Anomalous temperature dependence of the effective field at the nuclei of Dy^{3+} ions in DySb

V. G. Stankevich, I. I. Lukashevich, N. I. Filippov, and I. A. Gladkikh

(Submitted June 14, 1973)
Zh. Eksp. Teor. Fiz. **66**, 283–292 (January 1974)

The spectra of the resonant absorption of γ quanta of energy 25.7 keV by Dy^{161} nuclei in the antiferromagnet DySb ($T_N = 9.5$ °K) were measured in the temperature range 4.2–10.8 °K. An unusual temperature dependence of the effective field at the dysprosium nucleus was observed, and is attributed to perturbation of the wave functions of the lower Kramers double by the exchange field. On the basis of the experimental data, a complete calculation of the level structure of the Dy^{3+} ion in DySb is calculated in a crystal field of tetragonal symmetry with allowance for the exchange interaction.

1. INTRODUCTION

It is known that the character of the hyperfine structure (hfs) spectra, from which the effective field H_{eff} at the nuclei can be determined directly, depends essentially on the relative values of the period τ_L of the Larmor precession and on the electron-spin relaxation time τ_{rel}. We distinguish between the following limiting situations.

In the case when $\tau_L > \tau_{rel}$, the effective field is determined by dynamic averaging over all the sublevels of the ion in accordance with their populations (see, e.g.,[1])

$$H_{\text{eff}}(T) = \sum_{i=1}^{2J+1} H_i(T) \exp\left(-\frac{E_i}{kT}\right) \Big/ \sum_{i=1}^{2J+1} \exp\left(-\frac{E_i}{kT}\right). \tag{1}$$

Here $H_i(T)$ is the field produced at the nuclei by an ion in a state with energy E_i; k is the Boltzmann constant, and the summation is carried out over all $2J + 1$ levels of the ion. Taking the proportionality of the magnetic field to the magnetic moment of one and the same sublevel into account, we can easily verify that the effective field $H_{eff}(T)$ at the nuclei depends on the temperature in exactly the same manner as the spontaneous magnetic moment of the ion [1].

In this case the temperature dependence of the effective field $H_{eff}(T)/H_{eff}(0)$ can be used to determine the ordering point and the temperature dependences of the sublattice magnetizations of different antiferromagnets. An example of a temperature dependence of this type, very frequently encountered in Mossbauer experiments, is the relation $H_{eff}(T)/H_{eff}(4.2°K)$ obtained from the hfs spectra of metallic dysprosium [2].

In the other case, when the period of the Larmor precession is shorter than the electron-spin relaxation time, $\tau_L < \tau_{rel}$, no averaging similar to (1) takes place, and the effective field is determined completely by the wave functions of the populated Stark levels. In this case, too, an hfs is observed in the paramagnetic region, in accord with the Afanas'ev and Kagan relaxation theory [3].

If the wave functions of the lower populated levels do not change significantly on going from the ordered into the paramagnetic region, then the effective field is independent of the temperature and the ordering point is not distinguished in any way in the Mossbauer spectra. Such a temperature dependence was obtained by us in $DyVO_4$ [4]. A similar situation also takes place in DyAlG [5]. It can be assumed that if an appreciable change of the wave functions of the lower sublevels takes place on going through the ordering point, as a result of the perturbation by the exchange field, then the temperature dependence of the effective field can have an intermediate form wherein the effective field decreases somewhat with increasing temperature in the ordered region and is independent of the temperature in the paramagnetic region.

The results of the present experiment have confirmed this assumption, and a temperature dependence of the predicted unusual type was first observed by us in dysprosium antimonide DySb. This compound is a highly anisotropic antiferromagnet [6] with an ordering point $T_N = 9.5°K$ [7]. We have previously established [8] that the magnetic moment per dysprosium ion in DySb, at 4.2°K, is close to the maximum possible for the Dy^{3+} ion in a magnetically ordered medium, namely $\mu = 10\ \mu_B$ (μ_B is the Bohr magneton).

The results of an x-ray structural analysis [9] have shown that at high temperatures, dysprosium antimonide has a face-centered lattice of the NaCl type ($a_0 = 6.154$ Å), which experiences tetragonal distortions ($c/a = 0.993$) when the temperature is lowered to $T_{cr} \sim 12°K$. It is suggested in the same paper that the magnetic phase transition coincides with the crystallographic transition, and consequently, in contradiction to the results of the magnetic measurements [7], it takes place at a temperature $T_N \sim 12°K$.

2. EXPERIMENT

To obtain the Mossbauer spectra, we used, as before [4,8], the 25.7-keV resonant γ transition in Dy^{161}. The γ-quantum source was prepared from gadolinium oxide Gd_2O_3 enriched to 97% Gd^{160} and irradiated in a reactor. The absorber was the dysprosium antimonide that was previously used in the measurement at 4.2°K [8]. The Mossbauer spectra were registered by a γ-resonance spectrometer with an NTA-512B multichannel analyzer [4,10]. The spectrometer operated in the constant-acceleration mode.

The measurements were performed in the temperature region 4.2–10.8°K. The absorber was placed in the cryostat illustrated in Fig. 1. The cryostat had a helium bath 1 with approximate volume 4 liters surrounded by an external nitrogen dewar 2. The investigated sample 3 was secured in a copper ring with heater 4 and placed in the vacuum space. The copper ring was connected by a thermal junction 5 to the copper bottom of the helium bath. The thermal junction was a copper wire 0.3 mm in diameter. To decrease the intake of heat by radiation, the ring was surrounded with a copper screen 6 kept at liquid-nitrogen temperature.

The γ-quantum beam passed through hermetically sealed windows 7 of lavsan polyester 80 μ thick and

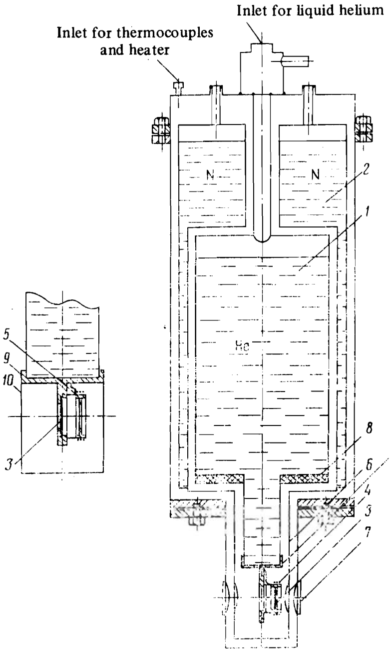

FIG. 1. Helium cryostat. On the left is shown the method used to mount the sample for measurement at temperatures below 4.2°K. 1—helium bath; 2—nitrogen dewar; 3—investigated sample; 4—copper ring with heater; 5—thermal junction; 6—copper screen kept at the temperature of liquid nitrogen; 7—windows of lavsan and aluminum foil; 8—carbon getter; 9—copper holder; 10—additional copper screen.

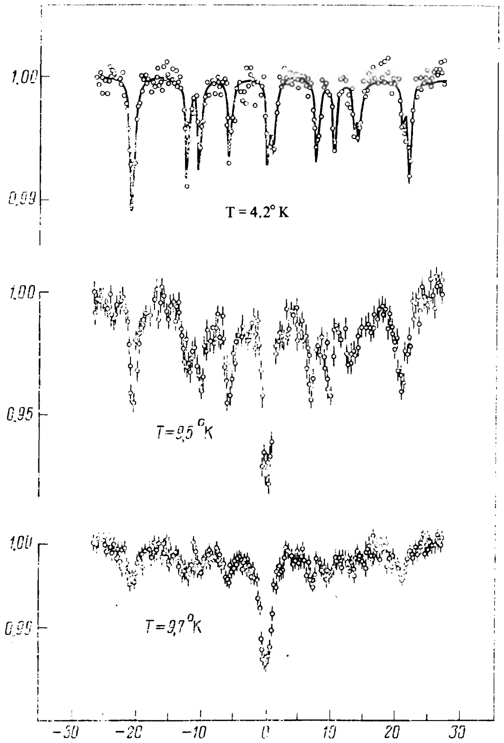

FIG. 2. Experimental Mossbauer spectra of DySb.

thin (δ ~ 2 μ) aluminum foil. The vacuum in the cryostat was maintained with a carbon getter 8. The rate of evaporation of the liquid helium was 0.07 liter/hour. This made it possible to carry out continuous measurements for two days.

To obtain temperatures higher than 4.2°K at the samples, we used a heater 4, connected to a stabilized current source capable of maintaining the temperature accurate to ~0.1°K. It should be noted that our cryostat can also be used for measurements at temperatures below 4.2°K, by pumping out the liquid-helium vapor. To this end it was necessary to secure the investigated sample in a copper holder 9, which was sealed into the bottom of the helium bath, and to install an additional copper screen 10 having the temperature of liquid helium. The temperatures were measured with the aid of a miniature germanium thermometer attached directly to the sample.

3. RESULTS AND DISCUSSION

Figure 2 shows some of the experimentally obtained hfs spectra of DySb. The first was observed in the ordered region and the second was observed at a temperature such that, in accordance with the magnetic-measurement data [7], magnetic ordering sets in, while the third was observed in the paramagnetic region.

We note the following main features of the behavior of the Mossbauer spectra. First, the spectra have a well-resolved hfs, in both the ordered and in the paramagnetic regions. The presence of the most intense extreme peaks in the Mossbauer spectra could be observed at the temperature 10.8°K. This is evidence of long electron-spin relaxation times of the Dy^{3+} ion in DySb. The latter is due to the small probability of the spin-spin relaxation in compounds having high anisotropy of the lower populated Kramers doublets [5,4]. Second, a broadening of the individual lines and a change in their relative intensities is observed with increasing temperature, thus confirming the major role played by the spin-lattice mechanism in the relaxation of the electron spin of Dy^{3+} in DySb.

We proceed now to consider the temperature dependence of the effective field $H_{eff}(T)$ at the nuclei; this field, as is well known, is proportional to the parameter of the magnetic hyperfine interaction (HFI). The latter can easily be obtained from the Mossbauer spectra, in which the line position is described with sufficient accuracy by a model Hamiltonian of well-known form (see, e.g., [11]):

$$\hat{\mathscr{H}}_{\mathrm{HFI}} = -\frac{\mu}{I}\hat{I}_z H_{\mathrm{eff}} + \frac{e^2 qQ}{4I(2I+1)}[3\hat{I}_z^2 - I(I+1)]. \tag{2}$$

Here μ and Q are respectively the magnetic and quadrupole moments of the nucleus, I and I_z are the spin of the nucleus and its z-component, and q is the gradient of the electric field at the nucleus.

It should be noted that the effective-field approximation is valid at low temperatures in the ordered region (when only one lower sublevel is populated) as well as in the paramagnetic region, where the highly-anisotropic Kramers doublet can be regarded as isolated. On the other hand, in the ordered region, where the fields H_i of the sublevels of the lower doublet differ not in the polarity alone, the effective-field approximation is, strictly speaking, not valid. Recognizing, however, that the absolute values of the fields of these sublevels, which have comparable populations, differ insignificantly and cause only a small broadening of the lines in the spectrum, we can use the effective-field approximation also in this temperature region.

The experimental temperature dependence $H_{eff}(T)/H_{eff}(4.2°K)$ obtained with the aid of (2) is shown

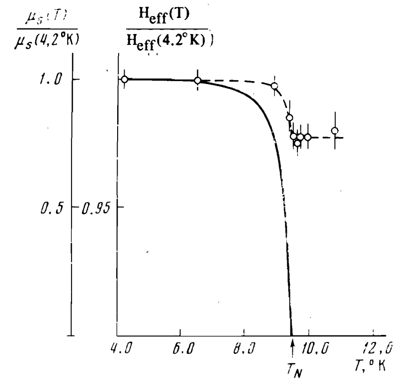

FIG. 3. Temperature dependence of the effective field $H_{eff}(T)/H_{eff}(4.2°K)$ at the Dy^{3+} ion in DySb. Solid curve—calculated temperature dependence of the sublattice magnetization (see the text).

in Fig. 3. It is quite unusual in form. Thus, in the ordered region the effective field decreases somewhat as $T_N = 9.5°K$ is approached, and in the paramagnetic region it is independent of the temperature. It is important to note that for this compound, unlike $DyVO_4$ [4], the ordering point $T_N = 9.5°K$ is distinctly pronounced on the $H_{eff}(T)/H_{eff}(4.2°K)$ curve. Therefore, assuming that the crystallographic phase-transition point $T_{cr} \simeq 11.8°K$ has been correctly determined [9], we can conclude that the latter does not coincide with the magnetic phase transition point.

Let us examine the temperature dependence of the effective field in the ordered region. Owing to the low rate of the spin relaxation, $H_{eff}(T)$ is not determined in this case by Boltzmann averaging of (1) over all the levels of the ions, and is therefore not proportional to the spontaneous magnetic moment. It is obvious that the observed dependence can be attributed to changes in the wave functions $|^2\Gamma_i\rangle$ of the lower populated sublevels as they approach the ordering point. These changes are caused by the fact that the principal term $^6H_{15/2}$ of the Dy^{3+} ion in a tetragonal-symmetry crystalline field is perturbed by the exchange interaction of the neighboring ions.

Thus, the obtained temperature dependence, on the one hand, separates the ordering point and, on the other hand, contains additional information on the states of the ion in the ordered and paramagnetic regions. This information can be used to calculate the concrete structure of the levels of the ion. An attempt at solving such a problem is described by Loh [12], who investigated the magnetic properties of $DyCo_2$ by γ-resonance spectroscopy. In this compound, however, an effective-field temperature dependence determined by expression (1) was observed, but this dependence did not contain enough information to solve the problem by using only Mossbauer measurements. In our case, on the other hand, the experimental data make it possible to carry out a complete calculation of the concrete structure of the Dy^{3+} ion levels in the investigated temperature range. We present below the scheme and the results of such a calculation for dysprosium antimonide.

It is known that the Hamiltonian of a tetragonal-symmetry crystal field can be expressed in the form [8]:

$$\hat{\mathscr{H}}_{\text{tetr}} = B_2^0\hat{O}_2^0 + B_4^0(\hat{O}_4^0 + 5\hat{O}_4^4) + B_6^0(\hat{O}_6^0 - 21\hat{O}_6^4), \tag{3}$$

where $\hat{O}_n^k$ are operators made up of the components of the total angular momentum of the ion **J** (their values are tabulated in [13]) while B_2^0, B_4^0, and B_6^0 are the parameters of the crystal field and describe respectively the contributions of the second, fourth, and sixth-order terms. Allowance for the anisotropic exchange interaction of the dysprosium spins directed along the z axis of the crystal [9] adds one more term to the Hamiltonian (3):

$$\hat{\mathscr{H}}_{\text{exch}} = g_J \mu_B H_m(T)\hat{J}_z, \tag{4}$$

where $H_m(T)$ is the molecular field produced by the neighboring ions of the given sublattice, $\hat{J}_z$ is the operator of the z-component of the total angular momentum of the ion, and g_J and μ_B are respectively the Lande factor and the Bohr magneton.

It is convenient in the calculations to take the parameter B_4^0 out in front of all the terms of the total Hamiltonian and to use it as a scale factor needed only to determine the level energies. The remaining parameters are then modified somewhat and the total Hamiltonian of the ion takes the form

$$\begin{gathered} \hat{\mathscr{H}} = B_4^0[c(T)\hat{J}_z/J + \alpha_4^2\hat{O}_2^0 + \hat{O}_4^0 + 5\hat{O}_4^4 + \alpha_4^6(\hat{O}_6^0 - 21\hat{O}_6^4)]; \\ c(T) = g_J\mu_B J H_m(T)/B_4^0, \quad \alpha_n^k = B_k^0/B_n^0. \end{gathered} \tag{5}$$

The total Hamiltonian (5) determines completely the structure of the levels, whose wave functions and energies can be calculated as the eigenfunctions and eigenvalues of the operator $\hat{\mathscr{H}}$.

Thus, the concrete structure of the levels of the ion is determined in the general case by the four parameters c(T), α_4^2, α_4^6, and B_4^0, the first of which is a function of the temperature. It is best to fit them first in the paramagnetic region. The Dy^{3+} ion is in this case in a pure crystalline field, so that we need consider only two parameters (α_4^2 and α_4^6) out of the four in the calculation of the wave functions. These parameters were chosen such that the magnetic moment of the lower Kramers doublet $\mu = g_J\mu_B\langle^2\Gamma|J_z|^2\Gamma\rangle$ was equal to the value $\mu_{exp} = 9.76\ \mu_B$ obtained from the experimental spectra of the paramagnetic region, as in [8].

The magnitude and the temperature dependence of the parameter c(T) were determined on the basis of the experimentally obtained $H_{eff}(T)/H_{eff}(4.2°K)$ in the ordered region with allowance for the proportionality of the effective field to the magnetic moment at the same sublevel [1]. The scale parameter B_4^0 was obtained from the condition that the temperature dependences of the perturbing exchange field c(T) coincide with the temperature dependence of the spontaneous magnetic moment $\mu_s(T)$, the latter being calculated with the aid of Boltzmann averaging over all the sublevels of the ion.

As a result of computer calculations, we obtained the following experimental values of the crystal-field parameters and of the exchange interaction of the Dy^{3+} ions in DySb:

$$B_2^0 = -(0.128 \pm 0.008)°\,\text{K}, \quad B_4^0 = -(0.0045 \pm 0.0005)°\,\text{K},$$
$$B_6^0 \approx 0, \quad g_J\mu_B J H_m(4.2°\,\text{K}) = -(16 \pm 1)°\,\text{K}.$$

As a result of the calculations, we also obtained the temperature dependence shown in Fig. 3 for the magnetization of the dysprosium-antimonide sublattices, which is described by practically identical functions $c(T)/c(4.2°K)$ and $\mu_s(T)/\mu_s(4.2°K)$. It must be emphasized that this dependence does not agree with the temperature dependence of the effective field, which is shown in the same figure.

An analysis of the parameters estimated above shows that they agree fairly well with the results reported in

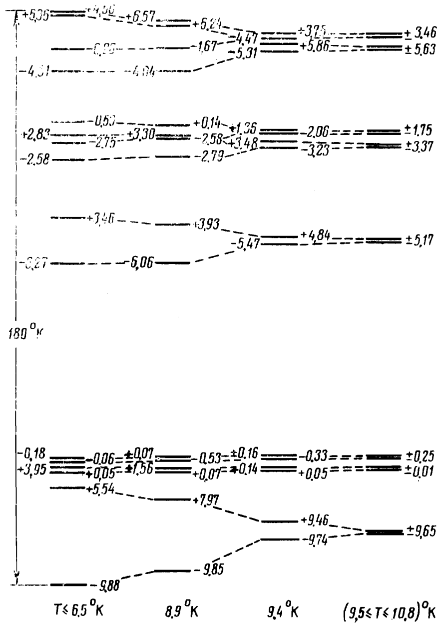

FIG. 4. Level scheme of the Dy^{3+} ion in DySb at different temperatures. The numbers indicate the values of the magnetic moments of the sublevels $\mu_i = g_J\mu_B \langle {}^k\Gamma_i|J_z|{}^k\Gamma_i\rangle$.

other papers. Thus, on the basis of Trammell's approximation [14], Levy and Vogt [9] estimated the order of magnitude of the crystal-field constant V_2^0 in accordance with the measured value of the tetragonal distortion: $V_2^0 \approx -30\ \text{cm}^{-1}$. Using furthermore the known relation between V_2^0 and B_2^0 as well as the factor $\langle J\|\alpha\|J\rangle$ calculated by Elliot and Stevens for Dy^{3+} [15], it is easy to calculate the value of B_2^0 on the basis of the indicated estimate of V_2^0:

$$B_2^0 = V_2^0\langle J\|\alpha\|J\rangle = -0.133^\circ\ \text{K}. \tag{6}$$

There is an obvious agreement between the estimate calculated in this manner and the optimal value of the parameter $B_2^0 = -(0.128 \pm 0.008)^\circ$K obtained in our experiments.

The zero value of the parameter B_6^0 agrees well with the conclusion drawn by Bleaney: that the sixth-order terms make a small contribution to the Hamiltonian (4) [16].

To compare the experimentally obtained exchange-interaction energy $E_{\text{exch}} = g_J\mu_B J H_m(4.2^\circ\text{K})$, we have estimated this quantity in elementary fashion by using the molecular-field theory. Using the paramagnetic Curie temperature indicated by Busch for dysprosium antimonide, $\Theta_p = -4^\circ$K, we easily obtain $E_{\text{exch}} \approx -10.5^\circ$K. This rough estimate agrees only in order of magnitude with the experimental exchange energy $E_{\text{exch}} = -(16 \pm 1)^\circ$K.

A calculation based on the experimental data yielded the concrete level structures shown in Fig. 4 for the Dy^{3+} ion at different temperatures. The horizontal lines representing the level positions are marked here by the values of their magnetic moments

$$\mu_i = g_J\mu_B\langle {}^k\Gamma_i|J_z|{}^k\Gamma_i\rangle$$

($|{}^k\Gamma_i\rangle$ is the wave function of the given level). In the right-hand side of the figure, which shows the paramagnetic region, one observes in natural fashion the double Kramers degeneracy of the levels, which is lifted in the ordered region. Simultaneously with lifting of the degeneracy, a certain restructuring takes place in the wave functions of the sublevels. This is particularly clearly seen in the case when the distance between the sublevels is comparable with the exchange-interaction energy.

An example of such a phenomenon is the change occurring in the wave functions (and consequently also in the magnetic moments) of the second and third Kramers doublets ($\mu_2 = \pm 0.01\ \mu_B$., $\mu_3 = \pm 0.25\ \mu_B$). As seen from the figure, the magnetic moments of the sublevels of these doublets change significantly when the temperatures are lowered, and some of them even reverse sign. It is also interesting to note the following features of the obtained level structure: first, the total Stark splitting amounts to $(160 \pm 20)^\circ$K in the paramagnetic region and is ~20°K larger in the ordered region; second, as was suggested by us earlier [8], it is possible to separate in the considered structure a special group of closely-lying lower levels, located ~60°K away from the remaining levels; third, the energy distance between the lower Kramers doublet and the two neighboring ones is $\Delta = (20 \pm 5)^\circ$K and is comparable with the exchange-interaction energy.

Taking into account all the foregoing features of the structure, we can formulate qualitative conditions for the existence of a temperature dependence of the effective field similar to the dependence observed in DySb (see Fig. 4). To this end it is necessary that the compound have a high magnetic anisotropy sufficient for the observation of an hfs in the paramagnetic region, and the distance between the lowest Kramers doublets should be comparable with the exchange-interaction energy. This condition is satisfied, for example, by dysprosium arsenide DyAs and by dysprosium phosphide DyP, and it appears that it is therefore possible to observe in them a temperature dependence of unusual type.

We now dwell briefly on paramagnetic-relaxation processes in DySb. The hfs spectra have shown that in the paramagnetic region the positions of the individual lines do not vary with temperature, and the relaxation process leads only to a change in the intensities and the widths. This behavior of the Mossbauer spectra has given grounds for hoping that only the sublevels of the lower Kramers doublet participate in the relaxation processes of this compound, just as in $DyVO_4$ [4]. We have attempted to calculate the experimental spectra in the paramagnetic region with the aid of such a two-level relaxation model. It turned out that the theoretical spectra are in worse agreement with the experimental ones than in the case of $DyVO_4$. This discrepancy can be attributed to the fact that sublevels other than those of the lower Kramers doublet take part in the relaxation processes.

In conclusion, the authors are indebted to V. V. Sklyarevskiĭ for interest in the work and for a discussion, and to V. D. Gorobchenko and A. M. Afanas'ev for useful discussions.

---

[1] S. Ofer, I. Nowik, and S. G. Cohen, in Chemical Applications of Mössbauer Spectroscopy, ed. by V. I. Goldanski and R. H. Herber, Acad. Press, N.Y., 1968.
[2] A. J. F. Boyle, D. St. P. Bunbury, C. Edwards, and H. E. Hall, Proc. 2nd Intern. Conf. ME, Saclay, France, 1961, p. 182.
[3] A. M. Afanas'ev and Yu. Kagan, Zh. Eksp. Teor. Fiz. **45**, 1660 (1963) [Sov. Phys.-JETP 18, 1139 (1964)].
[4] V. D. Gorobchenko, I. I. Lukashevich, V. G. Stankevich,

E. V. Mel'nikov and N. I. Filippov, Fiz. Tverd. Tela **14**, 2468 (1972) [Sov. Phys.-Solid State **14**, 2140 (1973)].
[5] I. Nowik and H. H. Wickman, Phys. Rev. **140**, N 3A, 869 (1965).
[6] G. Busch and O. Vogt, J. Appl. Phys. **39**, 1334 (1968).
[7] G. Busch, J. Appl. Phys. **38**, 1386 (1967).
[8] V. D. Gorobchenko, I. I. Lukashevich, V. G. Stankevich, N. I. Filippov, V. I. Chukalin, and E. I. Yarembash, Fiz. Tverd. Tela **13**, 1085 (1971) [Sov. Phys.-Solid State **13**, 901 (1971)].
[9] F. Levy and O. Vogt, Phys. Letters **24A**, 444 (1967).
[10] K. P. Aleshin, A. N. Artem'ev, and E. P. Stepanov, Prib. Tekh. Eksp. No. 4, 54 (1972).
[11] G. Wertheim, Mossbauer Effect: Principles and Applications, Acad. Press, 1964.
[12] E. L. Loh, in Nuclear Reactions in Light Nuclei and Mössbauer Studies, Johns Hopkins University, 1970, NYO-2028-5, p. 144.
[13] M. T. Hutchings, Sol. St. Phys. **16**, 227 (1966).
[14] G. T. Trammell, Phys. Rev. **131**, 922 (1963).
[15] R. J. Elliott, and K. W. H. Stevens, Proc. Roy. Soc. A-**218**, 553 (1953).
[16] B. Bleaney, Proc. Roy. Soc. A-**276**, 28 (1963).

Translated by J. G. Adashko
29