



Fast-track Communication

The impact of quadrupole moment of 4f shell on the hyperfine interactions anisotropy in RAl_2 ($R=Sm, Tb$) intermetallic compounds

N.N. Delyagin*, A.L. Erzinkyan

Institute of Nuclear Physics, Moscow State University, 119992 Moscow, Russia

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ABSTRACT

The magnetic hyperfine interactions for ^{119}Sn impurity atoms in SmAl_2 and TbAl_2 ferromagnetic compounds have been investigated by Mössbauer spectroscopy technique. These compounds have the same structure but differ in the sign of the quadrupole moment of the R^{3+} ion. In both cases, the spectrum contains two magnetic subspectra with the ratio of the intensities 1:3, which correspond to a and b Al sites with significantly different hyperfine parameters. The phenomenon change the order the component of inversion component of the Mössbauer spectra was found. This phenomenon is explained by the influence of the quadrupole moment 4f-shell of R^{3+} ions on the electron density distribution in the valence band. The degree of overlap of electron wave functions being on hybrid orbitals greatly depends on the sign of the 4f-shell quadrupole moment, which gives rise to huge anisotropy in the hyperfine magnetic field and the electric field gradient. Quadrupole deformation induced by the 4f quadrupole moment and the electric field gradient, greatly affects the d-like and p-like components of the electron wave functions, but little effect on the its s-components.

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1. Introduction

It is well known that the charge distribution of the rare-earth (R) 4f-electrons lies deep inside the R^{3+} ions. The effective radius of the 4f-shell is 10–30% of the ionic radius. Nevertheless, the size and the shape of 4f-electron distribution may have an important effect on some properties of the rare-earth systems. In the metallic state, the effect is governed by strong 4f–5d–6s-electrons hybridization [1,2]. For example, it was shown that the magnitude of the effective radius of 4f-shell has profound effect on the transfer of electron polarization from magnetic 4f-electrons to valence electron orbitals [3]. The phenomenon leads to huge deviation from the proportionality between the transferred magnetic hyperfine field and the spin of R^{3+} ion.

Of particular interest are the phenomena caused by the presence of the electric quadrupole moment of R^{3+} ions. Quadrupole moment is present in all ions with orbital angular momentum is nonzero. Non-sphericity of R^{3+} ion characterized by the second-order Steven's factor α [4], which is associated with the quadrupole moment $Q(4f)$ by the equation:

$$Q(4f)/a_0^2 = \alpha \langle R_{4f} \rangle^2 (2J^2 - J)/a_0^2 \quad (1)$$

Here $\langle R_{4f} \rangle$ is the effective radius of 4f-shell, J is angular momentum of the R^{3+} ion, a_0 is Bohr radius. Normalized quadrupole moment $Q(4f)/a_0^2$ is a dimensionless parameter describing the deviation of the 4f-distribution from a spherical shape. Quadrupole moment changes its magnitude and sign depending on the number of electrons in the 4f-shell of the ion. The shape of the 4f electron charge density is an oblate spheroid when $\alpha < 0$ or a prolate spheroid when $\alpha > 0$. In this regard, the series of rare-earth elements provides a good opportunity to study the quadrupole effects. For several decades ago, it was discovered the effect of quadrupole moment on the anisotropic magnetoresistance of dilute alloys of gold containing rare-earth impurities [5]. Recently, very interesting magnetic phenomena were discovered in a series of studies pseudobinary $(R, R')Al_2$ compounds in which R and R' ions have opposite signs of the second order Steven's factors (see [6–8] and references therein). Compounds containing a combination of two rare earth elements, which are represented by the opposite signs of the second-order Steven's factors, exhibit unusual electronic and magnetic properties which can be attributed to the presence of competing contributions to a single-ion magnetic anisotropy. Multiple magnetic ordering observed in these pseudobinary compounds strongly correlated with the values and signs of the quadrupole moments of the R^{3+} ions.

In this paper, we present data on a new phenomenon: the influence of the quadrupole moment of the R^{3+} ion on the anisotropy of the hyperfine interaction parameters. The data obtained by the Mössbauer spectroscopy of impurity atoms ^{119}Sn in

* Corresponding author.

E-mail address: delyagin@srd.sinp.msu.ru (N.N. Delyagin).

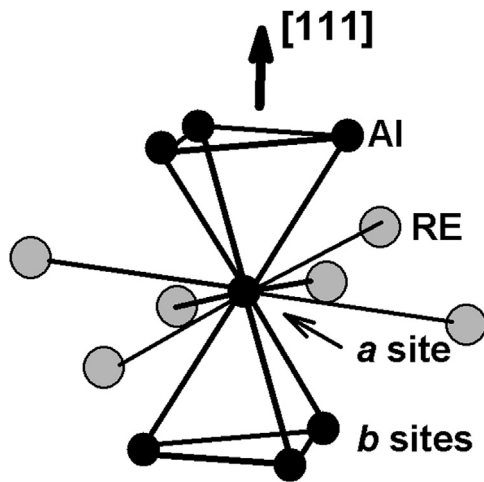


Fig. 1. A fragment of the crystal structure SmAl₂ and TbAl₂ compounds. Each *a*-site has six nearest R³⁺ neighbors; *b*-sites have the same near magnetic environment, but which is oriented at an angle of 70.5° relative to the axis of magnetization [111].

ferromagnetic intermetallic compounds RAl₂. Anisotropy of the magnetic hyperfine field for Sn atoms has been discussed repeatedly in the literature (see, for example, [9,10] and references therein). However, the effect of the quadrupole moment of the R³⁺ ion on the parameters of the hyperfine interactions has never been observed and discussed. The subjects of this study were selected compounds SmAl₂ and TbAl₂ with the largest quadrupole moments of opposite sign (+0.37 for Sm and −0.55 for Tb).

The RAl₂ Laves-phase compounds crystallize in cubic C15 structure (MgCu₂-type). In this structure, the Al atoms located at the vertices of tetrahedra which center the octants of the cubic lattice of the R atoms. All the Al sites structurally equivalent and possess rhombohedral point symmetry, with the third-order axis pointing along one of the [111] axes. The nearest magnetic neighbors of the Al atoms are six R atoms located near the equatorial plane perpendicular to the local [111] axis (Fig. 1). For each Al site, the principal axis of the electric field gradient (EFG) tensor is directed along the local threefold axis of symmetry (i.e. towards the center of tetrahedron). The SmAl₂ and TbAl₂ are collinear ferromagnetic compounds, in which the magnetic moments of R³⁺ ions are oriented along the crystallographic [111] axis [11,12]. In this case, the structurally equivalent Al sites are essentially nonequivalent from the point of view of the parameters of the hyperfine interactions. Two groups of nonequivalent Al sites (sites *a* and *b* in Fig. 1) with population ratio *a*:*b*=1:3 arise. The principal axis of EFG tensor for *a* sites coincides with the magnetization direction (and with the magnetic hyperfine field, *B*_{hf}), whereas for *b* sites principal axis of EFG tensor makes an angle $\theta=70^\circ32'$ ($\cos\theta=1/3$) with the *B*_{hf} direction.

It was previously shown that Sn impurity atoms are localized exclusively in the Al sites of RAl₂ compounds [13]. Anisotropy of the hyperfine interactions occurs as a result of the asphericity of the electron density distribution of the valence electrons on hybrid bonds Sn–R. This asphericity results in significantly different degrees of the overlapping distributions of electron density in the valence orbitals. This allows observing the anisotropy of the hyperfine interactions by analyzing the Mössbauer spectra for polycrystalline samples without the application of an external magnetic field.

2. Experimental details

Polycrystalline samples of SmAl₂ and TbAl₂ compounds were prepared by arc melting of high-purity metals under argon atmosphere. The 0.3 at% fraction of Al was substituted by Sn enriched by

the ¹¹⁹Sn isotope. In order to ensure appropriate homogeneity the ingots were turned over and remelted several times. The samples were annealed at 1200 K for 48 h and at 900 K for 72 h. In order to check the purity of the alloys the samples were examined by X-ray powder diffraction. Analysis of the data showed the MgCu₂-type structure without visible contamination by the other phase. The purity of the samples confirmed the results of the analysis of the Mössbauer spectra, which is not detected any foreign components.

Mössbauer absorption spectra were measured at 5 K using 23.9 keV radiation from a CaSnO₃ source. In order to enhance the effect of resonance absorption and resolution in detecting the Mössbauer spectra, a resonance CaSnO₃-based detector was used. The spectra were least-squares fitted with a superposition of discrete magnetic subspectra. Three hyperfine parameters (hyperfine field, *B*_{hf}, quadrupole shift, *QSH*, and isomer shift, *IS*), as well the linewidths and the intensities of subspectra were the adjustable parameters.

3. Results and discussion

The Mössbauer spectra of ¹¹⁹Sn in SmAl₂ and TbAl₂ compounds measured at 5 K are shown in Fig. 2. The obtained hyperfine parameters of the magnetic subspectra are listed in Table 1. Each of the two spectra comprises two subspectra with intensity ratio 1:3. Thus, these two subspectra clearly identified as relevant to the impurity atoms Sn localized in *a*- and *b*- Al sites, respectively (as shown in Fig. 2). As seen from Table 1, the hyperfine parameters of *a*- and *b*- Sn (Al) sites are significantly different. Since all the sites are structurally equivalent, the observed difference of the hyperfine parameters must be explained anisotropy of Sn–R interatomic interaction.

The inspection of Fig. 2 shows an unusual behavior of the components of the Mössbauer spectra ¹¹⁹Sn in SmAl₂ and TbAl₂ compounds. Namely, there is the phenomenon change the order of the arrangement components of the magnetic hyperfine structure in the spectra. As seen from Fig. 2, in SmAl₂ magnetic hyperfine field is larger for *b*-sites than for *a*-sites while in TbAl₂ situation is the opposite: the hyperfine field for *a*-sites greater than for *b*-sites. Since both compounds, SmAl₂ and TbAl₂, have the same crystallographic and magnetic structures, observed inversion of the component of the hyperfine structure should be explained by the difference of intra-atomic properties of Sm³⁺ and Tb³⁺ ions. The most important difference is the opposite of the sign of the quadrupole moment. The 4f charge density of Sm³⁺ ion is a prolate spheroid, whereas the 4f charge density of Tb³⁺ is shaped as oblate spheroid (with respect to the magnetic axis [111]). Following the original Campbell's hypothesis [1], it should be taken into account the dominant influence of the 4f–5d exchange interaction on the interatomic bonds in the rare-earth systems. Nonsphericity of 4f electron density induces a proper nonsphericity of the electron distribution in the valence orbitals, which polarization is responsible for the hyperfine fields. This nonsphericity should depend on the sign of the quadrupole moment R³⁺ ion.

There are two sources of nonsphericity of the valence electron density. The first of them is determined by EFG at Sn(Al) site. In Mössbauer spectra the quadrupole interaction is manifested as a shift component of the magnetic hyperfine structure. In the case of axially symmetric EFG, quadrupole shift and quadrupole coupling constant e^2qQ , where *e* is the electron charge, *q* is the electric field gradient and *Q* is nuclear quadrupole moment, are connected by the equation:

$$QSH = (e^2qQ/8)(3\cos^2\theta - 1) \quad (2)$$

Thus, for the Sn atoms localized in *a*- and *b*- sites the quadrupole shifts are equal to:

$$QSH(a) = e^2qQ/4 \text{ and } QSH(b) = -e^2qQ/12 \quad (3)$$

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