Evidence for a critical end point in [111]-stressed RbCaF₃

J.Y. Buzaré, W. Berlinger, K.A. Müller

► To cite this version:

J.Y. Buzaré, W. Berlinger, K.A. Müller. Evidence for a critical end point in [111]-stressed RbCaF₃. Journal de Physique Lettres, 1985, 46 (5), pp.201-205. 10.1051/jphyslet:01985004605020100 . jpa-00232500

HAL Id: jpa-00232500

<https://hal.science/jpa-00232500>

Submitted on 1 Jan 1985

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification

Physics Abstracts

64.60K — 64.70K — 76.30K

Evidence for a critical end point in [111]-stressed RbCaF₃

J. Y. Buzaré (*), W. Berlinger and K. A. Müller

IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

(Reçu le 23 novembre 1984, accepté le 14 janvier 1985)

Résumé. — Dans RbCaF₃, pour une contrainte $\sigma > \sigma_E$ appliquée suivant [111], une ligne de transitions de type Ising sépare une phase pseudo-cubique d'une phase trigonale. Elle rencontre sous un angle fini une ligne de transitions de premier ordre qui borde une phase pseudo-tétraгонаle. On localise ainsi un point critique terminal à $\sigma_E = 0,10 \pm 0,01$ kbar et $T_E = 196,3 \pm 0,1$ K. Le saut du paramètre d'ordre est monotone le long de la ligne de premier ordre. Pour établir le diagramme de phase on a utilisé la Résonance Paramagnétique électronique du centre $Gd^{3+}-O^{2-}$.

Abstract. — In RbCaF₃, a [111] stress $\sigma > \sigma_E$ induces an Ising line separating the pseudo-cubic from the trigonal phase which impinges at finite angle on a first-order boundary to the tetragonal phase. Thus, a critical end point (CEP) occurs sited at $\sigma_E = 0.10 \pm 0.01$ kbar and $T_E = 196.3 \pm 0.1$ K. The discontinuity jump of the order parameter along this boundary is monotonous across the CEP. The Paramagnetic Resonance of the $Gd^{3+}-O^{2-}$ centre was used as a symmetry probe to establish the phase diagram.

Multicritical points of various topologies have recently attracted considerable attention [1], the critical end points (CEP) especially attracting theoretical interest [2]. Blankschtein and Mukamel [3] have investigated theoretically structural phase transitions which are first-order cubic-to-tetragonal at zero stress. They found the phase diagram exhibited a CEP under [111] compressional stresses : a $q = 3$ state Potts transition line which should be of first-order character, and an Ising line impinging on it at a finite stress. They predicted this phase diagram to be realizable in BaTiO₃, KMnF₃ and RbCaF₃. The idea was tested in KMnF₃ by specific-heat measurements [4]. Preliminary results were interpreted in this way, locating a CEP at $\sigma_E \simeq 0.2$ kbar and $T_E \simeq 187.35$ K, but the nature of the high-temperature transition has not been firmly established. In addition, the symmetry of the phases remained unknown. Furthermore, despite the transition at zero stress being continuous, EPR [5] and neutron-scattering [6] experiments indicated this kind of behaviour in [111]-stressed SrTiO₃. But the CEP is not sufficiently resolved in as much as the angle under which the Ising line joins the Potts line is concerned.

In this Letter, we present conclusive EPR investigations of the phase diagram for [111]-stressed RbCaF₃ confirming the theory. The EPR technique is known to provide accurate measurements of components of the order parameter, and clear determination of the phase symmetries.

(*) Permanent address : Laboratoire de Spectroscopie du Solide (E.R.A. CNRS, n° 682), 72017 Le Mans Cedex, France.

RbCaF_3 is a compound with perovskite structure undergoing a slightly first-order phase transition [7] from the cubic O_h^1 to the tetragonal D_{4h}^{18} space group. The order parameter of the transition is the rotational angle of the CaF_6 octahedra ϕ which has three components $\phi_{[100]}$, $\phi_{[010]}$ and $\phi_{[001]}$. This transition should be continuous according to mean-field theory and may be explained to be driven first-order by critical fluctuations : the strongly anisotropic soft-mode behaviour is connected with nearly two-dimensional correlated (100), (010) and (001) octahedral sheets which tend to keep the crystal cubic [8]. However, the crossover from first-order to continuous transition through a tricritical point (TCP) could be induced by symmetry-breaking fields of near [001] stress [9, 10] : the TCP is believed to be of Lifshitz type owing to the strongly quartic character of the soft phonon dispersion [11].

RbCaF_3 crystals doped with Gd_2O_3 were grown by one of us (J. Y. B.) by the Bridgman-Stockbarger method. In this experiment, a compressional stress σ was applied along a [111] cubic direction. Therefore, the sample is a cylinder machined to a diameter of 2.9 mm and a height of 4.7 mm with carefully polished parallel (111) end planes. The EPR experiments were carried out at microwave K-band in the IBM multipurpose cavity where the stress is applied with a stainless-steel hollow force transmitting tube and the various accessories as previously described ; the sample temperature is kept constant to better than 10^{-4} K [12]. At room temperature, the sample shows two different EPR spectra : one results from Gd^{3+} ions on Ca^{2+} sites, the other from $\text{Gd}^{3+}\text{-O}^{2-}$ electrically neutral pairs substituted to $\text{Ca}^{2+}\text{-F}^-$ bonds. The geometry of the apparatus allows application of the stress perpendicular to the external magnetic field $\mathbf{H}$. In such a case, the EPR spectrum of Gd^{3+} is insensitive to the octahedra rotations around [111], whereas the $\text{Gd}^{3+}\text{-O}^{2-}$ pair is sensitive thereto. The spectrum exhibits strong axial lines corresponding to a large quadrupolar parameter b_2^0 in the spin Hamiltonian. This yields a strong dependence of the line positions on the angle between the magnetic field and the pair axis [7]. In the cubic phase for $\mathbf{H}$ along [110], the lines owing to pairs pointing along [100] and [010] coincide. In the tetragonal phase, octahedral rotations by $\pm \phi$ around [001] result in a splitting of these lines proportional to ϕ , whereas rotations around [100] and [010] leave the lines at their cubic-phase positions. We can then infer that when the magnetic field is along a twofold cubic axis, for any octahedral rotational vector, the line splitting is induced by this vector component which lies along the fourfold cubic axis perpendicular to the magnetic field.

Throughout this work, owing to our particular geometry, $\mathbf{H}$ is kept along $[1\bar{1}0]$. Then the [001] components of the octahedral rotational vectors are monitored. We concentrate on the EPR line occurring at $H \simeq 3\,500$ G in the cubic phase : its splitting resulting from octahedral rotations is given by $\Delta H = B\phi_{[001]}$ with $B = (125 \pm 1)$ G/degree.

At zero stress, the well-known slightly first-order tetragonal-to-cubic transition is observed at $T_c = 196.05 \pm 0.10$ K for this newly grown crystal. Application of [111] stress at sufficiently low temperature leaves the tetragonal phase almost unchanged. An EPR spectrum is shown in figure 1a for $\sigma_{[111]} = 0.31$ kbar corresponding to the highest force (20 kg) applied on the crystal. The only difference from the stress-free spectrum concerns the inner lines. The observed splitting which increases on heating, gives evidence for removal of the tetragonal symmetry : the rotational vectors ϕ move slightly away from the fourfold axes towards [111] in each domain. Then the $\text{Gd}^{3+}\text{-O}^{2-}$ pairs rotated by $\pm |\phi|$ around near [100] and [010] directions become inequivalent. This splitting ΔH_i is proportional to the $\phi_{[001]}$ component figures 1a and 1e. The two outer lines result from pairs located in domains with near [001] order-parameter direction. Their splitting ΔH_o is proportional to the $\phi_{[001]}$ component. The angle α by which the ϕ 's are rotated away from the fourfold axes may be estimated from $\text{tg } \alpha = \sqrt{2}\phi_{[001]}/\phi_{[001]} = \sqrt{2} \Delta H_i/\Delta H_o$. This leads to $\alpha \simeq 16.4^\circ$ at $T = 196.35$ K and 8.7° at 195 K for $\sigma_{[111]} = 0.31$ kbar. At a critical temperature T_p ($T_p = 196.45$ K for this stress), the spectrum changes discontinuously to figure 1b. The lines observed above and below this critical temperature coexist. This has to be seen as evidence for a first-order transition. Above T_p , two lines are recorded (Fig. 1c). They result from alternate

Fig. 1. — (a), (b) and (c) : EPR line evolution at the first-order transition (T_p). (a) $T \simeq T_p$, tetragonal phase (including explanations of the splittings ΔH_0 and ΔH_i); (b) $T \simeq T_p$, tetragonal and trigonal phase coexistence; (c) $T \gtrsim T_p$, trigonal phase. (d) EPR line evolution at the second-order transition (T_1). (e) Geometry of rotational order-parameter vectors and their [001] projection in the pseudo-tetragonal phase.

rotations of the octahedra around the $[111]$ direction parallel to the stress. Thus, we obtain a monodomain RbCaF_3 sample with $R\bar{3}c$ structure. The splitting between the two lines is proportional to the order parameter $\varphi_{[111]}$ in this $R\bar{3}c$ phase. It decreases continuously down to zero when T is raised up to $T_1 = (198.95 \pm 0.10)$ K (Fig. 1d). For $T \geq T_1$, only one line is observed. It results from $\text{Gd}^{3+} - \text{O}^{2-}$ pairs along $[100]$ and $[010]$ which are equivalent in the pseudo-cubic phase. Therefore, T_p is the temperature at which the jump from the tetragonal to the trigonal phase occurs. Determination of T_1 is not so straightforward owing to overlapping and broadening of the EPR lines as the trigonal-cubic transition is approached. We locate it for the temperature at which an inflection point is observed in the variation of the peak-to-peak distance of the EPR line *versus* temperature after the splitting has become unresolved.

The temperature dependence of the spectra was analysed for a large variety of applied stresses. Our results are summarized in figure 2 where the phase diagram is plotted. From the data, it may be seen that the slightly first-order cubic-tetragonal phase transition extends to $\sigma_E = (0.10 \pm 0.01)$ kbar. In this stress range ($\sigma < \sigma_E$), the transition temperature T_c is but slightly modified by the applied stress ($dT_c/d\sigma_{[111]} \gtrsim 0$). Furthermore, the order-parameter discontinuity at T_c remains constant within the experimental error (Fig. 3). Thus, these small compressional $[111]$ -applied stresses do not alter the octahedral sheet correlations. For $\sigma > \sigma_E$, a trigonal phase arises and we have two phase boundaries. At low temperature, a first-order line (T_p) separates the pseudo-tetragonal from the trigonal phase, merging the T_c line. Note that T_p is essentially stress independent. Along the T_p line, no change of the $\varphi_{\sigma[001]}$ order-parameter component is

Fig. 2. — Phase diagram (σ , T) of [111]-stressed RbCaF_3 .

Fig. 3. — (a) Component $\phi_{0[001]}$ of the order parameter in the tetragonal phase at $T \lesssim T_c$ or T_p deduced from ΔH_0 (●); $\phi_{1[111]}$ at $T \gtrsim T_p$ deduced from the line splitting (■) and measured by rotating $\mathbf{H}$ in the (111) plane (□) versus $\sigma_{[111]}$. (b) Order-parameter evolution at the T_p transition for three applied stresses.

observed (Fig. 3a) whereas the $\phi_{1[001]}$ increases : therefore $|\phi|$ and α increase with the applied stress, while the order-parameter discontinuity $\Delta\phi$ and the ϕ direction jump from near fourfold cubic axes towards [111] decrease. In figure 3a, the variations of $\phi_{1[111]}$ versus $\sigma_{[111]}$ along the T_p line are also plotted. Except for the neighbourhood of σ_E , the experimental points lie on a straight line which seems to pass through the origin with a slope equal to $4.6^\circ/\text{kbar}$. These results for some applied stresses are summarized in figure 3b. They corroborate the first-order character of the transition. The second boundary is a second-order line between the trigonal and the cubic phases. It meets the former line at $\sigma_E = 0.10 \pm 0.01$ kbar, and $T_E = 196.3 \pm 0.1$ K at a finite angle

thus locating a multicritical point. At this multicritical point, a continuous first-order line meets a second-order line T_1 : this is a CEP. Except close to this point, T_1 varies linearly with $\sigma_{[111]}$ according to $dT_1/d\sigma_{[111]} = (11.8 \pm 0.1) \text{ K/bar}$.

Qualitatively, the gross features of this phase diagram may be quite easily understood. They arise from the competition between ordering along [100] directions favoured at zero stress and ordering along [111] favoured by the uniaxial stress $\sigma_{[111]}$. For convenience, in the following discussion let us choose the components of ϕ as ϕ_1 along [111] and ϕ_2 and ϕ_3 in the (111) plane. As the temperature is lowered at constant $\sigma > \sigma_E$, ϕ_1 orders first through a continuous Ising-like ($n = 1$) transition : the stress wins. Lowering the temperature further, ϕ_2 and ϕ_3 also order at a first-order transition : the natural ordering wins. Furthermore, owing to the threefold symmetry of the ordering in the (111) plane for $T < T_p$ this transition may be seen as three-state Potts-like [13]. For stresses $\sigma < \sigma_E$, the disappearance of the trigonal phase indicates that the applied stresses are definitely too small to compete with the « natural » ordering.

In conclusion, one can state that these compressional [111]-stress EPR results in RbCaF_3 corroborate the topology of the predicted phase diagram and its CEP [3, 14]. It is similar to the diagram in KMnF_3 [4], but in the RbCaF_3 EPR experiments the amount and direction of the order parameter in the tetragonal and trigonal phases has been measured and awaits quantitative theoretical computation.

Acknowledgments.

One of us (J. Y. B.) would like to acknowledge the hospitality of the IBM Zurich Research Laboratory where he was visiting when this work was performed.

References

- [1] See : *Proc. NATO Adv. Study Inst. Multicritical Phenomena, Geilo 1983*, R. Pynn and A. Skjeltorp eds. (Plenum, New York) 1984.
- [2] KERSZBERG, M. and MUKAMEL, D., *Phys. Rev. Lett.* **43** (1979) 293 and *Phys. Rev. B* **23** (1981) 3943 and 3953.
- [3] BLANKSCHTEIN, D. and MUKAMEL, D., *Phys. Rev. B* **25** (1982) 6939.
- [4] FOSSHEIM, K., in [1].
- [5] MUELLER, K. A., BERLINGER, W. and SLONCZEWSKI, J. C., *Phys. Rev. Lett.* **25** (1970) 734 ; MUELLER, K. A. and BERLINGER, W., *Z. Phys. B* **46** (1982) 81.
- [6] CURRAT, R., MUELLER, K. A., BERLINGER, W. and DENOYER, F., *Phys. Rev. B* **17** (1978) 2937.
- [7] BUZARÉ, J. Y., ROUSSEAU, J. J. and FAYET, J. C., *J. Physique Lett.* **38** (1977) L-445 ; BUZARÉ, J. Y., FAYET-BONNEL, M. and FAYET, J. C., *J. Phys. C* **13** (1980) 857 ; BUZARÉ, J. Y., FAYET-BONNEL, M. and FAYET, J. C., *J. Phys. C* **14** (1981) 67.
- [8] NATTERMANN, T., *J. Phys. C* **9** (1976) 3337.
- [9] AHARONY, A. and BRUCE, A. D., *Phys. Rev. Lett.* **42** (1979) 462.
- [10] BUZARÉ, J. Y., FAYET, J. C., BERLINGER, W. and MUELLER, K. A., *Phys. Rev. Lett.* **42** (1979) 465.
- [11] ROUSSEAU, M., NOUET, J. and ALMAIRAC, R., *J. Physique* **38** (1977) 1423.
- [12] BERLINGER, W. and MUELLER, K. A., *Rev. Sci. Instrum.* **48** (1977) 1161.
BERLINGER, W., *Magn. Res. Rev.* (1984) in press.
- [13] AHARONY, A., MUELLER, K. A. and BERLINGER, W., *Phys. Rev. Lett.* **38** (1977) 33.
- [14] Note the phase diagram shown in figure 3b of [3] is schematic and therefore only the general topology is relevant.