

EFFECTS OF HYDROSTATIC PRESSURE AND OF JAHN-TELLER DISTORTIONS ON THE MAGNETIC PROPERTIES OF RbFeF₃(*)

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Résumé. — Nous avons déterminé dans RbFeF₃ les rapports $(\Delta T_i/\Delta H_a)_p = 0,35$ et $0,19^\circ/\text{kOe}$ ($\Delta T_i/\Delta P)_H = 0,18$ et $-0,81^\circ/\text{kbar}$ pour les transitions de premier ordre à $T_1 = 40^\circ\text{K}$ et $T_2 = 87^\circ\text{K}$. Les chaleurs latentes correspondantes sont $0,006$ et $0,04$ cal/g ; les variations des volumes relatifs sont $\Delta V_i/V_i = 1,5 \times 10^{-6}$ et -22×10^{-6} . Nous expliquons l'inhomogénéité de la température de Néel, les structures cristallographiques, le ferromagnétisme faible au-dessous de T_2 , ainsi que l'anisotropie magnétique cubique mesurée pour des champs supérieurs à $0,5$ kOe.

Abstract. — RbFeF₃ exhibits first-order transitions at $T_1 = 40^\circ\text{K}$ and $T_2 = 87^\circ\text{K}$. We report $(\Delta T_i/\Delta H_a)_p = 0.35$ and $0.19^\circ/\text{kOe}$, $(\Delta T_i/\Delta P)_H = 0.18$ and $-0.81^\circ/\text{kbar}$ for T_1 and T_2 , respectively, corresponding to latent heats 0.006 and 0.04 cal/g and relative volume changes $\Delta V_i/V_i = 1.5 \times 10^{-6}$ and -22×10^{-6} . The inhomogeneity of the Néel temperature, the crystallographic structures, the weak ferromagnetism below T_2 , and the cubic magnetic anisotropy in an $H_a > 0.5$ kOe are interpreted.

I. Experimental. — RbFeF₃ has the cubic perovskite structure above its Néel temperature $T_N = 102^\circ\text{K}$ [1], but becomes tetragonal ($c/a > 1$) in the interval $T_2 < T < T_N$ [2]. For all $T < T_2 = 87^\circ\text{K}$, it exhibits weak ferromagnetism, the magnitude of σ_0 increasing abruptly below first-order transitions at $T_1 = 40^\circ\text{K}$ and $T_2 = 87^\circ\text{K}$ [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]. Nevertheless the magnetic anisotropy for σ_0 appears cubic (easy axes are pseudocubic $<100>$ axes if $T_1 < T < T_2$, $<110>$ axes if $T < T_1$) in applied fields $H_a = 5$ kOe [4]. Although the dominant magnetic structure is a simple Type G antiferromagnet for all $T < T_N$ [5], Mössbauer measurements below T_2 distinguish two types of iron sites [1]. Different values for $\Delta T_2/\Delta H_a$ have been reported : $0.56^\circ/\text{kOe}$ [1] and $0.125^\circ/\text{kOe}$ [2], as well as a $\Delta T_1/\Delta H_a = 0.35^\circ/\text{kOe}$ [1].

We have measured the magnetic properties of RbFeF₃ in the vicinity of the first-order transformations as functions of both applied field and hydrostatic pressure. The powder sample used was obtained by grinding a single crystal grown by J.-R. O'Connor. The measurements were performed on a vibrating-coil magnetometer used in conjunction with a helium-gas pressure-generating unit. This system permits the direct measurement of magnetic moment while freely varying applied field, temperature and pressure [6].

Magnetization vs temperature curves were in good accord with previous measurements. In the temperature range $90 < T < 120^\circ\text{K}$ and in fields

$$1 < H_a \leq 10 \text{ kOe}$$

at both atmospheric pressure and at 5 kbars, the magnetization vs temperature curves show no kink in the vicinity of T_N , which supports the conclusion of Wertheim et al. [1] that T_N varies spatially as a result of lattice strains produced by crystallographic distortions accompanying short-range magnetic order.

Hydrostatic pressure, though shifting T_1 and T_2 ,

does not significantly change the magnitudes of the weak ferromagnetic components as a function of $(T_1 - T)$ or $(T_2 - T)$, where $T_1 \approx 41^\circ\text{K}$ in our sample. T_1 and T_2 varied linearly with applied field and pressure in the ranges $1 < H_a \leq 12$ kOe and $1 < P < 6$ kbars. The resultant slopes are listed in Table I. The measured sharp increases in ferromagnetic moment $\Delta\sigma_1$ and $\Delta\sigma_2$ on cooling through T_1 and T_2 were 2.0 and 3.5 e. m. u./g. (Testardi et al [2] found 5 e. m. u./g at T_2). Substitution of these values into the Clausius-Clapeyron equations permits determination of the latent heats L_i and volume changes V_i listed in Table I. The 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.

TABLE I
Parameters of the two first-order transitions
in RbFeF₃

T_i (°K)	$(\partial T_i/\partial H)_p$ (deg/kOe)	$(\partial T_i/\partial p)_H$ (deg/kbar)	L_i (cal/g)	$(\Delta V_i/V_i)$ ($\times 10^6$)
41	0.35	0.18	.006	1.5
87	0.19	-0.81	.04	-22

II. Interpretation. — In a cubic crystalline field, octahedral-site Fe^{2+} ions have a threefold-degenerate $^5T_{2g,1}(t_{2g}^4 e_g^2)$ ground state even after spin-orbit coupling has been included. At those temperatures $T < T_N$ where the spins are aligned collinearly, magnetic order insures a cooperative elastic distortion to either trigonal ($\alpha < 60^\circ$) or tetragonal ($c/a > 1$) local symmetry [7]. These distortions do not quench the spin-orbit coupling, but introduce a very large magnetic anisotropy stabilizing the Fe^{2+} -ion spin axis parallel to the unique local axis ($g_{\parallel} > g_{\perp}$). Whether the local distortions are to trigonal or tetragonal symmetry depends on second-order considerations. Therefore, although KFeF_3 is rhombohedral ($\alpha < 60^\circ$) below T_N , it is reasonable to assume that in RbFeF₃ the Jahn-Teller distortion is to tetragonal ($c/a > 1$) symmetry in the interval $T_1 < T < T_N$ and to trigonal ($\alpha < 60^\circ$) symmetry below T_1 .

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