Hyperfine interactions at ^{119}Sn nuclei in metallic Gd

S. I. Reĭman, N. I. Rokhlov, V. S. Shpinel', and E. P. Kaminskaya

Scientific-Research Institute of Nuclear Physics at the M. V. Lomonosov State University, Moscow

(Submitted 3 June 1983)
Zh. Eksp. Teor. Fiz. **86**, 330–337 (January 1984)

The hyperfine interaction for ^{119}Sn impurity atoms (~ 0.5 at.%) in metallic gadolinium has been investigated by emission Mössbauer spectroscopy in the temperature range 4.5 to 320 K. At 4.5 K the magnetic hyperfine field $H_{\mathrm{hf}} = -32.34 \pm 0.04$ T, the quadrupole interaction is close to zero, and the isomeric shift with respect to $\mathrm{CaSnO_3}$ is 1.91 ± 0.01 mm/sec. Below 170 K the $H_{\mathrm{hf}}(T)/H_{\mathrm{hf}}(0)$ dependence agrees well with the behavior of the reduced magnetization of the matrix corrected for the depolarizing effect of the nonmagnetic impurity. It was concluded from this that the proportionality coefficients relating $H_{\mathrm{hf}}(T)$ to the polarization of the matrix conduction electrons $\sigma(T)$, and $\sigma(T)$ to the mean of the Gd ion spins $\langle S_z \rangle$, do not depend on T. An appreciable negative anomaly was observed in the temperature range 200 to T_c ($T_c = 291$ K). The direction of H_{hf} changes on varying the temperature and follows the rotation of the easy magnetization axis of the Gd matrix. The features of the behavior of the Mössbauer spectra of tin in an external magnetic field indicate the noncollinear nature of the ordering of the Gd spin moments at $T > 230$ K. The connection between the hyperfine magnetic field and the magnitude of the conduction electron polarization is discussed.

1. INTRODUCTION

The magnitudes of the hyperfine (hf) fields at nonmagnetic impurities in heavy rare-earth metals (REM) at absolute zero depart from proportionality to the magnitude of the projection of the REM ion spin onto the total moment[1–5]

$$H_{\mathrm{hf}} \propto (g_J - 1) J. \qquad (1)$$

Studies of the temperature dependence of these fields, $H_{\mathrm{hf}}(T)$, showed that it is appreciably different from that of the magnetization of the matrix, $M(T)$.[2,4,5] The observed departures can be connected both with the nature of the interaction which leads to magnetic ordering, and with the mechanism by which hf fields arise at the impurity nuclei. In this connection it is important to establish reliably whether there is proportionality between the magnitudes of H_{hf} and the polarization of the conduction electrons. For this purpose, in the present work measurements have been carried out of the temperature dependence of the hf fields on the nuclei of tin impurity atoms in metallic gadolinium, using the method of Mössbauer emission spectroscopy. Since the Gd^{3+} ion in the metal is in the $^8S_{7/2}$ state (with a small admixture of the $^6P_{7/2}$ first excited state), the exchange interaction Hamiltonian should in this case be of the pure spin form:

$$\mathscr{H} = -J\mathrm{Ss}. \qquad (2)$$

The polarization of the conduction electrons, σ, should thus be proportional to the mean value of the spin of the ion $\langle S \rangle$ with the condition that the corresponding coefficient of proportionality should be independent of temperature. If $H_{\mathrm{hf}}(T)$ is then proportional to $\sigma(T)$, the temperature dependence of H_{hf} should agree with the dependence of the matrix magnetization. Measurements of hf fields on a Sn impurity in Gd were made earlier,[6] but they did not cover the whole temperature range of magnetic ordering and were not sufficiently accurate.

As is known, metallic gadolinium has a close-packed hexagonal crystal structure and the symmetry does not change on passing through the Curie point. There has been much work on the magnetic properties of gadolinium. An anomaly was found[7] in the magnetization of polycrystalline Gd around 210 K. The authors ascribed this anomaly to the existence of a helicoidal spin structure which even in a rather small (≈ 15 Oe) external magnetic field changed into ferromagnetic. However, neutron diffraction studies[8,9] did not show reflections corresponding to a spiral spin structure. From these and other investigations it could be concluded that Gd below T_c is a normal ferromagnet, but the direction of easy magnetization depends appreciably on temperature. It was also shown in some other work[10,11] that in the temperature region T_c–230 K, the magnetic ordering in Gd is probably of a more complicated nature than had been suggested earlier.

2. THE EXPERIMENTS

The specimens for the investigation were prepared in two variants: in the form of an absorber and in the form of a source. The stable isotope ^{119}Sn (0.5 at.% by calculation) was introduced into Gd (99.6% purity) by threefold remelting in an argon arc furnace. The alloy was ground with a diamond needle file in an inert atmosphere into a chip which was then deposited on an aluminum substrate from a solution of BF-2 adhesive in alcohol. The source specimen was prepared by melting weighed quantities of gadolinium and radioactive ^{119m}Sn on a tantalum substrate in an argon atmosphere in an induction furnace. The calculated tin concentration was also not more than 0.5 at.% in this case. After melting, the specimen and the tantalum substrate were rolled down to a thickness of 0.1–0.2 mm and then heated briefly (1–2 sec) at ~ 1000 °C (the temperature was not monitored) in an induction furnace and wrapped in aluminum foil.

Mössbauer spectra were measured with a spectrometer operating with constant acceleration, the speed being cali-

0038-5646/84/010190-05$04.00

brated with a laser interferometer.[12] The spectra were recorded with a gas discharge proportional resonance counter having a cathode covered with the compound $Ca^{119}SnO_3$. The counter was fixed in a light frame which was in turn fixed to the shaft of the vibrator. While the absorption spectra were being measured, a Mössbauer source in the form of the compound $Ca^{119}SnO_3$ was fixed to the side of the frame opposite the detector, and a cryostat with the absorber was housed inside the frame between the detector and source. The source specimen was placed in the cryostat to measure emission spectra, while the $Ca^{119}SnO_3$ source was removed from the frame. The specimen temperature was maintained constant to an accuracy of ± 0.1 K. The spectra were analyzed by a computer using the method of least squares.

RESULTS AND DISCUSSION

We first note that gadolinium has a low Debye characteristic temperature ($\Theta_D = 173$ K, according to Rosen[13]). Raising the temperature of the specimen above Θ_D thus leads to a sharp reduction in the probability of the Mössbauer effect and, as a consequence, to a fall in the resonance effect to a small value (a few percent in the case of the absorber at 4.5 K). This makes the obtaining of reliable results from absorption spectra difficult. The main measurements were therefore made on the source specimen, since a better signal to noise ratio could be obtained then and the spectra measured to high accuracy over the whole temperature interval of interest to us.

Some Mössbauer spectra of the source specimen are shown in Fig. 1. At 4.5 K (Fig. 1, curve 1) the spectra consist of six resonance lines, the position of which is characteristic of Mössbauer spectra of the ^{119}Sn nucleus when a high magnetic field $H_{hf} = -32.34 \pm 0.4$ T acts on it. The symmetric disposition of the lines relative to the isomer shift $\delta = 1.91 \pm 0.01$ mm·sec^{-1} indicates the absence of any appreciable quadrupole interaction ($\Delta E \leqslant 0.05$ mm·sec^{-1}). The fact that the spectrum in the paramagnetic region at 300 K has a single resonance line at $\delta = 1.87 \pm 0.01$ mm·sec^{-1} with width $\Gamma = 1.13$ mm·sec^{-1} also points to this.

Increasing the specimen temperature leads to a reduction in the splitting in the spectrum, but the spectrum retains its shape to 100 K. Another resonance line with an isomer shift $\delta = 1.85 \pm 0.01$ mm·sec^{-1} appears in the spectrum above 100 K (see Fig. 1, curve 2), with relative intensity $\approx 30\%$ of the overall intensity of the spectrum. This line gradually broadens below 100 K and is completely absent at 77 K. As can be seen from curve 1 in Fig. 1, the position of the lines from this phase then coincide with the positions from the main phase, so that the spectrum at $T < 77$ K is well described by a single sextet.

It seems that most of the Sn atoms are dissolved in Gd and occupy regular sites of the crystal lattice. This is confirmed by the fact that the magnetic ordering temperature of 291 ± 1 K determined from the Mössbauer spectra according to the start of broadening of the spectral line, agrees well with the known T_c for Gd. The other, smaller fraction of the Sn atoms are either in a nonequivalent position in the gadolinium lattice (in interstitial sites associated with defects and impurities) or form a separate phase. The fraction of these atoms depends on the history of the specimen preparation: for example, they are fewer for a higher rate of cooling of the melt after fusion, while on the other hand the fraction of this phase increases on annealing. We shall only discuss below, the Mössbauer spectra of tin lying on regular sites of the Gd matrix.

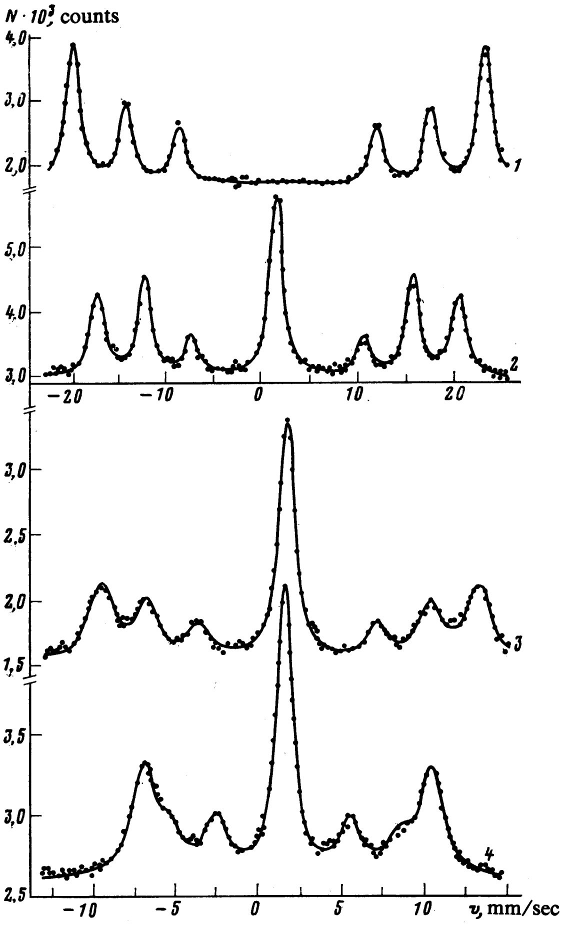

FIG. 1. Emission Mössbauer spectra of ^{119}Sn nulcei in gadolinium at different temperatures: 1) 4.5, 2) 120, 3) 215, 4) 240 K.

On the whole, the values of the parameters H_{hf}, δ and ΔE agree, within the limits of error, when calculated from absorption and from emission spectra. At the same time, some features are observed in the source spectra. As can be seen from the spectra in Fig. 1, the intensity of the second and fifth lines of the sextet changes on varying the temperature. On raising the specimen temperature, the intensity of these lines first increases, reaches a maximum value in the range 120–180 K and then decreases again almost to zero for $T > 230$ K. These changes can be explained if one takes into account that the ratio of the intensities of the lines of the sextet depends on the angle θ between the vector of the magnetic field at a tin nucleus and the direction of the γ-ray beam in the following way:

$$^3/_4(1+\cos^2\theta) : \sin^2\theta : {}^1/_4(1+\cos^2\theta). \tag{3}$$

Two extreme cases can be distinguished here. When $\theta = 0$

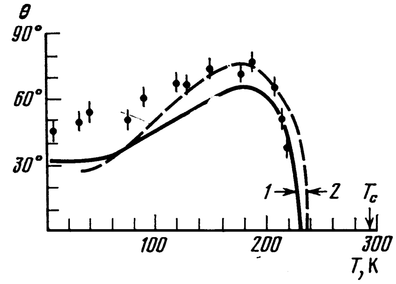

FIG. 2. Temperature dependence of the angle θ between the direction of the γ-ray beam (c axis of the crystal) and the direction of the hyperfine magnetic field vector at ^{119}Sn nuclei (points) and the dependence of the angle between the c axis and the magnetic moment of gadolinium according to neutron scattering data[8]—curve 1, and according to magnetocrystalline measurements[14]—curve 2.

the ratio of intensities is 3:0:1, and if $\theta = 90°$ it is 3:4:1. It is natural to associate the change in the ratio between the line intensities of the sextet observed by us with the formation of a texture in the source specimen. As a result of the rolling and subsequent thermal treatment, a preferred orientation of the gadolinium crystallites evidently arises.[1)] Since we observed a ratio close to 3:0:1 at temperatures above 230 K it can be concluded that the crystallographic c axis is, in our case, oriented perpendicular to the plane of the specimen (in the direction of propagation of the γ-ray beam), since it is known from neutron diffraction data[8,9] that in the temperature region T_c–230 K the direction of the magnetic moment is oriented along the c axis. This conclusion is, naturally, only valid under the assumption that the direction of the magnetic field at the tin nuclei is determined by the direction of the spins of the neighboring gadolinium atoms.

The temperature dependence of the angle θ, calculated according to Eq. (3) is shown in Fig. 2 as confirmation of this assumption. In this figure the variation of the angle φ between the Gd magnetic moment and the c axis is shown, derived from neutron diffraction[8] and from magnetic measurements.[14] Comparison of these results shows good qualitative agreement, although some disagreement is seen at low temperatures. These departures can be explained by several causes. First, it is possible that there is incomplete ordering of the specimen. Second, even in the measurement of the angle φ by different authors using one and the same method there is not good qualitative agreement, and more so among measurements by different methods.[8,9,14] These differences can be ascribed to differences in thermal treatment of the specimens studied, the existence of internal strains and also the composition and amount of impurities. The nature of the impurity is probably important since, for example, in the temperature range 15–200 K no change in the angle between the direction of the magnetic hyperfine field and the principal axis of the tensor of the electric field gradient[15] (the c axis of the Gd crystal) was observed for ^{111}Cd nuclei in Gd.

Figure 3 shows the dependence of reduced hyperfine field $H_{\rm hf}(T)/H_{\rm hf}$ (4.5 K) at Sn nuclei in Gd on the reduced temperature T/T_c; results of Gotthardt *et al.*[6] are also shown there. The variation of the spontaneous magnetization of Gd, M/M_0, according to Nigh *et al.*[16] is shown in the

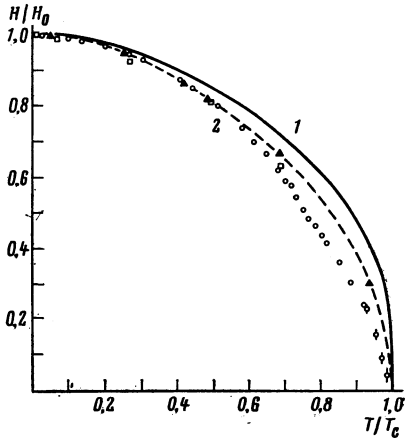

FIG. 3. Dependence on reduced temperature of: reduced magnetization of gadolinium M/M_0 (Ref. 16)—continuous curve 1; reduced magnetization of a gadolinium ion next to a nonmagnetic impurity M_1/M_0 (Ref. 17)—dashed curve 2; reduced hyperfine magnetic field at ^{119}Sn nuclei in Gd: ○) our measurements, □) according to Gotthardt *et al.*[6]; ▲) the analogous dependence for ^{111}Cd in Gd[15].

same figure and the calculated[17] reduced magnetization of a gadolinium ion next to a nonmagnetic impurity M_1/M_0. Comparison of these results shows that in the temperature range 4.5–170 K the $H_{\rm hf}(T)/H_{\rm hf}$ (4.5 K) dependence agrees with that of M_1/M_0. However, an appreciable divergence is observed at higher temperatures between the reduced hyperfine field on Sn and both M/M_0 and M_1/M_0, so that the difference

$$H_{\rm hf}(T)/H_{\rm hf}(4.5\ {\rm K}) - M/M_0 \tag{4}$$

is a negative quantity (negative anomaly) and reaches a value of 0.2. If we subtract M_1/M_0 and not M/M_0, then the difference reaches 0.1.

We note here some features of the Mössbauer spectra at temperatures above 230 K. For example, application of an external magnetic field $H_0 = 0.02$ T perpendicular to the γ-ray beam in the range 230–260 K, not only leads to reorientation of $H_{\rm hf}$ by 90°, but also to its increasing by $\approx 5\%$ ($H_{\rm hf} = 0.7$–0.5 T, Fig. 4). That such a small value of H_0 is sufficient to turn the axis of easy magnetization is due to the well known small magnetocrystalline anisotropy in gadolinium in this temperature range. The increase in $H_{\rm hf}$ at tin nuclei can be explained by the anisotropic nature of the hf magnetic interaction. As has been shown,[18] the field $H_{\rm hf}$ at tin nuclei in $\rm Gd_{0.95}Tm_{0.05}$ is less by $4 \pm 1\%$ than in $\rm Gd_{0.97}Tb_{0.03}$, in which the magnetization direction is directed perpendicular to the c axis. The magnitude and sign of $\Delta H_{\rm hf}$ found by us agrees well with the results of Balabanov *et al.*,[18] but the observed anomaly in $H_{\rm hf}(T)/H_{\rm hf}(0)$ cannot be completely explained by anisotropy in the hf interaction, since the disagreement is appreciably less. Besides, the change $\Delta H_{\rm hf}$ in an applied field $H_0 = 0.35$ T is double (taking the sign of $H_{\rm hf}$ into account) that for $H_0 = 0.02$ T. This fact can be understood if non-collinearity of the magnetic moments in Gd is assumed, which evidently decreases on applying an external magnetic field. Actually, neutron diffraction studies showed[19] that the angle φ fluctuates above 235 K and that

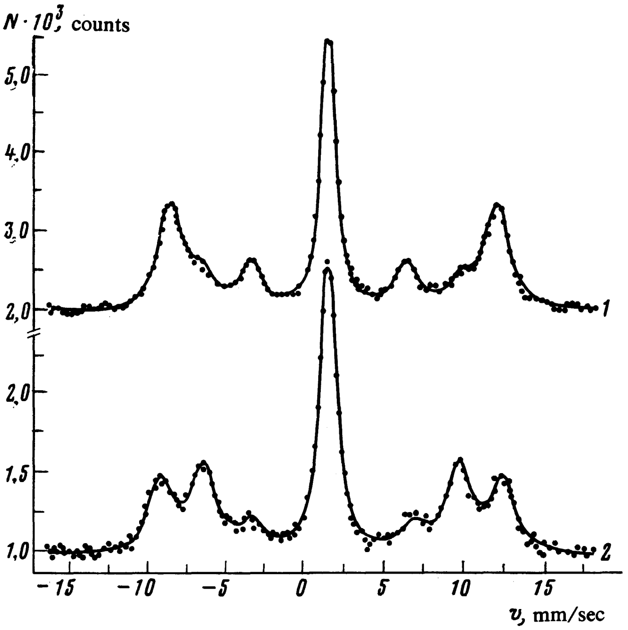

FIG. 4. Emission Mössbauer spectra of ^{119}Sn nuclei in Gd at 230 K: 1) without external field, 2) in a magnetic field of 0.02 T applied perpendicular to the γ-ray beam.

only on the average is φ equal to zero.

The shapes of the Mössbauer spectra obtained at $T > 230$ K indicates the existence of at least two magnetically nonequivalent sites for tin in Gd with relative populations 3:1, and the tin nuclei in the less populated sites have $H_{\mathrm{hf}} \approx 20\%$ less than for sites with the larger population. Unfortunately, a detailed interpretation of these spectra is complicated by the overlap of lines from two sextets, which increases with increasing temperature. Nevertheless, the features enumerated above confirm the earlier suggestions[7,11,17] that Gd is not a simple ferromagnet in the range T_c–230 K.

4. DISCUSSION

The $H_{\mathrm{hf}}(T)$ dependence for ^{111}Cd over the whole temperature range up to T_c and for ^{119}Sn in the temperature range $T < 170$ K agrees with the magnetization curve for Gd, corrected for the depolarizing effect of the impurity, i.e., $H_{\mathrm{hf}}(T) = a\langle S_z\rangle$, where a is a constant. At $T = 0$ the polarization of the conduction electrons $\sigma(0)$ is proportional to the spin S, according to the Hamiltonian of Eq. (2), while $H_{\mathrm{hf}}(0)$ is usually taken to be proportional to $\sigma(0)$, i.e., $\sigma(0) = \chi_1(0)S$ and $H_{\mathrm{hf}}(0) = \chi_2(0)\sigma(0)$. If the coefficients χ_1 and χ_2 depend on temperature, then

$$\sigma(T) = \chi_1(T)\langle S_z\rangle \text{ and } H_{\mathrm{hf}}(T) = \chi_2(T)\sigma(T).$$

Consequently the condition $\chi_1(T)\chi_2(T) = a$ is required. The existence of such a connection between these coefficients which characterize completely different forms of interaction (exchange and hyperfine) is quite unreasonable if χ_1 and χ_2 depend on T. The condition obtained thus indicates that $\chi_1(T) = \mathrm{const}$ and $\chi_2(T) = \mathrm{const}$. Consequently, $H_{\mathrm{hf}}(T)$ on the nonmagnetic impurities Sn and Cd is proportional to the polarization of the conduction electrons of the matrix, $\sigma(T)$. It can also be deduced that $\sigma(T)$ is proportional to the magnetization of the matrix $\langle S_z\rangle$ for a fixed magnetic structure, while the negative temperature anomaly in $H_{\mathrm{hf}}(T)$ for tin in the temperature region $T > 170$ K is explained by a decrease in the matrix polarization, associated with the rotation of the axis of easy magnetization and readjustment of the magnetic structure of Gd.

In other REM's, as distinct from Gd, large deviations of the temperature dependence $H_{\mathrm{hf}}(T)$ at an impurity atom were observed from the magnetization curve.[2,3] Assuming the proportionality between H_{hf} and $\sigma(T)$, we come to the conclusion that the temperature anomalies in hf field in REM's indicate the absence of proportionality between $\langle S_z\rangle$ and $\sigma(T)$. This suggests that the interaction between the 4-f ions and the conduction electrons (k-f interaction) is not pure spin, but contains contributions associated with the orbital momenta and the conduction electrons.[20,21] It has been shown[20] that the dependence of H_{hf} at nonmagnetic impurities in a number of isomorphic REM compounds on the total momentum of the ion, J, is well described by the three-term formula

$$H_{\mathrm{hf}} = [(g_J - 1)H_{01} + (2 - g_J)H_{10} + c_n H_{21}]\langle \mathbf{J}\rangle, \qquad (5)$$

where the first term is the usual spin contribution to the conduction electron polarization, while the second and third are, respectively, the orbital and spin-dipole contributions. We obtained Eq. (5) independently, starting from the general formulation of Hirst.[21] If account is taken of higher terms in the expansion, proportional to odd powers of $\mathbf{J}$,[22] then it can be shown that the departure of the $H_{\mathrm{hf}}(T)$ curve from $\langle \mathbf{J}\rangle$ must depend appreciably on the orbital momentum of the REM ion. This statement is also to some extent valid for Gd since the Gd ion is not in a pure S state.

[1)] This effect arises, although to a smaller extent, in other control specimens.

[1] A. S. Kuchma and V. S. Shpinel', Zh. Eksp. Teor. Fiz. **62**, 1054 (1972) [Sov. Phys. JETP **35**, 556 (1972)].
[2] S. K. Godovikov, M. G. Kozin, V. V. Turovtsev, and V. S. Shpinel, Phys. Status Solidi B **78**, 103 (1976); P. V. Bogdanov, S. K. Godovikov, M. G. Kozin, N. I. Moreva, and V. S. Shpinel, Hyp. Int. **5**, 333 (1978).
[3] P. V. Bogdanov, S. K. Godovikov, M. G. Kozin, V. V. Turovtsev, and V. S. Shpinel', Zh. Eksp. Teor. Fiz. **72**, 2120 (1977) [Sov. Phys. JETP **45**, 1113 (1977)].
[4] B. Perscheid and M. Forker, Z. Phys. B **31**, 49 (1978).
[5] M. Forker and J. B. Fechner, Phys. Status Solidi B **65**, K9 (1974).
[6] V. Gotthardt, H. S. Möller, and R. L. Mössbauer, Phys. Lett. A **28**, 480 (1969).
[7] K. P. Belov and A. V. Ped'ko, Zh. Eksp. Teor. Fiz. **42**, 87 (1962) [Sov. Phys. JETP **15**, 62 (1962)].
[8] J. W. Cable and E. O. Wollan, Phys. Rev. **165**, 733 (1968).
[9] V. M. Kuchin, V. A. Semenkov, S. Sh. Shil'shteĭn, and Yu. V. Patrikeev, Zh. Eksp. Teor. Fiz. **55**, 1241 (1968) [Sov. Phys. JETP **28**, 649 (1969)].
[10] I. I. Gurevich, A. I. Klimov, V. N. Maĭorov, E. A. Meleshko, B. A. Nikol'skiĭ, A. V. Purogov, V. S. Roganov, V. I. Selivanov, and V. A. Suetin, Zh. Eksp. Teor. Fiz. **69**, 1453 (1975) [Sov. Phys. JETP **42**, 741 (1975)].
[11] H. R. Child, Phys. Rev. B **18**, 1247 (1978).
[12] S. I. Reĭman and K. P. Mitrofanov, Prib. Tekh. Eksp. No. 2, 66 (1980)

[Instrum. and Exp. Tech. **23**, 358 (1980)].

[13] M. Rosen, Phys. Rev. Lett. **19**, 695 (1967).

[14] W. D. Corner, W. C. Roe, and K. N. R. Taylor, Proc. Phys. Soc. London **80**, 927 (1962).

[15] L. Boström, G. Liljegren, B. Jonsson, and E. Karlsson, Phys. Scripta **3**, 175 (1971).

[16] H. E. Nigh, S. Legvold, and F. H. Spedding, Phys. Rev. **132**, 1092 (1963).

[17] H. P. van de Braak and W. J. Caspers, Phys. Status Solidi, **24**, 733 (1967).

[18] A. Balabanov, I. Felner, and I. Nowik, Solid State Commun. **18**, 823 (1976).

[19] J. W. Cable and W. Koehler, J. Appl. Phys. **53**, 1904 (1982).

[20] B. D. Dunlap, I. Nowik, and P. M. Levy, Phys. Rev. B **7**, 4232 (1973).

[21] L. L. Hirst, Adv. Phys. **27**, 231 (1978).

[22] E. Belorizky, J. J. Niez, and P. M. Levy, Phys. Rev. B **23**, 3360 (1981).

Translated by R. Berman