Gigantic effect of magnetic vacancies on a phase transition of the Morin type in rare-earth orthoferrites

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An extremely strong influence of nonmagnetic ions (Al^{3+}) on the magnetic anisotropy has been detected in the orthoferrite $DyFeO_3$; it leads to a considerable change of the Morin temperature. The observed results are interpreted by means of a "magnetic vacancy" model. Within the framework of this model, the anisotropy energy and the shift of the Morin temperature are calculated as functions of the concentration of nonmagnetic substituent ions. An experimental investigation is made of reorientation transitions induced in $DyFe_{1-x}Al_xO_3$ by an external magnetic field.

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INTRODUCTION

The explanation of the role of impurity ions in shaping the magnetic properties of a material constitutes one of the most important problems of magnetism. Their behavior in a magnetic crystal is the subject of many experimental and theoretical investigations. It is known, for example, that the anisotropy energy of certain magnetic materials (iron garnets, orthoferrites, etc.) is strongly influenced by Co^{2+} and Fe^{2+} ions,[1] which have an orbitally degenerate or nearly degenerate ground state. Much attention has also been given to other magnetic ions in the investigation of anisotropy.

We have observed a very strong influence of nonmagnetic ions on the magnetic properties of certain rare-earth orthoferrites. In the rare-earth orthoferrites (ROF) $RFeO_3$ there are two types of magnetic ions, Fe^{3+} and R^{3+}, forming respectively the "iron" and "rare-earth" (RE) magnetic lattices. In the vicinity of each rare-earth ion (RI) there are eight nearest neighbors, Fe^{3+} ions. We shall suppose that instead of an Fe^{3+} ion there "sits" on a definite site a nonmagnetic ion (for example Al^{3+}, Ga^{3+}, ...). Then such an impurity substitution ion may be regarded as a vacancy in the magnetic lattice, since at this site of the magnetic lattice a magnetic ion is absent (Fig. 1). For brevity, we shall hereafter call such a nonmagnetic impurity ion of the substitution type a magnetic vacancy.

The diversity of the properties of ROF is determined primarily by R–Fe interaction. The exchange interaction of a pair of ions Fe^{3+} and R^{3+} can be separated into two parts: the isotropic interaction and the anisotropic, which also includes antisymmetric exchange. Usually the isotropic part considerably exceeds the anisotropic. As regards the interaction of R^{3+} with all the nearest neighbors, by virtue of the antiferromagnetic ordering of the magnetic moments of the Fe^{3+} ions the resultant isotropic exchange field on R^{3+} vanishes,$^{1)}$ since the fields produced by ions with antiparallel moments compensate each other. But complete compensation of the anisotropic and antisymmetric interactions does not occur; therefore the resultant field on R^{3+} is nonzero, though small (~10^3–10^4 Oe).

The situation changes abruptly when in the vicinity of the R^{3+} ion there is a magnetic vacancy (Fig. 1). In this case, the compensation of the isotropic exchange interaction is destroyed; there arises an isotropic exchange field $\mathbf{H}_{mv}$ acting on R^{3+}:

$$H_{mv}=\eta a G, \qquad (1)$$

where G is the antiferromagnetism vector of the Fe^{3+} ions; $\eta=\pm 1$, depending on the type of site occupied by the magnetic vacancy; and $a \gtrsim 10^4$ Oe.

The field $\mathbf{H}_{mv}$ magnetizes the rare-earth ions that are nearest neighbors of the magnetic vacancy. If within the crystal the magnetic vacancies are distributed randomly on the iron sublattice, then it is obvious that the total magnetic moment of the rare-earth ions (RI) induced by them (the magnetic vacancies) will be zero. The additional free energy of the RI produced by the magnetic vacancies is an even function of $\mathbf{H}_{mv}$ and therefore does not vanish on averaging over a random distribution of magnetic vacancies. RI in ROF usually have strong anisotropy of the susceptibility (or anisotropy of the *g* factor); in this case the additional free energy will depend on the orientation of $\mathbf{H}_{mv}$, and consequently on that of the antiferromagnetism vector, with respect to the crystal axes. This means that the magnetic vacancies produce additional anisotropy. We shall estimate this anisotropy energy for the case of extremely anisotropic, Ising ions. The direction of the magnetic moment of an Ising ion coincides with a definite axis (the axis of quantization) for arbitrary direction of the external and exchange fields that act upon it. In ROF such ions as Dy^{3+}, Tb^{3+}, and

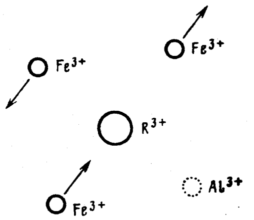

FIG. 1. Schematic representation of a "magnetic vacancy."

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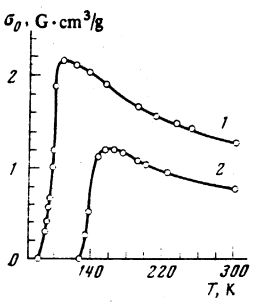

FIG. 2. Temperature variation of the spontaneous magnetization of $DyFe_{1-x}Al_xO_3$. Curve 1, $x=0.027$; Curve 2, $x=0.1$.

Ho^{3+} can be described with good accuracy in the approximation of the Ising model. The axis of quantization of these ions in ROF lies in the *ab* plane (a reflection plane of the crystalline field for the RI) and makes an angle ± α with the crystallographic *a* axis. The signs ± correspond to different, nonequivalent positions of the RI. When this is taken into account, the additional free energy produced by magnetic vacancies randomly distributed on the Fe sublattice with concentration[2)] x, in the quadratic approximation with respect to the field $\mathbf{H}_{mv}$ determined by (1), can be expressed in the form (per RI)

$$\Delta\mathcal{F}=-zx\frac{\mu^2a^2}{2T}\frac{(\mathbf{Gn}^+)^2+(\mathbf{Gn}^-)^2}{2}, \tag{2}$$

where $\mathbf{n}^\pm$ are unit vectors determining the direction of the local RI axis for the two nonequivalent locations (±); $z=8$ is the number of nearest RI in the vicinity of a magnetic vacancy. The additional anisotropy energy, for example in the *ab* plane, has according to (2) the value

$$\Delta\mathcal{F}_{ab}=\Delta K_{ab}G_x^2=\left[-\frac{zx\mu^2a^2\cos 2\alpha}{2T}\right]G_x^2.$$

We shall compare this additional anisotropy caused by magnetic vacancies with the anisotropy energy K in the *ab* plane of the Fe sublattice in $DyFeO_3$, which does not exceed $5\cdot10^4$ erg/cm³.[2,3] Setting $\mu=10\mu_B$, $a=10^4$ Oe, $\cos2\alpha=-\frac{1}{2}$, we determine the concentration x^* of magnetic vacancies for which $\Delta K_{ab}=K$:

$$x^*(T)=\frac{4KT}{z\mu^2a^2}\approx\frac{T[\mathrm{K}]}{5\cdot10^3}. \tag{3}$$

For $T=50$ K, we have $x^*=1\%$. This example illustrates the "gigantic" anisotropy introduced by magnetic vacancies.

EXPERIMENTAL RESULTS

To investigate the change of anisotropy caused by magnetic vacancies, investigations were made of the magnetic and magneto-elastic properties of monocrystals of dysprosium orthoferrite (Dy^{3+} is the Ising ion) with small additions of Al^{3+} ions. In order to determine any effect of the Al^{3+} ions on the Fe^{3+} spin sublattice that was not caused by interaction with rare-earth ions, magnetic anisotropy was also studied in monocrystals of aluminum-substituted yttrium orthoferrite (the Y^{3+} ion is nonmagnetic). Monocrystals of $DyFe_{1-x}Al_xO_3$ ($x=0.027$; 0.1) and $YFe_{0.95}Al_{0.05}O_3$ were grown from solution in a melt of lead compounds. The amount of Al^{3+} ion content was determined with an x-ray spectrum analyzer JPX-3 to accuracy 0.01%. Magnetostriction measurements were made on the monocrystals by the method of remote piezoelectric sensing, and measurements of torque curves by piezosensing, in pulsed magnetic fields ~100 kOe. Measurements of torque curves were also made in static magnetic fields up to 12 kOe with a magnetic torsion balance with autocompensation.

As the measurements showed, the anisotropy constant of $YFe_{0.95}Al_{0.05}O_3$ in the *ac* plane at 78 K was $4\cdot10^5$ erg/cm³; that is, somewhat diminished in comparison with unsubstituted yttrium orthoferrite ($K_{ac}=5\cdot10^5$ erg/cm³). The decrease of the anisotropy constant is perhaps due to the fact that the ionic radius of Al^{3+}(0.57 Å) is smaller than that of Fe^{3+}(0.67 Å); consequently, replacement of Fe^{3+} ions by Al^{3+} in yttrium orthoferrite should decrease the rhombic distortion of the crystal. A considerably more pronounced effect on the anisotropy was observed on introduction of Al^{3+} ions into dysprosium orthoferrite. It is known that in $DyFeO_3$, lowering of temperature causes a spin-reorientation transition from the weakly ferromagnetic state (G_xF_z) to a purely antiferromagnetic (G_y) (a transition of the Morin type[4]).

A small replacement of Fe^{3+} ions by Al^{3+} leads to a substantial increase of the $G_xF_z-G_y$ transition temperature. As is seen from Fig. 2, the transition temperatures for $x=0.027$ and $x=0.1$ are 105 and 135 K respectively, whereas for pure $DyFeO_3$ we have $T_M=42$ K. On application of an external magnetic field $\mathbf{H}\parallel c$-axis below T_M, when the crystal is antiferromagnetic, a transition to the weakly ferromagnetic state (G_xF_z) is induced. The process of rotation of the spins in the *ab* plane, as in the case of *ac* reorientation, is accompanied by magnetoelastic deformations. In addition to the magnetostriction due to the Fe^{3+} ions, in the case of orthoferrites with magnetic RE ions there occurs RE magnetostriction, due to the paramagnetism of the RE ions and proportional to $(\chi H)^2$ (Fig. 3).

By replotting the curves of Fig. 3 in coordinates $\lambda=f(H^2)$, where the paramagnetic component is linear, and extrapolating the resulting relations to $H=0$, one can separate out in pure form the magnetostriction due to rotation of the magnetic sublattices of Fe^{3+} ions; it amounted to $\Delta l/l=0.8\cdot10^{-5}$. The magnetostriction values obtained coincide in sign with, and are close in value to, those observed in unsubstituted dysprosium orthoferrite during the spin-reorientation transition $G_y-G_xF_z$.[2] From the field dependence of the magnetostriction we determined also the threshold field $H_{th}(T)$, at which the

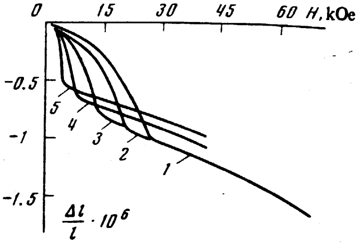

FIG. 3. Field dependence of magnetostriction of $DyFe_{0.973}Al_{0.027}O_3$ at various temperatures. Curve 1, 81 K; 2, 86 K; 3, 90 K; 4, 96 K; 5, 100 K.

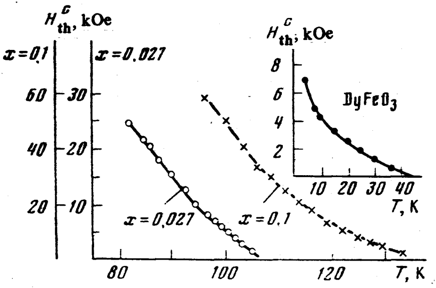

FIG. 4. Phase diagram $H_{th}^{c}(T)$ for $DyFe_{1-x}Al_xO_3$ monocrystals.

process of spin rotation began. Figure 4 shows the phase diagrams $H_{th}(T)$ for $x=0.027$ and $x=0.1$. It is seen that the threshold field and consequently the anisotropy constant increase with increasing distance from T_M; T_M, in accordance with Fig. 2, is displaced sharply upward with replacement of Fe^{3+} ions by Al^{3+}. An explanation of the so pronounced influence of small substitutions on the Morin transition in $DyFe_{1-x}Al_xO_3$, and also a calculation of the change of the anisotropy constant in the *ab* plane on introduction of nonmagnetic ions (magnetic vacancies) into dysprosium orthoferrite, will be given in the following section.

THEORY AND DISCUSSION OF RESULTS

We shall consider the behavior of the system $DyFe_{1-x}Al_xO_3$ in greater detail on the basis of the magnetic-vacancy model discussed in the Introduction.

According to Ref. 2, the exchange-interaction Hamiltonian of the RI in the unsubstituted ROF can be expressed in the form

$$\mathscr{H}_0 = z\mu_B \mathbf{S}_R[A(\mathbf{L})\mathbf{F}+B(\mathbf{L})\mathbf{G}], \tag{4}$$

where $A(\mathbf{L})$ is a symmetric and $B(\mathbf{L})$ an antisymmetric function, with respect to reflection in the plane C_s, of the orbital angular momentum operator $\mathbf{L}$. We assume that the presence of a magnetic vacancy in a nearest neighborhood does not greatly change the R–Fe exchange interaction with the other ions and the crystalline field that acts on the RI. In this case, the Hamiltonian of the exchange interaction of the RI with the uncompensated nearest Fe^{3+} neighborhood can be represented as follows:

$$\mathscr{H} = (z-2)\mu_B \mathbf{S}_R[A(\mathbf{L})\mathbf{F}+B(\mathbf{L})\mathbf{G}]+\mu_B \mathbf{S}_R[A(\mathbf{L})+\eta B(\mathbf{L})](\mathbf{F}+\eta\mathbf{G}), \tag{5}$$

where the first term describes the interaction of the RI with the z-2 compensated Fe^{3+} magnetic moments, and the second describes the interaction with the uncompensated Fe^{3+} ion, which, in the operation of reflection in the plane C_s, takes the place of the magnetic vacancy; $\eta = \pm 1$. In the following calculations, we shall omit from the Hamiltonian (5) the small term ~ $B(\mathbf{L})\mathbf{F}$.

It has been established experimentally[5] that the ground doublet of the Dy^{3+} ion in $DyFeO_3$ is described with good accuracy by wave functions of the form $\psi_0^{\pm} = |\pm\frac{15}{2}\rangle$, with an axis of quantization that lies in the *ab* plane at an angle $\alpha = \pm 60°$ to the *a* axis. Because of this specific form of the wave functions of the ground doublet, its splitting because of antisymmetric exchange interaction is zero, and the splitting caused by symmetric exchange is small. In this connection, as was mentioned in Ref. 2, an important role is played by Van Vleck interaction of the ground doublet with the excited ones; this produces additional anisotropy in $DyFeO_3$, which stabilizes the configuration Γ_1 and determines a phase transition of the Morin type ($\Gamma_4 \to \Gamma_1$) at $T = 42$ K. The principal contribution to the Van Vleck interaction comes from the first excited doublet ($E_1 \approx 50\ cm^{-1}$), whose wave functions,[3] from analysis of experimental data on the temperature dependence $\chi_c(T)$, are $\psi_1^{\pm} = |\pm\frac{13}{2}\rangle$.

We shall calculate the spectrum of the Dy^{3+} ions, with allowance for exchange interaction, with the Hamiltonian (5), restricting ourselves to the ground and first excited doublets.[3)] In the representation of the wave functions of these doublets, the matrix of the operator $\mathscr{H}$ has the form

$$\mathscr{H} = \begin{pmatrix} \langle\frac{15}{2}|\mathscr{H}|\frac{15}{2}\rangle & 0 & \langle\frac{15}{2}|\mathscr{H}|\frac{13}{2}\rangle & 0 \\ 0 & \langle-\frac{15}{2}|\mathscr{H}|-\frac{15}{2}\rangle & 0 & \langle-\frac{15}{2}|\mathscr{H}|-\frac{13}{2}\rangle \\ \langle\frac{13}{2}|\mathscr{H}|\frac{15}{2}\rangle & 0 & \langle\frac{13}{2}|\mathscr{H}|\frac{13}{2}\rangle & 0 \\ 0 & \langle-\frac{13}{2}|\mathscr{H}|-\frac{15}{2}\rangle & 0 & \langle-\frac{13}{2}|\mathscr{H}|-\frac{13}{2}\rangle \end{pmatrix}. \tag{6}$$

As a result of diagonalization of the matrix (6), to the second order of perturbation theory, the energy levels of the Dy^{3+} ions in whose neighborhoods there are magnetic vacancies are determined as follows:

$$E_0^{1,2} = -\Delta E \pm \tilde{\Delta}_0, \quad E_1^{1,2} = E_1 + \Delta E \pm \tilde{\Delta}_1, \tag{7}$$

where

$$\begin{gathered} \tilde{\Delta}_0 = g\mu_B |[(z-1)a\mathbf{F}+\eta a\mathbf{G}]\mathbf{n}_\sigma|, \\ \tilde{\Delta}_1 = g_1\mu_B |[(z-1)a\mathbf{F}+\eta a\mathbf{G}]\mathbf{n}_\sigma + {}^2/_{13}(z-1)b\mathbf{G}\mathbf{l}_\sigma|, \\ \Delta E = \frac{\chi_{VV}^{c}}{2}\{[((z-1)a\mathbf{F}+\eta a\mathbf{G})\mathbf{l}_\sigma + (z-1)b\mathbf{G}\mathbf{n}_\sigma]^2 \\ +[((z-1)a\mathbf{F}+\eta a\mathbf{G})\mathbf{m}_\sigma]^2\}, \end{gathered} \tag{8a}$$

$$\begin{gathered} \chi_{VV}^{0} = \frac{2\mu_B^2(g')^2}{E_1}, \quad g = \frac{15}{2}g_L, \quad g_1 = \frac{13}{15}g, \quad g' = g_L\frac{\sqrt{15}}{2}, \\ ga = \langle {}^{15}/_2|A(\mathbf{L})\mathbf{S}_R\mathbf{n}_\sigma|{}^{15}/_2\rangle, \\ g'b = i\langle {}^{15}/_2|B(\mathbf{L})\mathbf{S}_R\mathbf{n}_\sigma|{}^{13}/_2\rangle, \end{gathered} \tag{8b}$$

$\mathbf{n}_\sigma$, $\mathbf{m}_\sigma$, $\mathbf{l}_\sigma$ are unit vectors; $\mathbf{n}_\sigma$ is directed along the RI axis; $\mathbf{m}_\sigma$ and $\mathbf{n}_\sigma$($\mathbf{m}_\sigma \perp \mathbf{n}_\sigma$) lie in the *ab* plane; $\mathbf{l}_\sigma \parallel c$-axis; $\sigma = \pm$ determines nonequivalent locations. In the calculation of the matrix elements from the operator $A(\mathbf{L})$, only the isotropic part was taken into account in the latter.

To determine the energy levels of Dy^{3+} ions in whose neighborhood there are no magnetic vacancies is easy: in formulas (7) and (8), replace $(z-1)$ by z and set the term $\eta a\mathbf{G}$ equal to zero.

We shall represent the free energy of the system $DyFe_{1-x}Al_xO_3$ in the form of a sum of the free energy $\mathscr{F}_{Fe}$ of the subsystem of iron ions, by analogy with Ref. 2, and of the free energy of the rare-earth subsystem. At not too high temperatures ($T \leq 100$ K), if we restrict ourselves to the ground and first excited doublets of Dy^{3+}, under the condition that the splitting of the doublets and the shift of their "center of gravity" is small in comparison with the distance E_1 between them, we can represent the free energy $\mathcal{F}_R$ in the form (per RI)

$$\mathcal{F}_R=-\frac{1-zx}{2}\sum_{\sigma=\pm}\left[\frac{\Delta_0^2}{2T}f_0(T)+\frac{\Delta_1^2}{2T}f_1(T)+\Delta E\,\mathrm{th}\frac{E_1}{2T}\right]$$
$$-\frac{zx}{4}\sum_{\substack{\eta=\pm 1\\ \sigma=\pm}}\left[\frac{\tilde{\Delta}_0^2}{2T}f_0(T)+\frac{\tilde{\Delta}_1^2}{2T}f_1(T)+\Delta\tilde{E}\,\mathrm{th}\frac{E_1}{2T}\right], \tag{9}$$

where

$$f_0(T)={}^1\!/_2\exp(E_1/2T)/\mathrm{ch}(E_1/2T),$$
$$f_1(T)={}^1\!/_2\exp(-E_1/2T)/\mathrm{ch}(E_1/2T).$$

By substituting in (8) the values of the corresponding quantities from (7) and omitting the terms independent of the angles, we express the total free energy of the system as follows:

$$\mathcal{F}=\frac{AF^2}{2}a_1F_x^2+a_2F_y^2+a_3F_z^2+(b_1+\Delta b_1)G_x^2+(b_2+\Delta b_2)G_y^2$$
$$+(b_3+\Delta b_3)G_z^2+d_1G_xF_z+d_3G_zF_x. \tag{10}$$

The coefficients a_i, b_i, and d_i in (10), which vary with concentration as $(1-2x+x/z)$, may for small x be considered equal to the corresponding quantities for pure DyFeO$_3$. The quantities $\Delta b_i\sim x$; they are due to the presence of magnetic vacancies in the neighborhood of the RI.

By minimizing the free energy (10) with respect to **F** under the condition $\mathbf{F}\cdot\mathbf{G}=0$, $G^2=f-F^2\approx 1$,[4] and also omitting the terms of the type $a_iF_i^2$, which are unimportant at high temperatures, we determine the anisotropy constant of the vector **G** in the ab plane $(\mathcal{F}_{ab}=K_{ab}G_x^2)$:

$$K_{ab}\approx K_{ab}^{\mathrm{Fe}}+\chi_{VV}^0H_{\mathrm{ex}}^2\,\mathrm{th}\frac{E_1}{2T}+\frac{xza^2}{4}[\chi_Tf_0(T)+\chi_T'f_1(T)], \tag{11}$$

where

$$\chi_T=g^2\mu_B^2/T,\qquad \chi_T'=g_1^2\mu_B^2/T,\qquad H_{\mathrm{ex}}=zb/2.$$

It is evident from (11) that the presence of the additional anisotropy will stabilize the phase Γ_1 and will lead to a rise of the temperature T_M of the phase transition of the Morin type $(\Gamma_4\to\Gamma_1)$.

We shall estimate this temperature from the condition $K_{ab}(T_M)=K_2$,[7] where K_2 is the fourth-order anisotropy constant of the iron sublattice. For very small concentrations x, when the rise of the Morin transition temperature is not large in comparison with T_M^0 in pure DyFeO$_3$, the relative shift $\Delta T_M/T_M^0$ of the transition temperature is determined as

$$\frac{\Delta T_M}{T_M^0}\approx\frac{xz\mu_B^2g^2a^2}{2E_1\chi_{VV}^0H_{\mathrm{ex}}^2}\mathrm{ch}^2\frac{E_1}{2T_M^0}\ . \tag{12}$$

For concentrations x at which the Morin temperature T_M rises appreciably (to 100 K and above), it may be supposed that the ground and excited doublet levels of Dy^{3+} are populated about equally. In this case the temperature T_M can be estimated with the formula

$$T_M\approx\frac{1}{2}\left[\chi_{VV}^0H_{\mathrm{ex}}^2E_1+\frac{xza^2\mu_B^2}{4}(g^2+g_1^2)|\right]\Big/\ |K_{ab}^{\mathrm{Fe}}-K_2|. \tag{13}$$

The value of a is determined from the condition $|za\mathbf{F}|=|\lambda\mathbf{F}|\approx 10^3$ Oe[2]; $H_{\mathrm{exc}}\approx 10^4$ Oe according to an estimate made in Ref. 2; $K_{ab}^{\mathrm{Fe}}-K_2\approx-1.8\cdot 10^4$ erg/g is determined from the condition $K_{ab}(T_M^0)=K_2$ for pure DyFeO$_3$. On substituting in (13) the numerical values of the quantities that occur there, we get for T_M the expression $T_M=52+2500x$[K]. For $x=0.027$ this formula gives $T_M=119$ K, which agrees not too badly with experimental data. At larger concentrations, formula (13) leads to too high values of T_M; for example, for $x=0.1$ we have $T_M=300$ K. This is due to the fact that the calculation presented above is correct only for the case $x\ll 1/z=0.125$, when it may be supposed that in the vicinity of each RI there is no more than one magnetic vacancy.

In conclusion, we note that such decompensation of the exchange interaction occurs not only on replacement by nonmagnetic ions, but also in the case of other defects, for example dislocations or defects on the surface of the crystal, etc. This can lead to a strong influence of such defects on the anisotropy energy and other magnetic properties.

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[1] A small weakly ferromagnetic canting of the magnetic moments of the Fe^{3+} ions leads to the result that complete compensation of the isotropic exchange does not occur in the weakly ferromagnetic phase; the resulting isotropic exchange field is $\lesssim 10^3$ Oe.

[2] Because we are considering a magnetic structure that is uniform throughout the specimen, there is a lower bound to x, which can be estimated from the following qualitative considerations. The nonuniformity $\delta\mathbf{G}$ of the antiferromagnetism vector that is produced by a magnetic vacancy is propagated into the crystal, by exchange interaction, over a region with linear dimensions of order $(A/K)^{1/2}$, where A is the exchange constant between Fe^{3+} ions and K is the anisotropy constant of the vector **G**. Hence it follows that when $x\gg a_0^3(K/A)^{3/2}$ (a_0 is the interatomic distance), the dependence of **G** on the coordinates may be neglected. For ROF this condition is satisfied when $x\gg 10^{-3}$ to 10^{-4}.

[3] In these calculations we do not take the R–Fe dipole interaction into account, because our interest is in the reorientation of the vector **G** in the ab plane. In DyFeO$_3$, the R–Re interaction does not produce anisotropy in the ab plane.[6] This follows automatically from the character of the wave functions of the ground doublet $(\Psi_0^\pm=|\pm 15/2\rangle)$, with axis of quantization in the ab plane.

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Superconductivity and structural instability of the ZrV_2 compound

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The electrical resistivity between 60 and 300 K and the superconducting transition temperature T_c are measured for samples of Laves-phase ZrV_2 with a C15 structure in quenched and annealed states. It is found that a structural transformation occurs at ~90 K in the annealed samples, whereas their T_c is 0.3° lower than for the quenched samples. The appearance of lattice instability and the lowering of T_c as a result of annealing at 1200°C is ascribed to an increase in the degree of atomic ordering in the crystal lattice of the ZrV_2 compound.

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Much attention is being paid lately to the problem of the interrelationship between superconductivity and lattice instability in compounds of the transition metals.[1,2] The interest in this problem is explained by the fact that high superconducting transition temperatures T_c occur, judging by numerous experimental data,[3–6] in intermetallic compounds with an unstable crystal lattice, although, apparently, there exists no mechanism at all for "an enhancement of superconductivity by structural instability."[2]

One must assume that considerable light could be shed on the question of the presence of a correlation between lattice instability and superconductivity by measurements of T_c in superconducting intermetallic compounds of identical chemical composition and crystal structure, but differ by whether or not a phase transition connected with a structural instability is realized in them.

In the present work we have successfully identified a class of objects in which the presence or absence of a structural transformation preceding the superconducting transition is determined solely by the character of the heat treatment of the samples. We have in mind the superconducting Laves phases of type $MgCu_2$ with a C15 structure (space group $O_h^7\text{-}Fd3m$), in which first-order phase transitions are observed at $T_m \gg T_c$, accompanied by a lowering of the symmetry of the crystal lattice.[7–9] In the present work the investigated samples were Laves-phase ZrV_2.

The intermetallic-compound samples were prepared by a method for alloying zirconium and vanadium in an arc furnace with a permanent electrode in an atmosphere of purified argon. The resulting ingots were cut with an electric-spark lathe. Some of the samples were annealed in a vacuum of $\sim 10^{-6}$ Torr at 1200 °C over a period of 24 hours. In the x-ray patterns of both the annealed and the unannealed samples contained only lines of the cubic phase of type C15 with parameter $a = 7.438 \pm 0.002$ Å.

The results of measurements, at 60–300 K, of the relative resistivity of the samples after arc melting (I) and of samples which had undergone additional annealing at 1200 °C (II) are presented in Fig. 1. It is clear that the $\rho(T)$ curves for the samples ZrV_2(I) and ZrV_2(II) are quite different[1]: The temperature dependence of the resistivity of the annealed sample has a distinct maximum at ~90 K (with rising temperature); on the curve for the unannealed sample there are no anomalies what-

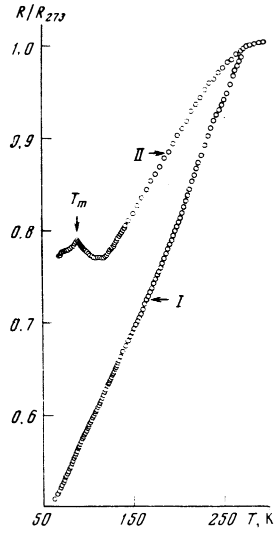

FIG. 1. Temperature dependence of the resistivity of ZrV_2: I—sample after arc heating, II—sample annealed in a vacuum at 1200 °C for 24 hours.