SOVIET PHYSICS JETP VOLUME 34, NUMBER 5 MAY 1972

MAGNETIC HYPERFINE INTERACTIONS OF DIAMAGNETIC ATOMS IN RARE EARTH ORTHOFERRITES

I. S. LYUBUTIN and Yu. S. VISHNYAKOV

Crystallography Institute, U.S.S.R. Academy of Sciences

Submitted June 3, 1971

Zh. Eksp. Teor. Fiz. 61, 1962–1969 (November, 1971)

Rare earth orthoferrites $R_{1-x}Ca_xFe_{1-x}Sn_xO_3$ in which some of the iron ions are replaced by tin ions are investigated by means of the Mössbauer effect. Strong magnetic fields H_{eff} are observed at the nuclei of the diamagnetic tin atoms. H_{eff} is found to depend strongly on the atomic number of the rare earth element. The field decreases by 100 kOe on changing from lanthanum orthoferrite to lutecium orthoferrite. The exchange integrals J in the molecular-field-theory approximation and high-temperature-expansion-theory approximation are derived from the temperature dependence of the effective magnetic fields at the iron and tin nuclei. The values of the critical parameters β and D for substituted orthoferrites are also determined.

1. INTRODUCTION

RECENTLY, great interest has been aroused by the discovery of the effect of induction of strong magnetic fields at diamagnetic-atom nuclei introduced into iron-garnet[1-5] and iron-spinel[6,7] crystal lattices. In such compounds, the diamagnetic and ferromagnetic atoms are not neighbors but are separated by an intermediate oxygen atom. There is therefore no direct interaction here between the diamagnetic atom and the ferromagnetic one, and all the spin polarization mechanisms that do not take spin transfer into account are not very effective. At the same time, these compounds are dielectrics, and spin transfer with the aid of the conduction electrons is completely excluded here. The mechanism of induction of magnetic fields at diamagnetic atoms in such compounds is not yet clear.[8,9,6] At the same time, a study of similar effects can yield interesting information concerning the delocalization of the spin density in ferromagnetic dielectrics.

We report here investigations, with the aid of the Mössbauer effect, of the magnetic fields at the nuclei of diamagnetic tin atoms introduced into the crystal lattices of rare-earth orthoferrites.

Unlike iron garnets and spinels, rare-earth orthoferrites are antiferromagnets with weak ferromagnetism.[10] These are compounds with the general chemical formula $RFeO_3$ (where R is a rare-earth element or yttrium), having an orthorhombic structure of the type of the distorted perovskite structure.[11] All the iron ions are in crystallographically equivalent locations in an octahedral surrounding of oxygen ions, and form two magnetic sublattices, the moments of which are almost antiparallel. The magnetic structure of orthoferrites is such that each Fe^{3+} ion is surrounded by six Fe^{3+} ions of the other sublattice. The Fe–O–Fe indirect exchange interaction is most favored here, since the exchange-coupling angle is close to 180°.[12]

Our preliminary investigations of yttrium and gadolinium orthoferrites[13] have shown that in this case a strong magnetic field is likewise induced at the nuclei of the diamagnetic tin ions. However, unlike the garnets, the magnitude of the induced field in orthoferrites depends strongly on the rare-earth element.

We have investigated the Mössbauer effect on the nuclei Sn^{119} and Fe^{57} in the orthoferrites of practically all rare-earth elements in a wide temperature interval from 78°K to the Neel point.

2. EXPERIMENTAL PROCEDURE, SAMPLES

We synthesized polycrystalline samples of substituted orthoferrites, in which some of the iron ions were replaced by tin ions: $R_{1-x}Ca_xFe_{1-x}Sn_xO_3$. Here R = La, Pr, Nd, Sm, Gd, Tb, Ho, Er, Yb, Lu and Y, and the value of x ranged from 0.05 to 0.3. All the samples were enriched with Sn^{119} and Fe^{57}. The single-phase character of the samples was monitored with the aid of a Toshiba AFV-201 x-ray diffractometer. An x-ray analysis has shown that all the synthesized compounds have a distorted structure of the perovskite type and have the same structure as the orthoferrite $GdFeO_3$[11] (space group P_{bnm}). The unit-cell parameters a, b, and c for compositions with x = 0.1 are given in Table I together with the parameters for the nonsubstituted orthoferrites $RFeO_3$.[14] The values of a, b, and c for the substituted orthoferrites are somewhat larger than for the pure compounds $RFeO_3$. In a number of rare-earth elements, the parameters a and c decrease monotonically with decreasing radius of the R^{3+} ion. The parameter b varies little and has a blurred maximum in the gadolinium region.

The Mössbauer absorption spectra of Sn^{119} and Fe^{57} were obtained with a spectrometer of the electrodynamic type in the constant-acceleration regime. The spectra were recorded in 256 channels of the LP-4050 multichannel analyzer. The γ-quantum sources were Sn^{119m} in $BaSnO_3$ and Co^{57} in a platinum matrix.

For measurements in the high-temperature region, we constructed a special oven ensuring gradient-free heating of the sample up to 1000°C.[15] The temperature was measured with a chromel-alumel thermocouple. The accuracy of the temperature stabilization and the measurement was ±0.5°.

Table I. Lattice parameters (in Å) and Neel temperatures (in °K) for substituted and nonsubstituted orthoferrites

Compound	a	b	c	T_N^*
$LaFeO_3$	5,556	5.565	7.862	740
$La_{0,9}Ca_{0,1}Fe_{0,9}Sn_{0,1}O_3$	5.572	5.572	7.882	651
$NdFeO_3$	5.441	5.573	7,753	687
$Nd_{0,9}Ca_{0,1}Fe_{0,9}Sn_{0,1}O_3$	5.476	5,608	7.788	615
$GdFeO_3$	5,346	5.616	7.668	657
$Gd_{0,9}Ca_{0,1}Fe_{0,9}Sn_{0,1}O_3$	5.380	5.632	7.708	583
$TbFeO_3$	5.328	5,600	7.636	647
$Tb_{0,9}Ca_{0,1}Fe_{0,9}Sn_{0,1}O_3$	5.366	5.618	7.684	—
$YFeO_3$	5,302	5.589	7.622	640
$Y_{0,9}Ca_{0,1}Fe_{0,9}Sn_{0,1}O_3$	5,318	5.614	7,652	568
$HoFeO_3$	5.278	5,591	7.602	639
$Ho_{0,9}Ca_{0,1}Fe_{0,9}Sn_{0,1}O_3$	5,322	5.614	7.656	—
$ErFeO_3$	5,263	5.582	7.591	636
$Er_{0,9}Ca_{0,1}Fe_{0,9}Sn_{0,1}O_3$	5.304	5.610	7,636	564
$YbFeO_3$	5.233	5.557	7.570	627
$Yb_{0,9}Ca_{0,1}Fe_{0,9}Sn_{0,1}O_3$	5.276	5.590	7,624	—
$LuFeO_3$	5.213	5.547	7.565	623
$Lu_{0,9}Ca_{0,1}Fe_{0,9}Sn_{0,1}O_3$	5.262	5.580	7,620	555

---

*The values of T_N for the nonsubstituted orthoferrites were taken from [16].

3. EXPERIMENTAL RESULTS AND DISCUSSION

Low-temperature Region

Figure 1 shows the Mössbauer spectrum of the Sn^{119} nuclei in the compound $Nd_{0.95}Ca_{0.05}Fe_{0.95}Sn_{0.05}O_3$ at 78°K. The figure shows a well resolved magnetic hyperfine line splitting due to the action of a strong effective magnetic field ($H_{\text{eff}}^{\text{Sn}} = 217$ kOe) on the Sn^{119} nucleus. In the spectra of the orthoferrites with a large content of the Sn^{4+} ions, the Mössbauer lines are broadened.

The temperature dependence of $H_{\text{eff}}^{\text{Sn}}$ for different orthoferrites with the composition $R_{0.9}Ca_{0.1}Fe_{0.9}Sn_{0.1}O_3$ is shown in Fig. 2. An interesting feature of this dependence is that when the fields are extrapolated to zero temperature, the values of $H_{\text{eff}}^{\text{Sn}}(0\,°\text{K})$ do not tend to a single value, but remain essentially different for different rare-earth elements. At the same time, the effective magnetic fields $H_{\text{eff}}^{\text{Fe}}$ at the iron nuclei at 0 °K, differ slightly for the different orthoferrites (Fig. 3). Figure 4 shows the dependence of the effective magnetic field $H_{\text{eff}}^{\text{Sn}}$ at 0 °K on the number of the rare-earth element R. A strong decrease of $H_{\text{eff}}^{\text{Sn}}(0\,°\text{K})$ is observed in the series of rare-earth elements. The field decreases by 100 kOe on going from lanthanum to lutecium.

It is known that in rare-earth orthoferrites the crystal lattice becomes deformed with decreasing radius of the rare-earth ion. In an almost ideal cubic lattice, in the case of lanthanum orthoferrite, rhombic distortions appear, which increase on going to lutecium. It should be noted that the Neel temperature of the rare-earth orthoferrites decreases at the same time, in spite of the fact that the parameters of the unit cell decrease (see Table I).

Apparently, the lattice distortions are accompanied by a change in the angle of the Fe–O–Fe (or Fe–O–Sn) exchange coupling. This angle deviates from 180° and becomes smaller the stronger the distortions.[16] The indirect exchange interaction becomes weaker, and therefore the Neel point drops. Apparently, the effective magnetic field $H_{\text{eff}}^{\text{Sn}}$ is also directly dependent on the Fe–O–Sn exchange-coupling angle, a change of which alters the overlap of the atomic orbitals of the iron, oxygen, and tin.

According to theoretical calculations by Bersuker and Ogurtsov,[9] the magnetic field at the nucleus of a diamagnetic atom in such a system can be due to the transfer of the spin density from the iron atom to the tin atom. This transfer, in the MO LCAO approximation is due to hybridization of the s, p, and d electrons, and should apparently depend on the degree of overlap of the orbitals of these electrons.

High-temperature Region

From the temperature dependence of the effective magnetic fields at the Sn^{119} nuclei, we determined the Neel points of the investigated orthoferrites. The Neel temperatures, determined from the vanishing of the magnetic field at the Sn nucleus (see Fig. 2) are listed in Table I. Special experiments, in which the Mössbauer effect was measured simultaneously on the two isotopes Fe^{57} and Sn^{119} in the same sample, have shown that the magnetic fields at the iron and tin nuclei vanish simultaneously.

Using the experimental Neel temperatures T_N, we estimated the parameters of the exchange interaction J for our orthoferrites, using two methods, the molecular-field theory and the Rushbrook and Wood method of high-temperature expansion.[17]

In the molecular-field theory, the exchange integral for an antiferromagnet can be estimated from the relation

$$|J| = 3kT_N / nS(S+1). \qquad (1)$$

Here k is Boltzmann's constant, n the number of nearest neighbors, and S the spin, equal to $5/2$ for the Fe^{3+} ions. The exchange integral |J| is determined by the Hamiltonian $\mathscr{H} = +|J| \sum_{\langle i,j \rangle} S_i S_j$, where each pair of near-

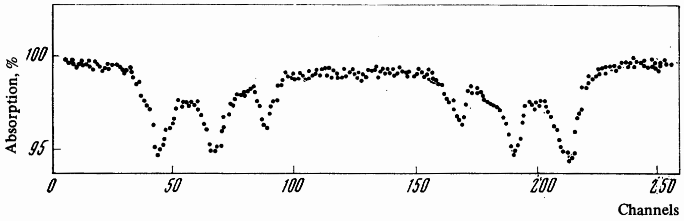

FIG. 1. Mossbauer spectrum of Sn^{119} nuclei in the orthoferrite $Nd_{0.95}Ca_{0.05}Fe_{0.95}Sn_{0.05}O_3$ at 78°K.

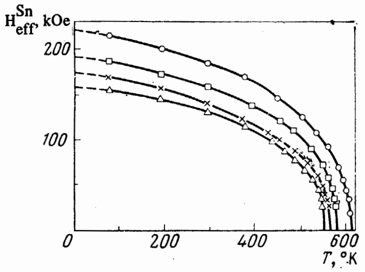

FIG. 2. Temperature dependence of the effective magnetic field H_{eff}^{Sn} at the tin nuclei for different orthoferrites with composition $R_{0.9}Ca_{0.1}Fe_{0.9}Sn_{0.1}O_3$. O–Nd, □–Gd, X–Y, Δ–Lu.

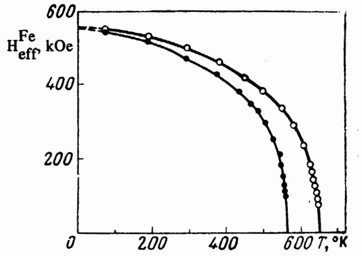

FIG. 3. Temperature dependence of effective magnetic field H_{eff}^{Fe} at the iron nuclei for the orthoferrites $La_{0.9}Ca_{0.1}Fe_{0.9} \times Sn_{0.1}O_3$ and $Er_{0.9}Ca_{0.1}Fe_{0.9}Sn_{0.1}O_3$. O–La, ●–Er.

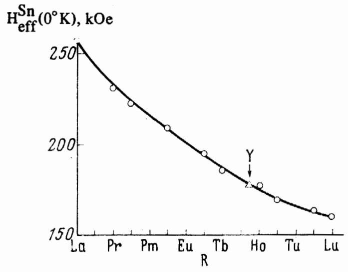

FIG. 4. Dependence of the effective magnetic field H_{eff}^{Sn} at 0°K on the number of the rare-earth element R in the orthoferrites $R_{0.9}Ca_{0.1}Fe_{0.9}Sn_{0.1}O_3$.

est magnetic atoms ⟨i, j⟩ appears in the sum only once.

In the orthoferrite structure, each magnetic Fe atom has in his nearest surrounding six neighboring Fe atoms of the other sublattice. Therefore n = 6 for the pure (nonsubstituted) orthoferrite $RFeO_3$. For an orthoferrite in which some of the iron ions are replaced by diamagnetic ions, the estimate of the parameter J becomes formally more complicated because the exact value of n is not known. However, if the nonmagnetic ions substitute uniformly the iron ions in the sublattices, then this difficulty can be eliminated by introducing the effective nearest-neighbor number n_{eff}, which depends on the substitution. For $R_{1-x}Ca_xFe_{1-x}Sn_xO_3$ orthoferrites, we have $n_{eff} = (1 - x)n$. For example, for x = 0.1, i.e., when one-tenth of the iron ions is replaced by tin ions, we have $n_{eff} = 5.4$.

Table II lists the exchange integrals calculated both for substituted orthoferrites at x = 0.1 ($R_{0.9}Ca_{0.1}Fe_{0.9}Sn_{0.1}O_3$, $n_{eff} = 5.4$) and for pure orthoferrites ($RFeO_3$, n = 6). There is a surprising agreement between the values obtained for J.

At the present time, the most direct approach to the problem of magnetic phase transitions is the method of high-temperature expansions developed by Rushbrook and Wood.[17, 19] In the theory of high-temperature expansions, for an antiferromagnet with a simple cubic lattice, the relation between the exchange integral and the Neel temperature is given by the expression[17]

$$T_N = \frac{|J|}{k}\frac{5}{192}(n-1)\,[11S(S+1)-1]\left[1+\frac{0{,}63}{nS(S+1)}\right]. \qquad (2)$$

For a nonsubstituted orthoferrite (n = 6 and S = 5/2), expression (2) reduces to

$$|J|/k = T_N/12.5512. \qquad (3)$$

Table II. Values of the exchange integrals |J|/k, (°K) for substituted and nonsubstituted orthoferrites

R	Molecular-field theory		High-temperature-expansion theory	
	$RFeO_3$ $n = 6$	$R_{0,9}Ca_{0,1}Fe_{0,9}S_{0,1}O_3$ $n_{eff} = 5.4$	$RFeO_3$ $n = 6$	$R_{0,9}Ca_{0,1}Fe_{0,9}Sn_{0,1}O_3$ $n_{eff} = 5.4$
La	42.4	41.4	59.0	58.9
Nd	39.3	39,1	54.7	55.6
Gd	37.6	37.0	52.3	52.7
Y	36.6	36.1	51,0	51.3
Er	36.4	35.8	50,7	51.0
Lu	35.6	35.3	49.6	50.2

For substituted orthoferrites, $R_{1-x}Ca_xFe_{1-x}Sn_xO_3$, the exchange integral can be determined by introducing, as before, the effective number of nearest neighbors n_{eff}. Then for x = 0.1, $n_{eff} = 5.4$ and S = 5/2 expression (2) reduces to

$$|J|/k = T_N/11.0593. \qquad (4)$$

The exchange integrals calculated in this manner turn out again, just as in the molecular-field theory, to be very close for substituted and pure orthoferrites (Table II).

As expected, the values of the parameters J, calculated by the high-temperature expansion method, are higher and apparently more exact than the values of J obtained in the molecular-field approximation.[18] Calculation shows that the value of |J| drops from 58.8 to 50.8°K on going from the lanthanum orthoferrite to the lutecium orthoferrite.

The fact that the exchange integrals calculated for substituted orthoferrites turned out to coincide with the corresponding values of J for pure orthoferrites indicates that the theory as considered above can apparently be applied also to complex substituted systems, provided the corresponding values of n_{eff} can be chosen in a reasonable manner.

Temperature Dependence of Effective Magnetic Fields

It is customarily assumed at present that the effective magnetic field at the Fe^{3+} ion nuclei, as a function of the temperature, is proportional to the magnetization of that sublattice in which the iron ion is situated.[20, 21]

It is of interest to compare the temperature dependence of the effective magnetic fields at the Fe nuclei, and also at the Sn nuclei in different orthoferrites. Figure 5 shows the dependence of the reduced field $H_{eff}(T)/H_{eff}(0)$ on the reduced temperature T/T_N for certain orthoferrites with composition $R_{0.9}Ca_{0.1}Fe_{0.9}Sn_{0.1}O_3$. Attention should be called to the following features of these curves: 1) for all the investigated orthoferrites the fields at the iron nuclei have approximately the same temperature dependence; a similar result was also observed for nonsubstituted orthoferrites;[16] 2) the fields at the tin nuclei decrease more rapidly with increasing temperature than the fields at the iron nuclei (Fig. 5).

It can apparently be assumed that the field at the nucleus of a diamagnetic atom reflects the magnetic state of the iron ions surrounding this atom. On the other hand, the state of these iron ions differs in that they have at least one diamagnetic atom in their nearest surroundings. Consequently, their exchange interaction

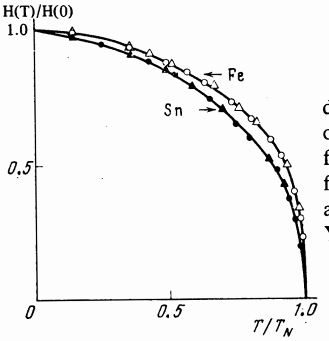

FIG. 5. Dependence of the reduced magnetic field $H_{eff}(T)/H_{eff}(0)$ on the reduced temperature T/T_N for Sn and Fe nuclei in the orthoferrites $Er_{0.9}Ca_{0.1}Fe_{0.9} \times Sn_{0.1}O_3$ and $Y_{0.9}Ca_{0.1}Fe_{0.9}Sn_{0.1}O_3$. ○, ●—Y; △, ▲—Er.

becomes weaker and the temperature dependence of the magnetic moment should be stronger. It can be assumed as a rough approximation that the temperature dependence of the field at a tin nucleus (Fig. 5) reflects the temperature dependence of the magnetic moment of those iron ions which have weakened exchange couplings. This apparently can explain the singularities of (2) (Fig. 5).

As shown experimentally[22, 23] and theoretically,[24, 25] the temperature dependence of the magnetization near the Neel point can be expressed in the form

$$\sigma_s(T)/\sigma_s(0) = D(1 - T/T_N)^{\beta}.$$

Different theories predict different values of the parameters β and D (see Table IV of [16]). For example, β can assume values $1/2$, $1/8$, $5/16$, and $1/3$. To give preference to any particular theoretical model, it is necessary to know the experimental values of the parameters β and D for different substances.

Recent[16] Mössbauer investigations have shown that for pure (nonsubstituted) orthoferrites the value of the parameter β in the temperature interval $0.60 < T/T_N < 0.99$ is 0.348 ± 0.005. The coefficient D ranges from 1.11 to 1.17.

We attempted to determine the values of the critical parameters β and D for the substituted orthoferrite $Y_{0.9}Ca_{0.1}Fe_{0.9}Sn_{0.1}O_3$, assuming that the field at the nucleus has the same temperature dependence as the magnetization. Figure 6 shows in a doubly-logarithmic scale a plot of $H_{eff}(T)/H_{eff}(0)$ against $(1 - T/T_N)$ both for the fields at the iron nuclei and for the fields at the tin nuclei. Both plots are linear in the temperature interval $0.60 < T/T_N < 0.985$, but differ somewhat in slope. The values of the parameters β and D calculated from the temperature dependences of the fields at the iron and at the tin nuclei turn out to be somewhat different:

$$\beta^{Fe} = 0{,}315 \pm 0{,}005, \quad D^{Fe} = 1{,}13 \pm 0{,}02, \quad 0{,}60 < T/T_N < 0{,}985;$$

$$\beta^{Sn} = 0{,}380 \pm 0{,}01, \quad D^{Sn} = 1{,}17 \pm 0{,}02, \quad 0{,}60 < T/T_N < 0{,}985.$$

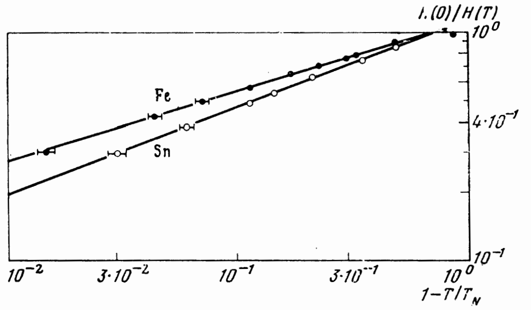

FIG. 6. Dependence of the field $H_{eff}(T)/H_{eff}(0)$ on the quantity $1-T/T_N$ in the orthoferrite $Y_{0.9}Ca_{0.1}Fe_{0.9}Sn_{0.1}O_3$. The scales of both coordinates are logarithmic.

Thus, for substituted orthoferrites as well, the magnetization as a function of the temperature in the region $0.6 < T/T_N < 0.985$ varies approximately in accordance with the $1/3$ law, and not the $1/2$ law predicted by the molecular-field theory.

The authors are grateful to Professor K. P. Belov and Professor L. M. Belyaev for interest in the work and for useful discussions of the results, and to L. S. Garashina for help with the x-ray investigation of the samples.

---

[1] K. P. Belov and I. S. Lyubutin, ZhETF Pis. Red. **1**, No. 1, 26 (1965) [JETP Lett. **1**, 16 (1965)].

[2] I. S. Lyubutin, Fiz. Tverd. Tela **8**, 643 (1966) [Sov. Phys.-Solid State **8**, 519 (1966)].

[3] K. P. Belov and I. S. Lyubutin, Zh. Eksp. Teor. Fiz. **49**, 747 (1965) [Sov. Phys.-JETP **22**, 518 (1966)].

[4] V. I. Gol'danskiĭ, M. N. Devisheva, V. A. Trukhtanov and V. F. Belov, ZhETF Pis. Red. **1**, No. 1, 31 (1965) [JETP Lett. **1**, 19 (1965)].

[5] V. A. Golovnin, S. M. Irkaev, R. N. Kuz'min, and B. V. Mill', ibid. **11**, 35 (1970) [**11**, 21 (1970)].

[6] S. L. Ruby, B. E. Evans, and S. S. Hafner, Sol.Stat. Comm. **6**, 277 (1968).

[7] G. V. Novikov, V. A. Trukhtanov, L. Cher, S. I. Yushchuk, and V. I. Gol'danskiĭ, Zh. Eksp. Teor. Fiz. **56**, 743 (1969) [Sov. Phys.-JETP **29**, 403 (1969)].

[8] I. S. Lyubutin, The proceedings of the Conference for Application of Mössbauer Spectroscopy, Hungary, Tuhan, 1969.

[9] I. B. Bersuker and I. Ya. Ogurtsov, Zhurn. Teor. Eksp. Khim. **4**, 48 (1968).

[10] K. P. Belov, M. A. Belyanchikova, R. Z. Levitin, and S. A. Nikitin, Redkozemel'nye ferro- i antiferromagnetiki (Rare-earth Ferro- and Antiferromagnets), Nauka, 1965.

[11] S. Geller, J. Chem. Phys. **24**, 1236 (1956).

[12] W. C. Koehler and E. O. Wollan, J. Phys. Chem. Sol. **2**, 100 (1957).

[13] I. S. Lyubutin and Yu. S. Vishnyakov, ZhETF Pis. Red. **12**, 508 (1970) [JETP Lett. **12**, 355 (1970)].

[14] S. Geller and E. A. Wood, Acta Cryst. **9**, 563 (1956); D. Treves, J. Appl. Phys. **36**, 3 (1965).

[15] I. S. Lyubutin and Yu. S. Vishnyakov, Pribory i Tekh. Eksperim. No. 5, 221 (1970).

[16] M. Eibschütz, S. Shtrikman, and D. Treves, Phys. Rev. **156**, 562 (1967).

[17] G. S. Rushbrook and P. J. Wood, Mol. Phys. **6**, 409 (1963).

[18] J. S. Smart, Effective Field Theories of Magnetism, Philadelphia–London, 1966.

[19] G. S. Rushbrook and P. J. Wood, Mol. Phys. **1**, 257 (1958).

[20] V. Jaccarino, Magnetism, Acad. Press, Inc., N. Y. Vol. **11A**.

[21] J. J. Van Loef, Physica **32**, 2102 (1966).

[22] M. Eibschütz, S. Shtrikman, and D. Treves, Sol. Stat. Comm. **4**, 141 (1966).

[23] P. Heller and G. Benedek, Phys. Rev. Lett. **14**, 71 (1965).

[24] J. W. Essam and M. F. Fisher, J. Chem. Phys. **38**, 802 (1963).

[25] E. Callen and H. Callen, J. Appl. Phys. **36**, 1140 (1965).

Translated by J. G. Adashko
205