

below the sensitivity of an x-ray determination. The latent heats  $L_i$  are also small: The values given in Table I correspond to approximately 0.4 and 3 cm<sup>-1</sup>/molecule at  $T_1$  and  $T_2$ , respectively.

These small changes are consistent with a microscopic model for the transitions in which magnetoelastic forces play a critical role in determining the relative stabilities of the phases. Indeed, it is notable that  $\Delta V_2/V_2$  is comparable to the magnetostrictive strain observed at 77°K.<sup>4</sup>

### III. INTERPRETATION

In a cubic crystalline field, octahedral-site Fe<sup>2+</sup> ions have a threefold-degenerate  ${}^5T_{2g,1}(t_{2g}^4e_g^2)$  ground state even after spin-orbit coupling has been included. Since the ground state is not a Kramers doublet, the energy is reduced by a Jahn-Teller distortion to lower point symmetry at lower temperatures. Distortions of the octahedra to either tetragonal or trigonal symmetry can remove the degeneracy. It is customary to define the noncubic component of the crystalline-field energy as

$$V_{nc} = \delta(L_z^2 - \frac{2}{3}), \quad (2)$$

where  $\delta$  may be either positive or negative. In the case of octahedral-site Fe<sup>2+</sup> ions, a  $\delta < 0$  corresponds to a tetragonal ( $c/a > 1$ ) or a trigonal ( $\alpha < 60^\circ$ ) distortion that stabilizes a Kramers doublet without quenching the spin-orbit-coupling energy. A  $\delta > 0$ , on the other hand, reverses the signs of the distortions and stabilizes a singlet state, thereby quenching the spin-orbit coupling. If a Jahn-Teller distortion occurs above a magnetic-ordering temperature, a distortion having  $\delta > 0$  is stabilized, since distortions that conserve the spin-orbit coupling are not cooperative when the spins are disordered, whereas the elastic coupling between neighboring interstices strongly favors cooperative distortions. On the other hand, if there is no distortion above  $T_N$ , then there will be a distortion having  $\delta < 0$  at those temperatures  $T < T_N$  where the spins are aligned collinearly. Here the magnetic order provides the long-range order that ensures a cooperative elastic distortion if the spin-orbit coupling is not quenched.

It can be shown<sup>7</sup> that the spectroscopic splitting factor for the effective spin  $S' = 1$  has the components

$$\begin{aligned} g_{||} &= (3 + \frac{1}{2}k_c) + 0.52(1 + \frac{1}{2}k_c)(\delta/3k_c\lambda), \\ g_{\perp} &= (3 + \frac{1}{2}k_c) - 0.26(1 + \frac{1}{2}k_c)(\delta/3k_c\lambda), \end{aligned} \quad (3)$$

where  $k_c \approx 0.9$  is a factor that takes account of covalent mixing and  $\lambda < 0$  is the spin-orbit-coupling constant for the atomic Fe<sup>2+</sup> ion. In the magnetically ordered state, the internal field  $\mathbf{H}_i$  produces a Zeeman splitting

$$\mu_B \mathbf{H}_i \cdot \vec{g} \cdot \mathbf{S}' = (\psi_\theta, H_Z \psi_\theta), \quad (4)$$

where the Zeeman energy is

$$H_Z = \mu_B \mathbf{H}_i \cdot (-k_c \mathbf{L} + 2\mathbf{S}). \quad (5)$$

Therefore, the Zeeman splitting in the molecular fields

is maximized by making  $(\delta/\lambda) > 0$  so that  $g_{||}$  increases and  $g_{\perp}$  decreases. Since  $\lambda < 0$ , this means a  $\delta < 0$ . Note that from Eqs. (3) and (4), the energy change goes as the first power of the atomic-displacement parameter  $\delta$ , whereas the elastic restoring forces go as  $\delta^2$ . This guarantees a finite macroscopic distortion below the magnetic-ordering temperature where the spins order collinearly. It also introduces a large crystalline anisotropy ( $g_{||} \neq g_{\perp}$ ) for the axis and magnitude of the atomic moments. A crystallographic distortion associated with an antiferromagnetic to paramagnetic transition may produce a first-order transition at  $T_N$ .

In Fe<sub>1- $\delta$</sub> O and KFeF<sub>3</sub>, there is a cubic to trigonal ( $\alpha < 60^\circ$ ) transition with decreasing temperature at the Néel temperature  $T_N$ . However, whether the microscopic interstices are distorted to trigonal ( $\alpha < 60^\circ$ ) or to tetragonal ( $c/a > 1$ ) symmetry depends upon second-order considerations. Therefore, it is reasonable to assume that the cubic to tetragonal ( $c/a > 1$ ) transition at  $T_N$  in RbFeF<sub>3</sub> is due to a Jahn-Teller stabilization in the presence of internal molecular fields. The only surprising feature is that the transition is second order and poorly defined.

Levinstein *et al.*<sup>8</sup> have demonstrated that extensive twinning takes place in RbFeF<sub>3</sub> below  $T_N$ , the extent of the twinning increasing with the  $c/a$  ratio as  $T$  is decreased. This observation indicates that strong magnetoelastic coupling is present right through  $T_N$ , dynamically cooperative Jahn-Teller distortions occurring within regions of short-range magnetic order above  $T_N$ . Since adjacent regions of short-range order may have their spin axes aligned perpendicular, cooling through the Néel temperature introduces twin planes. Creation of these twin planes requires energy, so the temperature at which long-range magnetic order sets in depends upon the energy required to create twin planes for the relief of internal stresses created by the magnetoelastic coupling. This energy requirement varies from region to region within any real crystal, thereby leading to the spatial variation of  $T_N$  suggested by Wertheim *et al.*<sup>1</sup>

In oxides with the perovskite structure, distortions to orthorhombic symmetry are common.<sup>9</sup> They represent a reduction in the anion coordination of the larger cation and can be correlated satisfactorily with the relative size and electronegativity of this cation. In the absence of a Jahn-Teller distortion, the general symmetry sequence with decreasing temperature in oxides is cubic  $\rightarrow$  rhombohedral  $\rightarrow$  orthorhombic. Although this sequence is not found in RbFeF<sub>3</sub>, where a Jahn-Teller distortion is present, it is reasonable to assume that any orthorhombic symmetry has the  $Pbnm$  space group of GdFeO<sub>3</sub>.<sup>10</sup> This symmetry permits the existence of a Dzialoshinskii vector  $\mathbf{D}$  parallel to the orthorhombic axis  $\mathbf{b}_0$ , and hence a canting of the spins to produce weak ferromagnetism for certain combinations of magnetic order and spin direction. In particular, with type-G magnetic order, spins parallel to  $\mathbf{c}_0$  may be

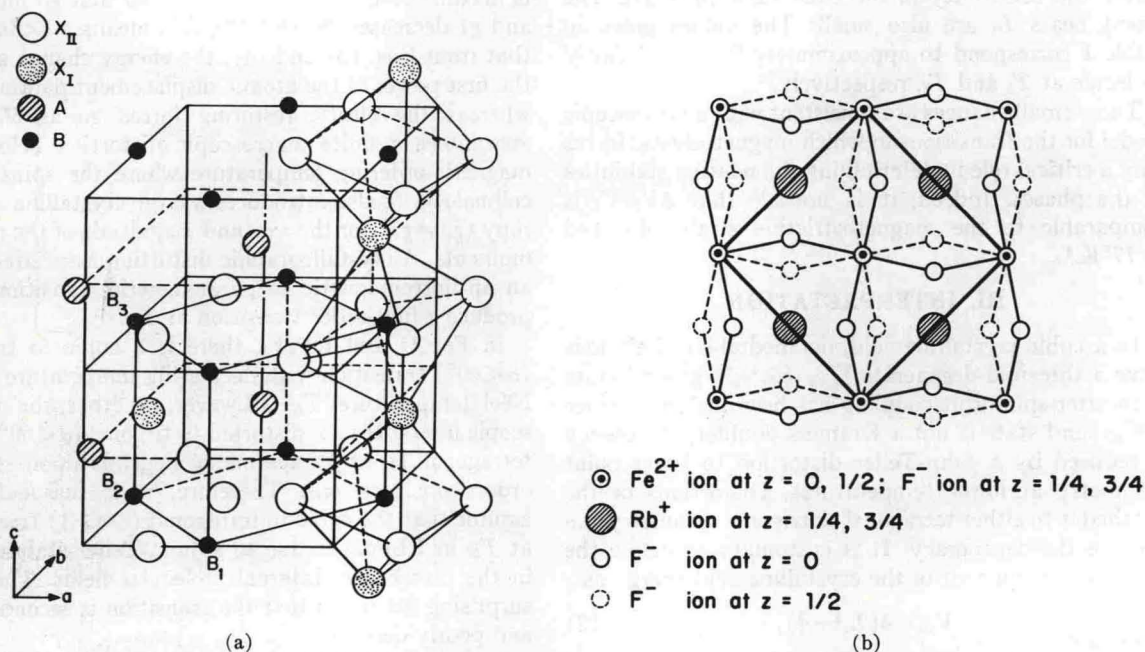


FIG. 2. Two  $Rb^+$ -ion-induced distortions of the perovskite structure: (a) Orthorhombic  $Pbnm$ . (b) Tetragonal ( $c_T' = 2c_T$ ) projected on (001).

canted so as to give a net ferromagnetic moment parallel to  $\mathbf{a}_0$  and spins parallel to  $(\mathbf{a}_0 \pm \mathbf{b}_0)$  will cant in the  $\mathbf{a}_0$ - $\mathbf{c}_0$  plane to give a net ferromagnetic moment parallel to  $\mathbf{c}_0$ . This immediately provides a mechanism for the appearance of weak ferromagnetism below  $T_2$ . Furthermore, Levinstein *et al.*<sup>8</sup> have observed directly that at  $T_2$  ferromagnetism is associated with the orthorhombic phase and that this ferromagnetic phase boundary moves across the twin planes of the tetragonal phase so as to include some regions having  $\mathbf{c}_T \rightarrow \frac{1}{2}\mathbf{c}_0$  and others having  $\mathbf{c}_T \rightarrow \frac{1}{2}(\mathbf{a}_0 + \mathbf{b}_0)$ .

Since the  $RbFeF_3$  crystals are heavily twinned below  $T_N$ , there are approximately equal volumes of material having  $\mathbf{c}_T$  directed along each of the three pseudocubic  $\langle 100 \rangle$  axes. Although additional twinning may occur below  $T_2$ , it was found that those twin planes associated with the orthorhombic distortion are mobile in applied magnetic fields.<sup>8</sup> In fact, for  $H_a > 0.5$  kOe, essentially all of these mobile twin planes are removed,<sup>4</sup> so that the specimen appears macroscopically orthorhombic. Nevertheless, it still contains the twins due to the Jahn-Teller distortion. In those regions of the specimen where  $\mathbf{c}_T \rightarrow \frac{1}{2}\mathbf{c}_0$ , spin canting would give a spontaneous ferromagnetic moment  $\sigma_0^0$  parallel to  $\mathbf{a}_0$ , which is along a pseudocubic  $\langle 110 \rangle$  axis. Where  $\mathbf{c}_T \rightarrow \frac{1}{2}(\mathbf{a}_0 \pm \mathbf{b}_0)$ , spin canting gives a spontaneous ferromagnetic moment  $\sigma_0^0/\sqrt{2}$  parallel to  $\mathbf{c}_0$ , which is along a pseudocubic  $\langle 100 \rangle$  axis. This moment is reduced by  $1/\sqrt{2}$  because only the component of the spin parallel to  $\mathbf{a}_0$  contributes to the spin canting. Furthermore, it has been observed<sup>4</sup> that

applied fields of 5 kOe are insufficient either to rotate the weak ferromagnetic moment more than about  $2^\circ$  from the easy axis of magnetization or to induce a spin flip, although they are sufficient to move twin planes associated with the orthorhombic phase. This model then suggests a net magnetization, after application of a field  $H_a = 5$  kOe parallel to  $[001]$ ,

$$\sigma^0 = \frac{1}{\sqrt{2}} \{ (0, 0, 1) + (0, 0, 1) + (1, 1, 0) \} \sigma_0^0, \quad (6)$$

where the Miller indices refer to the pseudocubic unit cell, and the orthorhombic axes are

$$\mathbf{c}_0 \parallel (0, 0, 1), \mathbf{a}_0 \parallel \frac{1}{\sqrt{2}}(1, 1, 0), \mathbf{b}_0 \parallel \frac{1}{\sqrt{2}}(\bar{1}, 1, 0). \quad (7)$$

However, Gyorgy *et al.*<sup>4</sup> have found that the torque curves for an "apparently single" crystal of  $RbFeF_3$  give cubic symmetry with  $\langle 100 \rangle$  easy axes and a  $\cos\theta$  dependence. This observation is clearly incompatible with Eq. (6), which means that some modification of the model is required.

Modification of the model begins with the observation that the distortions to "orthorhombic" symmetry are much smaller than the Jahn-Teller distortion to tetragonal ( $c/a > 1$ ) symmetry and that our assignment of the  $Pbnm$  space group was an assumption. In oxides, the orthorhombic symmetry  $Pbnm$  occurs where the larger cation is relatively small. It reduces the near-neighbor anion configuration about the larger cation from 12 to  $(5+2+5)$ , as illustrated in Fig. 2(a). This