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N N Delyagin and V I Krylov

Institute of Nuclear Physics, Moscow State University, 119992 Moscow, Russian Federation

E-mail: delyagin@srd.sinp.msu.ru

Abstract
The magnetic hyperfine interaction of the ^{119}Sn probe nucleus on the R site of the ferro- and ferrimagnetic RFe$_2$ (R = Sm–Tm, Lu, Zr, Hf and U) and RCo$_2$ (R = Gd–Er) compounds has been investigated by Mössbauer spectroscopy technique. It was found that the magnetic hyperfine fields (B_{hf}) exhibit quite different behaviours in the two series of the compounds. For the RFe$_2$ compounds, the ratio B_{hf}/μ_{3d} remains essentially constant across the series at a value of 30 T/μ_B (within ±4%), also for nonmagnetic R = Zr, Lu and Hf. This means that a contribution to B_{hf} from the 4f magnetic moments of the R sublattice is absent. In RCo$_2$ compounds, the total hyperfine field is the sum of two contributions: one is the 4f contribution (B_{4f}) and the other is 3d contribution (B_{3d}). The 3d and 4f contributions have the same relative sign; both contributions are positive with respect to the 3d moments direction. The B_{4f} contribution is relatively large: the ratio B_{4f}/B_{3d} varies from about 0.4 (ErCo$_2$) to about 0.7 (GdCo$_2$). The results demonstrate that the transfer of the electron polarization from the R atoms to the hybrid bonds is extremely sensitive to the features of the 3d electrons of the transition-metal subsystem.

1. Introduction

The cubic Laves-phase RFe$_2$ and RCo$_2$ (R is a rare-earth element) compounds have the same crystal structure (C15, MgCu$_2$ type); however, they show quite different magnetic behaviours. In the RFe$_2$ compounds, the strong Fe–Fe exchange interaction dominates over the Fe–R and R–R interactions and the transition-metal atoms carry a well-established magnetic moment of the order 1.5–1.8 μ_B. The compounds have rather high Curie temperatures (up to 800 K for GdFe$_2$). These properties depend only slightly on the R atom type. In the cubic RFe$_2$ compounds with nonmagnetic R atoms (R = La, Y, and Zr) the magnetic moment of the Fe atom equals 1.5–1.6 μ_B and the Curie temperature exceeds 500 K. For the RCo$_2$ compounds, a

quite different behaviour has been found. The magnetic properties of these compounds depend strongly on the R atom. When R is a nonmagnetic rare earth, RCo_2 are exchange-enhanced paramagnets, while the compounds with magnetic rare earths are ferro- or ferrimagnets, in which the observed Co moment of about 1 μ_B is entirely induced through R–Co exchange interaction. This phenomenon is called itinerant electron metamagnetism (see the review [1]). In contrast to the RFe_2 compounds, the Curie temperature of the RCo_2 compounds increases strongly with R spin, from ∼40 K ($ErCo_2$) to ∼400 K ($GdCo_2$). The prominent difference in magnetic behaviour of the two series of isostructural compounds is due to the peculiarities of the interactions between 3d and 4f magnetic sublattices. It is generally believed that a hybridization between the 3d electrons of the transition metal and valence electrons of a rare-earth atom plays a crucial role. In the RCo_2 compounds, the itinerant electron metamagnetism is directly related to a strong hybridization between the 3d states of the Co atoms and the spin polarized 5d states of neighbouring R atoms [1].

Measurements of magnetic hyperfine interactions are a useful tool for investigation of the properties of magnetically ordered compounds. In particular, the important source of information on the spin polarization are experiments with nonmagnetic probe atoms. For nonmagnetic sp-elements, the hyperfine interaction parameters are quite sensitive to peculiarities of magnetic and electronic structure of the magnetic host. In this case, the magnetic hyperfine field (B_{hf}) is created by the transferred electron polarization produced by the magnetic moments of the adjacent magnetic atoms. Therefore, the hyperfine interaction parameters should be directly associated with the spin density of the hybrid electron orbitals, as well as with the features of the exchange interaction.

In this paper, we present extensive Mössbauer spectroscopy studies of the magnetic hyperfine fields at [119]Sn probe nuclei on the cubic R sites of the Laves-phase RFe_2 and RCo_2 compounds. In these compounds, in many cases the impurity Sn atoms preferentially occupy Fe or Co sites; however, recently we have demonstrated that samples with a sufficient amount of Sn atoms on the R sites can be obtained [2]. For several R–transition-metal compounds, very large hyperfine fields equal to 46–56 T were observed. Very recently, rather important data for [111]Cd probe nuclei on the R sites of the RCo_2 compounds were obtained by perturbed angular correlation spectroscopy [3]; now, the data for [111]Cd will also be discussed.

2. Experiment

Intermetallic compounds RFe_2 (R = Sm–Tm, Lu, Zr, Hf and U) and RCo_2 (R = Gd–Er) were prepared by arc melting of the metallic constituents in an atmosphere of high-purity argon. The concentration of the tin impurity (which was enriched to 96% in the [119]Sn isotope) was 0.3–0.5 at.%. The samples were re-melted several times for homogenization. The weight loss during arc melting was less than 0.1%. The ingots were annealed at the elevated temperatures; at the end of the annealing process, the ingots were water-quenched. As a rule, quenching is needed to produce a sufficient amount of Sn atoms on the R sites of the compounds. For RCo_2 compounds, in specific cases the best results were obtained with slightly nonstoichiometric, Co-excessive alloys. For Fe-based compounds, most of the results were obtained using the emission Mössbauer spectroscopy technique, which allows us to reduce the tin impurity concentration down to 0.1 at.% (in this case, the radioactive isotope [119m]Sn was used as the tin impurity). In different samples, the obtained fraction of the tin impurity atoms in the R sites is varied from 10 to 60%. X-ray diffraction showed the $MgCu_2$-type pattern without visible contamination by other phases. The transmission Mössbauer spectra were measured using a $CaSnO_3$ source. In order to enhance the effect of resonance absorption and resolution in detecting the 23.9 keV Mössbauer radiation, a resonance $CaSnO_3$-based detector was used.
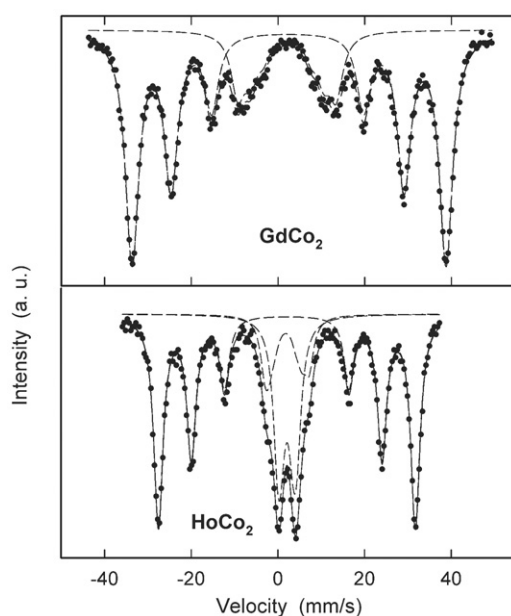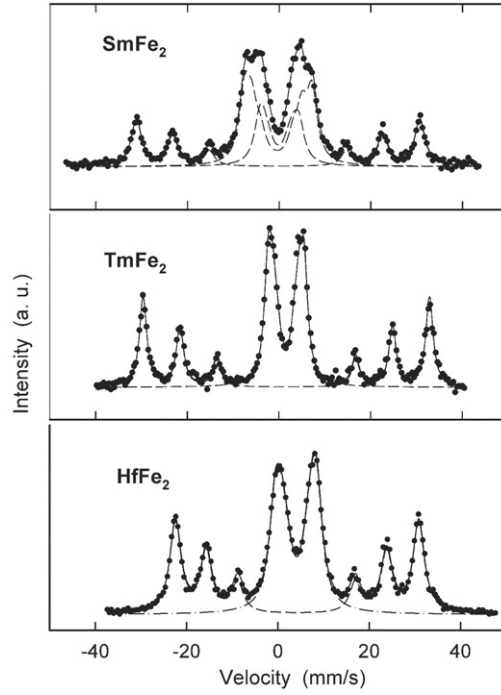
Figure 1. Mössbauer spectra of ^{119}Sn on R sites of the GdCo$_2$ (top) and HoCo$_2$ (bottom) compounds at 5 K.

For Fe-based compounds, the control ^{57}Fe Mössbauer measurements were carried out. For all of the compound, the spectra were measured at 5 K. For some of the compound, the temperature dependence of the B_{hf} was measured from 5 to 300 K. The sign of B_{hf} was determined by applying an external magnetic field up to 1.5 T. It should be noted that the sign of B_{hf} is determined with respect to the macroscopic magnetization of the sample. Most of the above-mentioned compounds are ferrimagnets, in which the magnetic moments of R atoms are antiparallel to 3d moments of the transition-metal atoms. Therefore, if the magnetization of the R sublattice dominates, the measured sign of B_{hf} is bound to be opposite to the sign defined with respect to the 3d moment direction.

3. Results

Representative ^{119}Sn transmission Mössbauer spectra of the RCo$_2$ compounds at 5 K are displayed in figure 1. Figure 2 shows the emission Mössbauer spectra of RFe$_2$ compounds. For all of the compounds, the spectra appear to consist of two distinct components with rather different hyperfine splitting. The centrally located low-field component corresponds to Sn impurity atoms localized on the transition-metal sites of the compounds [2, 4]. This component is beyond the scope of the present paper. Now, we will discuss only the high-field component which corresponds to Sn impurity atoms localized on the R sites. In all cases, well-fitting data were obtained with the assumption of a single hyperfine field value for Sn atoms on the R site. The quadrupole interaction was too small to be observed (no more than 0.1 mm s^{-1}) which corresponds to the point symmetry of the R sites. Tables 1 and 2 summarize the values B_{hf} measured at 5 K. For all compounds studied, it was found that the hyperfine field is positive with respect to the 3d moments direction. The observed hyperfine fields are very large; their values are several time larger than is commonly observed for Sn in other Fe- and Co-based intermetallic compounds. The origin of the huge positive hyperfine fields for Sn atoms on

Figure 2. Mössbauer emission spectra of ^{119}Sn on R sites of the SmFe$_2$ (top), TmFe$_2$ (middle) and HfFe$_2$ (bottom) compounds at 5 K.

Table 1. Magnetic hyperfine field B_{hf} of ^{119}Sn impurity atoms on R sites of the RFe$_2$ intermetallic compounds at 5 K. μ_{Fe} is the magnetic moment of the Fe atom. The mean-square errors for B_{hf} are equal to about 0.6 T.

| R	Sm	Gd	Tb	Dy	Ho	Er	Tm	Zr	Lu	Hf	U
B_{hf} (T)	45.6	52.6	51.2	48.8	47.5	48.0	46.1	50.0	45.0	39.3	18.1
μ_{Fe} (μ_B)	1.5	1.8	1.7	1.7	1.6	1.6	1.5	1.6	1.5	1.3	0.6
B_{hf}/μ_{Fe} (T/μ_B)	30.5	29.2	30.1	28.7	29.7	30.0	29.7	31.2	30.0	30.2	30.2
Average $B_{hf}/\mu_{Fe} = 30.0$ T/μ_B											

Table 2. Magnetic hyperfine field B_{hf} of ^{119}Sn impurity atoms on R sites of the RCo$_2$ intermetallic compounds at 5 K. For all the compounds, the value of the magnetic moment of the Co atom is accepted to be equal to 1 μ_B.

R	Gd	Tb	Dy	Ho	Er
B_{hf} (T)	52.1	47.9	45.0	43.4	41.3
B_{4f} (T)	22.1	17.9	15.0	13.4	11.3

the R site of R–Co and R–Fe compounds has been discussed in [2]. In order to analyse the results, knowledge of the accurate values of the 3d magnetic moments is needed. For the RCo$_2$ compounds, the magnetic moment of the Co atom is equal to about 1 μ_B [1]. For the RFe$_2$ compounds, there is a large number of measurements of the Fe moments; however, the published values show considerable scatter in some case. The accepted values of μ_{Fe} are tabulated in table 1.
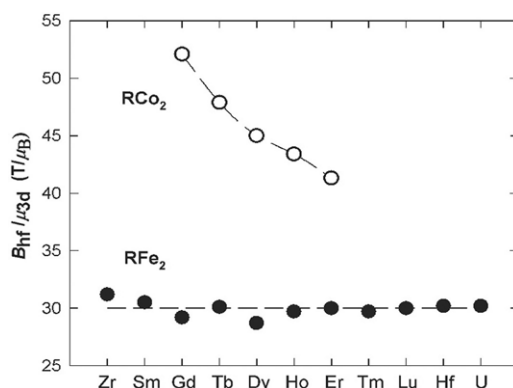
Figure 3. The B_{hf}/μ_{3d} ratio for ^{119}Sn probe atoms on the R sites of RFe$_2$ (full circles) and RCo$_2$ (open circles) compounds.

4. Discussion and conclusions

The magnetic hyperfine fields at the nuclei of nonmagnetic atoms arise from the hybridization between the valence states of the probe atom and the polarized electron states of the neighbouring magnetic atoms. The hybridization leads to the formation of bonding and antibonding states in the local density of states of the probe atom. The magnitude and sign of the B_{hf} are determined by competition between the negative contribution of the bonding states and positive contribution of the antibonding states. For Sn atoms the positive contribution to the B_{hf} dominates when the interatomic distance exceeds 0.28–0.29 nm [2]. In the RT$_2$ (T = Fe or Co) compounds, two magnetic subsystems are present; therefore, it is expected that, in principal, the polarization of the hybrid orbitals of the Sn impurity atom is governed by both 3d and 4f magnetic sublattices. However, for the RT$_2$ compounds, the relation between 3d and 4f contributions to the B_{hf} is not yet known.

In the MgCu$_2$-type structure, the R atoms occupy one crystallographic site which has 12 nearest-neighbouring Fe (Co) atoms at a distance of about 0.3 nm and four neighbouring R atoms at a somewhat larger distance. On this account, the contribution to the B_{hf} from the Fe (Co) atoms (B_{3d}) should be predominant. Following a commonly accepted approach, let us assume that the value of the B_{3d} contribution is proportional to the magnetic moment value of the T-atom (μ_{3d}). Then, $B_{3d} = 12\,\mu_{3d}\,p(R)$, where $p(R)$ is the partial contribution to B_{hf} (in units of T/μ_B), and R is the distance between the Sn atom and the neighbouring Fe or Co atoms. For all of the RFe$_2$ and RCo$_2$ compounds, the R distances are nearly identical; therefore, in the absence of a contribution from the 4f sublattice, the ratio B_{hf}/μ_{3d} should be a constant. The observed values of B_{hf}/μ_{3d} are shown in figure 3 (see also table 1). It is seen that the B_{hf} exhibit quite different behaviours in the two series of compounds. For the RFe$_2$ compounds, the ratio B_{hf}/μ_{3d} remains essentially constant across the series at a value of 30 T/μ_B (within $\pm 4\%$), likewise for nonmagnetic R = Zr, Lu and Hf. (It is interesting to note that the data for the UFe$_2$ compound is also in good agreement with the common regularity.) These surprising results show unambiguously that, in the RFe$_2$ compounds, a contribution to B_{hf} from the magnetic moments of the R atoms is absent.

In RCo$_2$ compounds, a quite different behaviour of B_{hf} is observed. As seen in figure 3, the ^{119}Sn hyperfine field increases strongly with increasing R^{3+} spin. This means that a large contribution to the B_{hf} from the rare-earth sublattice, B_{4f}, is present. From ErCo$_2$ to GdCo$_2$, the increase in B_{hf} is about 11 T. It is seen also that the 3d and the 4f contribution to the total

B_{hf} have the same relative sign. Earlier, similar behaviour of the hyperfine field for ^{111}Cd probe atoms was discovered [3, 5]. From our data, it follows that both contributions, B_{3d} and B_{4f}, are positive (that is, parallel to the 3d moments directions). It is well known that the 3d and 4f spins are always antiparallel. Therefore, the B_{4f} contribution has negative sign with respect to the R^{3+} spin direction.

As a first approximation, we may assume that the B_{3d}/μ_{3d} ratios are identical for both RFe$_2$ and RCo$_2$ compounds. The values of the B_{4f} contribution calculated in the framework of this approximation are listed in table 2. As already mentioned in [3] for Cd, the B_{4f} values are not proportional to the projection S_z of the R^{3+} ion spin on the total angular momentum. For Sn probe atoms, the same situation is observed. The significant deviations from the proportionality between B_{4f} and S_z are typical for Sn probe atoms in the rare-earth compounds. According to the analysis of the experimental data, these deviations can be explained by the strong dependence of the 4f–5d overlap on the radius of the 4f shell [6], which favours Campbell's model of the short-range 4f–5d exchange interaction [7]. In the case of intra-atomic 4f–5d exchange, the magnetic hyperfine field is produced by the overlap of the spin-polarized 5d electrons with the valence electrons of the probe. It is important to note that, for Sn probe atoms on the R sites of the RCo$_2$ compounds, the calculated B_{4f} values are in close agreement with the B_{hf} values for Sn in the magnetic compounds between rare-earth elements and nonmagnetic sp elements [6]. This means that the mechanism responsible for the transferred electron polarization of the hybrid orbitals is substantially the same for both types of compound.

The experimental results obtained in the present work and in [3, 5] show that the features of the magnetic hyperfine interaction for both Sn and Cd probe atoms on the R sites of the RCo$_2$ compounds are qualitatively rather similar. However, the magnitudes of B_{hf}, B_{3d}, and B_{4f} for Sn are considerably larger than for Cd. This difference reflects the peculiarities of the filling of bonding and antibonding hybrid orbitals for the probe atoms with the different numbers of the valence electrons. It should be emphasized that, for both Sn and Cd, the B_{3d} and B_{4f} contributions to the total hyperfine field have the same relative sign. For Sn atom, this means that both contributions are positive with respect to the direction of the 3d magnetic moments. It might be expected that, for Cd, both contributions should have the same signs. To check this suggestion, a measurement of the sign of the B_{hf} for Cd in RCo$_2$ compounds is desirable.

The most striking result of our investigation is the absence of a contribution from the 4f sublattice to the hyperfine field for Sn atoms in the RFe$_2$ compounds. This result seems especially unexpected compared to the RCo$_2$ compounds where the large B_{4f} contribution is present. Evidently, this contrast in behaviour of the transferred hyperfine field reflects important peculiarities of the electron hybridization with the interaction between rare-earth elements and transition 3d metals. It is reasonable to suppose, for example, that the transfer of the electron polarization from the R atoms to the hybrid orbitals is extremely sensitive to the delocalization of the 3d electrons, which is much larger in RCo$_2$ compared to RFe$_2$.

In summary, the present study by means of the Mössbauer spectroscopy technique has identified important characteristic features of the magnetic hyperfine interaction for ^{119}Sn probe atoms on the R sites of the RFe$_2$ and RCo$_2$ compounds:

(i) The magnetic hyperfine fields are rather large; in the GdFe$_2$ and GdCo$_2$ compounds the B_{hf} value exceeds 50 T. In all cases the sign of B_{hf} is positive with respect to the direction of the 3d magnetic moments.

(ii) In RFe$_2$ compounds, a contribution to the hyperfine field from the 4f sublattice is absent. The B_{hf} value is completely determined by the 3d spins of the Fe atoms. The ratio B_{hf}/μ_{Fe} remains essentially constant across the series at a value of 30 T/μ_B (within ±4%), likewise for R = Zr, Lu, Hf and U.

(iii) In RCo_2 compounds, the total hyperfine field is the sum of two contributions: one is the 4f contribution (B_{4f}) and the other is the 3d contribution (B_{3d}). The 3d and 4f contributions have the same relative sign; both contributions are positive with respect to the 3d magnetic moment direction. The B_{4f} contribution is relatively large: the ratio B_{4f}/B_{3d} varies from about 0.4 ($ErCo_2$) to about 0.7 ($GdCo_2$).

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