

## Magnetic Symmetry of Rare-Earth Orthochromites and Orthoferrites

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A new magnetic symmetry of the rare-earth orthochromites and orthoferrites ( $RMO_3$ ) below the second Néel temperature due to the reordering of the rare-earth spins is proposed. It is shown that the magnetic symmetry group is lowered to the subgroup of index two, thereby keeping the unit cell invariant. The proposed symmetry is shown to be consistent with the previously observed spin configuration of  $RMO_3$  such as  $GdCrO_3$ ,  $DyFeO_3$ , and  $DyCrO_3$ , and would also be consistent with those of other  $RMO_3$ . Although symmetry arguments and the calculation of the free energy show that two spin configurations are stable, in  $GdCrO_3$ , a future measurement of the magnetoelectric tensor would determine which configuration  $GdCrO_3$  has. It is further predicted that the magnetoelectric effect should be observed in any  $RMO_3$  below the second Néel temperature.

### I. INTRODUCTION

One of the fundamental problems in the rare-earth orthochromites and orthoferrites ( $RMO_3$ ,  $R$  is a rare earth and  $M$  is Cr or Fe) is concerned with the magnetic symmetry below the second Néel temperature  $T_{N2}$  due to the reordering of  $R^{3+}$  spins, where according to existing theory<sup>1</sup> the magnetic symmetries of the observed  $M^{3+}$  and  $R^{3+}$  spin configurations are not compatible with each other.

$RMO_3$  are weak ferromagnets resulting from a small canting of the antiferromagnetic  $M^{3+}$  spins.<sup>1,2</sup> Just below the first Néel temperature  $T_{N1}$  (where the  $M^{3+}$  spins order), the  $M^{3+}$  sublattice moments and the net moment are observed to lie either along the  $a$  axis and the  $c$  axis, respectively, in most of  $RMO_3$ , or along the  $c$  axis and the  $a$  axis in some  $RCrO_3$  ( $R = Nd, Tb, Dy, Ho, Yb$ ).<sup>2</sup> The net moment of the  $R^{3+}$  spins is polarized parallel or antiparallel to the net  $M^{3+}$  moment by the  $M^{3+}$ - $R^{3+}$  magnetic interactions. Although the  $R^{3+}$  spins of this state are sometimes said to be polarized quasi-paramagnetically, they should be considered to have a magnetic ordering given in Table I. As the temperature is lowered, the  $R^{3+}$  moment increases and the spin reorientation occurs at  $T_2$  and  $T_1$  (or at  $T_r$ ) in most of  $RMO_3$ .<sup>2</sup> Finally, below  $T_{N2} = 1-4$  K, a different configuration of  $R^{3+}$  spins is caused by the  $R^{3+}$ - $R^{3+}$  interaction.

The  $R^{3+}$  spin configuration below  $T_{N2}$  can not be explained by the existing theory,<sup>1</sup> which assumes that the magnetic symmetry group is the same for both above and below  $T_{N2}$ . Bertaut *et al.*<sup>3-5</sup> have investigated the  $R^{3+}$  spin configurations in some  $RMO_3$  under the assumption that the magnetic unit cell is different from the paramagnetic one. For instance, the spin configuration of  $Tb^{3+}$  spin in  $TbCrO_3$ <sup>4</sup> is assumed to belong to a two-dimension-

al irreducible representation associated with the wave vector  $\vec{k} = (0, \frac{1}{2}, 0)$ , that is, the magnetic unit cell is twice the paramagnetic one in the direction of the  $b$  axis. Following the procedure of Bertaut *et al.*, we have to assume that the magnetic unit cell is different from material to material.<sup>5</sup>

Experiments on some  $RMO_3$  near  $T_{N2}$  have shown that the transition at  $T_{N2}$  is of second order.<sup>6,7</sup> Here, it should be noted that a phase transition is of second order if the symmetry of a crystal changes in such a way that the number of symmetry operations after the transition is reduced to half that before transition.<sup>8</sup> Lowering symmetry can be realized either by (i) a doubling of the unit cell for a given crystal class, or by (ii) a halving of the number of rotations and reflections for a given unit cell. Bertaut *et al.* have investigated just the first case to explain the magnetic symmetry below  $T_{N2}$ .<sup>3-5</sup> In this paper, we shall show that case (ii) is more plausible than case (i) to describe the magnetic symmetry below  $T_{N2}$  in  $RMO_3$ .<sup>9</sup>

### II. MAGNETIC SYMMETRY

#### A. Spin Structure

Table I gives all the spin configurations of  $RMO_3$  derived with the assumption that the magnetic and the paramagnetic unit cells are the same.<sup>1</sup> In  $RMO_3$  containing magnetic  $R^{3+}$  ions, the observed spin configuration just above  $T_{N2}$  belongs either to  $\Gamma_2(F_x, C_y, G_z; F_x^R, C_y^R)$  or to  $\Gamma_1(A_x, G_y, C_z; C_z^R)$  (Ref. 2) and is compatible with this table. Below  $T_{N2}$ , owing to the  $R^{3+}$ - $R^{3+}$  magnetic interaction, a new  $R^{3+}$  spin configuration appears, as will be shown below.

Now, we point out some experimental results requiring a new explanation of the magnetic symmetry below  $T_{N2}$ . (a) In  $GdCrO_3$ , where the single-ion

TABLE I. Compatible spin configurations in  $RMO_3$  for  $T \geq T_{N2}$ . (After Bertaut; see Ref. 1).

	$M^{3+}$	$R^{3+}$
$\Gamma_1$	$A_x, G_y, C_z$	$C_z^R$
$\Gamma_2$	$F_x, C_y, G_z$	$F_x^R, C_y^R$
$\Gamma_3$	$C_x, F_y, A_z$	$C_x^R, F_y^R$
$\Gamma_4$	$G_x, A_y, F_z$	$F_z^R$
$\Gamma_5$		$G_x^R, A_y^R$
$\Gamma_6$		$A_x^R, C_y^R$
$\Gamma_7$		$C_x^R, F_y^R$
$\Gamma_8$		$A_x^R, G_y^R$

anisotropy of the  $Gd^{3+}$  ion can be neglected, the magnetically observed results<sup>7</sup> show that the  $Gd^{3+}$  spin configuration below  $T_{N2} = 2.42$  K is antiferromagnetic along the  $c$  axis and ferromagnetic along the  $a$  axis, and that the  $Cr^{3+}$  spin configuration is  $(F_x, G_z)$  which belongs to the  $\Gamma_2$  configuration. However, we see from Table I that although the ferromagnetic  $Gd^{3+}$  spin configuration  $F_x^R$  is compatible with the  $Cr^{3+}$  configuration  $(F_x, G_z)$  mentioned above, the antiferromagnetic configuration of the  $Gd^{3+}$  spins along the  $c$  axis is forbidden. (b) In  $DyFeO_3$ , where the  $Dy^{3+}$  anisotropy is large, the Ising-like spin of  $Dy^{3+}$  ion will be confined to the direction of the anisotropy axis. The  $Dy^{3+}$  spin in  $DyAlO_3$  (nonmagnetic  $M^{3+}$  ion) has been analyzed to be confined in the  $a$ - $b$  plane, the angle between the  $Dy^{3+}$  spin and the  $b$  axis being  $33^\circ$ .<sup>10,11</sup> The  $Dy^{3+}$  spin configuration below  $T_{N2}$  is  $\Gamma_5(G_x^R, A_y^R)$ . How-

TABLE II. Symmetry operations for various spin configurations. The screw axis  $\tilde{C}_{2\alpha}$  ( $\alpha = x, y, z$ ) is parallel to the  $\alpha$  axis indicated in Fig. 1 of Ref. 2. The center of inversion  $i$  is at each  $M^{3+}$  site, and  $R$  is the time-reversal operation. (+) means that the spin configuration is invariant to the corresponding operations.

	$\Gamma_1$	$\Gamma_2$	$\Gamma_3$	$\Gamma_4$	$\Gamma_5$	$\Gamma_6$	$\Gamma_7$	$\Gamma_8$
$M^{3+}$	$A_x G_y C_z$	$F_x C_y G_z$	$C_x F_y A_z$	$G_x A_y F_z$				
$R^{3+}$	$C_z^R$	$F_x^R C_y^R$	$C_x^R F_y^R$	$F_z^R$	$G_x^R A_y^R$	$A_x^R$	$G_z^R$	$A_x^R C_y^R$
field		$H_x$	$H_y$	$H_z$		$E_x$	$E_y$	$E_z$
$E$	+	+	+	+	+	+	+	+
$\tilde{C}_{2x}$	+	+			+	+		
$\tilde{C}_{2y}$	+		+		+		+	
$\tilde{C}_{2z}$	+			+	+			+
$i$	+	+	+	+				
$i\tilde{C}_{2x}$	+	+					+	+
$i\tilde{C}_{2y}$	+		+			+	+	+
$i\tilde{C}_{2z}$	+			+		+	+	+
$R$					+	+	+	+
$R\tilde{C}_{2x}$			+	+			+	+
$R\tilde{C}_{2y}$		+		+			+	+
$R\tilde{C}_{2z}$		+	+				+	+
$iR$					+	+	+	+
$iR\tilde{C}_{2x}$			+	+	+	+		
$iR\tilde{C}_{2y}$		+		+	+		+	
$iR\tilde{C}_{2z}$		+	+		+		+	+

ever, the configuration of  $Fe^{3+}$  spins is  $\Gamma_1(A_x, G_y, C_z)$ , which is incompatible with that of  $Dy^{3+}$  spins. (c) The  $Cr^{3+}$  and  $Dy^{3+}$  sublattice spins of  $DyCrO_3$  favor the  $\Gamma_2(F_x, C_y, G_z)$  and  $\Gamma_5(G_x^R, A_y^R)$  configurations, respectively.<sup>7,10,11</sup> These two configurations are not compatible with each other. Furthermore, the observed spontaneous magnetization along the  $a$  axis<sup>7</sup> is too large for the weak ferromagnetic moment  $F_x$  of  $Cr^{3+}$  ions, and is too small for the  $Dy^{3+}$  ferromagnetic moment  $F_x^R$  of the  $\Gamma_2(F_x^R, C_y^R)$  configuration which is compatible with the  $Cr^{3+}$  configuration. Note that this  $\Gamma_2(F_x^R, C_y^R)$  configuration is the spin-flopped configuration of  $\Gamma_5(G_x^R, A_y^R)$ .

In order to explain the magnetic symmetry of  $RMO_3$  below  $T_{N2}$ , we assume that at  $T_{N2}$  Landau's second-order phase transition takes place and the magnetic symmetry group is lowered to the index-two subgroup, the magnetic and the paramagnetic unit cells remaining the same. Now the symmetry operations for  $RMO_3$  crystals above  $T_{N2}$  are given in Table II, where the transformation properties of the magnetic and electric fields are also given for later use. The order of magnetic groups  $\Gamma_1$  through  $\Gamma_8$  is eight for all. At  $T_{N2}$  Landau's second-order phase transition occurs and the number of symmetry operations is reduced to half that above  $T_{N2}$ . Thus, the order of the magnetic group below  $T_{N2}$  should be four. Table III gives the spin configurations and the magnetic symmetries compatible with our assumption.

(a) For instance, the two symmetry groups  $D_2(C_2)222$  of the  $\Gamma_{26}(F_x, C_y, G_z: F_x^R, C_y^R, A_z^R)$  configuration and  $C_{2v}(C_2)2m'm$  of the  $\Gamma_{27}(F_x, C_y, G_z: F_x^R, C_y^R, G_z^R)$  configuration are both the index-two subgroup of the group  $D_{2h}(C_{2h})m'm'm$  of the  $\Gamma_2$  configuration. The  $\Gamma_{26}$  and  $\Gamma_{27}$  configurations are invariant to operations  $(E, \tilde{C}_{2x}, R\tilde{C}_{2y}, R\tilde{C}_{2z})$  and  $(E, i\tilde{C}_{2x}, iR\tilde{C}_{2y}, R\tilde{C}_{2z})$ , respectively. If we apply these to  $GdCrO_3$ , Table II shows that the  $Gd^{3+}$  antiferromagnetic configuration along the  $c$  axis is either  $A_z^R$  for the  $\Gamma_{26}$  or  $G_z^R$  for the  $\Gamma_{27}$  configuration. (b) On the other hand, the symmetry group  $D_2(D_2)222$  of the  $\Gamma_{15}(A_x, G_y, C_z: G_x^R, A_y^R, C_z^R)$  configuration is the index-two

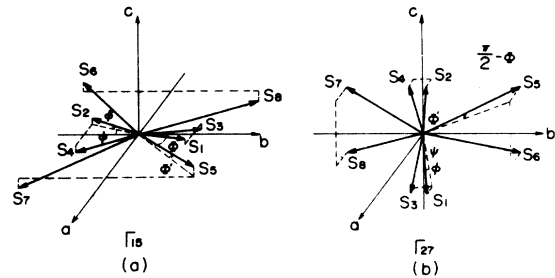


FIG. 1. Spin configuration in  $RMO_3$  below  $T_{N2}$ . (a) The  $\Gamma_{15}(A_x, G_y, C_z: G_x^R, A_y^R, C_z^R)$  configuration. (b) The  $\Gamma_{27}(F_x, C_y, G_z: F_x^R, C_y^R, G_z^R)$  configuration.

TABLE III. Magnetic symmetry of various spin configurations.

	Magnetic symmetry group	Spin configuration
$T \geq T_{N2}$	$D_{2h}(D_{2h})mmm$	$\Gamma_1$
	$D_{2h}(C_{2h})m'm'm'$	$\Gamma_2, \Gamma_3, \Gamma_4$
	$C_{2h}(C_{2h})2m$	$\Gamma_{12}, \Gamma_{13}, \Gamma_{14}$
	$C_{2h}(C_2)2m'$	$\Gamma_{23}, \Gamma_{24}, \overset{a}{\Gamma}_{34}$
$T \leq T_{N^*}$	$D_{2h}(D_2)m'm'm'$	$\Gamma_5^b$
	$D_{2h}(C_{2v})mmm'$	$\Gamma_6, \Gamma_7, \Gamma_8$
	$D_2(D_2)222$	$\Gamma_{15}^c$
	$D_2(C_2)222$	$\Gamma_{26}, \overset{d}{\Gamma}_{37}, \Gamma_{48}$
	$C_{2v}(C_{2v})2mm$	$\Gamma_{16}, \Gamma_{17}, \Gamma_{18}$
	$C_{2v}(C_2)2m'm'$	$\Gamma_{25}, \overset{e}{\Gamma}_{35}, \Gamma_{45}$
	$C_{2v}(C_2)2m'm'$	$\Gamma_{27}, \overset{d}{\Gamma}_{28}, \Gamma_{36}, \Gamma_{38}, \Gamma_{46}, \Gamma_{47}$
Not realized	$C_{2h}(C_2)2m'$	$\Gamma_{56}, \Gamma_{57}, \Gamma_{58}$
	$C_{2h}(C_2)2m$	$\Gamma_{67}, \Gamma_{68}, \Gamma_{78}$

<sup>a</sup>The spin reorientation region. See Ref. 2.

<sup>b</sup> $RAlO_3$  ( $R = Gd, Tb, Dy$ ) See Ref. 11.

<sup>c</sup> $DyFeO_3$ .

<sup>d</sup> $GdCrO_3$ .

<sup>e</sup> $DyCrO_3$ .

subgroup of that  $D_{2h}(D_{2h})m'm'm'$  of the  $\Gamma_1$  configuration. The  $\Gamma_{15}$  configuration is invariant to operations ( $E, \tilde{C}_{2x}, \tilde{C}_{2y}, \tilde{C}_{2z}$ ). This is applied to  $DyFeO_3$  and the  $(G_x^R, A_y^R)$  configuration of  $Dy^{3+}$  spins is compatible with the  $G_y$  configuration of  $Fe^{3+}$  spins. (c) Furthermore,  $DyCrO_3$  has the  $\Gamma_{25}(F_x, C_y, G_z; F_x^R, C_y^R; G_x^R, A_y^R)$  configuration, which means that the  $\Gamma_2(F_x, C_y, G_z; F_x^R, C_y^R)$  configuration is mixed with the  $\Gamma_5(G_x^R, A_y^R)$  configuration. The magnetic group of the  $\Gamma_{25}$  configuration is  $C_{2v}(C_2)2m'm'$ , which is the index-two subgroup of that  $D_{2h}(D_{2h})m'm'm'$  of the  $\Gamma_2$  configuration and consists of elements ( $E, \tilde{C}_{2x}, iR\tilde{C}_{2y}, iR\tilde{C}_{2z}$ ). More detailed discussion of  $DyCrO_3$  will be given in Sec. II(E). (d) Finally, any other  $RMO_3$  below  $T_{N2}$  would have one of the  $\Gamma_{ij}$  ( $i=1-4$  and  $j=5-8$ ) configurations given in Table III. The  $\Gamma_{15}$  and  $\Gamma_{27}$  spin configurations are illustrated in Figs. 1(a) and 1(b), respectively. The  $\Gamma_{26}$  configuration is obtained by exchanging the spins  $\tilde{S}_7$  and  $\tilde{S}_8$ .

### B. Hamiltonian

The Hamiltonian of our system is given as

$$\mathcal{H} = \mathcal{H}^M + \mathcal{H}^{M-R} + \mathcal{H}^R, \quad (1)$$

where the first term represents the Hamiltonian for  $M^{3+}$  ions which is shown, from the symmetry considerations, to be the same as those given in Ref. 2. The second term represents the Hamiltonian for the interaction between  $M^{3+}$  and  $R^{3+}$  ions and the third that for  $R^{3+}$  ions. The term  $\mathcal{H}^{M-R}$  consists of the isotropic, antisymmetric and anisotropic symmetric exchange interactions:

$$\mathcal{H}^{M-R} = \tilde{\mathcal{H}}_{1so} + \tilde{\mathcal{H}}_{ant1} + \tilde{\mathcal{H}}_{symm}. \quad (2)$$

The expression of this Hamiltonian is a little different from that of Ref. 2, since the inversion is no longer the symmetry operation of  $RMO_3$  below  $T_{N2}$ . The term  $\mathcal{H}^R$  consists of four parts, the isotropic, the antisymmetric, and the anisotropic-symmetric exchange interactions between  $R^{3+}$  spins and the anisotropy energy of  $R^{3+}$  ions whose site symmetry is  $C_s$ :

$$\begin{aligned} \mathcal{H}^R &= \mathcal{H}'_{1so} + \mathcal{H}'_{ant1} + \mathcal{H}'_{symm} + \mathcal{H}'_{an} \\ &= \sum_{\kappa k, \lambda l} J'_{kl}{}^{\kappa\lambda} \tilde{S}_k^\kappa \cdot \tilde{S}_l^\lambda + \sum_{\kappa k, \lambda l} \tilde{D}_{kl}{}^{\kappa\lambda} \cdot (\tilde{S}_k^\kappa \times \tilde{S}_l^\lambda) \\ &\quad + \sum_{\kappa k, \lambda l} \tilde{S}_k^\kappa \cdot \tilde{a}_{kl}{}^{\kappa\lambda} \cdot \tilde{S}_l^\lambda \\ &\quad + \sum_{\kappa k} \{ D_k{}^{\kappa\kappa} (S_{kx}^\kappa)^2 + E_k{}^{\kappa\kappa} [(S_{kx}^\kappa)^2 - (S_{ky}^\kappa)^2] \\ &\quad + p_k{}^{\kappa\kappa} (S_{kx}^\kappa S_{ky}^\kappa + S_{ky}^\kappa S_{kx}^\kappa) \} \\ &\quad + (\text{fourth-order terms}) \\ &\quad + (\text{sixth-order terms}). \end{aligned} \quad (3)$$

Now, we introduce average sublattice spins denoted by  $\tilde{S}_i$ , where

$$\tilde{S}_i = N^{-1} \sum_{\mu} \tilde{S}_i^{\mu} \quad (4)$$

and  $N$  is the number of unit cells in the crystal. Further, we use new isotropic exchange-interaction constants multiplied by the number of nearest-neighbor spins as follows<sup>2</sup>:

$$\tilde{J} = 2\tilde{J}'_{15}, \quad \tilde{J}'' = 2\tilde{J}'_{16}, \quad \tilde{J}' = 2\tilde{J}'_{17}, \quad \tilde{J}''' = 2\tilde{J}'_{18}, \quad (5a)$$

$$J'_A = 4J'_{55}, \quad J'_B = 2J'_{56}, \quad J'_C = 8J'_{57}, \quad J'_D = 4J'_{58}. \quad (5b)$$

Similarly, the antisymmetric and the anisotropic-symmetric exchange-interaction constants multiplied by the number of nearest-neighbor spins are used below in this paper. Symmetry considerations show that these constants are given as those in Table IV(a)–IV(f). Then, the Hamiltonians (2) and (3) are given in Appendix, where Bertaut's irreducible bases  $\tilde{F}$ ,  $\tilde{G}$ ,  $\tilde{C}$ , and  $\tilde{A}^{1,2}$  are used.

### C. Spin Configuration of $GdCrO_3$

We first consider the spin configuration of  $GdCrO_3$  below  $T_{N2}$ . The  $Gd^{3+}$  anisotropy energy of  $GdCrO_3$  is small as compared with other interaction energies such as the  $Cr^{3+}$ - $Gd^{3+}$  and  $Gd^{3+}$ - $Gd^{3+}$  exchange interactions.<sup>2,12,13</sup> Thus, the  $Gd^{3+}$  spin is not confined to its own single-ion anisotropy axis but to the direction of the effective field due to the magnetic interactions with  $Cr^{3+}$  and  $Gd^{3+}$  spins.

The Hamiltonian (1) is also written as<sup>2</sup>

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_a, \quad (6)$$

where

$$\mathcal{H}_0 = \frac{1}{2}(J_A - J_B + J_C - J_D)\tilde{G}^2 \quad (7)$$

TABLE IV. (a) Isotropic exchange interaction constants between  $M^{3+}$  and  $R^{3+}$  spins. {For  $T \geq T_{N2}$ ,  $\vec{J}'' = \vec{J}$  and  $\vec{J}''' = \vec{J}'$  [see Table I(d) of Ref. 2].} (b) Antisymmetric exchange interaction constants between  $M^{3+}$  and  $R^{3+}$  spins. {For  $T \geq T_{N2}$ ,  $\vec{D}'' = \vec{D}$  and  $\vec{D}''' = \vec{D}'$  [see Table I(e) of Ref. 2].}

	$\vec{S}_5$	$\vec{S}_6$	$\vec{S}_7$	$\vec{S}_8$	$\vec{S}_5$	$\vec{S}_6$	$\vec{S}_7$	$\vec{S}_8$
$\vec{S}_1$	$\vec{J}$	$\vec{J}''$	$\vec{J}'$	$\vec{J}'''$	$(\vec{D}_x, \vec{D}_y, \vec{D}_z)$	$(\vec{D}_x'', \vec{D}_y'', \vec{D}_z'')$	$(\vec{D}_x', \vec{D}_y', \vec{D}_z')$	$(\vec{D}_x''', \vec{D}_y''', \vec{D}_z''')$
$\vec{S}_2$	$\vec{J}''$	$\vec{J}$	$\vec{J}'''$	$\vec{J}'$	$(-\vec{D}_x'', -\vec{D}_y'', -\vec{D}_z'')$	$(-\vec{D}_x, -\vec{D}_y, -\vec{D}_z)$	$(-\vec{D}_x', -\vec{D}_y', -\vec{D}_z')$	$(-\vec{D}_x''', -\vec{D}_y''', -\vec{D}_z''')$
$\vec{S}_3$	$\vec{J}'''$	$\vec{J}'$	$\vec{J}''$	$\vec{J}$	$(-\vec{D}_x''', -\vec{D}_y''', -\vec{D}_z''')$	$(-\vec{D}_x, -\vec{D}_y, -\vec{D}_z)$	$(-\vec{D}_x', -\vec{D}_y', -\vec{D}_z')$	$(-\vec{D}_x, -\vec{D}_y, -\vec{D}_z)$
$\vec{S}_4$	$\vec{J}'$	$\vec{J}'''$	$\vec{J}$	$\vec{J}''$	$(\vec{D}_x', -\vec{D}_y', -\vec{D}_z')$	$(\vec{D}_x''', -\vec{D}_y''', -\vec{D}_z''')$	$(\vec{D}_x, -\vec{D}_y, -\vec{D}_z)$	$(\vec{D}_x'', -\vec{D}_y'', -\vec{D}_z'')$

TABLE IV. (c) Anisotropic-symmetric exchange interaction constants between  $M^{3+}$  and  $R^{3+}$  spins.  $\vec{a}_{xx} = -(\vec{a}_{xx}' + \vec{a}_{yy}')$ ,  $\vec{a}_{yy}' = -(\vec{a}_{xx}' + \vec{a}_{yy}')$ ,  $\vec{a}_{zz}' = -(\vec{a}_{xx}' + \vec{a}_{yy}')$ ,  $\vec{a}_{xx}'' = -(\vec{a}_{xx}'' + \vec{a}_{yy}'')$ ,  $\vec{a}_{yy}'' = -(\vec{a}_{xx}'' + \vec{a}_{yy}'')$ , and  $\vec{a}_{zz}'' = -(\vec{a}_{xx}'' + \vec{a}_{yy}'')$ . {For  $T \geq T_{N2}$ ,  $\vec{a}_{\alpha\beta} = \vec{a}_{\alpha\beta}' = \vec{a}_{\alpha\beta}''$  [see Table I(f) of Ref. 2].}

	$\vec{S}_5$	$\vec{S}_6$	$\vec{S}_7$	$\vec{S}_8$
$\vec{S}_1$	$\begin{pmatrix} \vec{a}_{xx} \\ \vec{a}_{xy} \\ \vec{a}_{yy} \\ \vec{a}_{zz} \end{pmatrix}$	$\begin{pmatrix} \vec{a}_{xx}'' \\ \vec{a}_{xy}'' \\ \vec{a}_{yy}'' \\ \vec{a}_{zz}'' \end{pmatrix}$	$\begin{pmatrix} \vec{a}_{xx}' \\ \vec{a}_{xy}' \\ \vec{a}_{yy}' \\ \vec{a}_{zz}' \end{pmatrix}$	$\begin{pmatrix} \vec{a}_{xx}''' \\ \vec{a}_{xy}''' \\ \vec{a}_{yy}''' \\ \vec{a}_{zz}''' \end{pmatrix}$
$\vec{S}_2$	$\begin{pmatrix} \vec{a}_{xx}'' \\ \vec{a}_{xy}'' \\ \vec{a}_{yy}'' \\ \vec{a}_{zz}'' \end{pmatrix}$	$\begin{pmatrix} \vec{a}_{xx} \\ \vec{a}_{xy} \\ \vec{a}_{yy} \\ \vec{a}_{zz} \end{pmatrix}$	$\begin{pmatrix} \vec{a}_{xx}' \\ \vec{a}_{xy}' \\ \vec{a}_{yy}' \\ \vec{a}_{zz}' \end{pmatrix}$	$\begin{pmatrix} \vec{a}_{xx}''' \\ \vec{a}_{xy}''' \\ \vec{a}_{yy}''' \\ \vec{a}_{zz}''' \end{pmatrix}$
$\vec{S}_3$	$\begin{pmatrix} \vec{a}_{xx}''' \\ \vec{a}_{xy}''' \\ \vec{a}_{yy}''' \\ \vec{a}_{zz}''' \end{pmatrix}$	$\begin{pmatrix} \vec{a}_{xx}'' \\ \vec{a}_{xy}'' \\ \vec{a}_{yy}'' \\ \vec{a}_{zz}'' \end{pmatrix}$	$\begin{pmatrix} \vec{a}_{xx}' \\ \vec{a}_{xy}' \\ \vec{a}_{yy}' \\ \vec{a}_{zz}' \end{pmatrix}$	$\begin{pmatrix} \vec{a}_{xx} \\ \vec{a}_{xy} \\ \vec{a}_{yy} \\ \vec{a}_{zz} \end{pmatrix}$
$\vec{S}_4$	$\begin{pmatrix} \vec{a}_{xx}' \\ \vec{a}_{xy}' \\ \vec{a}_{yy}' \\ \vec{a}_{zz}' \end{pmatrix}$	$\begin{pmatrix} \vec{a}_{xx}''' \\ \vec{a}_{xy}''' \\ \vec{a}_{yy}''' \\ \vec{a}_{zz}''' \end{pmatrix}$	$\begin{pmatrix} \vec{a}_{xx}'' \\ \vec{a}_{xy}'' \\ \vec{a}_{yy}'' \\ \vec{a}_{zz}'' \end{pmatrix}$	$\begin{pmatrix} \vec{a}_{xx} \\ \vec{a}_{xy} \\ \vec{a}_{yy} \\ \vec{a}_{zz} \end{pmatrix}$

TABLE IV. (d) Isotropic exchange constants between  $R^{3+}$  spins. (e) Antisymmetric exchange interaction constants between  $R^{3+}$  spins. (For  $T \geq T_{N2}$ ,  $B'_x = B'_y = C'_y = D'_x = 0$ , since the symmetry group contains the inversion operation.)

	$\tilde{S}_5$	$\tilde{S}_6$	$\tilde{S}_7$	$\tilde{S}_8$	$\tilde{S}_5$	$\tilde{S}_6$	$\tilde{S}_7$	$\tilde{S}_8$
$\tilde{S}_5$	$J_A$	$J_B$	$J_C$	$J'_B$				
$\tilde{S}_6$		$J_A$	$J'_D$	$J'_C$	$(B'_x, B'_y, 0)$	$(0, C'_y, C'_z)$	$(D'_x, 0, D'_z)$	
$\tilde{S}_7$			$J'_A$	$J'_B$	$(-D'_x, 0, D'_z)$	$(0, -C'_y, C'_z)$	$(0, -C'_y, C'_z)$	
$\tilde{S}_8$				$J'_A$			$(B'_x, -B'_y, 0)$	

TABLE IV. (f) Anisotropic-symmetric exchange interaction constants between  $R^{3+}$  spins,  $a'_{xx} = - (a'_{xx} + a'_{yy})$ ,  $b'_{xx} = - (b'_{xx} + b'_{yy})$ ,  $c'_{xx} = - (c'_{xx} + c'_{yy})$ , and  $d'_{xx} = - (d'_{xx} + d'_{yy})$ . (For  $T \geq T_{N2}$ ,  $a'_{xx} = a'_{yy} = c'_{yy} = d'_{xx} = 0$ , since the symmetry group contains the inversion operation.)

	$\tilde{S}_5$	$\tilde{S}_6$	$\tilde{S}_7$	$\tilde{S}_8$
$\tilde{S}_5$	$\begin{pmatrix} a'_{xx} & a'_{xy} & a'_{xz} \\ a'_{xy} & a'_{yy} & a'_{yz} \\ a'_{xz} & a'_{yz} & a'_{zz} \end{pmatrix}$	$\begin{pmatrix} b'_{xx} & b'_{xy} & 0 \\ b'_{xy} & b'_{yy} & 0 \\ b'_{xz} & 0 & b'_{zz} \end{pmatrix}$	$\begin{pmatrix} c'_{xx} & 0 & 0 \\ c'_{yy} & c'_{yy} & c'_{yz} \\ c'_{xz} & c'_{yz} & c'_{zz} \end{pmatrix}$	$\begin{pmatrix} d'_{xx} & 0 & d'_{xz} \\ d'_{xx} & d'_{yy} & 0 \\ d'_{xz} & 0 & d'_{zz} \end{pmatrix}$
$\tilde{S}_6$	$\begin{pmatrix} a'_{xx} & a'_{xy} & -a'_{xz} \\ a'_{xy} & -a'_{yy} & -a'_{yz} \\ a'_{xz} & -a'_{yz} & a'_{zz} \end{pmatrix}$	$\begin{pmatrix} a'_{xx} & a'_{xy} & -a'_{xz} \\ a'_{xy} & -a'_{yy} & -a'_{yz} \\ a'_{xz} & -a'_{yz} & a'_{zz} \end{pmatrix}$	$\begin{pmatrix} d'_{xx} & 0 & -d'_{xz} \\ d'_{xx} & d'_{yy} & 0 \\ d'_{xz} & 0 & d'_{zz} \end{pmatrix}$	$\begin{pmatrix} c'_{xx} & 0 & 0 \\ c'_{yy} & c'_{yy} & -c'_{yz} \\ c'_{xz} & -c'_{yz} & c'_{zz} \end{pmatrix}$
$\tilde{S}_7$			$\begin{pmatrix} a'_{xx} & -a'_{xy} & -a'_{xz} \\ a'_{xy} & a'_{yy} & a'_{yz} \\ a'_{xz} & a'_{yz} & a'_{zz} \end{pmatrix}$	$\begin{pmatrix} b'_{xx} & -b'_{xy} & 0 \\ b'_{xy} & b'_{yy} & 0 \\ b'_{xz} & 0 & b'_{zz} \end{pmatrix}$
$\tilde{S}_8$			$\begin{pmatrix} a'_{xx} & -a'_{xy} & a'_{xz} \\ a'_{xy} & a'_{yy} & -a'_{yz} \\ a'_{xz} & -a'_{yz} & a'_{zz} \end{pmatrix}$	$\begin{pmatrix} d'_{xx} & -a'_{xy} & a'_{xz} \\ a'_{xy} & a'_{yy} & -a'_{yz} \\ a'_{xz} & -a'_{yz} & a'_{zz} \end{pmatrix}$

TABLE IV. (g) Second-order single-ion anisotropy constants of  $R^{3+}$  ion.

	$\tilde{S}_5$	$\tilde{S}_6$	$\tilde{S}_7$	$\tilde{S}_8$
$D'$	$(S_x^R)^2$	$D'$	$D'$	$D'$
$E'$	$[(S_x^R)^2 - (S_y^R)^2]$	$E'$	$E'$	$E'$
$p'$	$(S_x^R S_y^R + S_x^R S_z^R)$	$p'$	$p'$	$-p'$

TABLE V. Orders of magnitudes of various exchange constants and of the single-ion anisotropy constants for  $\text{GdCrO}_3$ . Compare with Table II of Ref. 2.

	1	$\epsilon$	$\epsilon^2$	$\epsilon^3$	$\epsilon^4$
$M^{3+} - M^{3+}$	$J$	$\vec{D}$	$\vec{a}$		
$M^{3+}$			$K$		
$M^{3+} - R^{3+}$	$\vec{J}$	$\vec{D}$	$\vec{a}$		
$R^{3+} - R^{3+}$			$J'$	$\vec{D}'$	$\vec{a}'$
$R^{3+}$				$K'$	

is the unperturbed isotropic Hamiltonian given in Ref. 2 and  $\mathcal{H}_a$  is the anisotropic part of the Hamiltonian. The free energy  $\langle \mathcal{H} \rangle$  of the system is given, to the first-order perturbation of  $\mathcal{H}_a$ , by

$$\langle \mathcal{H} \rangle = -kT \ln \text{Tr} e^{-\beta \mathcal{H}_0} + \langle \mathcal{H}_a \rangle, \quad (8)$$

where the angular brackets denote the thermal average taken with respect to the density matrix  $\rho_0 = e^{-\beta \mathcal{H}_0} / \text{Tr} e^{-\beta \mathcal{H}_0}$ . Here, we approximate the mean value of the product of spin operators by the product of the mean values of spin operators:  $\langle \vec{S}_i \vec{S}_j \rangle = \langle \vec{S}_i \rangle \langle \vec{S}_j \rangle$ .

To simplify the calculation, it is convenient to know the order of magnitudes of parameters. For  $\text{GdCrO}_3$  they are given in Table V, where  $\epsilon$  represents  $|\vec{D}|/J \sim 10^{-2}$ , the order of magnitudes of the overt and hidden canting angles of  $\text{Cr}^{3+}$  spins. We assume that the antisymmetric and the anisotropic-symmetric exchange-interaction energies, respectively, between the orbitally nondegenerate ions such as  $\text{Gd}^{3+}$  and  $\text{Cr}^{3+}$  ions in  $\text{GdCrO}_3$  are one and two orders of magnitudes smaller than the corresponding isotropic exchange interaction energy. Furthermore, we assume the anisotropy term  $K' = (D', E', \rho')$  of  $\text{Gd}^{3+}$  ion<sup>13</sup> to be of the order of  $\epsilon^3$ .

Since the real spin configuration of  $\text{GdCrO}_3$  cannot be identified definitely by the magnetic data<sup>7</sup> alone, we assume in this subsection that  $\text{GdCrO}_3$  has the  $\Gamma_{27}(F_x, C_y, G_z; F_x^R, C_y^R, G_z^R)$  configuration below  $T_{N2}$ . From the Hamiltonians (9a)–(9d) of Ref. 2 and (A1)–(A7) of this paper, the normalized free-energy of the  $\Gamma_{27}$  spin configuration is found to be

$$\begin{aligned} F = \langle \mathcal{H} \rangle / \langle S_{Cr} \rangle^2 N \\ = \frac{1}{2}(J_A + J_B + J_C + J_D)F_x^2 + \frac{1}{2}(J_A + J_B - J_C - J_D)C_y^2 \\ + \frac{1}{2}(J_A - J_B + J_C - J_D)G_z^2 \\ + (D_y + B_y)F_x G_z - (B_x - C_x)C_y G_z + DG_z^2 \\ + s[(\vec{J} + \vec{J}'' + \vec{J}' + \vec{J}''')F_x F_x^R \\ + (\vec{J} + \vec{J}'' - \vec{J}' - \vec{J}''')C_y C_y^R \end{aligned}$$

$$\begin{aligned} - (\vec{D}_x + \vec{D}_x'' - \vec{D}_x' - \vec{D}_x''')G_x C_y^R \\ + (\vec{D}_y + \vec{D}_y'' + \vec{D}_y' + \vec{D}_y''')G_y F_x^R \\ + s^2[\frac{1}{2}(J'_A + J'_B + J'_C + J'_D)(F_x^R)^2 \\ + \frac{1}{2}(J'_A + J'_B - J'_C - J'_D)(C_y^R)^2 \\ + \frac{1}{2}(J'_A - J'_B + J'_C - J'_D)(G_z^R)^2], \quad (9) \end{aligned}$$

where terms smaller than the order of  $\epsilon^2$  are omitted.  $s$  is the ratio of the mean values of the  $\text{Gd}^{3+}$  and  $\text{Cr}^{3+}$  spins,  $\langle S_{Gd} \rangle / \langle S_{Cr} \rangle$ , which is the only parameter depending on the temperature.

In the classical-spin approximation, equilibrium directions of the sublattice spins are defined in terms of  $\psi, \phi, \Phi$ , and  $\Phi'$ , where  $\psi$  and  $\phi$  are the overt and hidden canting angles of  $\text{Cr}^{3+}$  spins, respectively,  $2\Phi$  is the angle between two sublattices of  $\text{Gd}^{3+}$  spins  $\vec{S}_5$  and  $\vec{S}_8$  or  $\vec{S}_6$  and  $\vec{S}_7$ ,  $2\Phi'$  is the angle between  $\vec{S}_5$  and  $\vec{S}_6$  or  $\vec{S}_7$  and  $\vec{S}_8$  which gives the  $G_x^R$  configuration [see Fig. 1(b)]. This angle  $\Phi'$  can be taken as an order parameter of the second-order phase transition at  $T_{N2}$ . Then, the normalized basis vectors are expressed in terms of  $\psi, \phi, \Phi$ , and  $\Phi'$  as follows:

$$F_x = \sin\psi \sim \psi, \quad (10a)$$

$$C_y = \cos\psi \sin\phi \sim \phi, \quad (10b)$$

$$G_z = -\cos\psi \cos\phi \sim -1, \quad (10c)$$

$$F_x^R = \cos\Phi, \quad (10d)$$

$$C_y^R = \sin\Phi \cos\Phi', \quad (10e)$$

$$G_z^R = \sin\Phi \sin\Phi'. \quad (10f)$$

The minus sign in Eq. (10c) shows that the up-spins of the  $G_x$  configuration of  $\text{Cr}^{3+}$  ions are  $\vec{S}_2$  and  $\vec{S}_4$  and the down-spins are  $\vec{S}_1$  and  $\vec{S}_3$ , which is the configuration below the spin-reorientation temperature of the  $\Gamma_4 - \Gamma_2$  type.<sup>2</sup> Inserting Eq. (10) into Eq. (9) and minimizing Eq. (9) with respect to  $\psi, \phi, \Phi$  and  $\Phi'$ , we obtain the expression for the free-energy as a function of the temperature  $T$ . Minimization of the free-energy with respect to these angles gives the following four equations:

$$\psi = [(D_y + B_y) - s(\vec{J} + \vec{J}'' + \vec{J}' + \vec{J}''')\cos\Phi] / 2(J_D + J_B), \quad (11)$$

$$\begin{aligned} \phi = -[(B_x - C_x) + s(\vec{J} + \vec{J}'' - \vec{J}' - \vec{J}''')\sin\Phi \\ \times \cos\Phi'] / 2(J_B - J_C), \quad (12) \end{aligned}$$

$$\begin{aligned} (J_B - J_C)(\vec{J} + \vec{J}'' + \vec{J}' + \vec{J}''')^2 (s_0 + s \cdot \cos\Phi) s \cdot \sin\Phi \\ + (J_D + J_B)(\vec{J} + \vec{J}'' - \vec{J}' - \vec{J}''')^2 (s'_0 - s \cdot \sin\Phi \cos\Phi') \\ \times s \cdot \cos\Phi \cos\Phi' \\ - 4(J_D + J_B)(J_B - J_C)s^2 \sin\Phi \cos\Phi [(J'_D + J'_B) \\ - (J'_B - J'_C)\cos^2\Phi'] = 0, \quad (13) \end{aligned}$$

$$\sin\Phi \sin\Phi' \cdot \{[(\bar{J} + \bar{J}'' - \bar{J}' - \bar{J}''')^2 - 4(J_B - J_C) - \bar{J}''']^2 s_0'\} = 0, \quad (14)$$

$$\times (J_B' - J_C') s \cdot \sin\Phi \cos\Phi' - (\bar{J}' + \bar{J}'' - \bar{J}') \quad \text{where}$$

$$s_0 = \frac{2(\bar{D}_y + \bar{D}_y'' + \bar{D}_y' + \bar{D}_y''')(J_D + J_B) - (\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''')(D_y + B_y)}{(\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''')^2}, \quad (15)$$

$$s_0' = \frac{2(\bar{D}_x + \bar{D}_x'' - \bar{D}_x' - \bar{D}_x''')(J_B - J_C) - (\bar{J} + \bar{J}'' - \bar{J}' - \bar{J}''')(B_x - C_x)}{(\bar{J} + \bar{J}'' - \bar{J}' - \bar{J}''')^2}. \quad (16)$$

The angles  $\Phi$  and  $\Phi'$  which are assumed to be generally of the order of 1 are determined by Eqs. (13) and (14). The stability conditions with respect to  $\psi$  and  $\phi$

$$\frac{\partial^2 F}{\partial \psi^2} = 2(J_D + J_B) > 0, \quad (17)$$

$$\frac{\partial^2 F}{\partial \phi^2} = 2(J_B - J_C) > 0 \quad (18)$$

are always satisfied.<sup>2</sup> For a stable configuration the following equations should be positive:

$$\begin{aligned} \frac{\partial^2 F}{\partial \Phi^2} &= [(\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''')^2 / 2(J_D + J_B)] \\ &\times (s_0 + s \cdot \cos\Phi) s \cdot \cos\Phi \\ &- [(\bar{J} + \bar{J}'' - \bar{J}' - \bar{J}''')^2 / 2(J_B - J_C)] \\ &\times (s_0' - s \cdot \sin\Phi \cos\Phi') s \cdot \sin\Phi \cos\Phi' \\ &- 2s^2 \cos 2\Phi \cdot [(J_D' + J_B') - (J_B' - J_C') \cos^2 \Phi'], \quad (19) \end{aligned}$$

$$\begin{aligned} \frac{\partial^2 F}{\partial \Phi'^2} &= s \cdot \sin\Phi \{ - [(\bar{J} + \bar{J}'' - \bar{J}' - \bar{J}''')^2 / 2(J_B - J_C)] \\ &\times (s_0' - s \cdot \sin\Phi \cos\Phi') \cos\Phi' \\ &+ 2(J_B' - J_C') s \cdot \sin\Phi \cos 2\Phi' \}. \quad (20) \end{aligned}$$

Equations (13) and (14) give an unstable solution (I), and two sets of stable solutions (II) and (III).

*Case I.*  $\sin\Phi = 0$ . In this case, Eq. (20) shows that the spin configuration is stationary and not stable. Following Eqs. (10d)–(10f), the configuration of  $\text{Gd}^{3+}$  spins is completely  $F_x^R$ , which means that the  $\text{Gd}^{3+}$  spins are polarized parallel or antiparallel to the net moment  $F_x$  of  $\text{Cr}^{3+}$  spins.

*Case II.*  $\sin\Phi' = 0$ . The angle  $\Phi$  is determined by Eq. (13):

$$\begin{aligned} (J_B - J_C)(\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''')^2 (s_0 + s \cdot \cos\Phi) s \cdot \sin\Phi \\ + (J_D + J_B)(\bar{J} + \bar{J}'' - \bar{J}' - \bar{J}''')^2 (s_0' - s \cdot \sin\Phi) s \cdot \cos\Phi \\ - 4(J_D + J_B)(J_B - J_C)(J_B' + J_C') s^2 \sin\Phi \cos\Phi = 0. \quad (21a) \end{aligned}$$

This equation is similar to Eq. (37a) of Ref. 2 except for the last term which results from the  $\text{Gd}^{3+}$ – $\text{Gd}^{3+}$  exchange interaction. Using the angle  $\Phi$  determined by Eq. (21a), the equilibrium values of

other angles are obtained as

$$\Phi' = 0, \quad (21b)$$

$$\psi = [(D_y + B_y) - s(\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''') \cos\Phi] / 2(J_D + J_B), \quad (21c)$$

$$\begin{aligned} \phi = -[(B_x - C_x) + s(\bar{J} + \bar{J}'' - \bar{J}' - \bar{J}''') \\ \times \sin\Phi] / 2(J_B - J_C). \quad (21d) \end{aligned}$$

This corresponds to the  $\Gamma_2(F_x, C_y, G_x: F_x^R, C_y^R)$  configuration above  $T_{N2}$ . The stability conditions of Eqs. (19) and (20) should be satisfied.

*Case II.* In this case we have

$$s \cdot \sin\Phi \cos\Phi' = B, \quad (22)$$

where

$$B = \frac{s_0'(\bar{J} + \bar{J}'' - \bar{J}' - \bar{J}''')^2}{(\bar{J} + \bar{J}'' - \bar{J}' - \bar{J}''')^2 - 4(J_B - J_C)(J_B' - J_C')}. \quad (23)$$

The angle  $\Phi$  is determined by the following equation:

$$\begin{aligned} (J_B - J_C)[(\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''')^2 - 4(J_D + J_B)(J_D' + J_B')] \\ \times s^3 \cos^3 \Phi + (J_B - J_C)(\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''')^2 s_0 s^2 \cos^2 \Phi \\ - \{ (J_B - J_C)[(\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''')^2 - 4(J_D + J_B)(J_D' + J_B')] s^2 \\ + (J_D + J_B)(\bar{J} + \bar{J}'' - \bar{J}' - \bar{J}''')^2 s_0' B \\ - (J_D + J_B)(\bar{J} + \bar{J}'' - \bar{J}' - \bar{J}''')^2 - 4(J_B - J_C)(J_B' - J_C') \\ \times B^2 \} s \cdot \cos\Phi - (J_B - J_C)(\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''')^2 s_0 s^2 = 0. \quad (24a) \end{aligned}$$

By using the angle  $\Phi$  determined by Eq. (24a), Eqs. (22), (11), and (12) give the other stable angles to be

$$\Phi' = \cos^{-1}[B / (s \cdot \sin\Phi)], \quad (24b)$$

$$\psi = [(D_y + B_y) - s(\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''') \cos\Phi] / 2(J_D + J_B), \quad (24c)$$

$$\phi = -[(B_x - C_x) + B(\bar{J} + \bar{J}'' - \bar{J}' - \bar{J}''')] / 2(J_B - J_C). \quad (24d)$$

This corresponds to the  $\Gamma_{27}(F_x, C_y, G_x: F_x^R, C_y^R, G_x^R)$  configuration below  $T_{N2}$ . Also in this case the stability conditions of Eqs. (19) and (20) should be satisfied.

Up to the order of  $\epsilon^2$ , the free-energies  $F(\Gamma_{\frac{1}{2}}^I)$ ,  $F(\Gamma_{\frac{1}{2}}^{II})$ , and  $F(\Gamma_{\frac{1}{2}}^{III})$  of three cases I, II, and III, respectively, are given as

$$F(\Gamma_{\frac{1}{2}}^I) = F^{Cr} - [(\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''')^2 / 2(J_D + J_B)] \\ \times s(s + s_0) + \frac{1}{2}(J'_A + J'_B + J'_C + J'_D)s^2, \quad (25a)$$

$$F(\Gamma_{\frac{1}{2}}^{II}) = F^{Cr} - [(\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''')^2 / 2(J_D + J_B)] \\ \times (s_0 + s \cdot \cos\Phi) s \cdot \cos\Phi + [(\bar{J} + J'' - \bar{J}' - \bar{J}''')^2 / \\ 2(J_B - J_C)] (s'_0 - s \cdot \sin\Phi) s \cdot \sin\Phi \\ + \frac{1}{2}[(J'_A + J'_B + J'_C + J'_D) \cos^2\Phi \\ + (J'_A + J'_B - J'_C - J'_D) \sin^2\Phi] s^2, \quad (25b)$$

$$F(\Gamma_{\frac{1}{2}}^{III}) = F^{Cr} - [(\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''')^2 / 2(J_D + J_B)] \\ \times (s_0 + s \cdot \cos\Phi) s \cdot \cos\Phi \\ + [(\bar{J} + \bar{J}'' - \bar{J}' - \bar{J}''')^2 / 2(J_B - J_C)] (s'_0 - B) B \\ + (J'_B - J'_C) B^2 + \frac{1}{2}[(J'_A + J'_B + J'_C + J'_D) \cos^2\Phi \\ + (J'_A - J'_B + J'_C - J'_D) \sin^2\Phi] s^2, \quad (25c)$$

where  $F^{Cr}$  is the free-energy of  $Cr^{3+}$  spin system:

$$F^{Cr} = F_0 + D - [4(J_D + J_B) - (J_A + J_B + J_C + J_D)] \\ \times (D_y + B_y)^2 / 8(J_D + J_B)^2 - [4(J_B - J_C) \\ - (J_A + J_B - J_C - J_D)] (B_x - C_x)^2 / 8(J_B - J_C)^2. \quad (25d)$$

Although the configuration of case I has been shown to be unstable, the free-energy  $F(\Gamma_{\frac{1}{2}}^I)$  is also given for comparison.

In the high-temperature phase,  $s$  is relatively small and the free energy  $F(\Gamma_{\frac{1}{2}}^{II})$  is the lowest. Then, the  $\Gamma_{\frac{1}{2}}(F_x, C_y, G_z; F_x^R, C_y^R)$  configuration is realized.<sup>2</sup> As the temperature is lowered,  $s$  increases and then the free energy of this configuration crosses that of the  $\Gamma_{27}(F_x, C_y, G_z; F_x^R, C_y^R, G_z^R)$  configuration at a critical point  $s_c$ , where the corresponding temperature is defined as  $T_{N2}$ . Then,  $\Phi'$  takes a nonzero value and a new antiferromagnetic configuration  $G_z^R$  of  $Gd^{3+}$  spins appears. The free energy  $F(\Gamma_{\frac{1}{2}}^{III})$  is the lowest for  $s$  larger than  $s_c$  and the  $\Gamma_{27}$  configuration is realized in the lower-temperature phase. Here, although we have no available values of parameters in Eq. (25), it seems that  $F(\Gamma_{\frac{1}{2}}^I)$  is higher than  $F(\Gamma_{\frac{1}{2}}^{II})$  or  $F(\Gamma_{\frac{1}{2}}^{III})$  for all values of  $s$ . The case I, therefore, is never realized.

Now, we can obtain the expressions of the derivatives of the angle  $\Phi$  with respect to the temperature  $T$  by differentiating Eqs. (21a) and (24a) for the high- and low-temperature phases, respectively. The resulting expression is lengthy and is not given here; its derivation is quite straightforward.  $\partial\Phi/\partial T$  has a finite discontinuity at  $T_{N2}$ . The derivative of the angle  $\Phi'$  is obtained from Eq. (22) as follows:

$$\partial\Phi'/\partial T = \frac{[(\partial s/\partial T)\sin\Phi + (\partial\Phi/\partial T)s \cdot \cos\Phi]\cos\Phi'}{(s \cdot \sin\Phi \sin\Phi')}, \quad (26)$$

using the derivative  $\partial\Phi/\partial T$  to be determined. At  $T_{N2}$ ,  $\Phi'$  is zero and Eq. (26) shows that  $\partial\Phi'/\partial T$  has an infinite discontinuity. This is characteristic of Landau's second-order phase transition.<sup>8</sup> Similar discussions are applicable to the case where  $GdCrO_3$  has the  $\Gamma_{26}$  configuration.

#### D. Spin Configuration of $DyFeO_3$

We next investigate the spin configuration  $DyFeO_3$  below  $T_{N2}$ , where the  $Dy^{3+}$  anisotropy is large enough as compared with the  $Fe^{3+}$ - $Dy^{3+}$  and  $Dy^{3+}$ - $Dy^{3+}$  magnetic interactions. Then, we can regard the  $Dy^{3+}$  spin as the Ising-like spin directed along its own anisotropy axis.

As mentioned previously, we assume that the spin configuration of  $DyFeO_3$  below  $T_{N2}$  is  $\Gamma_{15}(A_x, G_y, C_z; G_x^R, A_y^R)$ . Here, the  $C_z^R$  configuration of  $Dy^{3+}$  spins is omitted, since the  $Dy^{3+}$  Ising-like spin is confined to its anisotropy axis in the  $a$ - $b$  plane. The Hamiltonian of this  $\Gamma_{15}$  configuration is easily obtained from Eqs. (9a)-(9d) of Ref. 2 and from Eqs. (A1)-(A7) of this paper. Then, in this configuration the isotropic and the antisymmetric exchange interactions between  $Fe^{3+}$  and  $Dy^{3+}$  spins are absent and the anisotropic-symmetric exchange interaction is given as

$$\bar{\mathcal{H}}_{\text{symm}}/2N = (\bar{a}_{xx} - \bar{a}_{xx}'' + \bar{a}_{xx}' - \bar{a}_{xx}''') A_x G_x^R \\ + (\bar{a}_{yy} - \bar{a}_{yy}'' - \bar{a}_{yy}' + \bar{a}_{yy}''') G_y A_y^R \\ + (\bar{a}_{xy} - \bar{a}_{xy}'' + \bar{a}_{xy}' - \bar{a}_{xy}''') G_y G_x^R \\ + (\bar{a}_{xy} - \bar{a}_{xy}'' - \bar{a}_{xy}' + \bar{a}_{xy}''') A_x A_y^R \\ + (\bar{a}_{xz} - \bar{a}_{xz}'' + \bar{a}_{xz}' - \bar{a}_{xz}''') C_z G_x^R \\ + (\bar{a}_{yz} - \bar{a}_{yz}'' - \bar{a}_{yz}' + \bar{a}_{yz}''') C_z A_y^R. \quad (27)$$

Now, for the temperature above  $T_{N2}$ , symmetry arguments show that  $\bar{a}_{\alpha\beta}'' = \bar{a}_{\alpha\beta}$  and  $\bar{a}_{\alpha\beta}''' = \bar{a}_{\alpha\beta}'$ . Expecting that the same relations nearly hold for the temperature below  $T_{N2}$ , the anisotropic-symmetric exchange interaction is small enough to be neglected. Thus, since the  $Fe^{3+}$ - $Dy^{3+}$  interaction is nearly absent for this  $\Gamma_{15}$  configuration, we can treat two spin systems of  $Fe^{3+}$  and  $Dy^{3+}$  ions to be independent of each other. Therefore, the spin configurations of  $Fe^{3+}$  and  $Dy^{3+}$  ions in  $DyFeO_3$  are the same as those of  $Fe^{3+}$  ions in  $YFeO_3$  and of  $Dy^{3+}$  ions in  $DyAlO_3$ , respectively. The  $Fe^{3+}$  spin configuration is  $(A_x, G_y, C_z)$ . The hidden canting angles  $\phi$  and  $\phi'$  which give the  $A_x$  and  $C_z$  configurations, respectively, are given as follows<sup>14</sup>:

$$\phi = (D_z - C_z) / 2(J_D - J_C), \quad (28a)$$

$$\phi' = -(B_x - C_x) / 2(J_B - J_C). \quad (28b)$$

The  $Dy^{3+}$  spin configuration is  $(G_x^R, A_y^R)$ ; each spin



is confined in the  $a$ - $b$  plane and canted from the  $b$  axis by  $33^\circ$ .<sup>15</sup>

### E. Spin Configuration of DyCrO<sub>3</sub>

The Cr<sup>3+</sup> spins of DyCrO<sub>3</sub> have the  $\Gamma_2(F_x, C_y, G_z)$  configuration. Then, following Bertaut,<sup>1</sup> the compatible configuration of Dy<sup>3+</sup> spins should be  $\Gamma_2(F_x^R, C_y^R)$ . However, the Dy<sup>3+</sup> spins favor the  $\Gamma_5(G_x^R, A_y^R)$  configuration as mentioned previously. We assume that the Dy<sup>3+</sup> spins are confined to its own anisotropy axis. The free energy of the  $\Gamma_2(F_x^R, C_y^R)$  configuration is not so much higher than that of the  $\Gamma_5(G_x^R, A_y^R)$  configuration. The difference of free energies between two configurations is of the order of the Dy<sup>3+</sup>-Dy<sup>3+</sup> interaction  $J'$  which is calculated to be nearly  $0.2 \text{ cm}^{-1}$  by using the experimental data.<sup>11</sup> Here, the  $\Gamma_2$  configuration is the spin-flopped configuration of  $\Gamma_5$ . In fact, Holmes *et al.*<sup>11</sup> found in DyAlO<sub>3</sub> that with the magnetic field applied along the  $a$  axis, the metamagnetic transition which involves a simultaneous reversal of two spins takes place at a critical field  $H_c = 11 \text{ kOe}$  at the temperature  $T = 1.45 \text{ K}$  ( $T_{N2} = 3.52 \text{ K}$ ). Now, in DyCrO<sub>3</sub>, the weak ferromagnetic moment of Cr<sup>3+</sup> spins along the  $a$  axis induces the effective field acting on Dy<sup>3+</sup> spins along the  $a$  axis owing to the Cr<sup>3+</sup>-Dy<sup>3+</sup> interactions. The comparison with the observed data<sup>7</sup> shows that the magnitude of this effective field is  $7 \text{ kOe}$  which is smaller than  $H_c$ . Then, the Dy<sup>3+</sup> spin configuration would be mainly  $\Gamma_5(G_x^R, A_y^R)$ . However, this effective field induces the ferromagnetic moment  $F_x^R$  of Dy<sup>3+</sup> spins, resulting in the  $\Gamma_2(F_x^R, C_y^R)$  configuration in addition to  $\Gamma_5(G_x^R, A_y^R)$ . Thus, there is a possibility that the two spin configurations coexist stably.

This is also justified from symmetry arguments. Table II shows that the effective field and the induced Dy<sup>3+</sup> spins above  $T_{N2}$  both belong to the  $\Gamma_2(H_x: F_x^R, C_y^R)$  configuration whose magnetic symmetry group is  $D_{2h}(C_{2h})m'm'm$ . This magnetic group is invariant to operators ( $E, \bar{C}_{2x}, i, i\bar{C}_{2x}, R\bar{C}_{2y}, R\bar{C}_{2z}, iR\bar{C}_{2y}, iR\bar{C}_{2z}$ ). At  $T_{N2}$  the reordering of Dy<sup>3+</sup> spins takes place. Below  $T_{N2}$  the Dy<sup>3+</sup> spins favor the  $\Gamma_5(G_x^R, A_y^R)$  configuration in addition to  $\Gamma_2(F_x^R, C_y^R)$  due to the effective field from the Cr<sup>3+</sup> spins, resulting in the  $\Gamma_{25}(F_x^R, C_y^R; G_x^R, A_y^R)$  spin configuration, whose magnetic group is  $C_{2v}(C_2)2m'm'$ . The symmetry operations in this group are ( $E, \bar{C}_{2x}, iR\bar{C}_{2y}, iR\bar{C}_{2z}$ ). Thus, at  $T_{N2}$  Landau's second-order phase transition occurs and the number of symmetry operators is reduced to half that above  $T_{N2}$ . The spin configurations below and above  $T_{N2}$ ,  $\Gamma_{25}$  and  $\Gamma_2$ , respectively, are illustrated in Figs. 2(a) and 2(b).<sup>16</sup>

Now, we calculate the free-energy of the  $\Gamma_{25}(F_x, C_y, G_z: F_x^R, C_y^R; G_x^R, A_y^R)$  configuration. In DyCrO<sub>3</sub> containing orbitally degenerate Dy<sup>3+</sup> ion, the orders of magnitudes of interaction parameters

are given in Table II of Ref. 2. In a procedure similar to that in Sec. II C, we obtain the equilibrium values of the angles  $\psi$  and  $\phi$  which define the overt canting  $F_x$  and the hidden canting  $C_y$ , respectively, of Cr<sup>3+</sup> spins:

$$\psi = -[(D_y + B_y) + s(\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''')] \sin \Phi_0 / 2(J_D + J_B), \quad (29a)$$

$$\phi = -[(B_x - C_x) + s(\bar{J} + \bar{J}'' - \bar{J}' - \bar{J}''')] \sin \Phi_0 / 2(J_B - J_C), \quad (29b)$$

where  $s$  is the ratio of the induced Dy<sup>3+</sup> sublattice spin to the Cr<sup>3+</sup> sublattice spin and  $\Phi_0$  is the angle between the Dy<sup>3+</sup> anisotropy axis and the  $b$  axis. ( $\Phi_0$  is taken to be  $33^\circ$ .) Finally, from Eqs. (A1)–(A3), we obtain the effective field acting on the Dy<sup>3+</sup> spins along the  $a$  axis as follows:

$$H_{\text{eff}} = \langle S_{\text{Cr}} \rangle [(\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''')\psi + (\bar{D}_y + \bar{D}'_y + \bar{D}''_y + \bar{D}'''_y) + 2(\bar{a}_{xx} + \bar{a}''_{xx} + \bar{a}'_{xx} + \bar{a}'''_{xx})] \quad (30)$$

$$\sim \langle S_{\text{Cr}} \rangle \{2[(\bar{D}_y + \bar{D}'_y + \bar{D}''_y + \bar{D}'''_y) + 2(\bar{a}_{xx} + \bar{a}''_{xx} + \bar{a}'_{xx} + \bar{a}'''_{xx})] \times (J_D + J_B) - (\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''')(D_y + B_y)\} / 2(J_D + J_B) - \langle S_{\text{Dy}} \rangle (\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''')^2 / 2(J_D + J_B), \quad (30')$$

which is expected to amount to  $7 \text{ kOe}$  at  $T = 1.5 \text{ K}$  to fit the observed data.<sup>7</sup>

### III. MAGNETOELECTRIC EFFECT

In a material which exhibits the linear magneto-electric (ME) effect,<sup>17–21</sup> an applied electric field  $E$  induces a magnetization  $M$  which is proportional to  $E$ , and an applied magnetic field  $H$  induces an electric polarization  $P$  which is proportional to  $H$ . Since the qualitative nature of the ME tensors is determined by symmetry, measurement of these

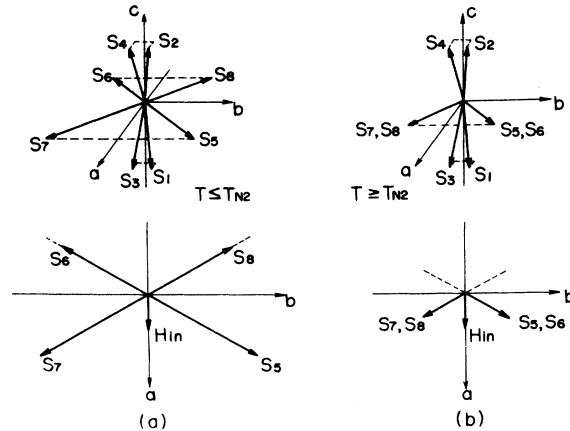


FIG. 2. Spin configuration in DyCrO<sub>3</sub>. (a) The  $\Gamma_{25}(F_x, C_y, G_z: F_x^R, C_y^R; G_x^R, A_y^R)$  configuration below  $T_{N2}$ . (b) The  $\Gamma_2(F_x, C_y, G_z: F_x^R, C_y^R)$  configuration above  $T_{N2}$ .

TABLE VI. Magnetoelectric susceptibility tensors for various spin configurations.

	ME tensor	Spin configuration
$T > T_{N2}$	$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$	$\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$ $\Gamma_{12}, \Gamma_{13}, \Gamma_{14}, \Gamma_{23}, \Gamma_{24}, {}^a \Gamma_{34}$
	$\begin{bmatrix} \alpha_{xx} & & \\ & \alpha_{yy} & \\ & & \alpha_{zz} \end{bmatrix}$	$\Gamma_5^b$ $\Gamma_{15}, {}^c \Gamma_{25}, {}^d \Gamma_{35}, \Gamma_{45}$
	$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha_{yz} \\ 0 & \alpha_{xy} & 0 \end{bmatrix}$	$\Gamma_6$ $\Gamma_{16}, \Gamma_{26}, {}^e \Gamma_{36}, \Gamma_{46}$
$T \leq T_{N2}$	$\begin{bmatrix} 0 & 0 & \alpha_{zx} \\ 0 & 0 & 0 \\ \alpha_{zx} & 0 & 0 \end{bmatrix}$	$\Gamma_7$ $\Gamma_{17}, \Gamma_{27}, {}^e \Gamma_{37}, \Gamma_{47}$
	$\begin{bmatrix} 0 & \alpha_{yx} & 0 \\ \alpha_{yx} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$	$\Gamma_8$ $\Gamma_{18}, \Gamma_{28}, \Gamma_{38}, \Gamma_{48}$

<sup>a</sup>The spin reorientation region.

<sup>b</sup>RAIO<sub>3</sub> ( $R = \text{Gd, Tb, Dy}$ ); see Ref. 11.

<sup>c</sup>DyFeO<sub>3</sub>.

<sup>d</sup>DyCrO<sub>3</sub>.

<sup>e</sup>GdCrO<sub>3</sub>.

tensors provides a powerful tool for justifying our arguments developed in Sec. II.

We can write the free energy of a ME material, the electric polarization, and the magnetization as

$$F = -\frac{1}{2} \sum_{i,j} \kappa_{ij} E_i E_j - \sum_{i,j} \alpha_{ij} E_i H_j - \frac{1}{2} \sum_{i,j} \chi_{ij} H_i H_j, \quad (31a)$$

$$P_i = -(\partial F / \partial E_i)_{H,T} = \sum_j \kappa_{ij} E_j + \sum_j \alpha_{ij} H_j, \quad (31b)$$

$$M_i = -(\partial F / \partial H_i)_{E,T} = \sum_j \chi_{ij} H_j + \sum_j \alpha_{ij} E_j, \quad (31c)$$

where  $\kappa_{ij}$  and  $\chi_{ij}$  are the usual electric and magnetic susceptibility tensors, respectively, and  $\alpha_{ij}$  is the ME susceptibility tensor.

By using symmetry considerations together with Tables II and III, the ME susceptibility tensors for various spin configurations are given in Table VI. (i) Above  $T_{N2}$ , the tensors vanish for all  $\Gamma_i$  ( $i=1-4$ ) and  $\Gamma_{ij}$  ( $i, j=1-4$ ) configurations, since the corresponding groups involve the inversion symmetry. (ii) However, below  $T_{N2}$ , all  $RMO_3$  crystals are expected to exhibit the ME effect due to the lack of the inversion symmetry. (iii) The nonvanishing ME tensor elements of the  $\Gamma_{15}$  and  $\Gamma_{25}$  type such as DyFeO<sub>3</sub> and DyCrO<sub>3</sub>, respectively, are  $\alpha_{xx}$ ,  $\alpha_{yy}$  and  $\alpha_{zz}$ . Thus, the magnetic and electric fields along any crystal axis induce polarization and magnetization, respectively, along the applied field. (iv) Since  $\alpha_{yz}$  and  $\alpha_{xy}$  are nonzero tensor elements for the  $\Gamma_{26}$  configuration, the applied magnetic and electric fields along the  $b$  axis (or the  $c$  axis) induce an ME polarization and mag-

netization, respectively, parallel to the  $c$  axis (or the  $b$  axis). For the  $\Gamma_{27}$  configuration  $\alpha_{xx}$  and  $\alpha_{yy}$  elements are nonzero. Therefore, future experiments on the ME effect of GdCrO<sub>3</sub> will clarify whether it has the  $\Gamma_{26}$  or  $\Gamma_{27}$  configuration. (v) All of the magnetic symmetry in  $RMO_3$  below  $T_{N2}$  are to be determined by the ME effect measurement by using Table VI.

#### IV. CONCLUDING REMARKS

Assuming that in  $RMO_3$  the magnetic and the paramagnetic unit cells are the same both above and below  $T_{N2}$ , we have clarified that the magnetic symmetry group is lowered to the index-two subgroup of that above  $T_{N2}$ . By calculating the free energy, the spin configuration corresponding to this magnetic group has been shown to be stable. Then, we have shown that GdCrO<sub>3</sub> has either the  $\Gamma_{26}(F_x, C_y, G_z; F_x^R, C_y^R, A_z^R)$  or the  $\Gamma_{27}(F_x, C_y, G_z; F_x^R, C_y^R, G_z^R)$  configuration, DyFeO<sub>3</sub> the  $\Gamma_{15}(A_x, G_y, C_z; C_x^R, A_y^R)$  configuration, and DyCrO<sub>3</sub> the  $\Gamma_{25}(F_x, C_y, G_z; F_x^R, C_y^R, G_z^R, A_x^R)$  configuration.

Furthermore, we have predicted that the ME effect may be observed in  $RMO_3$  below  $T_{N2}$ , although any  $RMO_3$  has no ME effect above  $T_{N2}$ . In DyFeO<sub>3</sub> and DyCrO<sub>3</sub> which have the  $\Gamma_{15}$  and the  $\Gamma_{25}$  configurations, respectively, a magnetic or an electric field along any crystal axis induces a polarization or a magnetization parallel to the applied field. In GdCrO<sub>3</sub> with the  $\Gamma_{26}$  configuration, the ME polarization and magnetization are induced along the  $b$  axis (or the  $c$  axis) with the applied magnetic and electric field along the  $c$  axis (or the  $b$  axis). If GdCrO<sub>3</sub> has the  $\Gamma_{27}$  configuration, the role of the  $b$  axis in the  $\Gamma_{26}$  configuration is replaced by that of the  $a$  axis. Thus, measurements of the ME tensor determine which configuration GdCrO<sub>3</sub> has. It is hoped that all the magnetic symmetry of other  $RMO_3$  could be determined by observing the ME effect.

#### ACKNOWLEDGMENTS

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#### APPENDIX: HAMILTONIANS FOR THE INTERACTION BETWEEN $M^{3+}$ AND $R^{3+}$ IONS AND FOR $R^{3+}$ IONS

$$\begin{aligned} \bar{\mathcal{H}}_{1so}^R / N = & (\bar{J} + \bar{J}'' + \bar{J}' + \bar{J}''') \bar{F} \cdot \bar{F}^R \\ & + (\bar{J} + \bar{J}'' - \bar{J}' - \bar{J}''') \bar{C} \cdot \bar{C}^R \\ & + (\bar{J} - \bar{J}'' + \bar{J}' - \bar{J}''') \bar{A} \cdot \bar{C}^R \\ & + (\bar{J} - \bar{J}'' - \bar{J}' + \bar{J}''') \bar{G} \cdot \bar{A}^R, \quad (A1) \\ \bar{\mathcal{H}}_{ant}^R / N = & (\bar{D}_x + \bar{D}_x'' + \bar{D}_x' + \bar{D}_x''') (A_y F_x^R - A_z F_y^R) \end{aligned}$$

$$\begin{aligned}
& + (\bar{D}_x + \bar{D}_x'' - \bar{D}_x' - \bar{D}_x''') (G_y C_x^R - G_x C_y^R) \\
& + (\bar{D}_x - \bar{D}_x'' + \bar{D}_x' - \bar{D}_x''') (F_y G_x^R - F_x G_y^R) \\
& + (\bar{D}_x - \bar{D}_x'' - \bar{D}_x' + \bar{D}_x''') (C_y A_x^R - C_x A_y^R) \\
& + (\bar{D}_y + \bar{D}_y'' + \bar{D}_y' + \bar{D}_y''') (G_x F_x^R - G_x F_y^R) \\
& + (\bar{D}_y + \bar{D}_y'' - \bar{D}_y' - \bar{D}_y''') (A_x C_x^R - A_x C_y^R) \\
& + (\bar{D}_y - \bar{D}_y'' + \bar{D}_y' - \bar{D}_y''') (C_x G_x^R - C_x G_y^R) \\
& + (\bar{D}_y - \bar{D}_y'' - \bar{D}_y' + \bar{D}_y''') (F_x A_x^R - F_x A_y^R) \\
& + (\bar{D}_z + \bar{D}_z'' + \bar{D}_z' + \bar{D}_z''') (C_x F_x^R - C_y F_x^R) \\
& + (\bar{D}_z + \bar{D}_z'' - \bar{D}_z' - \bar{D}_z''') (F_x C_y^R - F_y C_x^R) \\
& + (\bar{D}_z - \bar{D}_z'' + \bar{D}_z' - \bar{D}_z''') (G_x G_y^R - G_y G_x^R) \\
& + (\bar{D}_z - \bar{D}_z'' - \bar{D}_z' + \bar{D}_z''') (A_x A_y^R - A_y A_x^R) ,
\end{aligned}$$

(A2)

$$\begin{aligned}
\bar{H}'_{\text{symm}}/2N &= (\bar{a}_{xx} + \bar{a}_{xx}'' + \bar{a}_{xx}' + \bar{a}_{xx}''') F_x F_x^R \\
& + (\bar{a}_{xx} + \bar{a}_{xx}'' - \bar{a}_{xx}' - \bar{a}_{xx}''') C_x C_x^R \\
& + (\bar{a}_{xx} - \bar{a}_{xx}'' + \bar{a}_{xx}' - \bar{a}_{xx}''') A_x G_x^R \\
& + (\bar{a}_{xx} - \bar{a}_{xx}'' - \bar{a}_{xx}' + \bar{a}_{xx}''') G_x A_x^R \\
& + (\text{terms where } x \rightleftharpoons y) \\
& + (\text{terms where } x \rightleftharpoons z) \\
& + (\bar{a}_{xy} + \bar{a}_{xy}'' + \bar{a}_{xy}' + \bar{a}_{xy}''') (C_x F_y^R + C_y F_x^R) \\
& + (\bar{a}_{xy} + \bar{a}_{xy}'' - \bar{a}_{xy}' - \bar{a}_{xy}''') (F_x C_y^R + F_y C_x^R) \\
& + (\bar{a}_{xy} - \bar{a}_{xy}'' + \bar{a}_{xy}' - \bar{a}_{xy}''') (G_x G_y^R + G_y G_x^R) \\
& + (\bar{a}_{xy} - \bar{a}_{xy}'' - \bar{a}_{xy}' + \bar{a}_{xy}''') (A_x A_y^R + A_y A_x^R) \\
& + (\bar{a}_{yz} + \bar{a}_{yz}'' + \bar{a}_{yz}' + \bar{a}_{yz}''') (A_y F_z^R + A_z F_y^R) \\
& + (\bar{a}_{yz} + \bar{a}_{yz}'' - \bar{a}_{yz}' - \bar{a}_{yz}''') (G_y C_z^R + G_z C_y^R) \\
& + (\bar{a}_{yz} - \bar{a}_{yz}'' + \bar{a}_{yz}' - \bar{a}_{yz}''') (F_y G_z^R + F_z G_y^R) \\
& + (\bar{a}_{yz} - \bar{a}_{yz}'' - \bar{a}_{yz}' + \bar{a}_{yz}''') (C_y A_z^R + C_z A_y^R) \\
& + (\bar{a}_{zx} + \bar{a}_{zx}'' + \bar{a}_{zx}' + \bar{a}_{zx}''') (G_x F_z^R + G_z F_x^R) \\
& + (\bar{a}_{zx} + \bar{a}_{zx}'' - \bar{a}_{zx}' - \bar{a}_{zx}''') (A_z C_x^R + A_x C_z^R) \\
& + (\bar{a}_{zx} - \bar{a}_{zx}'' + \bar{a}_{zx}' - \bar{a}_{zx}''') (C_x G_z^R + C_z G_x^R) \\
& + (\bar{a}_{zx} - \bar{a}_{zx}'' - \bar{a}_{zx}' + \bar{a}_{zx}''') (F_x A_z^R + F_z A_x^R) ,
\end{aligned}$$

(A3)

$$\begin{aligned}
H'_{\text{iso}}/N &= \frac{1}{2} (J'_A + J'_B + J'_C + J'_D) (\bar{F}^R)^2 \\
& + \frac{1}{2} (J'_A - J'_B + J'_C - J'_D) (\bar{G}^R)^2 \\
& + \frac{1}{2} (J'_A + J'_B - J'_C - J'_D) (\bar{C}^R)^2 \\
& + \frac{1}{2} (J'_A - J'_B - J'_C + J'_D) (\bar{A}^R)^2 ,
\end{aligned}$$

(A4)

$$H'_{\text{ant1}}/N = (B'_x + D'_x) (G_y^R F_x^R - G_x^R F_y^R)$$

$$\begin{aligned}
& + (B'_x - D'_x) (A_y^R C_x^R - A_x^R C_y^R) \\
& + (B'_y + C'_y) (A_x^R F_x^R - A_x^R F_y^R) \\
& + (B'_y - C'_y) (G_x^R C_x^R - G_x^R C_y^R) \\
& + (D'_x + C'_x) (C_x^R F_y^R - C_y^R F_x^R) \\
& + (D'_x - C'_x) (G_x^R A_y^R - G_y^R A_x^R) ,
\end{aligned}$$

(A5)

$$\begin{aligned}
H'_{\text{symm}}/N &= (a'_{xx} + b'_{xx} + c'_{xx} + d'_{xx}) (F_x^R)^2 \\
& + (a'_{xx} - b'_{xx} + c'_{xx} - d'_{xx}) (G_x^R)^2 \\
& + (a'_{xx} + b'_{xx} - c'_{xx} - d'_{xx}) (C_x^R)^2 \\
& + (a'_{xx} + b'_{xx} - c'_{xx} + d'_{xx}) (A_x^R)^2 \\
& + (\text{terms where } x \rightleftharpoons y) \\
& + (\text{terms where } x \rightleftharpoons z) \\
& + 2(a'_{xy} + b'_{xy}) (F_x^R C_y^R + F_y^R C_x^R) \\
& + 2(a'_{xy} - b'_{xy}) (G_x^R A_y^R + G_y^R A_x^R) \\
& + 2(a'_{yz} + c'_{yz}) (F_y^R G_z^R + F_z^R G_y^R) \\
& + 2(a'_{yz} - c'_{yz}) (C_y^R A_z^R + C_z^R A_y^R) \\
& + 2(a'_{zx} + d'_{zx}) (F_x^R A_z^R + F_z^R A_x^R) \\
& + 2(a'_{zx} - d'_{zx}) (C_x^R G_z^R + C_z^R G_x^R) ,
\end{aligned}$$

(A6)

$$\begin{aligned}
H'_{\text{an}}/N &= D' [(F_x^R)^2 + (G_x^R)^2 + (C_x^R)^2 + (A_x^R)^2] \\
& + E' [(F_x^R)^2 + (G_x^R)^2 + (C_x^R)^2 + (A_x^R)^2] \\
& - (F_y^R)^2 - (G_y^R)^2 - (C_y^R)^2 - (A_y^R)^2 \\
& + 2p' (F_x^R C_y^R + F_y^R C_x^R + G_x^R A_y^R + G_y^R A_x^R) \\
& + (\text{fourth-order terms}) \\
& + (\text{sixth-order terms}) ,
\end{aligned}$$

(A7)

where  $N$  is the number of unit cells in crystal, and

$$\begin{aligned}
\bar{a}_{xx} &= -(\bar{a}_{xx} + \bar{a}_{yy}) , & \bar{a}'_{xx} &= -(\bar{a}'_{xx} + \bar{a}'_{yy}) , \\
\bar{a}''_{xx} &= -(\bar{a}''_{xx} + \bar{a}''_{yy}) , & \bar{a}'''_{xx} &= -(\bar{a}'''_{xx} + \bar{a}'''_{yy}) , \\
a'_{xx} &= -(a'_{xx} + a'_{yy}) , & b'_{xx} &= -(b'_{xx} + b'_{yy}) , \\
c'_{xx} &= -(c'_{xx} + c'_{yy}) , & d'_{xx} &= -(d'_{xx} + d'_{yy}) .
\end{aligned}$$

For  $T \geq T_{N2}$ , the symmetry group contains the inversion operation. Then,

$$\begin{aligned}
\bar{J}'' &= \bar{J} , & \bar{J}''' &= \bar{J}' , & \bar{D}'' &= \bar{D} , & \bar{D}''' &= \bar{D}' , \\
\bar{a}'' &= \bar{a} , & \bar{a}''' &= \bar{a}'
\end{aligned}$$

and

$$B'_x = B'_y = C'_y = D'_x = a'_{xx} = a'_{yy} = c'_{yz} = d'_{zx} = 0 .$$

Therefore, for  $T \geq T_{N2}$ , Eqs. (A1)–(A3) coincide with Eqs. (9e)–(9g) of Ref. 2, respectively.

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- <sup>9</sup>In the spin-reorientation of the  $\Gamma_4 \rightarrow \Gamma_2$  type discussed in Ref. 2, the magnetic symmetry group of the spin-reorientation region ( $T_1 \leq T \leq T_2$ ) is the index-two subgroup of those in the high- and low-temperature phases, where the magnetic unit cell is the same as the paramagnetic one. At the spin-reorientation temperatures  $T_1$  and  $T_2$ , the second-order phase transition takes place. See Ref. 2.
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- <sup>15</sup>We assume that  $\text{Dy}^{3+}$  spins are confined to their own anisotropy axes in the  $a$ - $b$  plane. Then, the spin configuration of  $\text{DyFeO}_3$  above  $T_{N2}$  is  $\Gamma_1(A_x, G_y, C_z)$ , where  $C_z^R$  vanishes, that is,  $\text{Dy}^{3+}$  spins are really paramagnetic.
- <sup>16</sup>Above  $T_{N2}$  the  $\text{Dy}^{3+}$  spins are polarized due to the magnetic interactions between  $\text{Dy}^{3+}$  and  $\text{Cr}^{3+}$  spins. The polarized  $\text{Dy}^{3+}$  spins might direct along the effective field induced by the  $\text{Cr}^{3+}$  moment. However, since the  $\text{Dy}^{3+}$  single-ion anisotropy is large enough, the polarized  $\text{Dy}^{3+}$  spins are confined to their easy axes and the net moment of  $\text{Dy}^{3+}$  spins is along the net effective field from the  $\text{Cr}^{3+}$  spins, that is, along the  $a$  axis. The resulting configuration of the  $\text{Dy}^{3+}$  spins is  $\Gamma_2(F_x^R, C_y^R)$ .
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