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EFFECTS OF HYDROSTATIC PRESSURE AND OF JAHN-TELLER DISTORTIONS ON THE MAGNETIC PROPERTIES OF $RbFeF_3$(*)

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Résumé. — Nous avons déterminé dans $RbFeF_3$ les rapports $(\Delta T_i/\Delta H_a)_p$ = 0,35 et 0,19°/kOe $(\Delta T_i/\Delta P)_H$ = 0,18 et — 0,81°/kbar pour les transitions de premier ordre à T_1 = 40 °K et T_2 = 87 °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 crystallographiques, le ferromagnétisme faible au-dessous de T_2, ainsi que l'anisotropie magnétique cubique mesurée pour des champs supérieurs à 0,5 kOe.

Abstract. — $RbFeF_3$ exhibits first-order transitions at T_1 = 40 °K and T_2 = 87 °K. We report $(\Delta T_i/\Delta H_a)_p$ = 0.35 and 0.19 °/kOe, $(\Delta T_i/\Delta P)_H$ = 0.18 and — 0.81°/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.** — $RbFeF_3$ has the cubic perovskite structure above its Néel temperature T_N = 102 °K [1], but becomes tetragonal ($c/a > 1$) in the interval $T_2 < T < T_N$ [2]. For all $T < T_2$ = 87 °K, it exhibits weak ferromagnetism, the magnitude of σ_0 increasing abruptly below first-order transitions at T_1 = 40 °K and T_2 = 87 °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°/kOe [1] and 0.125°/kOe [2], as well as a $\Delta T_1/\Delta H_a$ = 0.35°/kOe [1].

We have measured the magnetic properties of $RbFeF_3$ 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 $90 < T < 120$ °K and in fields

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

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 $T_1 \approx 41$ °K in our sample. T_1 and T_2 varied linearly with applied field and pressure in the ranges $1 < H_a \leqslant 12$ 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 $RbFeF_3$

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 $^5T_{2g,1}(t_{2g}{}^4e_g^2)$ 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 ($\alpha < 60°$) 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 ($\alpha < 60°$) below T_N, it is reasonable to assume that in $RbFeF_3$ the Jahn-Teller distortion is to tetragonal ($c/a > 1$) symmetry in the interval $T_1 < T < T_N$ and to trigonal ($\alpha < 60°$) symmetry below T_1.

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