

Phase Transitions in the Canted Antiferromagnet*

C. W. FAIRALL† AND J. A. COWEN

Department of Physics, Michigan State University, East Lansing, Michigan 48823

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We have made a theoretical study of the transitions induced by a magnetic field for the two-sublattice canted antiferromagnet at 0 K. The Hamiltonian for the system includes isotropic exchange, uniaxial single-ion anisotropy, and Dzyaloshinsky-Moriya $\mathbf{D} \cdot \mathbf{S}_1 \times \mathbf{S}_2$ antisymmetric exchange. The problem is solved in the molecular-field approximation with \mathbf{D} perpendicular to the antiferromagnetic easy axis. The equations of equilibrium and stability are solved numerically by computer. The antiferromagnetic to spin-flop transition occurs when the net moment reaches a critical angle $\alpha_{sh}(h_D)$. The paramagnetic transition is destroyed by the Dzyaloshinsky-Moriya (DM) interaction unless the field is applied parallel to \mathbf{D} . For \mathbf{H} not parallel to \mathbf{D} , we observe a quasiparamagnetic transition which manifests itself as an inflection point in the susceptibility.

I. INTRODUCTION

Studies of the phase transitions of the uniaxial antiferromagnet have been made in the molecular-field approximation,^{1,2} in the spin-wave approximation,³ and in the Green's-function random phase approximation (RPA), and Callen decoupling approximations.⁴ More recently, the canted antiferromagnet with a Dzyaloshinsky-Moriya (DM) antisymmetric exchange interaction⁵ has been considered in the small- D approximation.⁶⁻⁸ However, three important questions remain unresolved: (1) Does the antiferromagnetic axis undergo a true spin-flop discontinuity? (2) What are the effects of a large DM interaction? (3) What happens to the paramagnetic boundaries?

II. HAMILTONIAN

The magnetic field dependence of the phase boundaries has been studied using a Heisenberg Hamiltonian, retaining all types of second-order interaction⁹:

$$H = H_{\text{ex}} + H_{aK} + H_{aL} + H_D + H_z, \quad (1)$$

where

$$H_{\text{ex}} = \frac{1}{2} \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (\text{isotropic exchange}), \quad (2a)$$

$$H_{aK} = \frac{1}{2} \sum_{ij} K_{ij} S_i^z S_j^z \quad (\text{anisotropic exchange}), \quad (2b)$$

$$H_{aL} = -\frac{1}{2} L' \sum_i [(S_i^z)^2 - \frac{1}{3} S(S+1)] \quad (\text{uniaxial anisotropy}), \quad (2c)$$

$$H_D = \frac{1}{2} \sum_{ij} D_{ij} (S_i^z S_j^x - S_i^x S_j^z) \quad (\text{DM antisymmetric exchange, } \mathbf{D} = D\hat{y}), \quad (2d)$$

$$H_z = -g\mu_B \mathbf{H} \cdot \sum_i \mathbf{S}_i \quad (\text{Zeeman interaction}). \quad (2e)$$

The total Hamiltonian is

$$H = \frac{1}{2} \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \frac{1}{2} \sum_{ij} K_{ij} S_i^z S_j^z - \frac{1}{2} L' \sum_i [(S_i^z)^2 - \frac{1}{3} S(S+1)] + \frac{1}{2} \sum_{ij} D_{ij} (S_i^z S_j^x - S_i^x S_j^z) - g\mu_B \mathbf{H} \cdot \sum_i \mathbf{S}_i. \quad (3)$$

Following the formalism of Rohrer and Thomas,² we rewrite the Hamiltonian as a free energy in molecular fields:

$$\begin{aligned} \epsilon' = E/N = S^2 [& J_1 \cos(\alpha_1 - \alpha_2) \\ & - \frac{1}{2} (L - K_2) (\cos^2 \alpha_1 + \cos^2 \alpha_2) + K_1 \cos \alpha_1 \cos \alpha_2 \\ & + D \cos \theta \sin(\alpha_1 - \alpha_2) + J_2 - \frac{1}{3} L] \\ & - g\mu_B S [H^x (\sin \alpha_1 + \sin \alpha_2) \cos \theta + H^y (\sin \alpha_1 + \sin \alpha_2) \sin \theta \\ & + H^z (\cos \alpha_1 + \cos \alpha_2)]. \quad (4) \end{aligned}$$

The angles are defined according to Fig. 1. N is the number of spins per sublattice, α_1 denotes the A sublattice, $a \in A$. α_2 denotes the B sublattice, $b \in B$,

$$J_1 = \sum_{a \in A} J_{ab} = \sum_{b \in B} J_{ab}, \quad (5a)$$

$$J_2 = \sum_{a \in A} J_{aa'} = \sum_{b \in B} J_{bb'}, \quad (5b)$$

$$K_1 = \sum_{a \in A} K_{ab} = \sum_{b \in B} K_{ab}, \quad (5c)$$

$$K_2 = \sum_{a \in A} K_{aa'} = \sum_{b \in B} K_{bb'}, \quad (5d)$$

$$D = \sum_{a \in A} D_{ab} = \sum_{b \in B} D_{ab'}, \quad D_{ab} = -D_{ba} \quad (5e)$$

$$L = L'(1 - 1/2S). \quad (5f)$$

We can define the molecular fields

$$H_E = J_1 S / g\mu_B, \quad (6a)$$

$$H_L = (L - K_2) S / g\mu_B, \quad (6b)$$

$$H_K = K_1 S / g\mu_B, \quad (6c)$$

$$H_D = DS / g\mu_B. \quad (6d)$$

We then transform the angles to a more convenient set and rewrite the energy as a dimensionless quantity.

$$\begin{aligned} \epsilon = E/N S^2 J_1 = & -\cos 2\phi - h_L (\cos 2\phi \cos^2 \alpha + \sin^2 \phi) \\ & - h_K (\cos^2 \alpha - \sin^2 \phi) - h_D \cos \theta \sin 2\phi \\ & - 2h^x \sin \phi \cos \alpha \cos \theta - 2h^y \sin \phi \cos \alpha \sin \theta \\ & + 2h^z \sin \alpha \sin \phi, \quad (7) \end{aligned}$$

where

$$h_L = H_L/H_E, \text{ etc.}, \quad (8)$$

and

$$\alpha_1 = \alpha + \phi, \quad (9a)$$

$$\alpha_2 = \pi + \alpha - \phi. \quad (9b)$$

Our problem is now reduced to solving the equilibrium and stability equations. The equilibrium equations are

$$\partial\epsilon/\partial\eta_i = 0. \quad (10)$$

The stability equations are

$$S(\eta_i, \eta_j) = (\partial^2\epsilon/\partial\eta_i^2)(\partial^2\epsilon/\partial\eta_j^2) - [\partial^2\epsilon/\partial\eta_i\partial\eta_j]^2 \geq 0, \quad (11)$$

where $\boldsymbol{\eta} = (\phi, \theta, \alpha)$.

III. ZERO-TEMPERATURE PHASES

We wish to solve for the phase boundaries of a uniaxial antiferromagnet, with the z axis being the easy axis, whose xy -plane symmetry has been broken by a DM interaction with D vector in the y direction. The zero-field equilibrium configuration has both spin sublattices lying in the xz plane, "antiferromagnetically" aligned but each canted toward the x axis an angle ϕ_0 , producing a net moment in the x direction.

(a) $\mathbf{h} = (0, 0, h)$ shall be referred to as the parallel or easy axis case. From symmetry we can see that $\theta = 0$. The first-order transition is characterized by discontinuities in the energy or magnetization and a magnetic hysteresis. There is no unique spin-flop critical field but a region in which both the antiferromagnetic and spin-flop states are stable. The upper boundary of this region is h_{sh} and the lower boundary is h_{sc} . If one increases the applied field from zero, the AF state re-

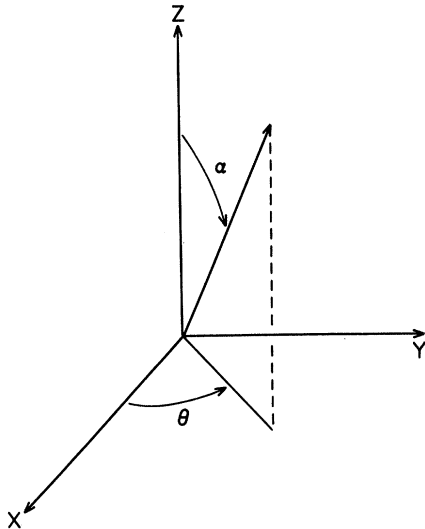


FIG. 1. Spin array with angles defined in Eq. (4).

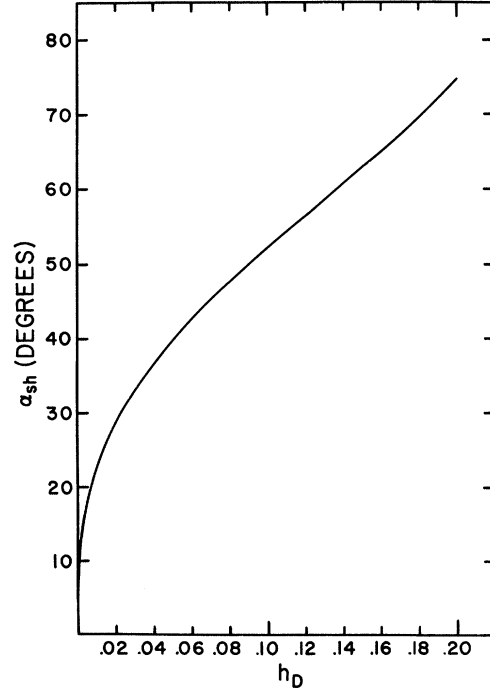


FIG. 2. Critical angle $\alpha_{sh}(h_D)$ for $h_K=0$ and $h_L=0.1$ versus h_D .

mains stable up to h_{sh} , analogous to the superheated liquid-gas transition. If one then reverses the process, reducing the field, the SF state remains stable down to h_{sc} , analogous to the supercooled gas-liquid transition. The energies of the AF and SF states are equal at the thermodynamic critical field h_{th} , implying that if $h_{th} < h < h_{sh}$, the AF state is metastable, and if $h_{sc} < h < h_{th}$, the SF state is metastable.

The equilibrium conditions are

$$\begin{aligned} \partial\epsilon/\partial\phi = (2+h_K+h_L \cos 2\alpha) \sin 2\phi \\ - 2h_D \cos 2\phi + 2h \sin \alpha \cos \phi = 0, \end{aligned} \quad (12)$$

$$\partial\epsilon/\partial\alpha = (h_K+h_L \cos 2\phi) \sin 2\alpha + 2h \sin \phi \cos \alpha = 0. \quad (13)$$

The stability function is

$$\begin{aligned} S(\alpha, \phi) = \{ (2+h_K+h_L \cos 2\alpha) \cos 2\phi \\ + 2h_D \sin 2\phi - h \sin \alpha \sin \phi \} \{ (h_K+h_L \cos 2\phi) \cos 2\alpha \\ - h \sin \alpha \sin \phi \} - \{ h_L \sin 2\alpha \sin 2\phi - h \cos \alpha \cos \phi \}^2 \geq 0. \end{aligned} \quad (14)$$

The canting of the system in zero field is given by $h=0$, and $\alpha=0$ as

$$\tan 2\phi_0 = 2h_D / (2+h_K+h_L). \quad (15)$$

When $\cos \alpha \neq 0$, ϕ and α are related by Eq. 13:

$$\sin \alpha = -h \sin \phi / (h_K+h_L \cos 2\phi). \quad (16)$$

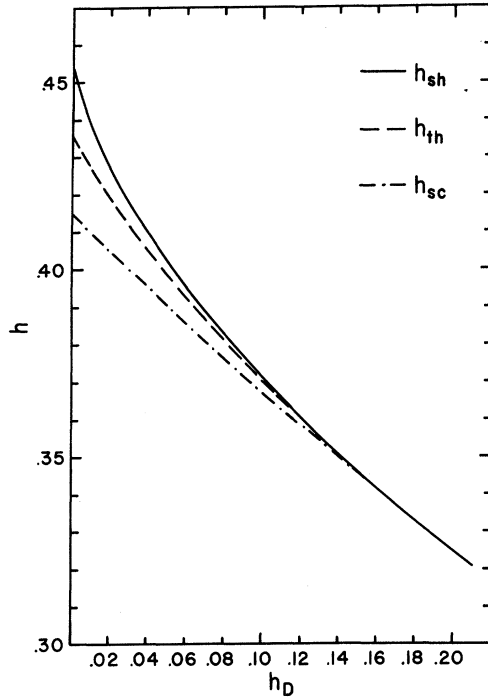


FIG. 3. Critical fields $h_{th}(h_D)$, $h_{sh}(h_D)$, and $h_{sc}(h_D)$ versus h_D for $h_K=0$ and $h_L=0.1$.

The transition from the antiferromagnetic state to the spin-flop state, called the superheated transition, is defined by the requirement that $S(\alpha, \phi)=0$. The solution with $h_D=0$ is well known and is given by

$$h_{sh}(0) = [(2+h_K+h_L)(h_K+h_L)]^{1/2}. \quad (17)$$

The $h_D=0$ case is characterized by $\alpha=0$ and $\phi=0$ for $h < h_{sh}(0)$ and $\alpha = -\frac{1}{2}\pi$ for $h > h_{sh}(0)$. When $h_D \neq 0$ there exists a net moment which is in the x direction in zero field but moves towards the z axis as the field is increased. Therefore, when $0 < h < h_{sh}(h_D)$, α and ϕ are not zero. As h approaches $h_{sh}(h_D)$, $|\alpha|$ becomes larger and approaches a critical angle $\alpha_{sh}(h_D)$. When h exceeds $h_{sh}(h_D)$, then $\alpha = -\frac{1}{2}\pi$ and a discontinuity in magnetization has taken place. The $h_D \neq 0$ equations were solved numerically by computer using Newton's method for three unknowns (Figs. 2 and 3).

The spin-flop state is defined by letting $\alpha = -\frac{1}{2}\pi$. The boundaries for this phase occur when $S(-\frac{1}{2}\pi, \phi) = 0$. When $h_D=0$, there are two phase boundaries, a spin flop to antiferromagnetic, or supercooled, boundary and a spin flop to paramagnetic boundary. The h_D solutions are

$$h_{sc}(0) = (2+h_K-h_L) [(h_K+h_L)/(2+h_K+h_L)]^{1/2}, \quad (18a)$$

$$h_p^{||}(0) = 2+h_K-h_L. \quad (18b)$$

The spin-flop state is stable, $S(-\frac{1}{2}\pi, \phi) \geq 0$, when $h_{sc}(0) < h < h_p^{||}(0)$.

The equations with $h_D \neq 0$ were solved numerically (Fig. 3). The paramagnetic transition, which corresponds to $\phi = \frac{1}{2}\pi$ or a spin saturation, does not exist because the DM interaction will lower the energy if the spins cant slightly. To see this, examine the energy when h is large and $\phi = \frac{1}{2}\pi - \delta$, $\delta \simeq h_D/h \ll 1$:

$$\epsilon \simeq 1 + h_K - h_L - 2h - h_D \delta. \quad (19)$$

No matter how large h is, $\delta \neq 0$ will give a lower energy.

Experimentally, one almost always observes the thermodynamic transition defined by $\epsilon_{AF} = \epsilon_{SF}$. One usually argues that "nucleation centers" prevent passing of the equal energy point.¹⁰ The procedure for finding h_{th} is to define

$$\Delta = \epsilon_{AF} - \epsilon_{SF},$$

and solve for $\Delta=0$. When $h_D=0$, the solution is

$$h_{th}(0) = [(2+h_K-h_L)(h_K+h_L)]^{1/2}. \quad (20)$$

The $h_D \neq 0$ equations were solved numerically (Fig. 3). As one would expect, the critical angle α_{th} is less than α_{sh} . The critical fields obey $h_{sc} < h_{th} < h_{sh}$, but

$$h_{th} = (h_{sc} h_{sh})^{1/2}$$

only when $h_D=0$.

Taking proper care to include all second-order terms, one can obtain an approximation for $h_{sc}(h_D)$ where $h_D \ll 1$:

$$h_{sc}(h_D) \simeq \frac{1}{2} \{-h_D + [h_D^2 + 4h_{sc}^2(0)]^{1/2}\}. \quad (21)$$

Figure 4 compares Eq. (21) with the numerical results for $h_K=0$ and $h_L=0.1$.

(b) We now consider the case where $\mathbf{h} = (h, 0, 0)$ is perpendicular to the easy axis and the D vector. We use Eqs. (10) and (11) with $\alpha=0$ and $\theta=0$. When $h_D=0$ the paramagnetic transition occurs at

$$h_p^\perp(0) = 2+h_K+h_L. \quad (22)$$

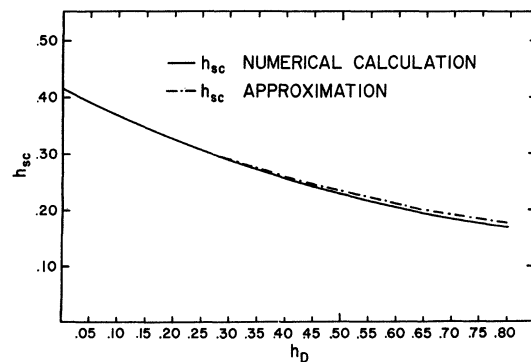


FIG. 4. Comparison of numerical value of $h_{sc}(h_D)$ and Eq. (21) for $h_K=0$ and $h_L=0.1$.

As in the previous case, $h_D \neq 0$ destroys the second-order paramagnetic transition.

(c) When $\mathbf{h} = (0, h, 0)$ we are able to obtain an exact solution. For $h_D = 0$ the problem is equivalent to (b). For $h_D \neq 0$,

$$\partial \epsilon / \partial \phi = (2 + h_K + h_L) \sin 2\phi - 2h_D \cos 2\phi \cos \theta - 2h \cos \phi \sin \theta = 0, \quad (23)$$

$$\partial \epsilon / \partial \theta = -2h \sin \phi \cos \theta + 2h_D \sin \theta \sin \phi \cos \phi = 0, \quad (24)$$

$$S(\theta, \phi) = [(2 + h_K + h_L) \cos 2\phi + 2h_D \sin 2\phi \cos \theta + h \sin \phi \sin \theta] (h \sin \phi \sin \theta + h_D \cos \theta \sin \phi \cos \phi) - (h_D \sin \theta \cos 2\phi - h \cos \phi \cos \theta)^2 \geq 0. \quad (25)$$

From Eq. 24,

$$\cos \theta = (h_D / h) \cos \phi \sin \theta.$$

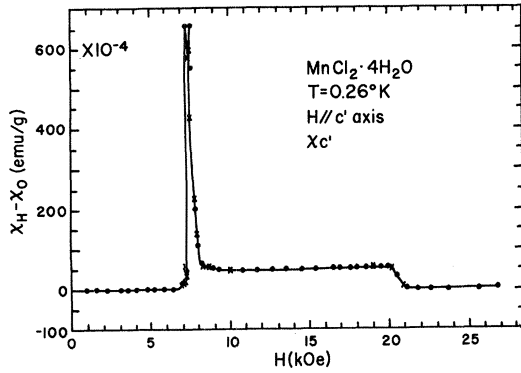


FIG. 5. χ^{\parallel} versus H for $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. $T = 0.26$ K, $H_{\text{th}} = 7.5$ kG, and $H_p^{\parallel} = 20.0$ kG (Ref. 11).

The solution to Eq. 23 and $S(\theta, \phi) = 0$ is $\theta = \phi = \frac{1}{2}\pi$ at a critical field:

$$h_p^{\pm} = \frac{1}{2} \{ h_p^{\pm}(0) + [(h_p^{\pm}(0))^2 + 4h_D^2]^{1/2} \}. \quad (26)$$

IV. SUSCEPTIBILITY

One method of experimentally determining the critical fields is to measure the susceptibility χ as a function of H . Rives's¹¹ data for χ versus H for $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ($h_K \simeq 0$, $h_D \simeq 0$, $h_L \simeq 0.2$) show anomalies at the spin-flop and paramagnetic boundaries (Fig. 5). For our system we can define a magnetization

$$\begin{aligned} M^x &= \sin \phi \cos \alpha \cos \theta, \\ M^y &= \sin \phi \cos \alpha \sin \theta, \\ M^z &= -\sin \phi \sin \alpha. \end{aligned} \quad (27)$$

The susceptibility is

$$\chi^i = dM^i / dh^i.$$

We have calculated χ^x and χ^z numerically as functions

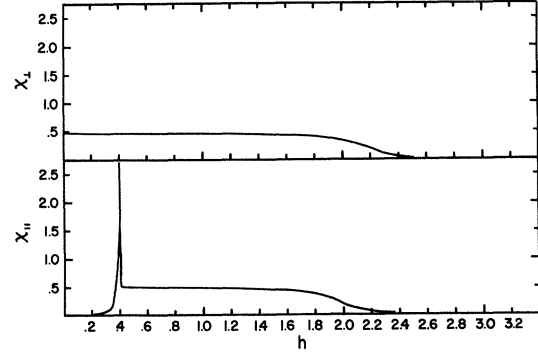


FIG. 6. Numerical calculations of χ versus h for $h_K = 0$, $h_L = 0.1$, and $h_D = 0.05$.

of h (Fig. 6). The zero-field susceptibility is given by

$$\chi_0^x = (\cos^2 \phi_0) / (h_p^{\pm}(0) \cos 2\phi_0 + 2h_D \sin 2\phi_0), \quad (28a)$$

$$\chi_0^y = 2 / (h_p^{\pm}(h_D) + h_p^{\pm}(0)), \quad (28b)$$

$$\chi_0^z = \sin^2 \phi_0 / (h_K + h_L \cos 2\phi_0). \quad (28c)$$

The inflection point in the susceptibility corresponding to a quasiparamagnetic transition was examined by numerically calculating $d\chi/dh$ (Fig. 7) as a function of h . The x and z susceptibilities can be expressed as

$$\chi = [h_p(0) + h_D \sin \phi (4 - \cos 2\phi / \cos^3 \phi)]^{-1}, \quad (29)$$

where we are assuming $h > h_{\text{sh}}(h_D)$:

$$\begin{aligned} h_p(0) &= h_p^{\pm}(0) = 2 + h_K + h_L, & \text{for } \chi^x \\ &= h_p^{\parallel}(0) = 2 + h_K - h_L & \text{for } \chi^z. \end{aligned}$$

The quasiparamagnetic boundary is given by

$$d^2 \chi^i / dh^2 = 0.$$

For $h_D \ll 1$ the approximate solution is

$$\cos^3 \phi_{qp} \simeq (4/5) [h_D / h_p(0)], \quad (30)$$

$$h_{qp} \simeq h_p(0) + 3(h_p(0) h_D^2 / 100)^{1/3}. \quad (31)$$

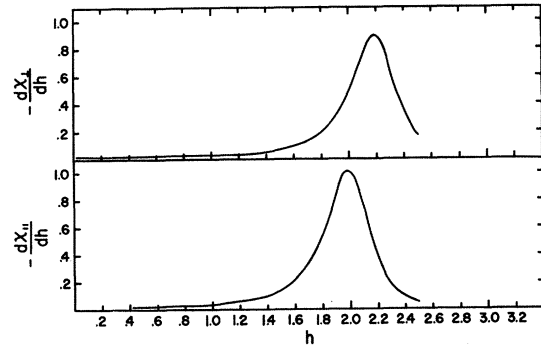


FIG. 7. Numerical calculation of $d\chi/dh$ versus h for $h_K = 0$, $h_L = 0.1$, and $h_D = 0.05$.

For the case illustrated in Fig. 7, the numerically computed inflection points occur at

$$h_{qp}^z = 1.990, \quad \phi_{qp}^z = 74.44^\circ,$$

$$h_{qp}^x = 2.195, \quad \phi_{qp}^x = 74.97^\circ,$$

where $h_K=0$, $h_L=0.1$, $h_D=0.05$. Equations (30) and (31) give

$$h_{qp}^z = 2.009, \quad \phi_{qp}^z = 74.0^\circ,$$

$$h_{qp}^x = 2.212, \quad \phi_{qp}^x = 74.5^\circ.$$

V. CONCLUSION

The addition of a DM interaction to the uniaxial antiferromagnet with anisotropic exchange yields a Heisenberg isotropic exchange Hamiltonian with general second-order anisotropy. The hysteresis of the first-order spin-flop transition is reduced as \mathbf{D} is increased and the paramagnetic transition only occurs when the field is applied parallel to \mathbf{D} . Experimentally, a quasi-paramagnetic transition would be observed as an inflection point in the susceptibility for fields not parallel to \mathbf{D} .

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† NDEA Title IV Fellow.

¹ T. Nagamiya, K. Yosida, and R. Kubo, *Advan. Phys.* **4**, 1 (1955).

² H. Rohrer and H. Thomas, *J. Appl. Phys.* **40**, 1025 (1969).

³ J. Feder and E. Pytte, *Phys. Rev.* **168**, 640 (1968).

⁴ F. B. Anderson and H. B. Callen, *Phys. Rev.* **136**, A1068 (1964).

⁵ T. Moriya, *Phys. Rev.* **120**, 91 (1960).

⁶ G. Cinader, *Phys. Rev.* **155**, 453 (1966).

⁷ M. S. Seehra and T. G. Castner, *Phys. Rev. B* **1**, 2289 (1970).

⁸ K. P. Belov, A. M. Kadomtseva, and R. Z. Bevitin, *Zh. Exprim. i Teor. Fiz.* **51**, 1306 (1966) [*Soviet Phys. JETP* **24**, 878 (1967)].

⁹ E. F. Bertaut, in *Magnetism*, edited by G. T. Rado and H. Shul (Academic, New York, 1963) Vol. III.

¹⁰ K. W. Blazey *et al.*, *Phys. Rev. Letters* **24**, 105 (1970).

¹¹ J. E. Rives, *Phys. Rev.* **162**, 491 (1967).

Effects of Hydrostatic Pressure and of Jahn-Teller Distortions on the Magnetic Properties of RbFeF_3 †

J. B. GOODENOUGH, N. MENYUK, K. DWIGHT, AND J. A. KAFALAS

Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173

(Received 19 June 1970)

The first-order transitions at $T_1=40^\circ\text{K}$ and $T_2=87^\circ\text{K}$ in RbFeF_3 have been measured as a function of hydrostatic pressure and applied magnetic field. It was not possible to observe the $T_N=102^\circ\text{K}$ transition with a magnetic-susceptibility measurement. It was found that $(\Delta T_1/\Delta H_a)_p=0.35^\circ/\text{kOe}$, $(\Delta T_2/\Delta H_a)_p=0.19^\circ/\text{kOe}$, $(\Delta T_1/\Delta P)_H=0.18^\circ/\text{kbar}$ and $(\Delta T_2/\Delta P)_H=-0.81^\circ/\text{kbar}$. These results correspond to latent heats of 0.006 and 0.04 cal/g at T_1 and T_2 , respectively, and relative volume changes $\Delta V_1/V_1=1.5\times 10^{-6}$, $\Delta V_2/V_2=-22\times 10^{-6}$. It is pointed out that a Jahn-Teller distortion to tetragonal ($c/a>1$) symmetry in the interval $T_2<T<T_N$ introduces a strong magnetoelastic coupling. This causes the heavy twinning that has been observed below T_N , and the resulting twinned structure is retained in the entire temperature interval $0<T<T_N$. In the temperature interval $T_1<T<T_2$, $\text{Rb}^+\text{-F}^-$ interactions induce distortions to orthorhombic or tetragonal symmetries that are superimposed on the Jahn-Teller distortion. The orthorhombic distortion is cooperative across twin boundaries caused by the Jahn-Teller distortion and also permits spin canting, which introduces a ferromagnetic component below T_2 . It is shown how the interplay of these distortions plus strong magnetoelastic coupling can explain the appearance of two sets of Mössbauer peaks below T_2 and results in macroscopic ferromagnetic components having cubic symmetry even though the microscopic crystallographic symmetry is "orthorhombic" ($T_1<T<T_2$). The Jahn-Teller distortion changes to rhombohedral ($\alpha<60^\circ$) for $T<T_1$; in combination with the existing orthorhombic structure, this produces monoclinic symmetry on a microscopic scale. Nevertheless, it is shown that the macroscopic magnetization retains its cubic symmetry, that the easy magnetization direction changes from $\langle 100 \rangle$ to the $\langle 110 \rangle$, that the apparent moment increases, and that there may still be two sets of Mössbauer peaks.

I. INTRODUCTION

Above its Néel temperature $T_N=102^\circ\text{K}$,¹ RbFeF_3 has the cubic perovskite structure, but it becomes tetragonal ($c/a>1$) in the interval $T_2<T<T_N$.² It undergoes first-order transitions at $T_1=40^\circ\text{K}$ and $T_2=87^\circ\text{K}$; it exhibits weak ferromagnetism at all $T<87^\circ\text{K}$.³ In the interval $T_1<T<T_2$, the structure appears to be

orthorhombic, and below T_1 it has lower symmetry, probably monoclinic.² The ferromagnetic moment has a preferred direction along the pseudocubic $\langle 100 \rangle$ axes in the interval $T_1<T<T_2$, along the pseudocubic $\langle 110 \rangle$ axes below T_1 .⁴ It is remarkable that these noncubic crystals exhibit a cubic macroscopic anisotropy of the weak ferromagnetism. A neutron-diffraction study on a polycrystalline sample shows the dominant magnetic