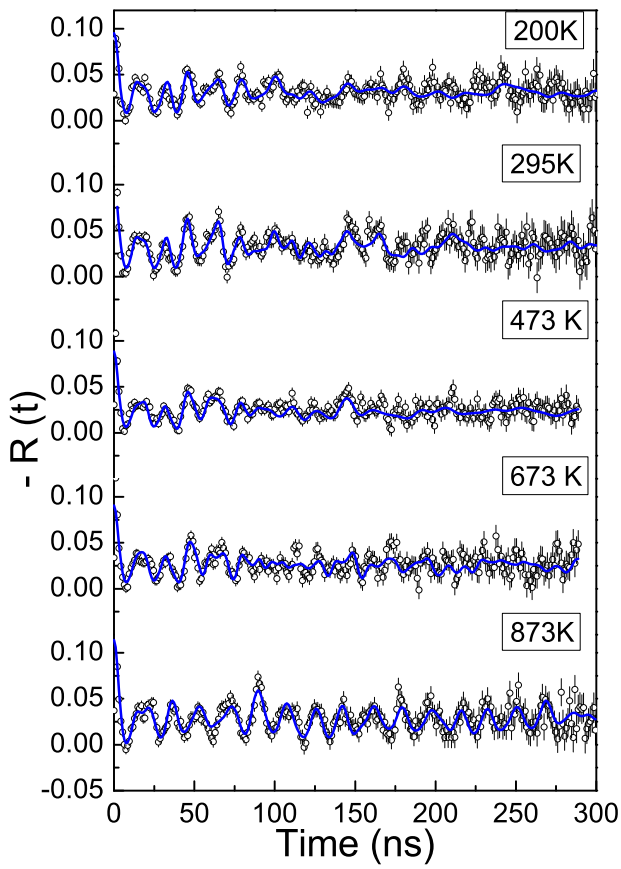

FIG. 2. Perturbation functions for ^{111}In(^{111}Cd) probes in $GdCo_5$ measured at different temperatures. Solid lines are the least squares fit of the theoretical functions to the experimental data.

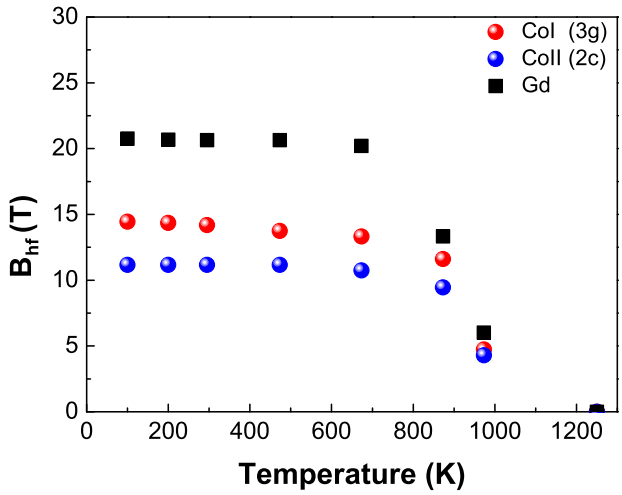

FIG. 3. Temperature dependence of B_{hf} for ^{111}Cd probes at three different sites in $GdCo_5$.

are formed by moments of both Gd and Co magnetic sublattices. Since the electron polarization in $GdCo_5$ are determined by the exchange interaction of the magnetic sublattices, it can be argued that the HFs on ^{111}Cd nuclei in this compound are induced by Gd-Co and Co-Co magnetic exchange interactions, and the HFs magnitudes are the result of competitive contributions to the HFs from these interactions. To determine the value of contributions from Gd and Co magnetic sublattice to the HFs on ^{111}Cd nuclei in $GdCo_5$ compound, further research on ^{111}Cd probes by PAC in the other compounds $RECo_5$ and measuring of HF's signs are required.

The temperature dependence of the HFs for (^{111}In)^{111}Cd probes (see Fig. 3) in Gd, Co_I, and Co_{II} sites of $GdCo_5$ compound are different from the temperature dependence of the spontaneous magnetization as well as from the dependence of Gd and Co magnetic moments as a function of temperature. In the range from 77 K to 670 K, the HFs are practically unchanged with increasing temperature. At the same temperature region, the magnetic moments of Co atoms, and especially Gd moments are decreased significantly faster.

These facts may indicate that the Gd and Co magnetic sublattices contribute to the HFs at ^{111}Cd nuclei with opposite signs. Such conclusion is consistent with the results of the HFs studies for ^{111}Cd probes localized at RE sites in $RECo_2$ compounds.[9,14] The authors of this investigation concluded that the total HF on ^{111}Cd nuclei is formed by two contributions of opposite signs: the contribution from Co magnetic moments and contribution from RE moments caused by indirect 4f-4f-magnetic exchange interaction.

It was established that the sign of HF for ^{111}Cd probes is positive for light and negative for heavy RE_2In.[16] In addition, the contributions from Gd sublattice to the HFs at ^{119}Sn probes in $GdCo_5$ are negative relatively to the Gd moments. Therefore, it should be expected that the contribution of the Gd sublattice to the HFs for ^{111}Cd probes in RCo_5 is also directed opposite to the Gd moments. As the total HFs for ^{111}Cd in RCo_5 consist of two contributions of opposite signs, and the Gd and Co moments are oriented opposite to each other, the contribution from the Co sublattice to the HF has to be negative with respect to Co moments for all three sites of ^{111}Cd localization.

The magnitude of contribution from Co sublattice to the HFs at ^{111}Cd probes prevails over Gd contribution, so that the total HF must be negative relative to the Co moment. The difference in the temperature dependence of the contributions from Gd and from Co magnetic moments leads to different temperature dependences for Gd and Co contributions to the HF at ^{111}Cd probes. The contribution from Gd sublattice to HF decreases more rapidly with the increase of temperature than the contribution from Co sublattice since the Gd magnetic moments decrease faster with the increase of temperature than Co moments. The fast decrease in the Gd contribution with the increase of temperature are compensated by a slow decrease in the Co contribution. For this reason a resulting field remains substantially constant with the increase of temperature over a wide range.

IV. CONCLUSION

We can make a conclusion about the similarity and the difference between the formation of the HFs for ^{119}Sn and ^{111}Cd probes in $GdCo_5$. Atoms of both probe nuclei are placed in all three inequivalent lattice positions. The HFs for ^{119}Sn and ^{111}Cd probes are formed by both contributions from Gd and Co magnetic sublattices. The contribution from Gd sublattice to the HFs is negative relative to the Gd magnetic moments for all three positions of ^{119}Sn and ^{111}Cd probes in $GdCo_5$. The contribution from Co sublattice to the HF is positive with respect to the Co magnetic moment and reaches +43 T for ^{119}Sn probes located at Gd sites. Conversely, the contribution from Co sublattice to the HFs is negative for all three sites of ^{111}Cd probes occupation. The contributions from Gd and Co magnetic sublattices to the HFs are competing with each other. With the increase of temperature, the reduction of the contributions is mutually compensated and, therefore, the resulting HFs for ^{111}Cd probes remain constant over a wide temperature range.

The difference in the values and in the sign of Co contributions to the HFs for ^{119}Sn and ^{111}Cd probes is consistent with the well-known dependence of the HFs on the atomic number Z of the impurity atoms, $B_{hf}(Z)$, in 3d host matrices: Fe, Co and Ni.[17] The HFs on ^{111}Cd probes in these matrices are more negative than the HFs on the ^{119}Sn probes. A similar trend is observed for the HFs on ^{119}Sn and ^{111}Cd probes in 3d-based alloys[18,19] and Heusler alloys.[20] Self-consistent calculations are needed (similar to the calculations of J. Kanamori *et al.*[21] of HFs for impurities in iron) to determine the features of the HFs formation for ^{119}Sn and ^{111}Cd probes in $GdCo_5$.

ACKNOWLEDGMENTS

Partial financial support for this research was provided by Fundação de Amparo a Pesquisa no Estado de São Paulo (FAPESP). BBS and AWC thankfully acknowledges the support provide by CNPq. GAC thankfully acknowledges the support provide by CAPES.

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