Theory of the magnetic properties of dysprosium orthoferrite

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A theory of non-Heisenberg R–Fe exchange interaction is developed for dysprosium orthoferrite, in which the ground state of the rare-earth ion Dy^{3+} is almost an Ising state. Use of a microscopic exchange Hamiltonian, obtained by symmetry considerations, and allowance for the specific properties of the wave functions of the lowest doublets of the Dy^{3+} ion make it possible to decrease effectively the number of parameters describing the R–Fe exchange. In particular, it is shown that in $DyFeO_3$ the exchange interaction causes practically no splitting of the ground doublet of Dy^{3+}, and that the chief role is played by Van Vleck terms in the energy; these determine the specific properties of the spontaneous spin reorientation ($\Gamma_4 \rightarrow \Gamma_1$) in this orthoferrite. The contribution of the Dy–Fe interaction to the thermodynamic potential is calculated, and the behavior of $DyFeO_3$ in a magnetic field is investigated. The basic exchange parameters of the theory are determined from experimental data.

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The rare-earth orthoferrites and orthochromites are materials in which the exchange interaction of the rare-earth ions (RI) with the d ions has a complicated non-Heisenberg form and depends strongly on the type of RI. This explains, in particular, the considerable diversity of their magnetic properties. The problem of $f-d$ exchange in antiferromagnets is very complicated, primarily because the isotropic component of this interaction, as a result of the antiferromagnetism of the d ions, is almost completely compensated,[1] and anisotropic, asymmetric interactions are advanced to first place. Therefore in general, description of the $f-d$ exchange in antiferromagnets requires a large number of parameters. Thus it has been shown[1] by use of symmetry theory that in orthoferrites, in the two-sublattice approximation for the d ion subsystem, nine such parameters are necessary (it was assumed that the RI can be described by consideration solely of the lowest doublet or quasidoublet that appears upon splitting of the ground multiplet by the crystalline field).

In certain cases, the spin Hamiltonian of $f-d$ exchange can be considerably simplified, and the number of exchange parameters needed can be decreased, by use of a microscopic approach, if the wave functions of the RI in the crystal are known. A suitable object for such an approach is $DyFeO_3$, where it has been established experimentally that the Dy^{3+} ion is with good accuracy an Ising ion and the wave functions of its ground state have been determined.[2,3] By analysis of the temperature variations of the components of the magnetic susceptibility tensor of $DyFeO_3$, one can determine the wave functions of the first excited state (see below). This information provides a good basis for a microscopic theory of the magnetic properties of $DyFeO_3$. In the present paper an attempt is made to develop such a theory, and it is shown that in this case two parameters suffice for description of the magnetic properties of the material that are dependent on $f-d$ exchange. As such parameters we may choose the exchange constants λ_F and λ_G that determine, respectively: a) the isotropic exchange field $H_F = \lambda_F F$, proportional to the weak ferromagnetic moment F; and b) the exchange field $H_G = \lambda_G G_{z'}$, proportional to the projection of the antiferromagnetism vec-

tor G on the Ising axis of the Dy^{3+} ion. In this paper, these fields[2] are estimated on the basis of known experimental data:

$$H_F \approx 10^3 \text{ Oe}, \quad H_G = \lambda_G G \approx 2 \cdot 10^4 \text{ Oe}.$$

It should be noted that the relative simplicity of the theory of $f-d$ exchange in this case is a specific property of $DyFeO_3$ and is a manifestation of the fact that Dy^{3+} in $DyFeO_3$ can be regarded as an Ising ion. A similar situation is apparently realized in $TbFeO_3$, $TbCrO_3$, and $DyCrO_3$. In other compounds of this type, description of the $f-d$ exchange requires a larger number of parameters.[3]

1. R-Fe INTERACTION IN ORTHOFERRITES

In orthoferrites, two mechanisms of R–Fe interaction are important: exchange and dipole. We shall consider them in turn.

A. The Hamiltonian of $R^{3+} - Fe^{3+}$ exchange interaction via an intermediate O^{2-} ion can be written in the form[4,5]

$$\hat{\mathscr{H}}_{R-Fe} = \sum_{k=0}^{6} \sum_{q=-k}^{k} a_{kq} Y_k^q(\hat{L}) \hat{S} \hat{S}_{Fe} \quad (k \text{ even}), \tag{1}$$

where $\hat{L}$ and $\hat{S}$ are the orbital and spin angular momentum operators of the RI, $\hat{S}_{Fe}$ is the spin operator of the iron ion (in the ground state of the Fe^{3+} ion, the orbital angular momentum $L = 0$), $Y_k^q(\hat{L})$ are irreducible tensor operators of rank k, and a_{kq} are exchange parameters.

In order to pass from (1) to the Hamiltonian of R – Fe exchange interaction in the crystal, it is necessary to sum (1) over all sets of three, $R^{3+} - O^{2-} - Fe^{3+}$, that couple a given RI with the nearest Fe^{3+} ions. In the case of orthoferrites, it is necessary to take into account that the spins of the iron ions are distributed over four sublattices: S_1, S_2, S_3, and S_4 (Fig. 1). On summing over bonds, it is possible to express the Hamiltonian of exchange interaction of the RI with the nearest Fe^{3+} ions in the form of a linear combination of interactions with normal modes G, F, A, and C ($G = S_1 - S_2 + S_3 - S_4$, $F = S_1 + S_2 + S_3 + S_4$, $A = S_1 - S_2 - S_3 + S_4$, $C = S_1 + S_2 - S_3 - S_4$,[6] characterizing the magnetic structure
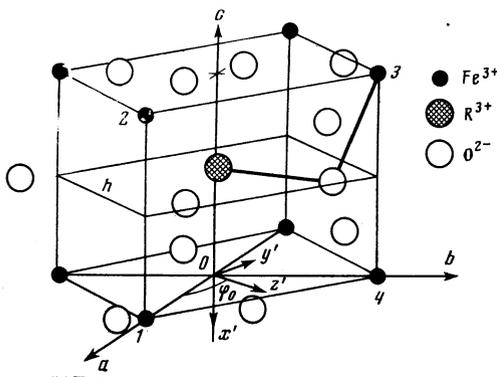
FIG. 1. Neighborhood of a rare-earth ion in orthoferrites. One of the $R^{3+}-O^{2-}-Fe^{3+}$ superexchange bonds is shown; h is the symmetry plane of the crystalline field; $abc \equiv xyz$ is the crystallographic coordinate system, $x'y'z'$ the local coordinate system (the z' axis is the Ising axis of the Dy^{3+} ion).

of the iron ions:

$$\hat{\mathscr{H}}_{05} = \Sigma \hat{\mathscr{H}}_{R-Fe} = \mu_B \hat{S} \{A_1(\hat{L})G + A_2(\hat{L})F + A_3(\hat{L})A + A_4(\hat{L})C\}. \tag{2}$$

Here $A_i(\hat{L})$ are certain linear combinations of operators $a_{kq} Y_k^q(\hat{L})$, with exchange parameters a_{kq} corresponding to various $R^{3+}-O^{2-}-Fe^{3+}$ bonds; the factor μ_B (the Bohr magneton) is introduced in order that the expression in wavy brackets may have the dimensions of magnetic field.

The symmetry of the crystal imposes limitations on the form of the exchange functions $A_i(\hat{L})$ in the Hamiltonian. Because in a reflection in the plane of symmetry of the crystalline field[4'] the sublattices of spins of Fe^{3+} ions change places, $S_1 \rightleftharpoons S_2$ and $S_3 \rightleftharpoons S_4$, it follows from the definition of the vectors G, F, A, and C that

$$\sigma_h G \hat{S} = -G \hat{S}, \quad \sigma_h F \hat{S} = F \hat{S}, \quad \sigma_h A \hat{S} = -A \hat{S}, \quad \sigma_h C \hat{S} = C \hat{S},$$

where σ_h is the transformation of reflection in the plane of symmetry. The Hamiltonian (2) must be invariant with respect to σ_h; therefore

$$\sigma_h A_{1,3}(\hat{L}) = -A_{1,3}(\hat{L}), \quad \sigma_h A_{2,4}(\hat{L}) = A_{2,4}(\hat{L}).$$

If we choose the axis of quantization along the direction perpendicular to the plane of symmetry (the c axis of the crystal), then the expansion of the operators $A_1(\hat{L})$ and $A_3(\hat{L})$ in irreducible tensor operators $Y_k^q(\hat{L})$ will contain only harmonics with odd q, and the expansion of $A_2(\hat{L})$ and $A_4(\hat{L})$ only harmonics with even q. For example,

$$A_1(\hat{L}) = b_1^+(L_+^+ \hat{L}_z + \hat{L}_z \hat{L}_+) + b_1^-(\hat{L}_- \hat{L}_z + \hat{L}_z \hat{L}_-) + \dots,$$
$$A_2(\hat{L}) = a_0 + a_2(3\hat{L}_z^2 - L(L+1)) + a_2^+ \hat{L}_+^2 + a_2^- \hat{L}_-^2 + \dots, \tag{3}$$
$$\hat{L}_\pm = \hat{L}_x \pm \hat{L}_y.$$

The product $a_0 F$ is the contribution of isotropic exchange to the R – Fe interaction. It is small ($\sim 10^3$ Oe) because of the smallness of the weak ferromagnetic moment of the iron. The quantity a_0 itself is the largest among the terms of the expansion (3). The terms with coefficients $b_1^\pm$, $a_2^\pm$, a_2, etc. are about an order of magnitude smaller. Nevertheless, the principal role in the exchange interaction is played by the coefficients in the expansion of $A_1(\hat{L})$, i.e. by the quantities $b_1^\pm$ etc. Although they are

smaller than a_0, in the Hamiltonian (2) they occur in combination with the antiferromagnetism vector G and thus produce appreciable exchange fields ($\sim 10^4$ Oe).

RI in orthoferrites are in a crystalline field of very low symmetry (C_s), and therefore their ground multiplets are split into doublets (Kramers ions) or singlets (non-Kramers ions); in the latter case, a quasidoublet structure of the spectrum is often observed experimentally.[7,8] A doublet (quasidoublet) can be described by use of an effective spin $S_{eff} = \frac{1}{2}$. By calculating the matrix of the exchange Hamiltonian (2) in two-state space and expanding it in Pauli matrices, we get the effective spin Hamiltonian of R – Fe interaction for a doublet. In the standard two-sublattice approximation for the subsystem of Fe^{3+} ions, it has the form

$$\tilde{\mathscr{H}}_{ex} = 2\mu_B \hat{S}_{eff}^\alpha \cdot (I_{\alpha\beta}^{(1)} G_\beta + I_{\alpha\beta}^{(2)} F_\beta), \tag{4}$$

where

$$\|I_{\alpha\beta}^{(1)}\| = \begin{bmatrix} 0 & 0 & I_{xz}^{(1)} \\ 0 & 0 & \pm I_{yz}^{(1)} \\ I_{zx}^{(1)} & \pm I_{zy}^{(1)} & 0 \end{bmatrix}, \quad \|I_{\alpha\beta}^{(2)}\| = \begin{bmatrix} I_{xx}^{(2)} & \pm I_{xy}^{(2)} & 0 \\ \pm I_{yx}^{(2)} & I_{yy}^{(2)} & 0 \\ 0 & 0 & I_{zz}^{(2)} \end{bmatrix} \tag{5}$$

(the signs $\pm$ distinguish nonequivalent positions of the RI). The exchange matrices $\|I_{\alpha\beta}^{(1)}\|$ and $\|I_{\alpha\beta}^{(2)}\|$ are in general asymmetric; that is, the effective spin Hamiltonian contains both anisotropic symmetric terms and antisymmetric ones.

Equation (4) can be put into the form

$$\tilde{\mathscr{H}}_{ex} = 2\mu_B \hat{S}_{eff}^\alpha g_{\alpha\beta} H_\beta^{ex}, \tag{6}$$

where $g_{\alpha\beta}$ are the components of the anisotropic g tensor of the doublet and where H^{ex} is the exchange field produced by the Fe^{3+} ions:

$$H_\beta^{ex} = \lambda_{\beta\gamma}^{(1)} G_\gamma + \lambda_{\beta\gamma}^{(2)} F_\gamma. \tag{7}$$

We note that the symmetry of the matrices $\|g_{\alpha\beta}\|$ and $\|\lambda_{\alpha\beta}^{(2)}\|$ is the same as that of the matrix $\|I_{\alpha\beta}^{(2)}\|$ in (4); the matrices $\|\lambda_{\alpha\beta}^{(1)}\|$ and $\|I_{\alpha\beta}^{(1)}\|$ also have the same symmetry.

B. The Hamiltonian of R – Fe dipole interaction has the following form:

$$\hat{\mathscr{H}}_{dip} = g_J \mu_B \hat{J} H^{dip}. \tag{8}$$

Here H^{dip} is the magnetic field produced at the corresponding sites by the magnetic moments of the Fe^{3+} ions, and $\hat{J}$ is the total angular momentum operator of the RI. The field H^{dip} depends strongly on the orientation of the magnetic moments of the iron sublattices with respect to the crystal axes. This dependence can be determined by use of the transformation properties of the vector H^{dip} with respect to the symmetry transformations of the space group of the orthoferrites.[1] The dipole field is represented as an expansion in the normal modes G, F, A, and C with tensor coefficients [analogous to the expansion (7) for the exchange field]. Direct calculations of H^{dip} show[9] that the contribution of the terms containing F, A, and C is negligibly small and that one can take account merely of the dependence of the dipole field on the orientation of the antiferro-

magnetism vector G:

$$H_\alpha^{dip} = \lambda_{\alpha\beta}^{dip} G_\beta, \quad \|\lambda_{\alpha\beta}^{dip}\| = \begin{bmatrix} 0 & 0 & \lambda_1^{dip} \\ 0 & 0 & \pm\lambda_2^{dip} \\ \lambda_1^{dip} & \pm\lambda_2^{dip} & 0 \end{bmatrix}. \qquad (9)$$

Numerical values of H_x^{dip} and H_y^{dip} in holmium orthoferrite are given in Ref. 9; they are

$$H_x^{dip} = 800 G_z/G \ [\text{Oe}], \quad H_y^{dip} = \pm 2727 G_z/G \ [\text{Oe}]. \qquad (10)$$

It is to be expected that the parameters of R– Fe dipole interaction will change only slightly within the orthoferrite series.

2. GROUND STATE AND WAVE FUNCTIONS OF RI IN DyFeO$_3$

The ground multiplet of the Dy^{3+} ion is $^6H_{15/2}$ ($L = 5$, $S = 5/2$). In a crystalline field of C_s symmetry, this multiplet is split into doublets with energies $E_0 = 0$, $E_1 = 52$ cm^{-1}, $E_2 = 147$ cm^{-1}, $E_3 = 225$ cm^{-1}, etc.[10] It has been established experimentally[2,3] that the ground doublet is described with sufficiently high accuracy by wave functions $\psi_{1,2}^{(0)} = |J = 15/2, M_J = \pm 15/2\rangle \equiv |\pm 15/2\rangle$, if the axis of quantization is chosen in the ab plane of the crystal at an angle $\varphi_0 \approx 60°$ to the a axis. This means that in the one-doublet approximation, the Dy^{3+} ion can be treated as an Ising ion with a direction of magnetization that coincides with the axis of quantization. In fact, by use of an effective spin $\hat{S}_{eff} = \frac{1}{2}$ the spin Hamiltonian of interaction of the RI with an external magnetic field H can be represented, for the ground doublet, in the form

$$\hat{\mathcal{H}}_{ext} = 2\mu_B \hat{S}_{eff}^\alpha g_{\alpha\beta} H_\beta, \qquad (11)$$

where the tensor $g_{\alpha\beta}$ (or the magnetic susceptibility tensor $\chi_{\alpha\beta}$) has a single nonvanishing component $g_{z'z'}$ ($\chi_{z'z'}$) (in the $x'y'z'$ coordinate system, z' is along the axis of quantization, x' along the c axis).

Interaction of the ground doublet with excited levels leads to the result that other components of the susceptibility tensor become nonzero. In particular,

$$\chi_{x'x'} = \chi_c = 2 \sum_{\substack{i \neq 0 \\ \nu = 1,2}} \frac{|\langle 15/2 | g_J \mu_B \hat{J}_{x'} | \psi_\nu^{(i)} \rangle|^2}{E_i - E_0}, \qquad (12)$$

where $\psi_{1,2}^{(i)}$ are the wave functions of the ith doublet. Knowing χ_c, one can estimate the nature of the wave functions of the excited doublets. Since the matrix elements $\langle M | \hat{J}_{x'} | M' \rangle$ are nonzero only when $\Delta M = \pm 1$, $\langle 15/2 | \hat{J}_{x'} | \psi_1^{(i)} \rangle = \langle 15/2 | \hat{J}_{x'} | 13/2 \rangle \alpha_i$, where α_i is the amplitude ("weight") of the state $|13/2\rangle$ in the wave function $\psi_1^{(i)}$ ($\Sigma \alpha_i^2 = 1$). Taking into account that the Kramers-conjugate wave functions of a doublet can always be chosen so that the state $|13/2\rangle$ occurs only in $\psi_1^{(i)}$, we get from (12)

$$\chi_c = 2 \sum_{i \neq 0} g_J^2 \mu_B^2 \alpha_i^2 \frac{|\langle 15/2 | \hat{J}_{x'} | 13/2 \rangle|^2}{E_i - E_0}$$
$$= 2.6 \cdot 10^{-4} (\alpha_1^2 + \alpha_2^2 E_1/E_2 + \alpha_3^2 E_1/E_3 + \dots) \ [G/g \cdot \text{Oe}] \qquad (13)$$

(it has been taken into account that $g_J = 4/3$ and $\langle 15/2 | \hat{J}_{x'} | 13/2 \rangle = \sqrt{15}/2$). It is obvious that when $T \ll E_1$, the susceptibility (13) must be practically independent of temperature. It has been established experimentally[11] that the susceptibility of the Dy^{3+} ions along the c axis in DyFeO$_3$ at low temperatures is in

fact independent of temperature and equal to $\chi_c = 2.8 \cdot 10^{-4}$ G/g Oe. By comparing this value and formula (13), one can easily show that best agreement of them is achieved when $\alpha_1 = 1$ and $\alpha_{i \neq 0} = 0$; that is, when the wave functions of the excited doublet are[5] $\psi_{1,2}^{(1)} = |\pm 13/2\rangle$. For this doublet,

$$g_{x'x'} = g_{y'y'} = 0, \quad g_{x'z'} = g_J \langle 15/2 | J_{x'} | 13/2 \rangle \approx 8.6.$$

3. THERMODYNAMIC POTENTIAL OF DyFeO$_3$

We shall write the thermodynamic potential (TP) in the form $\Phi = \Phi_{Fe} + \Phi_R$, where Φ_{Fe} is the TP of the iron sublattices,[13]

$$\Phi_{Fe} = \frac{1}{2}AF^2 + \frac{1}{2}b_z^{Fe}G_z^2 + \frac{1}{2}b_x^{Fe}G_x^2 + d_z^{Fe}G_zF_x + d_x^{Fe}G_xF_z - \text{FH} \qquad (14)$$

[fourth-order terms have been dropped in (14)], and where Φ_R is the TP determined by the energy spectrum of the Hamiltonian $\hat{\mathcal{H}} = \hat{\mathcal{H}}_{ex} + \hat{\mathcal{H}}_{dip} + \hat{\mathcal{H}}_{ext}$ [$\hat{\mathcal{H}}_{ex}$ from (2), $\hat{\mathcal{H}}_{dip}$ from (8), $\hat{\mathcal{H}}_{ext} = g_J \mu_B \text{JH}$] through the partition function:

$$\Phi_R = -T \ln \text{Sp}(\exp(-\hat{\mathcal{H}}/T)).$$

In the calculation of the matrix elements of the operator $\hat{\mathcal{H}}$, it is convenient to transform, by means of the Clebsch-Gordon coefficients, to the representation of $|LSM_LM_S\rangle \equiv |M_L\rangle|M_S\rangle$ in wave functions $|JM_J\rangle \equiv |M_J\rangle$:

$$|\pm^{15}/_2\rangle = |\pm 5\rangle|\pm^5/_2\rangle,$$
$$|\pm^{13}/_2\rangle = \gamma^{2}/_3}|\pm 4\rangle|\pm^5/_2\rangle + \gamma^{1}/_3}|\pm 5\rangle|\pm^3/_2\rangle.$$

Since the Hamiltonian $\hat{\mathcal{H}}$ is linear in $\hat{S}$, the only nonvanishing matrix elements will be those that satisfy the selection rule $M_S - M_S' = 0, \pm 1$. In view of this, we can write the matrix of the Hamiltonian $\hat{\mathcal{H}}$, in a representation that takes account only of the two lowest doublets of the Dy^{3+} ion, in the form

$$\begin{bmatrix} \langle^{15}/_2|\hat{\mathcal{H}}|^{15}/_2\rangle & 0 & \langle^{15}/_2|\hat{\mathcal{H}}|^{13}/_2\rangle & 0 \\ 0 & \langle-^{15}/_2|\hat{\mathcal{H}}|-^{15}/_2\rangle & 0 & \langle-^{15}/_2|\hat{\mathcal{H}}|-^{13}/_2\rangle \\ \langle^{13}/_2|\hat{\mathcal{H}}|^{15}/_2\rangle & 0 & E_1 + \langle^{13}/_2|\hat{\mathcal{H}}|^{13}/_2\rangle & 0 \\ 0 & \langle-^{13}/_2|\hat{\mathcal{H}}|-^{15}/_2\rangle & 0 & E_1 + \langle-^{13}/_2|\hat{\mathcal{H}}|-^{13}/_2\rangle \end{bmatrix}. \qquad (15)$$

In the usual two-sublattice approximation for the subsystem of Fe^{3+} ions, the first two terms in the expression (2) for the exchange Hamiltonian remain; and since $F \sim 10^{-2}G$, only the isotropic part a_0 is needed in the exchange function $A_2(\hat{L})$ [see (3)]. We then get for the term dependent on F in $\hat{\mathcal{H}}_{ex}$

$$\mu_B \hat{S} A_2(\hat{L}) F \approx \mu_B \hat{S} a_0 F = \mu_B g_J \hat{J} \left(\frac{g_J - 1}{g_J} a_0\right) F = \mu_B g_J \hat{J} \lambda F.$$

Noting also that the exchange function $A_1(\hat{L})$ is odd in $\hat{L}_{x'}$, we find the matrix elements

$$\langle^{15}/_2|\hat{\mathcal{H}}|^{15}/_2\rangle = -\langle-^{15}/_2|\hat{\mathcal{H}}|-^{15}/_2\rangle = \mu_0 \tilde{H}_{x'},$$

$$\langle^{13}/_2|\hat{\mathcal{H}}|^{13}/_2\rangle = -\langle-^{13}/_2|\hat{\mathcal{H}}|-^{13}/_2\rangle = \mu_1 \left(\tilde{H}_{x'} + \frac{\gamma 10}{26}MG_{x'}\right),$$

$$\langle^{15}/_2|\hat{\mathcal{H}}|^{13}/_2\rangle = \langle-^{15}/_2|\hat{\mathcal{H}}|-^{13}/_2\rangle^* = \mu_{10}\left(\tilde{H}_{x'} - i\tilde{H}_{y'} + \frac{\gamma 10}{4}MG_{z'}\right),$$

where

$$\mu_0 = g_J \mu_B \langle^{15}/_2|J_{z'}|^{15}/_2\rangle = 10\mu_B,$$
$$\mu_1 = g_J \mu_B \langle^{13}/_2|J_{z'}|^{13}/_2\rangle = ^{26}/_3\mu_B,$$
$$\mu_{10} = g_J \mu_B \langle^{15}/_2|J_{x'}|^{13}/_2\rangle = ^2/_3\sqrt{15}\mu_B,$$
$$\tilde{H} = H + H^{dip} + \lambda F, \quad M = \langle 5|A_1(\hat{L})|4\rangle.$$

It is easily shown that the Van Vleck susceptibility (13)

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(when $\alpha_1 = 1$) is $\chi_c = 2\mu_{10}^2/E_1$.

Diagonalization of the matrix (15) gives the following eigenvalues:

$$E_o^{(1,2)} = \mp\mu_o H_{z'} - \frac{\chi_o u^2}{2},$$

$$E_1^{(1,2)} = E_1 \mp \mu_1\left(H_{z'} + \frac{\sqrt{10}}{26}MG_{z'}\right) + \frac{\chi_o u^2}{2}, \qquad (16)$$

$$u^2 = \left(H_{z'} + \frac{\sqrt{10}}{4}MG_{z'}\right)^2 + H_{y'}^2.$$

We introduce the exchange parameters λ_G and λ_F by the relations $\lambda_G = (\sqrt{10}/4)M$, $\lambda_F = \lambda$. These parameters are related to the exchange fields $H_0 = \lambda_G G$ and $H_F = \lambda_F F$. The field H_G is determined by the exchange function $A_1(\hat{L})$ and produces the Van Vleck magnetization of the Dy^{3+} ion along the c axis of the crystal; H_F is the isotropic field.

From the energy spectrum (16) of the Hamiltonian $\hat{\mathscr{H}}$, we calculate the TP Φ_R. When $T \ll E_1$, we need only the contribution of the lowest doublet. We have

$$\Phi_R = -\frac{\chi_o}{2}\frac{u_+^2 + u_-^2}{2} - \frac{T}{2}\left[\ln\left(2\,\mathrm{ch}\frac{\Delta^+}{T}\right) + \ln\left(2\,\mathrm{ch}\frac{\Delta^-}{T}\right)\right], \qquad (17)$$

where $2\Delta^{\pm} = 2\mu_o H_{z'}$ is the Zeeman splitting of the ground doublet (the signs $\pm$ correspond to nonequivalent RI). On expanding (17) in $\Delta^{\pm}/T \ll 1$ to terms of the second order and then reducing the TP to standard form, we get for the complete TP of the system the expression

$$\Phi = \Phi_{Fe} + \Phi_R = \frac{1}{2}AF^2 + \frac{1}{2}\tilde{b}_1 G_x^2 + \frac{1}{2}\tilde{b}_3 G_z^2 + \tilde{d}_1 G_x F_z + d_3 G_z F_x$$
$$- \sum_{i=x,y,z} F_i(1+\eta_i)H_i - \tau_1 G_x H_z + \text{fourth-order terms}, \qquad (18)$$

where

$$\tilde{b}_1 = b_1^{Fe} + \chi_c(\lambda_G \sin\varphi_0 + \lambda_2^{dip})^2 - \chi_c(\lambda_G \cos\varphi_0 + \lambda_1^{dip})^2,$$

$$\tilde{b}_3 = b_3^{Fe} + \chi_c(\lambda_G \sin\varphi_0 + \lambda_2^{dip})^2 - \chi_{ab}(\lambda_1^{dip}\cos\varphi_0 + \lambda_2^{dip}\sin\varphi_0)^2,$$

$$\tilde{d}_1 = d_1^{Fe} - \chi_c(\lambda_G \cos\varphi_0 + \lambda_1^{dip})\lambda_F, \qquad \eta_x = \chi_{ab}\lambda_F \cos^2\varphi_0, \qquad \eta_z = \chi_c\lambda_F,$$

$$\tilde{d}_3 = d_3^{Fe} - \chi_{ab}\lambda_F \cos\varphi_0(\lambda_1^{dip}\cos\varphi_0 + \lambda_2^{dip}\sin\varphi_0), \qquad \eta_y = \chi_{ab}\lambda_F \sin^2\varphi_0,$$

$$\tau_1 = \chi_c(\lambda_G \cos\varphi_0 + \lambda_1^{dip}), \qquad \chi_{ab} = \mu_o^2/T.$$

In the complete TP (18), we have disregarded terms proportional to F_i^2, which are due to the weak splitting of the ground doublet ($\sim 1\ \mathrm{cm}^{-1}$) by the interaction $\mu_B \hat{S}A_2(\hat{L})F$; they are small down to temperatures $\sim 4K$.[6] When $T > 4K$, one can also neglect an insignificant renormalization of the exchange constant A. In the expressions for the renormalized TP parameters it has been taken into account that the Van Vleck susceptibilities of Dy^{3+} along the a and b axes of the crystal are small in comparison with χ_{ab}.

4. ANISOTROPY ENERGY AND ORIENTATIONAL TRANSITIONS IN DyFeO₃

On the basis of the TP (18), we shall consider the magnetic properties and phase transitions in $DyFeO_3$ at low temperatures.

Analysis of the experimental data shows that in

$DyFeO_3$ a spontaneous reorientation of the vector G and transitions induced by an external magnetic field, when $H \| c$ and when $H \| b$, occur in the ab plane; that is, at low temperatures ($T < 100$ K) the ab plane is an "easiest" plane of anisotropy. This is due to the fact that because of the specific properties of the wave functions of the ground doublet of the Dy^{3+} ion, the interaction $\mu_B \hat{S}A_1(\hat{L})G$ (which dominates in most orthoferrites) here does not lead to splitting of this doublet (the matrix elements of the interaction between wave functions of the doublet are zero).[7] In such a situation the Van Vleck interaction is promoted to first place, shifting the doublet as a whole downward. It is due to matrix elements of the type $\langle 15/2|\mu_B \hat{S}A_1(\hat{L})G|13/2\rangle$. According to (16), this Van Vleck interaction stabilizes the ab plane for G.

We obtain the anisotropy energy $K_{ab}(\varphi)$ in the ab plane after substituting in (18) the values $H = 0$, $G_x = G\cos\varphi$, $G_z = 0$, $F_z = F$ ($F \perp G$) and minimizing the TP with respect to F:

$$K_{ab}(\varphi) = \Phi(\varphi) = \frac{1}{2}(\tilde{b}_1 - \tilde{d}_1^2/A)G^2\cos^2\varphi + K_2\cos^4\varphi$$
$$= (K_{Fe} + K_R)\cos^2\varphi + K_2\cos^4\varphi, \qquad (19)$$

where

$$K_{Fe} = \frac{1}{2}\left[b_1^{Fe} - \frac{(d_1^{Fe})^2}{A}\right]G^2, \quad K = \frac{1}{2}(\tilde{b}_1 - b_1^{Fe})G^2 - \frac{1}{2}\left[\frac{\tilde{d}_1^2}{A} - \frac{(d_1^{Fe})^2}{A}\right]G^2.$$

The fourth-order anisotropy K_2 in (19) is determined by the iron sublattice. It is natural to suppose that K_{Fe} and K_2 vary little with temperature (when $T < 100$ K).

For the anisotropy K_R, recalling the form of the renormalized parameters in the TP (18), we get the following expression:

$$K_R = \frac{\chi_c G^2}{2}\left[(\lambda_G \sin\varphi_0 + \lambda_2^{dip})^2 - (\lambda_G \cos\varphi_0 + \lambda_1^{dip})^2\right.$$
$$\left. + \frac{2d_1^{Fe}}{A}\lambda_F(\lambda_G \cos\varphi_0 + \lambda_1^{dip}) - \frac{\chi_c}{A}\lambda_F^2(\lambda_G \cos\varphi_0 + \lambda_1^{dip})^2\right]. \qquad (20)$$

Here the last two terms in square brackets are produced by renormalization of the Dzyaloshinskiĭ constant d_1^{Fe} because of R – Fe interaction. From estimates that will be made below, it follows that the contribution of these terms to K_R is small ($\lesssim 10\%$); furthermore, the relations $\lambda_G \gg \lambda_1^{dip}$, λ_2^{dip} are satisfied. By use of these estimates, one can write a simpler approximate expression for K_R:

$$K_R \approx \frac{1}{2}\chi_c\lambda_G^2 G^2(\sin^2\varphi_0 - \cos^2\varphi_0) = \frac{1}{4}\chi_c(\lambda_G G)^2 = \frac{1}{4}\chi_c H_G^2. \qquad (21)$$

The magnitude and sign of the anisotropy K_R are to a substantial degree determined by the orientation of the Ising axis of the ion in the ab plane (the angle φ_0). An important factor is the fact that the Ising axis of the Dy^{3+} ion in $DyFeO_3$ lies in the ab plane, close to the b axis ($\varphi_0 = 60°!$); as is seen from (19) and (21), this provides a reason for a spontaneous transition $\Gamma_4 \to \Gamma_1$ on lowering of the temperature.[8]

It has been established experimentally that the spin-reorientation transition $\Gamma_4 \to \Gamma_1$ in $DyFeO_3$ is a phase transition of the first kind (this corresponds to $K_2 < 0$). The transition temperature can be found from the condition for equality of the TP of phase Γ_4 ($\varphi = 0$) and of phase Γ_1 ($\varphi = \pi/2$):

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$$K_{Fe}+K_R(T_M)+K_2=0.$$

The temperature dependence of the anisotropy K_R (which obviously has a Van Vleck origin) is determined by the temperature dependence of the susceptibility $\chi_c(T)$:

$$\chi_c(T)=\chi_c(0)\,\text{th}\,(E_1/2T).$$

We note that the susceptibility introduced above was $\chi_c \equiv \chi_c(0)$.

5. BEHAVIOR OF DyFeO$_3$ IN A MAGENTIC FIELD, AND DETERMINATION OF THE EXCHANGE CONSTANTS λ_G AND λ_F

A) A field $H\|c$ at $T<T_M$ induces a spin reorientation $\Gamma_1 \to \Gamma_{14} \to \Gamma_4$. The (H,T) phase diagram and the isotherms of magnetization and magnetostriction for this case were obtained in Ref. 11. Analysis of the magnetization and magnetostriction isotherms shows that the $\Gamma_{14} \to \Gamma_4$ transition line is a first-order phase transition line down to the lowest temperatures; the amount of the jump of the angle φ on this line is close to $\pi/2$ down to $T \approx 10$ K. Thus, for example, the jump of striction at $T\approx 10$ K is only 20% less than at $T=T_M$. All of this means that over the temperature interval $10\,\mathrm{K}<T<T_M$, in the Γ_{14} phase the deviation of the vector G from the b axis, induced by the external field, is small (that is, we may consider that $\cos\varphi \ll 1$).

When $H\|c$, the TP (18) minimized with respect to F takes the form

$$\Phi(H,T,\varphi)=K_{ab}(\varphi)-M_{c0}H\cos\varphi, \tag{22}$$

where

$$M_{c0}=F_0(1+\eta_z)+\tau_1 G=F_0+\chi_c[\lambda_F F_0+(\lambda_G\cos\varphi_0+\lambda_1^{dip})G] \tag{23}$$
$$=F_0+\chi_c(H_F+H_G\cos\varphi_0+H_z^{dip})$$

is the spontaneous magnetic moment of DyFeO$_3$ along the c axis in the Γ_4 phase; $K_{ab}(\varphi)$ is given by (19); and $F_0=|d_1^{Fe}|\,G/A$ is the weak ferromagnetic moment of the iron sublattices (we neglect the renormalization of the constant d_1^{Fe}).

The threshold field $H_{th}^c = H_{th}^c(T)$ of the transition $\Gamma_{14} \to \Gamma_4$ is determined from the system of equations

$$\Phi_\varphi'(H,T,\varphi)=0, \quad \Phi(H,T,\varphi)=\Phi(H,T,0) \tag{24}$$

by elimination of the angle φ. Making use of the smallness of $\cos\varphi$, we find from (24) the threshold field H_{th}^c and the equilibrium value of φ in the Γ_{14} phase:

$$H_{th}^c=\frac{2(K_{Fe}+K_R)}{M_{c0}}(1-[-K_2/(K_{Fe}+K_R)]^{1/2}), \tag{25}$$

$$\cos\varphi_{eq}=M_{c0}H/2(K_{Fe}+K_R). \tag{26}$$

B) When $H\|b$, the field induces in DyFeO$_3$ a transition of the "spin flop" type. The threshold field, which is given by the formula

$$H_{th}^b=\frac{[2(K_{Fe}+K_R+K_2)A]^{1/2}}{|1+\eta_y|} \tag{27}$$

and the magnetostriction isotherms for this case were obtained in Ref. 11. The flipping of the magnetic moments of the sublattices occurs in the ab plane; that is, a transition $\Gamma_1 \to \Gamma_4$ takes place.

The experimental data[11,14] on the behavior of DyFeO$_3$ in a magnetic field make possible a determination of the basic exchange parameters of the theory, λ_F and λ_G (or the exchange fields H_F and H_G). For this purpose we use the following values:

1) $M_{c0}=3.5$ G/g is determined from the magnetization isotherms by extrapolation of the measured $M_c(H)$ relations in the Γ_4 phase $(H>H_{th}^c)$ to $H=0$; this value varies very little with T when $T<T_M=42$ K.[11]

2) $F_0=1.1$ G/g.[14]

3) $\chi_c=2.6\cdot10^{-4}$ G/g Oe is determined from the slope of the $M_c(H)$ curves in the Γ_4 phase; it varies very little with T $(T<T_M)$.[11]

4) $A=10^5$ Oe g/G.

5) $\chi_{ab}\sin^2\varphi_0=2.2\cdot10^{-2}(T/\Theta+1)^{-1}$G/g Oe, $\Theta=5$K.[14]

6) $\chi(\Gamma_{14})=7.5$ G/g Oe is the susceptibility along the c axis in the Γ_{14} phase $(H<H_{th}^c)$ at $T=14.9$K.[11] Since in the Γ_{14} phase, $M_c(H)=M_{c0}\cos\varphi_{eq}+\chi_cH$, we get with the help of (26)

$$\chi(\Gamma_{14})=\chi_c+\chi_{rot}=\chi_c+\frac{M_{c0}^2}{2(K_{Fe}+K_R)}. \tag{28}$$

7) $H_{th}^c=3.5\cdot10^3$ Oe, $H_{th}^b=10^4$ Oe at $T=14.9$ K.[11]

Using the measured values of $\chi(\Gamma_{14})$, χ_c, and M_{c0}, we find from (28) the value of $K_{Fe}+K_R$ at $T=14.9$ K:

$$K_{Fe}+K_R=12.5\cdot10^3 \text{ erg/g.}$$

From formula (25) for H_{th}^c, by substitution in it of the known values of M_{c0}, H_{th}^c, and $K_{Fe}+K_R$, we get

$$K_2=-3.2\cdot10^3 \text{ erg/g.}$$

From formula (27) for H_{th}^b, it is now easy to find the value of the exchange parameter λ_F (we recall that $\eta_y=\lambda_F\chi_{ab}\sin^2\varphi_0$). We get

$$\lambda_F=-10^3 \text{ Oe}\cdot\text{g/G}, \quad H_F=1.1\cdot10^3 \text{ Oe.} \tag{29}$$

From formula (23) for M_{c0}, with the help of (9), (10), and (29), we find the exchange parameter

$$\lambda_G=2.2\cdot10^2 \text{ Oe}\cdot\text{g/G}, \quad H_G=2.2\cdot10^4 \text{ Oe.} \tag{30}$$

We have determined the exchange parameters by use of the experimental values of $\chi(\Gamma_{14})$, H_{th}^c, and H_{th}^b at $T=14.9$ K. At lower temperatures, an important role is played by Dy-Dy interaction, which has nowhere been taken into account in the present paper; and at $T\sim T_M$,
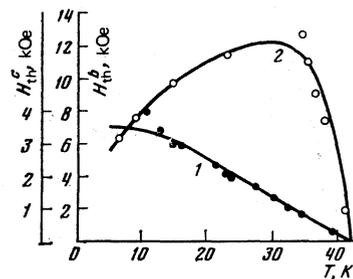

FIG. 2. Threshold fields of the spin-reorientation transitions in DyFeO$_3$: 1, $H\|c$; 2, $H\|b$. Points, experiment;[11] solid curve, theory.

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determination of the value of $\chi(\Gamma_{14})$ from the magnetization isotherms is difficult because a transition to the Γ_4 phase occurs even at small fields. The theoretical $H^c_{th}(T)$ and $H^b_{th}(T)$ curves calculated from the values of λ_F and λ_G that we have found show good agreement between theory and experiment over the whole temperature interval $10K < T < T_N$ (Fig. 2). We note that at a fixed temperature, formula (27) actually determines two values of λ_F: $\lambda_F > 0$ and $\lambda_F < 0$. The sign of the parameter λ_F in (29) was chosen precisely from the consideration of best agreement of the temperature behavior of the $H^b_{th}(T)$ curve with the experimental points.

As is seen from (29), (30), and (10), in $DyFeO_3$ the relations $H_G \gg H_F$, H^{dip} are satisfied; this justifies all the approximations made in the derivation of formula (21) for the anisotropy K_R.

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[1] A slight lack of compensation of it caused by weakly ferromagnetic cant of the d-ion sublattices.

[2] In $DyFeO_3$ there is still the dipole field exerted on the Dy^{3+} ions by the Fe^{3+} ions. It is calculated exactly (see below).

[3] Exceptions are $GdFeO_3$ and $GdCrO_3$, where the f-d exchange is practically isotropic, since the ground state of the Gd^{3+} ion is of S type.

[4] The plane parallel to the ab plane of the crystal and passing through the sites occupied by RI (Fig. 1).

[5] Analysis of the crystalline field in $DyFeO_3$ also leads to the same result.[12]

[6] The small terms $\frac{1}{2}a_1^{Fe}F_x^2$ and $\frac{1}{2}a_3^{Fe}F_z^2$ have already been discarded in the original TP (14) for the subsystem of Fe^{3+} ions.

[7] The interaction with F, $\mu_B \hat{8}A_2(\hat{L})F$, and also the R-Fe dipole

interaction may split the doublet when G departs from the ab plane; but the magnitude of these interactions is insufficient for a reorientation $\Gamma_4 \rightarrow \Gamma_2$ in $DyFeO_3$.

[8] We recall that in phase Γ_4, $G \| a$; in phase Γ_1, $G \| b$; and in phase Γ_2, $G \| c$. The symbols Γ_i denote the corresponding irreducible representations of the symmetry group of the orthoferrites; Γ_{14} is a reducible representation consisting of Γ_1 and Γ_4. In phase Γ_{14}, the vector G lies in the ab plane.

[1] A. K. Zvezdin, V. M. Matveev, and A. I. Popov, Proc. International Conference of Magnetism (ICM-73), Vol. 5, p. 285 (1974).

[2] G. Gorodetsky, B. Sharon, and S. Shtrikman, Solid State Commun. 5, 739 (1967).

[3] I. Nowik and H. J. Williams, Phys. Lett. 20, 154 (1966).

[4] P. M. Levy, Phys. Rev. 147, 311 (1966).

[5] R. J. Birgeneau, M. T. Hutchings, J. M. Baker, and J. D. Riley, J. Appl. Phys. 40, 1070 (1969).

[6] E. F. Bertaut, in: Magnetism, Vol. III (G. Rado and H. Suhl, ed.), Academic Press, 1963, p. 150.

[7] H. Schuchert, S. Hüfner, and R. Faulhaber, Z. Phys. 220, 280 (1969).

[8] J. C. Walling and R. L. White, Phys. Rev. B10, 4748 (1974).

[9] R. Bidaux, J. E. Bouree, and J. Hammann, J. Phys. Chem. Solids 35, 1645 (1974).

[10] H. Schuchert, S. Hüfner, and R. Faulhaber, Z. Phys. 220, 273 (1969).

[11] K. P. Belov, A. K. Zvezdin, A. M. Kadomtseva, and I. B. Krynetskiĭ, Zh. Eksp. Teor. Fiz. 67, 1974 (1974) [Sov. Phys. 40, 980 (1974)].

[12] V. M. Matveev, Dissertation, Moscow, Moscow State University, 1978.

[13] E. A. Turov, Fizicheskie svoĭstva magnitouproyadochennykh kristallov (Physical properties of magnetically ordered crystals), Izd. Akad. Nauk SSSR, 1963 (translation, Academic Press, 1965).

[14] I. B. Krynetskiĭ, Dissertation, Moscow, Moscow State University, 1974.

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Magnetic hyperfine interaction for Co impurity atoms in a PdAu matrix

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The oriented-nuclei procedure is used to measure the magnetic hyperfine fields for ^{60}Co in the ferromagnetic system $[Pd_{1-x}Au_x]_{0.99}Co_{0.01}$ with $0 \leq x \leq 0.15$. The data obtained indicate that the hyperfine field at Co remains practically unchanged when part of the Pd atoms is replaced by Au atoms, at least up to a concentration of 0.15 at.% Au. It can be concluded from these results that the Au atoms, just as the Pd atoms, produce a positive hyperfine field at the impurity Co atoms which have a localized magnetic moment. The concentration dependence of the hyperfine field can be described with an empirical formula consisting of a sum of contributions, viz., the polarization of the core and the partial contributions corresponding to the presence of the Pd or Au atoms in the first coordination sphere of the Co impurity atom in question. The possible mechanisms responsible for the positive hyperfine field at a $3d$ atom are briefly discussed.

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INTRODUCTION

The great interest in the investigations of magnetic hyperfine interaction for impurity $3d$ atoms in alloys with $4d$ and $5d$ metals is due to the fact that large pos-

itive hyperfine fields were observed for Co and Ni atoms in Pd matrices. This result turned out to be unexpected, since the only previously known values of the fields for $3d$ atoms were negative, a fact ascribed to the dominant contribution from the polarization of the