Magnetic hyperfine fields for tin atoms in RZn intermetallides

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The magnetic hyperfine (MHF) fields B for ^{119}Sn impurity atoms, replacing zinc atoms in the intermetallic compounds RZn (R = Sm, Gd, Tb, Dy, Ho), were measured by the method of Mössbauer spectroscopy. These fields and the MHF fields for ^{119}Sn atoms in rare-earth (RE) metals from gadolinium to holmium (Refs. 5–8) can be represented by linear superposition of the spin projection S_z and orbital angular momentum L_z of the RE ion: $B = aS_z + bL_z$. For ^{119}Sn atoms in RE metals and the intermetallides RZn and RAl_2 it was found that $b/a \approx -0.1$. The ratios of the strengths of the MHF fields for ^{119}Sn atoms in RE metals from gadolinium to holmium and their intermetallides RAl_2 (Ref. 3) and RZn, $B(R):B(RAl_2):B(RZn)$, do not depend on the specific RE element to within ~10%. This means that with the same accuracy the radial dependence of the partial contributions of gadolinium, terbium, dysprosium, holmium, and probably samarium ions to the MHF fields for ^{119}Sn atoms are identical.

1. INTRODUCTION

In order to construct models of the magnetic hyperfine (MHF) interaction for nonmagnetic atoms in intermetallides of rare-earth (RE) elements it is necessary to know how this interaction depends on different parameters of the matrix. The radial dependence of the partial contribution of gadolinium ions to the MHF field B for impurity tin atoms was investigated in Ref. 1 and 2. For this, the MHF fields were measured in compounds in which only the gadolinium ions have magnetic moments. It was conjectured that only this dependence is responsible for the variation in the field from one compound to another and that the field B is determined by gadolinium ions in the nearest-neighbor environment of the tin atom, i.e., according to existing experimental data (for example, Refs. 1–4) it is local. If rare-earth ions of the same type are present in the nearest-neighbor environment of the nonmagnetic atom and they are all located at the same distance from the nonmagnetic atom, then the partial contribution $p(r)$ of each RE ion to the MHF field is given simply by the ratio of the strength of this field to the number n of the nearest RE ions, i.e., $p(r) = B/n$. The range of distances between tin atoms, which replace the nonmagnetic atoms of the compounds, and their nearest-neighbor gadolinium ions was essentially the maximum possible range. The distance ranged from 0.360 nm in metallic gadolinium to 0.312 nm in GdZn.

The MHF fields for tin in heavy RE metals from gadolinium to holmium are known.[5–8] They have also been measured in RAl_2 compounds.[3] The distances between a tin atom and the RE ion closest to it are close to the maximum and minimum distances, respectively, in RE metals and RZn intermetallides and fall near the midpoint of their possible range in RAl_2 compounds. For this reason, measurements of MHF fields in RZn ferromagnets could allow the radial dependences of the partial contributions of RE ions to the field to be compared for tin atoms.

Another aim of the present work is to evaluate the spin and orbital contributions of the RE ions to the MHF field for impurity tin atoms in RZn intermetallides and to compare these contributions to the corresponding contributions to MHF fields for zinc atoms in the same compounds.[4]

In Ref. 3 it was established that the field B for impurity tin atoms in RAl_2 collinear ferromagnets with heavy and light RE elements varies, respectively, more rapidly and more slowly than linearly as a function of the spin projection S_z of the RE ion, where $B = a_0S_z$. Here $a_0 = B(GdAl_2)/7/2$, the ratio of the field in $GdAl_2$ to the spin projection of a free gadolinium ion 7/2. (The orbital angular momentum of this ion is equal to zero.) The deviations of the experimental values of the fields from this dependence were interpreted as being the result of the orbital contribution, taking into account different schemes for adding spin and the orbital angular momentum of light and heavy RE ions. The following expression was proposed for describing the MHF fields:

$$B=aS_z+ bL_z. \tag{1}$$

Here L_z is the projection of the orbital angular momentum of the RE ion, and a and b are constants, determined by fitting Eq. (1) to the experimental data.

All RZn intermetallides have a cubic structure of the CsCl form. These compounds with gadolinium and heavy RE elements are ferromagnets, and the compound with a samarium is an antiferromagnet.[9,10] It was established by means of neutron diffraction that TbZn has a collinear magnetic structure.[11]

2. EXPERIMENTAL PROCEDURE AND BASIC RESULTS

The RZn compounds were prepared by a well-known method.[4] The corresponding amounts of the RE metal, zinc and ^{119}Sn, wrapped in molybdenum foil, were heated in a quartz ampul with argon up to 1150 °C for 1 h, after which the ampul was quickly immersed in water. The tin content in the samples was equal to ~1 at. %. The purity of the samarium was 99.5%, and the purity of the other RE metals and zinc was at least 99.9%. X-ray structural analysis of the samples showed that they all have a structure of the CsCl form. Only the SmZn samples had a small admixture of an unidentified phase.

The Mössbauer absorption spectra were measured in the interval from 5 K up to magnetic-ordering temperatures on a constant-acceleration spectrometer with a $CaSnO_3$ resonance detector. The source, in the form of $CaSnO_3$, was at

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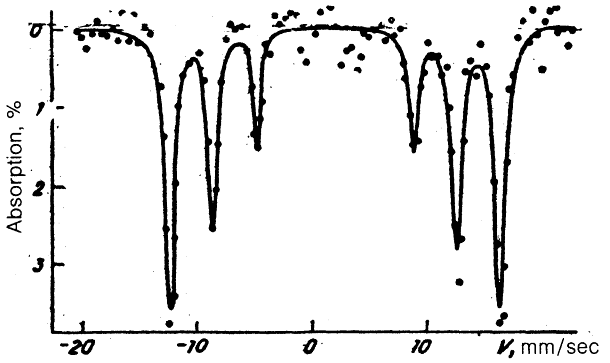

FIG. 1. Mössbauer absorption spectrum for ^{119}Sn impurity atoms in DyZn measured at 5 K.

room temperature. The samples were cooled in a continuous-flow helium cryostat.

The Mössbauer spectra include one magnetic sextet. At low temperatures the component widths are equal to ~1 mm/s, indicating that there is no significant spread in the hyperfine interaction parameters. The spectrum for tin in DyZn at 5 K is shown in Fig. 1. The spectra for tin in the other intermetallides studied had a similar form. For analysis the simple procedure of approximating the spectrum by a sum of Lorentzian lines was employed. The magnetic-ordering temperatures were determined from the temperature dependences of the MHF fields.

Our measurements with samples in an external longitudinal magnetic field up to 40 kOe at 4.2 K showed that the sign of the MHF field in TbZn is negative and they confirmed the antiferromagnetic character of the ordering of the magnetic moments in SmZn.

The basic experimental results are presented in Table I. The isomeric shifts for tin in the compounds RZn were measured relative to $CaSnO_3$, they do not depend on the RE element, and they are identical to the isomeric shifts for tin in the intermetallides of gadolinium[1,2] and RAl_2.[3]

The temperature dependences of the MHF fields B are shown in Fig. 2. They differ from the corresponding Brillouin functions. The temperature dependences $B(T)$ in GdZn, DyZn, and HoZn are close to one another and lie below the Brillouin function for spin 7/2. The temperature dependence $B(T)$ in GdZn is identical to that of the magnetization of this compound.[9]

The Curie temperatures T_C for DyZn and HoZn determined from the Mössbauer measurements are only a few degrees lower than the values determined from magnetic measurements. For TbZn and GdZn the value of T_C determined from Mössbauer measurements is less than the known values[9,10] by 10 and 20 K, respectively. The temperature of magnetic ordering in SmZn, which we measured, is higher than the value obtained from magnetic measurements of the Néel temperature (see Table I). The observed discrepancies in the magnetic-ordering temperatures could possibly reflect the differences in how they were measured.

Comparing the MHF fields for tin atoms in RE metals from gadolinium to holmium[5-8] and their RZn intermetallides gives the field ratio $B(\mathrm{RZn})/B(\mathrm{R}) = 1.10 \pm 0.10$. (For the fields in dysprosium and holmium the larger of the two values was taken, namely, 185 and 128 kOe.[7,8]) The same insensitivity to the specific RE element is characteristic for the field ratio in the RZn and RAl_2 intermetallides: $B(\mathrm{RZn})/B(\mathrm{RAl_2}) = 1.22 \pm 0.12$.

The RAl_2 (Ref. 3) and TbZn (Ref. 11) intermetallides are collinear ferromagnets. At low temperatures heavy RE metals are also collinear ferromagnets or their magnetic structure is such that the magnetic moments of the RE ions in the nearest coordination sphere do not deviate much from the direction determined by their vector sum.[12] For this reason, on the basis of the established fact that the ratios of the MHF field strengths for tin atoms in the RZn and RAl_2 compounds are constant, it can be conjectured that the intermetallides GdZn, DyZn, and HoZn, and also TbZn, have a collinear magnetic structure or at least a local magnetic structure that does not deviate much from a collinear structure.

The MHF field in the antiferromagnet SmZn was found to be ~1.3 times stronger than in the collinear $SmAl_2$ ferromagnet,[3] i.e., the ratio of the fields in these intermetallides is the same as in the ferromagnets RZn and RAl_2 with heavy RE elements, whose magnetic structure is collinear or is characterized by a small deviation from collinearity. Assuming that the MHF field is local, it is natural to explain the strength of the field in the anitferromagnet SmZn by the fact that the tin atoms are located in an environment of samarium ions, whose spins are close to one direction, which varies along the crystal lattice.

TABLE I. Magnetic hyperfine B fields and isomeric shifts (IS) relative to $CaSnO_3$ for ^{119}Sn impurity atoms in RZn intermetallic compounds at 5 K as well as the magnetic-ordering temperatures T_0 (Néel temperature for SmZn and Curie temperature for other intermetallides).

R	B, kOe (±2 кЭ)	IS, mm/s (±0.05 mm/s)	T_0, K (±2 K)	T_0, K (Ref. 10)
Sm	(+) 234	2,08	134	110—125
Gd	—355	2,05	248	268—270
Tb	—279	2,03	195	204—207
Dy	(—) 209	2,0	134	139—145
Ho	(—) 131	2,00	71	75—80

Note. The signs enclosed in parentheses are the proposed sign of the B field.

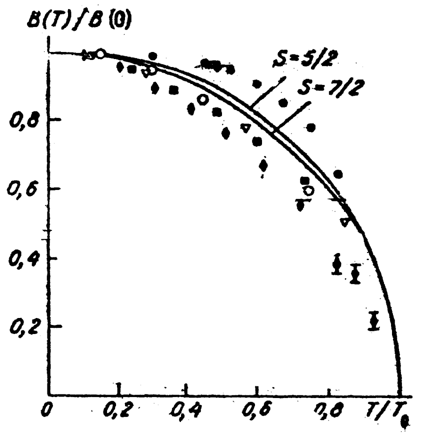

FIG. 2. Temperature dependences of the reduced magnetic hyperfine field $B(T)/B(0)$ for ^{119}Sn impurity atoms in the intermetallides SmZn (●), DyZn (○), HoZn (▽), GdZn (■), and TbZn (⧫); T_0 is the magnetic-ordering temperature (Néel temperature for SmZn and Curie temperature for other intermetallides).

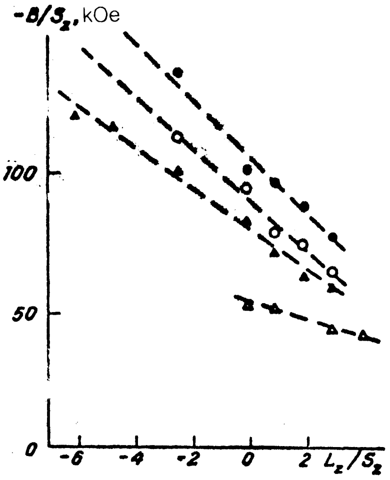

FIG. 3. $-B/S_z$ versus the ratio of the projections of the orbital angular momentum of the RE ion and its spin, L_z/S_z. The magnetic hyperfine fields B for ^{119}Sn impurity atoms in RE metals (○) and their intermetallides RAl$_2$ (+) and RZn (●) as well as for zinc atoms in RZn (×). The dashed lines were constructed by the method of least squares.

3. RADIAL DEPENDENCE OF THE PARTIAL CONTRIBUTION OF AN RE ION TO THE MHF FIELD FOR TIN ATOMS

From the established fact that the ratios of the MHF fields in gadolinium, terbium, dysprosium, holmium, and their intermetallides RAl$_2$ and RZn are the same it follows that the radial dependences of the partial contributions of the ions of three heavy RE elements and gadolinium to the MHF field for tin atoms are close to one another. The radial dependence of the partial contribution of the samarium ion to the MHF field for the same atoms is also close to them. This is indicated by the strengths of the fields in SmAl$_2$ (Ref. 3) and SmZn and the strength of the field $B = 150 \pm 20$ kOe for tin atoms in hexagonal ferromagnetic layers of samarium. It is conjectured that the field is determined by the nine samarium ions closest to the tin atom with ordered moments in adjacent hexagonal planes, while the contribution of the three other nearest samarium ions in the plane with local cubic site symmetry is equal to zero. The field B in samarium was obtained by extrapolating its measured temperature dependence to $T = 5$ K. In the range of possible distances between the nonmagnetic atom and the nearest RE ions, the partial contribution of the RE ions to the MHF field for tin atoms varies by a factor of ~ 1.7. The number of nearest RE neighbors decreases from 12 in RE metals to eight in the compounds RZn.

4. SPIN AND ORBITAL CONTRIBUTIONS TO THE MHF FIELD

In order to give a graphic illustration of the spin and orbital contributions to the MHF fields, the experimental values of the MHF fields divided by the spin projection of the RE ions, i.e., $-B/S_z$, are presented in Fig. 3 as a function of the ratio of the projections of the orbital angular momentum and the spin of the RE ion, L_z/S_z.

The values of the MHF fields for zinc in the RZn intermetallides (Ref. 4) and for tin in gadolinium and heavy RE metals (Refs. 5–8) as well as in the compound GdZn (Ref. 2) are negative. The negative sign of the field for tin in TbZn follows from our measurements in an external magnetic field. The sign of the field for tin atoms in the other cases studied was not determined. In the discussion below it is assumed that in the RZn compounds with heavy RE elements, just as in the RAl$_2$ intermetallides,[3] the B fields for tin atoms are negative. The sign of the MHF field for tin atoms in hexagonal ferromagnetic layers of metallic samarium and in the antiferromagnet SmZn is considered not relative to the total magnetization, but rather relative to the local magnetization of the nearest environment of tin atoms and is assumed to be positive.

Light RE metals have a complicated magnetic structure, and for this reason the MHF fields for tin atoms, induced by light RE ions with parallel magnetic moments, are unknown. However the results of our investigation of MHF fields in samarium[13] make it possible to evaluate the MHF field for a tin atom whose nearest-neighbor environment contains 12 samarium ions with parallel spins. The magnitude $B = 200 \pm 30$ kOe of this field follows from the extrapolated value of the MHF field for tin atoms in hexagonal ferromagnetic layers of samarium, when the magnetic moments of only 9 of the 12 nearest-neighbor samarium ions are aligned.

Estimates obtained from the experimental data were taken as the values of the projections of the spins and orbital angular momenta of heavy RE ions in RZn compounds.[14] The ratios of the estimated values of S_z and L_z are equal to their ratio for free ions. However, the difference of the estimated quantities S_z and L_z themselves from their values for free ions increases from TbZn to ErZn. In the first intermetallide the estimated values are equal to 97% of the values for the free ions and in the latter case the percentage is 76%. The extrapolated values, equal to 85% of the values for the free ion, were taken for the projections of the holmium ion in HoZn. The values for the free ion were taken for the spin and orbital angular momentum projections of the samarium ion in SmZn.

No estimates are available for the spin and orbital angular momentum projections of RE ions in RE metals, and the experimental values of their magnetic moments, as is well known, are several percent greater than the corresponding

TABLE II. Coefficients in the relation (2) for the MHF field for impurity tin atoms in RE metals and their intermetallides RZn and RAl_2 as well as for zinc atoms in the RZn intermetallides.

Matrix	Nonmagnetic atom	a, kOe/spin	b, kOe/orbital angular momentum	$-b/a$
R	Sn	−91	9,2	0,10
RAl_2	Sn	−81	7,2	0,089
RZn	Sn	−105	9,5	0,090
RZn	Zn	−53	3,2	0,061

values for the free ions. For this reason, the free-ion values of the projections were employed for ions in RE metals.

If the strength of the MHF field were proportional only to the projection of the spin of a RE ion, then the ratio B/S_z would not depend on the type of ion, i.e., the values of L_z/S_z for it. Meanwhile, the values of the ratio $-B/S_z$ for compounds with light and heavy RE metals (see Fig. 3) are greater and less, respectively, than in the analogous compound of gadolinium, whose ion has a zero orbital angular momentum. The schemes for adding the spin and orbital angular momentum of light and heavy RE ions in the ground states are different. These moments are parallel in heavy ions and antiparallel in light ions. From the data presented in Fig. 3 it is evident that the sign of the orbital contribution to the MHF field (bL_z) is opposite to that of the spin contribution (aS_z). The experimental data show clearly that for fields in compounds with light RE elements the spin and orbital contributions are added, while in intermetallides with heavy elements spin and orbital contributions subtracted. The sign of the MHF field B is opposite to that of the projection of the spin S_z of the RE ion, i.e., the field and spin are antiparallel.

It is obvious that the experimental data in Fig. 3 correspond quite well to the linear dependence of the field B on the spin and orbital angular momentum projections. For this reason we employ the relation (1) to compare the spin and orbital contributions to the MHF field for tin and zinc atoms in RZn compounds and for tin atoms in RE metals. The least-squares values of the coefficients a and b are presented in Table II.

The coefficient a is proportional to the strength of the field B in gadolinium and its intermetallides and its values reflect the changes in these fields. The ratios $-b/a$, of the coefficients, characterizing the ratio of the orbital and spin contributions, for fields at the tin nuclei in RE metals and their intermetallides are close and on the average equal to ~ 0.09. Thus the existing experimental data indicate that the ratios b/a of the coefficients for MHF fields at tin nuclei in RE intermetallides are independent of the distance between their atoms and RE ions closest to them.

The ratios $-b/a$ for MHF fields at tin nuclei are ~ 1.5 times greater than for fields on zinc nuclei in RZn compounds, but they are approximately the same as for fields at aluminum nuclei in RAl_2 compounds.[3] Our coefficients for MHF fields in RAl_2 intermetallides (see Table II) are somewhat different from those calculated in Ref. 3, since we employed the values given in Ref. 14 for the projections of the moments of the RE ions; this is important for representing data for compounds with neodymium and praseodymium.

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[1] N. N. Delyagin, G. T. Mudzhiri, V. I. Nesterov, and S. I. Reiman, Zh. Eksp. Teor. Fiz. **86**, 1016 (1984) [Sov. Phys. JETP **59** (3), 592 (1984)].

[2] N. N. Delagin, V. V. Krylov, G. T. Mujiri *et al.*, Phys. Status Solidi B **131**, 555 (1985).

[3] N. N. Delyagin, V. I. Krylov, N. I. Moreva *et al.*, Zh. Eksp. Teor. Fiz. **88**, 300 (1985) [Sov. Phys. JETP **61** (1), 176 (1985)].

[4] K. Eckrich, E. Dorman, A. Oppelt, and K. H. J. Buschow, Z. Phys. B **23**, 157 (1976).

[5] V. Gotthardt, H. S. Moller, and R. L. Mössbauer, Phys. Lett. A **28**, 480 (1969).

[6] M. Forker and K. Kruch, Hyperfine Interaction **9**, 399 (1981).

[7] S. K. Godovikov, M. G. Kozin, V. V. Turovtsev, and V. S. Spinel, Phys. Status Solidi B **78**, 103 (1976).

[8] S. K. Godovikov, P. V. Bogdanov, M. G. Kozin, and N. I. Moreva, Fiz. Tverd. Tela **23**, 990 (1981) [Sov. Phys. Solid State **23**, 573 (1981)].

[9] K. Kanemantsu, G. T. Alfieri, and E. Banks, J. Phys. Soc. Jpn. **26**, 244 (1969).

[10] K. H. J. Buschow, Rep. Progr. Phys. **42**, 1373 (1979).

[11] J. W. Cable, W. C. Koehler, and E. C. Wollan, Phys. Rev. **130**, 240 (1964).

[12] S. A. Nikitin, *Magnetic Properties of Rare-Earth Metals and Alloys* [in Russian], Moscow, 1989, p. 21.

[13] S. I. Reiman, N. I. Rokhlov, I. N. Rozantsev, and F. D. Khamdamov, Izv. Akad. Nauk SSSR, Ser. Fiz. **50**, 2392 (1986).

[14] E. Belorizky and Y. Berthier, J. Phys. F **16**, 637 (1986).

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