Shift of the first-order transition in RbCaF₃ under hydrostatic pressure

K. A. Müller*

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

W. Berlinger

IBM Zurich Research Laboratory, 8803 Ruschlikon, Switzerland

J. Y. Buzaré and J. C. Fayet

Laboratoire de Spectroscopie du Solide, European Research Associates No. 682, 72017 Le Mans-Cedex, France (Received 24 August 1979)

We have investigated the O_h^1 to D_{4h}^{18} structural phase transition in RbCaF₃ under hydrostatic pressure by monitoring the electron-paramagnetic resonance lines of Gd³⁺ ($S = \frac{7}{2}$) on Ca²⁺ sites. We find the first-order transition temperature shifts linearly by (3.6 ± 0.1) deg/kbar but neither the amount of the first-order discontinuity nor its character is altered up to the highest pressure $p_h = 1.2$ kbar we attained. The present experiment, which does not break the symmetry, confirms a uniaxial-stress experiment of Buzaré *et al.*, who reached a tricritical point at $\sigma_t = 0.19$ kbar, and attributed it to the symmetry-breaking stress effect on the highly anisotropic cubic fluctuations which induce the first-order transition.

RbCaF₃ undergoes the same type of structural phase transition (SPT) as SrTiO₃ from the cubic O_h^1 to the tetragonal D_{4h}^{18} space group.¹ Thereby octahedral units rotate in an antiferrodistortive manner for $T < T_c$ by angles $\phi_{\alpha}(\vec{x}, T)$ around principal cubic axes $\alpha = [100]$, [010], and [001] in the three possible tetragonal domains. This may be abbreviated by the shorthand notation, $\alpha = 1, 2, 3$, which constitutes the three components *n* of the order parameter $\vec{\phi}(\vec{x}, T)$.² The cubic Landau-Ginsburg-Wilson Hamiltonian which governs the transitions in RbCaF₃ and SrTiO₃ has, in d = 3 lattice dimensions, the form

$$\frac{H}{T} = \int d^{3}x \left[\frac{1}{2} r_{0} |\phi|^{2} + u |\phi|^{4} + v \sum_{\alpha=1}^{3} \phi_{\alpha}^{4} + \frac{1}{2} (\nabla \phi)^{2} - \frac{1}{2} f \sum_{\alpha=1}^{3} \left[\frac{\partial \phi_{\alpha}}{\partial x_{\alpha}} \right]^{2} \right] .$$
 (1)

The parameters v and f in H account for the cubic symmetry, the remaining terms being those of the n = d = 3 Heisenberg system. For v < 0 and f arbitrary, a tetragonal phase results below T_c . If u > 0and |v| and |f| are both not too large, a stable fixed point is found upon renormalization (of Heisenberg or cubic character, depending upon whether $n_c >$ or < 3).² The system thus shows a second-order transition as SrTiO₃ does, being a prototype of short-range order SPT and showing critical phenomena.³

In mean-field theory a second-order transition occurs for u + v > 0 (with v < 0).⁴ Including fluctuations but assuming negligible f, the boundary is pushed up to u + bv = 0 with $b < 1.^5$ It was first shown by Bruce,⁶ and by Nattermann and Trimper⁷ that increasing f towards its maximum value of 1 results in a more negative parameter v upon renormalization. One may express this by b(f) < b(0) = b. A detailed calculation was carried out by Nattermann,⁸ who obtained the amount of first-order character as a function of parameters u, v, and f.

The Fourier transformation of the "gradient terms" in Eq. (1) yields the dispersion of the soft-mode branch of rotations α at the *R* corner of the Brillouin zone (BZ):

$$\int dq^{3} \sum_{\alpha} \left(q^{2} - fq_{\alpha}^{2}\right) \phi_{q}^{\alpha} \phi_{-q}^{\alpha}$$
$$= \int dq^{3} \sum_{\alpha} \left(q_{\perp,\alpha}^{2} + aq_{\alpha}^{2}\right) \phi_{q}^{\alpha} \phi_{-q}^{\alpha} , \quad (2)$$

where we have $q_{\perp,\alpha}^2 = q^2 - q_{\alpha}^2$ and a = 1 - f. a = 0would indicate to second order complete flatness of the soft mode between the *R* and *M* points of the BZ, i.e., uncorrelated rotations of the octahedrons between (001) planes. Assuming that the dispersion is quadratic, very low values of *a* in RbCaF₃ and KMnF₃ have been extracted from the inelastic neutron data of $a = 0.013 \pm 0.07$ in both crystals as compared to a minimum of $a = 0.036 \pm 0.012$ in SrTiO₃.¹ The amount of first-order discontinuity in KMnF₃ agrees with the calculations of Nattermann for the known parameter a.⁸ Thus, the physical point in RbCaF₃ and KMnF₃ is below the u + b(f)v = 0boundary, whereas it is above in SrTiO₃.

Upon application of a symmetry-breaking field F, a

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cubic system whose physical point is below the u + bv boundary can be restored to a continuous transition. This was shown theoretically for not too large f's by Domany, Mukamel, and Fisher.⁹ For positive or negative F an n = 1 or n = 2 tricritical point is reached, respectively, at F = 0 there is a normal triple point. More recently, Aharony and Bruce¹⁰ investigated the properties of the Hamiltonian (1) in the presence of a uniaxial stress (symmetry-breaking field) for $f \approx 1$. They found that for $\nu < 0$ (tetragonal case) one can only reach a tricritical point if the symmetry-breaking stress induces a one-dimensional order parameter (n = 1). This was realized in RbCaF₃ by Buzaré *et al.*¹¹ under near-[001] stress σ in order to induce one $\{010\}$ domain below T_c . The tricritical point was reached at $\sigma_t = 0.19 \pm 0.03$ kbar and $T_t = 195.3 \pm 0.1$ K. Under uniaxial stress σ , elementary elasticity theory tells that a hydrostatic component of $p_h \approx \frac{1}{3}\sigma$ is also present. This component can change the parameters u and v to the extent that the physical point $u(p_h)$ and $v(p_h)$ shifts above the u + bv = 0 boundary. Then the cause of reaching the tricritical point at σ_t would not be the symmetrybreaking effect of σ but its hydrostatic component. To prove that this is not the case, the present hydrostatic pressure measurements were undertaken.

The order parameter was again probed by electron paramagnetic resonance (EPR) of the Gd^{3+} ions substitutional on octahedral Ca sites. The RbCaF₃:Gd³⁺ used in this experiment was from the same batch as that employed in the uniaxial-stress experiment.¹¹ It was ground to a (001) base of 1.3×1.5 mm² and a height of 2.7 mm. To guarantee a reproducible position of the sample in the presence of hydrostatic pressure its base was glued with some epoxy onto a hollow sample holder.

The EPR experiment was carried out at K-band frequency with a superheterodyne spectrometer and a high-pressure cavity similar to the one used by Wolbarst¹² operating in the circular TE_{01} mode. Pure sapphire was preferred over Lucalox as dielectric cavity material, the Lucalox showing base-line excursions due to spurious absorptions. A 1:1 mixture of pentane and isopentane¹³ served as pressure-transmitting fluid, and a 1% precision Bourdon gauge manometer monitored its pressure. The temperature was measured with a 2:1 at. % Au-Co/Cu thermocouple imbedded in the cavity wall near the sample. A proportional controller stabilized the temperature to 0.05 K. The magnetic field *H* was maintained along a [100] crystal direction, and the Gd³⁺ EPR $+\frac{7}{2} \leftrightarrow +\frac{3}{2}$ and $-\frac{5}{2} \leftrightarrow -\frac{3}{2}$ transitions d_1 and d_2 for a [010] domain were monitored, respectively. As previously¹¹ the quantity

$$\delta = \frac{1}{7} (|d_1| + 2|d_2|) \tag{3}$$

was calculated from the data. δ does not contain any

fourth-order crystal-field contributions b_n^4 . The latter are the only ones which change under hydrostatic pressure and temperature to a measurable extent above the phase transition. Thus δ was constant above T_c . The shift of δ below the transition $\Delta\delta(T) = \delta(T - T_c^{-}) - \delta(T_c^{-})$ is for symmetry reasons, under the geometry chosen, proportional to the square of the order parameter ϕ below the discontinuity, $\Delta\delta(T) = \rho [\phi(T)^2 - \phi(T_c^{-})^2]$.¹⁴ The proportionality constant was determined earlier¹¹ from a comparative study of $\phi(T)$ with the Gd³⁺-O⁻² center to be $\rho = (1.05 \pm 0.0)10^{-4} \text{ cm}^{-1} \text{deg}^{-2}$. In the present case, the crystal is strictly cubic above the transition and spontaneously distorted below T_c . Thus the above quadratic relation between $\Delta\delta(T)$ and ϕ^2 is rigorous. Furthermore, we found no EPR linewidth broadening due to fluctuations $\delta \phi(t)$. They can thus be neglected in the time-dependent form $\langle \phi(t)^2 \rangle = \langle [\langle \phi \rangle + \delta \phi(t)]^2 \rangle = (\langle \phi \rangle)^2 = \phi^2.$

The spectra were measured at hydrostatic pressures p_h of up to 1.2 kbar and varying the temperature T by approximately up to 0.5 K above and below the transition T_c . Our results are displayed in Fig. 1, where the quantity $\Delta\delta(T) \simeq b_2^0(T)$ is plotted versus T. Empirical "best fit" curves with $b_2^0/g\beta$ (gauss) = 5.31 $[T_c(p_h) + 0.42]^{0.33}$ are also shown. They fit the data points for each $T_c(p_h)$ fairly well. From Fig. 1 one sees that, up to the highest pressure applied, the transition remains first order. Neither the character of the transition as measured by $\Delta\delta(T)$ nor the jump in $\Delta\delta(T = T_c)$ changes up to the maximum hydrostatic pressure used. As the latter was six times the uniaxial stress $\sigma([100])$ needed to reach tricriticality, the present experiment is substantial proof in favor of the symmetry-breaking stress $\sigma([100])$ as being the cause to restore the continuous phase transition in the earlier experiment.

The shift in the first-order transition under hydrostatic pressure is shown in Fig. 2. It is linear with a slope of $\partial T/\partial p_h = 3.6$ deg/kbar. This is to be compared with the shift of $\partial T/\partial \sigma_{[100]} = 12$ deg/kbar



FIG. 1. Progression of axial EPR parameters $b_2^0/g\beta$ of Gd³⁺ in RbCaF₃ as a function of temperature in the presence of five different hydrostatic pressures of p_h : 0, 0.4, 0.6, 0.8, and 1.2 kbar.



FIG. 2. Shift of first-order transition temperature T_c as a function of hydrostatic pressure p_h .

in the first-order transition under uniaxial stress. Assuming the shift in T_c is caused in the latter experiment by the hydrostatic component of $\sigma_{[100]}$, i.e., $p_h \approx \frac{1}{3} \sigma_{[100]}$, one gets a shift of 36 deg/kbar. This is one order of magnitude larger than the value measured hydrostatically in the present experiment. This in effect rules out the possibility that the hydrostatic

*Permanent address: IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland.

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component in the uniaxial stress experiment changes the parameters u and v in the Hamiltonian (1) sufficiently to yield a tricritical point.

For an anisotropy parameter a = 1 - f = 0 one would expect tricritical Lifshitz behavior¹⁵ in the uniaxial-stress experiment,¹⁰ otherwise, normal Ising n = 1 tricritical behavior. The latter yields $\beta = \frac{1}{4}$ as generally observed¹⁶ except for ND₄Cl under hydrostatic pressure where $\beta = 0.14$ to 0.19 has been reported.¹⁷ The higher value is compatible with logarithmic corrections of the form $(t \ln |t|)^{1/4}$ in the range of measurements. Close enough to t = 0 such corrections should be present due to the marginal dimensionality $d^* = 3$ of the tricritical Ising system. However, such a behavior has so far only been reported for the ammonium-halide system. Furthermore, for ND₄Cl, NH₄Cl, and NH₄Br the recently reviewed dynamical critical exponents all differ from the theoretical one of zv = 1. Thus it has been argued that the ammonium halides show higher-order critical points.¹⁸ As the exponent $\beta = 0.18 \pm 0.2$ at the tricritical point in RbCaF₃ under uniaxial stress also differs considerably from 0.25, it appears less likely to be of normal tricritical Ising character. The theoretical alternative¹⁰ is the tricritical Lifshitz behavior which, to order $\epsilon_t = \frac{7}{2} - d$, yields $\beta = \frac{1}{8}$ to $\frac{1}{6}$.¹⁵ For higher stresses this should finally cross over to normal Lifshitz n = 1 behavior. To order $\epsilon = \frac{9}{2} - d$ the pre-diction is $\beta = \frac{1}{4}$ to $\frac{1}{3}$.¹⁹ However, most recent Monte Carlo simulations²⁰ have yielded $\beta = 0.21 \pm 0.03$ for the latter. This is well within the range of the observed $\beta = 0.18 \pm 0.2$ at and above the tricritical point. It could thus be that tricritical and normal Lifshitz behaviors are close enough to one another that no crossover is observable within the precision of the currently available data.

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