



FIG. 3. Two rhombohedral Jahn-Teller distortions superposed on orthorhombic $Pbnm$ structure: (a) $\beta < 90^\circ$, (b) $\alpha < 90^\circ$.

permits the formation of shorter metal-anion bonds. In fluorides, on the other hand, the anion is much more ionic, and the anion configuration about the larger cation tends to be maximized, particularly in the case of a large cation like Rb^+ . These observations suggest that the distortions below T_2 are induced by the Jahn-Teller distortion below T_N , which reduces the anion configuration about a Rb^+ ion from 12 to $(4+8)$. A distortion that would increase this again to $(4+4+4)$, possibly approaching $(8+4)$, is shown in Fig. 2(b). Note that there is a doubling of each of the pseudocubic axes to form a new tetragonal unit cell having $\mathbf{c}_T' = 2\mathbf{c}_T$. This has a larger near-neighbor anion configuration about each Rb^+ ion than would the space group $Pbnm$ of Fig. 2(a). Therefore this would appear to be the more stable alternative. However, if the unique axis \mathbf{c}_T' crosses a twin plane, then it is perpendicular to \mathbf{c}_T in the twin. In this case the distortion of Fig. 2(b) would give a near-neighbor anion configuration about each Rb^+ ion that is reduced to $(2+2+8)$, which would not be competitive with the $Pbnm$ configuration of Fig. 2(a). Since the twin planes associated with the "orthorhombic" distortion below T_2 move across the twin planes due to the Jahn-Teller distortion, it seems more consistent to assume that where \mathbf{c}_T would transform to $\frac{1}{2}(\mathbf{a}_0 \pm \mathbf{b}_0)$, the symmetry is $Pbnm$ as illustrated in Fig. 2(a); that where \mathbf{c}_T would transform to $\frac{1}{2}\mathbf{c}_0$, it transforms instead to $\frac{1}{2}\mathbf{c}_T'$ to produce the symmetry of Fig. 2(b). The change of structure from that of Fig. 2(a) to that of Fig. 2(b) is sufficiently subtle that for small oxygen displacements the x-ray techniques that identify a specimen as macroscopically a "single crystal" below T_N would identify specimens subjected to external fields $H_a > 0.5$ kOe as "probably orthorhombic."

This model accounts nicely for four puzzling experimental findings. First, the Fe^{2+} ions in regions where $\mathbf{c}_T \rightarrow \frac{1}{2}\mathbf{c}_T'$ would experience internal fields different from those of Fe^{2+} ions in regions where $\mathbf{c}_T \rightarrow \frac{1}{2}(\mathbf{a}_0 \pm \mathbf{b}_0)$, thus giving rise to the two different Mössbauer spectra reported by Wertheim *et al.*¹ while permitting the weak ferromagnetism to be due to spin canting. Second, since there is no weak ferromagnetism associated with the symmetry of Fig. 2(b), the modified model changes Eq. (6) to

$$\sigma^{(0)} = \frac{1}{3}\sqrt{2}(0, 0, 1)\sigma_0^0, \quad (6')$$

which does agree with the experimental torque curves. Similarly, application of an $H_a > 0.5$ kOe parallel to $(0, 1, 0)$ or $(1, 0, 0)$ would create a $\sigma^{(0)} = (\frac{1}{3}\sqrt{2})\sigma_0^0$ parallel to these directions because of a switching of \mathbf{c}_0 from $(0, 0, 1)$ to $(0, 1, 0)$ or $(1, 0, 0)$. Thus the apparent cubic symmetry of a noncubic "crystal" is due to switching of a unique crystallographic axis in the applied field H_a . Such a switching is possible because the "orthorhombic" component of the distortion is induced by the large magnetostriction associated with the Jahn-Teller distortions, which do not switch. This does not contradict the finding,⁴ from strain gauge measurements during switching, that the "c" axis does not follow σ , because only the small orthorhombic component of the distortion is involved. This component of the distortion has been observed directly by metallographic techniques to be switchable in fields $H_a > 0.5$ kOe.⁸ The "c" axis referred to above is essentially due to the Jahn-Teller component, which does not switch. Since the magnetic energy required to switch an "orthorhombic" \mathbf{c}_0 axis is only that needed to create and move a mobile twin plane, it may be 3 orders of

magnitude smaller than the latent heat at T_2 , as observed. Third, because switching is due to rotation of a unique crystallographic axis rather than to rotation of electron spins, the fact that the spins are rotated by less than 2.5° in an $H_a = 16$ kOe can be reconciled with a torque curve that shows switching from a $[100]$ to an $[010]$ direction in the $H_a = 5$ kOe.⁴ Fourth, because the "orthorhombic" distortion occurs to maximize the number of nearest neighbors at each Rb^+ ion, rather than to reduce the Rb-F bond length, a puckering that destroys the close-packed arrangement of RbF_3 layers expands the volume, which accords with our experimental results at T_2 .

Since the Jahn-Teller distortion may be to either tetragonal ($c/a > 1$) or rhombohedral ($\alpha < 60^\circ$) symmetry and since second-order terms in the energy stabilize the rhombohedral distortion in Fe_{1-x}O and KFeF_3 , it is reasonable to anticipate a spin reorientation to the pseudocubic $\langle 111 \rangle$ axes at lowest temperatures. The small latent heat at T_1 is compatible with a simple spin-flop transition. Superposition of a rhombohedral Jahn-Teller distortion onto the orthorhombic crystal symmetry of Fig. 2(a) would indeed lower the symmetry to monoclinic (see Fig. 3), since the projection of the unique pseudocubic $\langle 111 \rangle$ axis onto the a_0 - b_0 plane would be parallel to either a_0 or b_0 . Thus a_0 , b_0 , $c_0 \rightarrow a_M$, b_M , c_M and either $\alpha < 90^\circ$ or $\beta < 90^\circ$. Furthermore, the twin planes below T_2 would be both $\{110\}$, as in the interval $T_1 < T < T_N$, and $\{100\}$. Therefore below T_1 the original $\{110\}$ twin planes probably remain fixed, and an additional $\{100\}$ set may be added. Furthermore, note that there is no case where the unique axis due to the Jahn-Teller distortion coincides with an orthorhombic axis c_0 , so that below T_1 the Rb^+ -ion-induced component of the distortion probably has orthorhombic symmetry $Pbnm$ with $\mathbf{D} \parallel \mathbf{b}_M$ over the entire volume of the crystal.

If the principal spin axis is parallel to the pseudocubic $[111]$ axis and the a_M , b_M , c_M axes correspond to pseudocubic $[110]$, $[\bar{1}10]$, $[001]$ axes, then a $\mathbf{D} \parallel \mathbf{b}_M$ produces a net ferromagnetic moment σ_0^M along the $[11\bar{2}]$ axis and $\beta < 90^\circ$, as illustrated in Fig. 3(a). On the other hand, if the spin axis is the $[\bar{1}11]$ axis as in Fig. 3(b), then the net moment is $\sigma_0^M/\sqrt{3}$ (since only the component parallel to \mathbf{c}_M is rotated by $\mathbf{D} \parallel \mathbf{b}_M$) along the $[110]$ axis and $\alpha < 90^\circ$. Again it is assumed that the applied field strengths are not strong enough to either

flip or rotate the principal spin axes, and the net magnetization, after application of an $H_a > 0.5$ kOe parallel to $[110]/\sqrt{2}$, becomes

$$\begin{aligned} \sigma^M &= (1/4\sqrt{6}) \\ &\times \{ (1, 1, \bar{2}) + (1, 1, 0) + (1, 1, 2) + (1, 1, 0) \} \sigma_0^M \\ &= (\sigma_0^M/\sqrt{3}) [(1, 1, 0)/\sqrt{2}]. \end{aligned} \quad (8)$$

Thus for an $H_a > 0.5$ kOe applied along any pseudocubic $\langle 110 \rangle$ axis, a $\sigma^M = \sigma_0^M/\sqrt{3}$ is created parallel to that $\langle 110 \rangle$ axis. Consequently in an $H_a = 5$ kOe, the monoclinic phase will appear cubic with the $\langle 110 \rangle$ axes as equivalent axes of easy magnetization, which is what has been found experimentally.⁴ Furthermore, those regions of the crystal having $\alpha < 90^\circ$ can in principle have a different internal field at the Fe^{2+} ions than those having $\beta < 90^\circ$, so that again two distinguishable Mössbauer spectra are possible, though the differences would be less pronounced than in the interval $T_1 < T < T_2$.

Finally, it is significant that

$$(\sigma_{110}^M/\sigma_{100}^O) = (\sqrt{\frac{3}{2}})(\sigma_0^M/\sigma_0^O) \approx \sqrt{\frac{3}{2}}, \quad (9)$$

which accounts nicely for the rise in the weak ferromagnetic moment on passing from the orthorhombic to the monoclinic phase. In fact the ratio $\sqrt{\frac{3}{2}}$ appears to be in reasonable quantitative agreement with the measurements of Testardi *et al.*² and with our observed ratio of 1.3.

In conclusion, the rather extraordinary properties of RbFeF_3 can be understood as an interesting interplay of three well-known phenomena: (i) a Jahn-Teller distortion below T_N that preserves the spin-orbit coupling, thus inducing a large magnetocrystalline coupling, (ii) an orthorhombic distortion due to ionic-size considerations that permits the existence of a Dzialoshinskii vector, and hence spin canting (except in those regions where \mathbf{c}_0 would be parallel to tetragonal \mathbf{c}_T axis due to a Jahn-Teller distortion), and (iii) a spin flop due to a change in the orientation of the Jahn-Teller distortion as a result of the temperature dependence of the elastic constants.

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