Anisotropic hyperfine interaction for ^{119}Sn impurity atoms in the ferrimagnet TmFe$_2$

N. N. Delyagin, G. T. Mudzhiri, V. I. Nesterov, and A. K. Churakov

Institute of Nuclear Physics of the M. V. Lomonosov State University, Moscow

(Submitted 24 May 1985)
Zh. Eksp. Teor. Fiz. **89**, 2149–2155 (December 1985)

A Mössbauer spectroscopy study is made of the magnetic hyperfine interaction (MHI) for ^{119}Sn atoms substituted for Fe atoms in the ferrimagnetic intermetallic compound TmFe$_2$. At 77 K the local magnetic fields for the Sn atoms in the *a* and *b* sites of the Fe sublattice are 8.32 ± 0.03 and 5.50 ± 0.02 T, respectively. The magnetic hyperfine fields (found after correcting for the dipole field) are $B_{\rm hf}(a) = 9.72$ T and $B_{\rm hf}(b) = 4.99$ T. The isotropic and anisotropic components of $B_{\rm hf}$ are 6.17 T and 3.55 T, respectively. The magnetic hyperfine field is antiparallel to the magnetization of the Fe sublattice. Analysis of the temperature dependence of $B_{\rm hf}$ and the structure of the Mössbauer spectra of ^{119}Sn in the alloys (Tm,Y)Fe$_2$, (Tm,Gd)Fe$_2$, and Tm(Fe,Al)$_2$ implies that the MHI for Sn impurity atoms in TmFe$_2$ is determined entirely by the Fe sublattice. The parameters found for the MHI and the giant anisotropy of $B_{\rm hf}$ are interpreted with the aid of a two-component model of the MHI.[4] The lack of a contribution to $B_{\rm hf}$ from the Tm sublattice is treated as a consequence of the correlation between the MHI parameters and the peculiar features of the chemical bond of the Sn impurity atom with neighboring magnetic atoms.

1. INTRODUCTION

We have recently reported the results of a study of the magnetic hyperfine interaction (MHI) for ^{119}Sn impurity atoms in the ferromagnetic intermetallides of gadolinium[1,2] and in the intermetallides RAl$_2$ (R is a rare earth element).[3] It follows from these results, in particular, that the MHI for a nonmagnetic atom in rare earth magnets is characterized by an extremely small effective radius. The partial contributions to the magnetic hyperfine field $B_{\rm hf}$ fall off rapidly with increasing Sn–R distance (approximately as r^{-5}) and become negligible for $r \gtrsim 6$ Å. For Sn atoms $B_{\rm hf}$ is determined entirely by the magnetic R atoms in the nearest coordination spheres. These results are in sharp contrast to the data on the MHI for Sn atoms in alloys of *d* transition metals, where, in addition the negative contribution to $B_{\rm hf}$ from the nearest magnetic atoms, there is a large positive contribution proportional to the average magnetization of the alloy, and due to the more remote magnetic neighbors.[4] Such a sharp difference in the properties of the MHI for two systems of metallic magnets is unexpected and is hard to explain in the framework of the traditional theoretical models.

The standard procedure used to interpret the MHI for nonmagnetic atoms in metallic magnets is based on consideration of the Fermi contact interaction with the polarized *s* electrons of the conduction band. Such an approach would seem to be particularly correct for rare earth magnets, in which, in accordance with the assumption, there is clearly no direct overlap of the wave functions of the magnetic 4*f* electrons and the electrons of neighboring atoms. In this approximation one expects that the MHI for a nonmagnetic atom in magnetic alloys of the rare earth elements will be determined exclusively by the interaction with the conduction electrons, which is usually treated as a long-range interaction covering a large number of lattice sites. However, the experimental data imply that it is precisely in rare earth magnets that the MHI for a nonmagnetic atom is most highly local in character.

To explain this paradoxical result it seems necessary, in particular, to elucidate the nature of the collective (nonlocal) positive contribution to $B_{\rm hf}$ in alloys of *d* transition metals and to find out why this contribution is absent in rare earth magnets. It has been conjectured[2] that a possible means of achieving this goal is to study the MHI in magnets of this kind containing both *R* atoms and magnetic 3*d* atoms. Among the systems of this kind the intermetallides RFe$_2$, which have a simple crystal structure and a high concentration of both components, seem especially convenient for study. In this paper we report the first results obtained in this program of studies, for Sn impurity atom in the ferrimagnetic intermetallide TmFe$_2$.

We note that it is often quite difficult to obtain solid solutions of tin in rare earth intermetallides. In the process of melting, the tin interacts energetically with the components of the alloy, forming intermetallides of unknown composition. A subsequent annealing will by no means always decompose these intermetallides and stabilize the solid solution.[1-3] For alloys between rare earths and transition metals the difficulties here are especially great. The Tm–Fe phase diagram is one of the most favorable in this regard, and we were able to obtain a stable solid solution of tin in TmFe$_2$ and to made a detailed study of the MHI for ^{119}Sn impurity atoms in this system.

2. PROPERTIES OF TmFe$_2$. EXPERIMENTAL TECHNIQUES

The basic properties of the intermetallides TmFe$_2$ are well known. It has a *C* 15 cubic structure (of the MgCu$_2$ type, with a lattice constant of 7.247 Å) and is a ferrimagnet with a Curie temperature $T_C = 566$–580 K (Ref. 5). At low tem-

0038-5646/85/121240-04$04.00

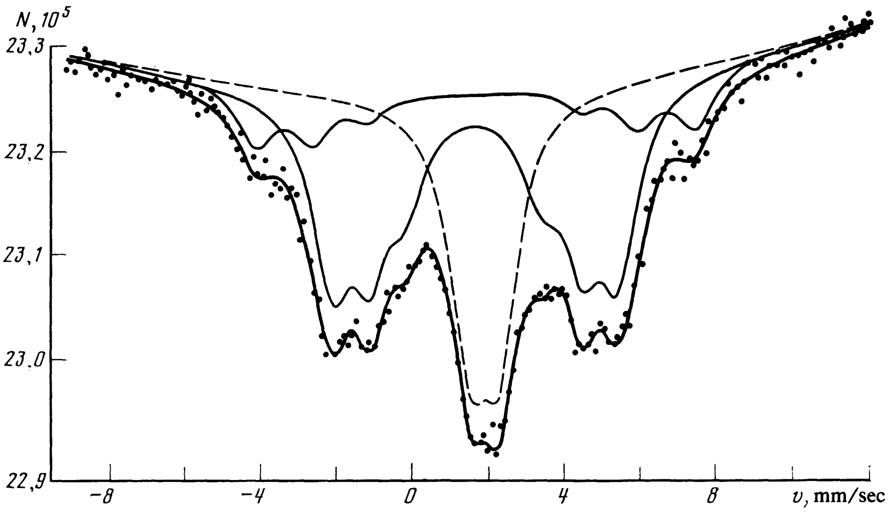

FIG. 1. Mössbauer absorption spectrum for ^{119}Sn impurity atoms in TmFe$_2$, measured at 77 K. The light solid curves show the two partial spectra corresponding to Sn atoms in the *a* and *b* sites of the Fe sublattice. The dashed curve shows the nonmagnetic doublet of an extraneous phase (see text).

peratures the magnetization of the Tm sublattice is higher than that of the Fe sublattice, but as the temperature is raised the magnetic moment of the Tm^{3+} ion decreases rapidly, and at temperatures above 240 K (the compensation point) the direction of the resultant moment is determined by the Fe sublattice.[6] According to the Mössbauer spectroscopy data[7,8] and the results of magnetic measurements of single crystals,[6] the spontaneous magnetic moment is oriented along the crystallographic axis [111].

At low temperatures the saturation magnetic moment per formula unit is $3.72\mu_B$ (Ref. 6). Analysis of the hyperfine interaction parameters for Tm has shown[8] that the magnetic moment μ(Tm) in TmFe$_2$ is $7.0\mu_B$, practically the same as the value for the free Tm^{3+} ion (see also Ref. 9). Taking this value, we obtain the value $\mu(\mathrm{Fe}) = 1.64\mu_B$ for the moment of the Fe atom. The hyperfine interaction for Fe and Tm in TmFe$_2$ has been studied in detailed by Bleaney *et al.*[8]

In this study we used Mössbauer spectroscopy to investigate the MHI for ^{119}Sn impurity atoms substituted for Fe atoms in TmFe$_2$. The alloys were prepared by arc or induction melting in argon. The metals used were at least 99.9% pure. Metallic tin enriched with the isotope ^{119}Sn was introduced into the iron prior to the melting. Several alloys were prepared, with small variations in the concentrations of the components (in most cases with an excess of thulium) but the results were practically independent of the degree of stoichiometry of the nominal composition. We also studied the alloys $(\mathrm{Tm}_{1-x}\mathrm{R}_x)\mathrm{Fe}_2$ and $\mathrm{Tm}(\mathrm{Fe}_{1-x}\mathrm{Al}_x)_2$ (R = Y, Gd; $x = 0.05$ and 0.10). The ingots were annealed in vacuum at temperatures of 700–800 °C for 100 hours. Measurements of the Mössbauer spectra for ^{57}Fe revealed that such an annealing was sufficient to yield well-ordered single-phase alloys. The parameters found for the Mössbauer spectra of ^{57}Fe in TmFe$_2$ are in good agreement with the data of Ref. 8. The concentration of impurity tin in the alloys varied from 0.4 to 1.5 at. %. The parameters of the hyperfine structure depended weakly on the tin concentration, but at high concentrations we observed a broadening of the hyperfine-structure components. The data discussed below is for alloys containing not more than 0.5 at. % Sn.

The spectra of the Mössbauer absorption of the 23.9-keV gamma rays of ^{119}Sn were measured in the temperature range 77–450 K for a CaSnO$_3$ source kept at room temperature. To determine the sign of B_{hf} the spectra were measured in an external magnetic field with an induction of 0.9 T; the sign of the field was determined at temperatures of 77 and 293 K (below the above the compensation point). To determine the parameters of the hyperfine structure we used the procedure of approximating the spectra by the sum of the Lorentzian lines using the program described in Ref. 10. The other details of the experimental and data-processing techniques are given in our previous papers.[1–3]

The features of the Mössbauer spectra of ^{119}Sn in cubic Laves phases with the *C* 15 structure have been considered previously.[1,3] If (as in the case of TmFe$_2$) the magnetic axis is [111], the localization of the Sm atoms in the Fe sites should lead to the observation of two sextets with an intensity ratio of 1:3 (the *a* and *b* sites in the tetrahedra formed by the Fe atoms). For Fe sites in the *C* 15 structure do not have a cubic local symmetry, and their nonequivalence is due to the anisotropy of the dipolar magnetic field and hyperfine interaction. The spectra for Sn in TmFe$_2$ had just such a character, clearly indicating that the impurity atoms were localized in the Fe sites. (We note that a similar type of localization occurs in the cubic phases of RAl$_2$, where the Sn impurity atoms substitute for Al atoms[1,3].)

As we mentioned in the Introduction, during the preparation of rare earth intermetallides with tin impurities a certain portion of the tin, as a rule, does not form a solid solution and is present in the form of an extraneous phase. In the present case this circumstance led to the appearance of a nonmagnetic doublet in the central part of the spectrum, with an intensity that varied depending on the tin concentration. In the processing of the spectrum this doublet was approximated by two Lorentzian lines of arbitrary intensity.

3. RESULTS AND DISCUSSION

Figure 1 shows the measured Mössbauer absorption spectrum for ^{119}Sn in TmFe$_2$ at 77 K. As expected for the case of impurity atoms localized in Fe sites, the spectrum consists of two sextets with an intensity ratio of 1:3. The

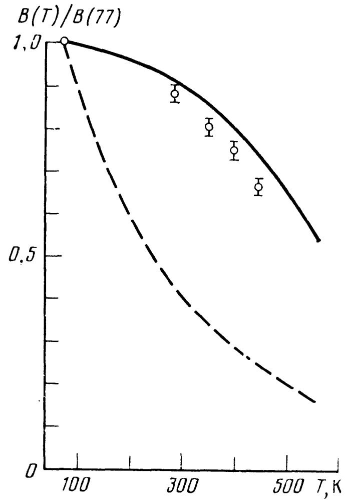

FIG. 2. Temperature dependence of $B_{\mathrm{eff}}(T)$ for Sn impurity atoms in $\mathrm{TmFe_2}$. The experimental points correspond to Sn atoms in the b sites of the Fe sublattice. The lines show the temperature curves of B_{hf} measured by Bleaney *et al.*[8] for Fe atoms (solid curve) and Tm atoms (dashed curve).

observed magnetic field B_{eff} for the two nonequivalent sites are substantially different, indicating that the MHI is highly anisotropic on account of the dependence of B_{eff} on the angle θ between the magnetic axis and the local threefold symmetry axis.[1,3] For the a sites ($\theta = 0°$) we have $B_{\mathrm{eff}} = 8.32 \pm 0.03$ T, and for the b sites ($\theta = 70.5°$) $B_{\mathrm{eff}} = 5.50 \pm 0.02$ T. The sign of B_{eff} is positive at 77 K (below the compensation point). This means that the magnetic hyperfine field is antiparallel to the orientation of the magnetic moments $\mu(\mathrm{Fe})$.

Figure 2 shows the temperature dependence of the magnetic field $B_{\mathrm{eff}}(T)$. For comparison, we also show the temperature curves $B_{\mathrm{hf}}(T)$ for Fe and Tm; the latter are to good accuracy proportional to the temperature curves for the corresponding atomic magnetic moments.[8] It is seen that over the entire range of temperatures studied, $B_{\mathrm{eff}}(T)$ is nearly the same as the temperature dependence of the spontaneous magnetization of the Fe sublattice. (The slight difference of these curves may be due to the temperature dependence of the dipole field; see below). This result means that B_{hf} for Sn atoms in $\mathrm{TmFe_2}$ is determined by the Fe sublattice; the contribution from the Tm sublattice is too small to be observable (if not absent altogether). Otherwise the $B_{\mathrm{eff}}(T)$ curve would be substantially sharper, since the moment $\mu(\mathrm{Tm})$ is very strongly temperature dependent. This conclusion is all the more unexpected since the rare earth ions in the intermetallides $\mathrm{RAl_2}$ create large hyperfine fields at the Sn nuclei.[1,3] If the role of the rare earth sublattice in $\mathrm{TmFe_2}$ were analogous to that in the $\mathrm{RAl_2}$ intermetallides, the contribution to B_{hf} from the Tm sublattice in $\mathrm{TmFe_2}$ would be close to 9 T; this would be easily detected experimentally.

To check this result we made some measurements with the alloys $\mathrm{(Tm,Y)Fe_2}$ and $\mathrm{(Tm,Gd)Fe_2}$, in which the Tm atoms were partially replaced by either Y atoms, which are nonmagnetic, or Gd atoms, which have a larger spin. It was found that such a substitution of atoms in the rare earth sublattice had no effect on the shape of the spectrum or on the value of B_{eff} for the Sn impurity atoms. Thus it was confirmed that the MHI for Sn in $\mathrm{TmFe_2}$ is entirely determined by the iron sublattice. The partial replacement of the Fe atoms by the nonmagnetic atoms Al is accompanied by a very strong decrease in B_{eff} for the Sn impurity atoms. the Mössbauer spectra of $^{119}\mathrm{Sn}$ in the alloys $\mathrm{Tm(Fe_{1-x}Al_x)_2}$ ($x = 0.05$ and 0.10) were compared to the model spectra calculated under various assumptions about the relationship between the local and collective contributions to B_{hf}. The results of the comparison showed that the replacement of one Fe atom among the nearest neighbors of an Sn atom by a nonmagnetic Al atom decreases B_{hf} by approximately one-half. Clearly, such a strong influence of the atoms of the nearest coordination sphere on B_{hf} is possible in the case when B_{hf} is actually the sum of two large contributions of opposite sign (as is the case for Sn atoms in transition metal alloys[4]).

For quantitative interpretation of the data we must determine the value of B_{hf} after correcting for the dipolar magnetic field B_d (which in this case is not small compared to the hyperfine field B_{hf}). The observable field $\mathbf{B}_{\mathrm{eff}}$ is the vector sum

$$\mathbf{B}_{\mathrm{eff}} = \mathbf{B}_{\mathrm{hf}} + \mathbf{B}_d, \tag{1}$$

where the magnitude and orientation of $\mathbf{B}_d$ is different for the a and b sites of the Fe sublattice. The vector components of $\mathbf{B}_d$ were calculated by a method discussed by Bowden and co-workers.[11] For the a sites the vectors $\mathbf{B}_{\mathrm{hf}}$ and $\mathbf{B}_d$ are collinear and antiparallel; the absolute value of $\mathbf{B}_d$ is 1.4 T. Thus to determine the magnitude of B_{hf} at the a sites we must add -1.4 T to $B_{\mathrm{eff}}(a)$, i.e., $B_{\mathrm{hf}}(a) = -9.72$ T. (The sign of B_{hf} is given relative to the direction of the magnetic moments of the Fe atoms.) For each of the b sites there is one nonzero projection of $\mathbf{B}_d$ onto the axes of the cubic coordinate system, i.e., in this case the vector $\mathbf{B}_{\mathrm{hf}}$ and $\mathbf{B}_d$ form an angle of 54.7°. From relation (1) for this case we find $B_{\mathrm{hf}}(b) = -4.99$ T. The fact tht $B_{\mathrm{hf}}(a)$ is almost twice as large as $B_{\mathrm{hf}}(b)$ means that the anisotropy of the hyperfine interaction is unusually high.

To determine the isotropic and anisotropic components of B_{hf} we use the same formula for the angular dependence of B_{hf} that was used to examine the anisotropy of the hyperfine interaction in the $\mathrm{RAl_2}$ intermetallides[3]:

$$B_{\mathrm{hf}}(\theta) = B_{is} + B_{an}(3\cos^2\theta - 1)/2, \tag{2}$$

where B_{is} and B_{an} are the isotropic and anisotropic components of the hyperfine field, θ is the angle between the magnetic axis and the local threefold symmetry axis (for the a and b sites the angle θ is equal to 0 and 70.5°, respectively). Using the values of $B_{\mathrm{hf}}(a)$ and $B_{\mathrm{hf}}(b)$ found above, we find from (2) that

$$B_{is} = -6.17\ \mathrm{T}, \quad B_{an} = -3.55\ \mathrm{T}, \quad B_{an}/B_{is} = 0.58,$$

i.e., the anisotropic component of B_{hf} is almost 60% of the isotropic component. At first glance such a large anisotropy of B_{hf} seems unexpected and hard to explain. We shall show that both the value of B_{hf} and its anisotropy find a natural explanation in terms of a two-component model based on analysis of the experimental data on the MHI for Sn atoms in alloys of d transition metals.[4]

According to this model, B_{hf} can be represented as the sum of contributions of comparable size and opposite sign: a negative contribution due to the nearest magnetic neighbors, and a positive contribution determined by more remote magnetic atoms and proportional to the average magnetic moment of the alloy. In TmFe_2 the nearest neighbors of the tin atom are 6 iron atoms at a distance of 2.56 Å, and the expression for B_{hf} has the following form[4]:

$$B_{\text{hf}} = 6\mu(\text{Fe})\,p(2.56) + 20\bar{\mu}, \qquad (3)$$

where $\mu(\text{Fe}) = 1.64\mu_B$, $\bar{\mu}$ is the average atomic moment of the alloy, equal to $1.09\mu_B$, and $p(2.56)$ is the partial contribution to B_{hf} from a moment of $1\mu_B$ located a distance of 2.56 Å away. Substituting $B_{\text{hf}} = B_{is} = -6.17$ T into (3), we find $p(2.56) = -2.8\ T/\mu_B$, in good agreement with the data obtained previously for Sn atoms in transition metal alloys (see Table II in Ref. 4). Thus we arrive at the conclusion that the MHI for Sn atoms in TmFe_2 not only is determined entirely by the Fe sublattice but also quantitatively obeys the same rules which govern the behavior of B_{hf} in systems which do not contain magnetic $4f$ electrons. The presence of the Tm^{3+} ions, with their large magnetic moment, has no influence on either the negative (local) or positive (collective) contribution to B_{hf} in TmFe_2.

In the framework of the two-component model the giant anisotropy of B_{hf} is to a certain extent only apparent, since the anisotropic component B_{an} should be compared in relative size not to the resultant (observable) field B_{hf} but to the partial contributions to B_{hf}, each of which is much larger than the observed field B_{hf}. It follows from (3) that the negative and positive contributions to B_{hf} are -28 and $+21.8$ T, and so the anisotropy in fact does not exceed 20%. Approximately the same value has been observed[12] for Sn impurity atoms in SmAl_2. In a previous discussion of the anisotropic contribution to B_{hf} in the RAl_2 intermetallides,[3,12] it was assumed that at least part of the anisotropic component B_{an} is due to a nonspherical distribution of the $4f$ electrons of the R^{3+} ions. Since the Tm^{3+} ions in TmFe_2 do not contribute to the MHI, this factor cannot be important in the present case, and the anisotropy of the MHI should be determined by the anisotropic polarization of the electrons in the Sn–Fe interaction. It is extremely likely that the strong anistropy is characteristic of the negative (local) contribution to B_{hf}, but more definite conclusions will require additional experimental data.

An unexpected result of this study is the conclusion that there is no contribution to the MHI from the thullium sublattice. There is no reason to doubt that the magnetic $4f$ electrons of the Tm^{3+} ions make a definite contribution to the polarization of the conduction electrons, but this polarization is not transferred to the Sn site. This peculiar feature of the hyperfine interaction is difficult to explain in terms of the traditional concept that a nonmagnetic atom is a charged "probe" which interacts with the collectivized electrons of the conduction band of the host. A more realistic analysis of the MHI for a nonmagnetic atoms should evidently take into account the specific features of the interatomic interaction at small distances.

A qualitative explanation can be given for the lack of an influence of the thullium on the local contribution to B_{hf}. We have previously called attention[2,3] to the existence of a correlation between the MHI parameters and the peculiar features of the chemical bond for the Sn impurity atom (which is reflected, in particular, in the size of the isomer shift of the Mössbauer line). For Sn in TmFe_2 the isomer shift is 1.69 ± 0.02 mm/sec, which is close the typical values for Sn in alloys of iron but substantially smaller than the value ≈ 2 mm/sec typical of the Sn–R interaction.[1–3] It can therefore be assumed that there is no direct Sn–Tm interaction in TmFe_2, and for this reason the transfer of electronic polarization from the nearest-neighbor Tm^{3+} ions to the Sn atom goes to zero. The situation for the positive (collective) contribution, which is presumably due to the polarization of the collectivized electrons, is less clear. The absence of an influence of the thulium on the positive contribution does not seem so unexpected, though, if it is recalled that no such contribution is observed at all in the gadolinium intermetallides.[2] It is quite likely that a necessary condition for the appearance of a contribution to B_{hf} from the remote magnetic atoms is a high concentration of magnetic $3d$ electrons, which are magnetic-moment carriers in the transition metal alloys. We assume that more-detailed information on this subject can be obtained in experiments with quasibinary solutions (e.g., RAl_2–RFe_2), in which one can observe a gradual transition from a system with a purely local hyperfine interaction (RAl_2) to a system with competing contributions of opposite sign.

[1] N. N. Delyagin, V. I. Nesterov, and S. I. Reĭman, Zh. Eksp. Teor. Fiz. **84**, 1580 (1983) [Sov. Phys. JETP **57**, 922 (1983)].

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

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

[4] N. N. Delyagin, V. I. Krylov, and V. I. Nesterov, Zh. Eksp. Teor. Fiz. **79**, 1049 (1980) [Sov. Phys. JETP **52**, 532 (1980)].

[5] B. Barbara, J. P. Giraud, J. Laforest, *et al.*, Physica $B + C$ **86/88**, 155 (1977); E. Burzo, Phys. Rev. B **17**, 1414 (1978).

[6] R. Ablundi and A. E. Clark, J. Appl. Phys. **49**, 1969 (1978).

[7] U. Atzmony, M. P. Dariel, E. R. Bauminger *et al.*, Phys. Rev. B **7**, 4220 (1973).

[8] B. Bleaney, G. J. Bowden, J. M. Cadogan, *et al.*, J. Phys. F **12**, 795 (1982).

[9] D. J. Germano and R. A. Butera, Phys. Rev. B **24**, 3912 (1981).

[10] A. K. Churkov, A. A. Byalko, N. G. Volkov, *et al.*, Preprint 10-83-852 [in Russian], Joint Institute for Nuclear Research, Dubna (1983).

[11] G. J. Bowden, D. St. P. Bunbury, A. P. Guimaraes, and R. E. Snyder, Proc. Phys. Soc. London C **1**, 1376 (1968); G. J. Bowden, J. Phys. F **3**, 2206 (1973).

[12] N. N. Delyagin, V. I. Krylov, N. I. Moreva, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 430 (1984) [JETP Lett. **39**, 521 (1984)].

Translated by Steve Torstveit