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Abstract. The influence of hydrostatic pressure on the cubic-to-tetragonal phase transition in RbCaF$_3$ is studied by monitoring the EPR spectra of the Gd^{3+}–O^{2-} pairs and Gd^{3+} centres. The phase transition remains of first order up to 800 MPa and the discontinuity of the order parameter φ at T_c slightly increases with increasing pressure. Similarly, the non-linearity of the cubic parameter $b_4^0(T)$, caused by the rotational fluctuations, near T_c becomes larger under pressure. The pressure shift of the phase transition temperature is determined: $dT_c/dp = (36.5 \pm 0.3)$ K GPa^{-1}. The values of T_c as well as dT_c/dp are interpreted within the rigid-sphere model.

1. Introduction

Influence of hydrostatic pressure on the structural phase transition in RbCaF$_3$ ($T_c = 195$ K) from a cubic phase to a tetragonal phase was first studied using the EPR of Gd^{3+} centres (Müller *et al* 1980). It was found that up to 120 MPa the transition temperature increases linearly at 36 K GPa^{-1}, but neither the magnitude of the first-order discontinuity parameter nor its character is altered by pressure. Similar conclusions have been drawn from our preliminary pressure EPR studies of the critical phenomena in the vicinity of the phase transition in RbCaF$_3$:Gd^{3+}–O^{2-} at 400 MPa (Krupski and Buzaré 1991). Nevertheless, from EPR experiments on RbCaF$_3$:Gd^{3+} crystals, the crossover from the first-order to continuous transition was observed under the uniaxial stress applied along [001] (Buzaré *et al* 1979). The critical end point was found in [111]-stressed RbCaF$_3$ by monitoring the EPR lines of Gd^{3+}–O^{2-} pairs (Buzaré *et al* 1985).

One may ask whether it is possible to change the order of the phase transition with hydrostatic pressure. Some theoretical considerations indicate that it is possible (Benguigui 1973). To answer this question, Trokiner and Zanni-Theveneau (1988) performed NMR experiment under hydrostatic pressure up to 540 MPa. They suggest a crossover of some critical exponents towards tricritical values with increasing hydrostatic pressure. This result and the disappearance of the phase coexistence at high pressures are interpreted as the occurrence of a tricritical point near 540 MPa above which the transition should become continuous.

The aim of this study is to examine whether this prediction is justified. The effect of the hydrostatic pressure on the critical behaviour of RbCaF$_3$ will be studied up to 800 MPa.

2. Experiment

Single crystals of $RbCaF_3$ doped with Gd_2O_3 were prepared by the Bridgman–Stockbarger technique in the Equipe de Physique de l'Etat Condensé (Le Mans) with the technical assistance of G Niesseron. The Gd^{3+} ion enters the Ca^{2+} octahedral site and the Gd^{3+}–O^{2-} pair substitutes for the Ca^{2+}–F^- bond.

EPR measurements at a frequency of 9.5 GHz under high hydrostatic pressures were carried out using the special spectrometer station constructed recently in the Institute of Molecular Physics in Poznań. This equipment is a modified version of the apparatus used previously (Stankowski *et al* 1976). Now, the cylindrical corundum resonator TE_{112} mode is coupled to a microwave (X-band) coaxial line and placed inside a reinforced pressure chamber made of hardened beryllium bronze. Because of these improvements it is possible to perform a high-pressure EPR experiment up to 800 MPa in the temperature range 80–400 K. The pressure of the transferring liquid is produced within the steel high-pressure cylinder and delivered to the pressure chamber via a capillary. Petroleum ether is used as the pressure-transmitting medium. The pressure is monitored with a standard manometer to the accuracy of 2 MPa. The desired temperature within the chamber is established by adjusting the rate of liquid-nitrogen flow through the heat exchanger placed immediately upon the pressure chamber. The temperature is controlled with an accuracy better than 0.1 K and measured with a copper–constantan thermocouple. 80 Hz magnetic field modulation is provided by modulation coils mounted outside the pressure chamber. A relatively higher filling factor of the corundum resonator partly compensates for the lower sensitivity; compared with the standard EPR cavity system and 100 kHz modulation, the EPR signal is only reduced by half.

The samples of $RbCaF_3$ with Gd^{3+} and Gd^{3+}–O^{2-} centres were cut along [001] axis into 5 mm rods of 1.5 mm diameter. Each sample was placed in the centre of the corundum resonator with the cylindrical axis perpendicular to the direction of the static magnetic field.

3. Results

The influence of hydrostatic pressure on the phase transition temperature T_c in $RbCaF_3$ and on the rotation angle φ of the fluorine octahedra (the order parameter) has been studied by monitoring the Gd^{3+}–O^{2-} EPR spectra up to 800 MPa. The magnetic field was perpendicular to the [001] direction and at an angle $\theta = 16°$ from the [100] axis. In this direction the line previously labelled A (Buzaré *et al* 1981) is highly sensitive to rotation of the octahedra in the (001) plane. From the angular dependence of the EPR lines in $RbCaF_3$:Gd^{3+}–O^{2-} crystals (Buzaré *et al* 1981) we find that the slope of the A-line anisotropy at $\theta = 16°$ is (6.8 ± 0.4) mT deg^{-1}. At the phase transition, alternate rotation of CaF_2 octahedra around one of the fourfold axes yields two orientations of the Gd^{3+}–O^{2-} centres, $\theta \pm \varphi$, below T_c. Thus, in the tetragonal phase, the A line splits into two components. This splitting allows us to determine the angle of rotation of the fluorine octahedra, i.e. the order parameter of the transition.

Figure 1 shows the temperature evolution of the A line when passing through the phase transition under a constant pressure of 800 MPa. At temperatures above T_c the broadening of the EPR line is observed near T_c. At T_c we observe the sudden onset of two satellite signals, one on each side of the central line. The splitting between these lines increases during further cooling. Such spectrum results from the multiple-domain structure of the sample in the tetragonal phase. The satellite signals correspond to the [001] domains, while
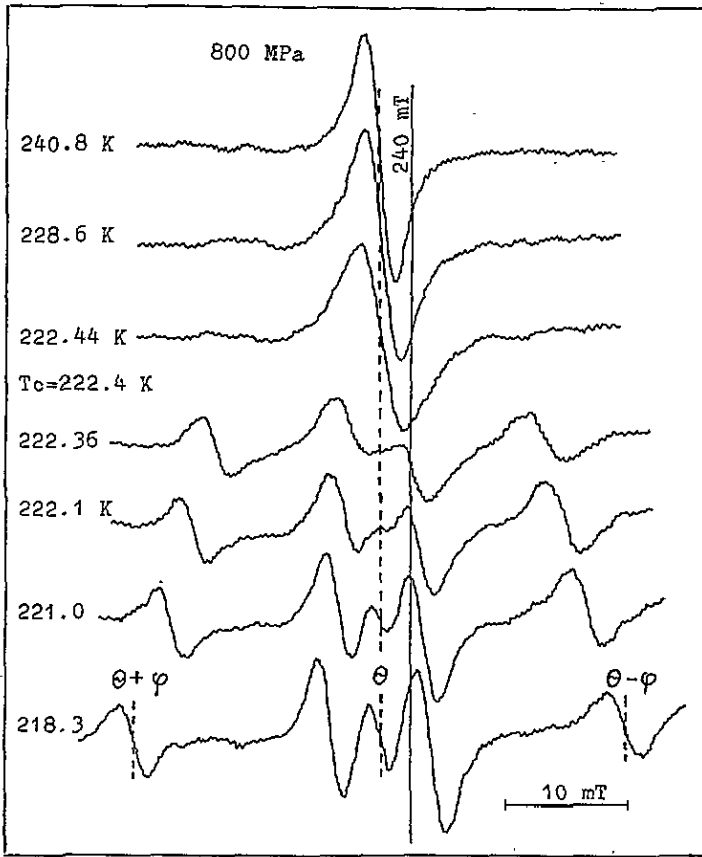
Figure 1. Temperature changes in the EPR spectra (A line for $\Theta = 16°$) of $RbCaF_3:Gd^{3+}-O^{2-}$ at 800 MPa ($\nu = 9.5$ GHz) in the vicinity of the phase transition.

the central signal is assigned to the [100] and [010] domains. The central line should remain unsplit when the static magnetic field H is in the (001) plane. Small misalignment of the sample causes the apparent splitting of the central line (figure 1) which does not contribute to the satellite [001] domains.

The behaviour of the order parameter φ as a function of temperature below T_c at five constant pressure settings, namely 0.1 MPa (atmospheric), 350 MPa, 600 MPa, 700 MPa and 800 MPa, is shown in figure 2. At T_c a sudden splitting of the A line is observed for all pressure values and φ jumps from zero to φ_c, its initial value.

In order to compare our measurements with those obtained by Trokiner and Zanni-Theveneau (1988) we assume that the temperature dependence of the order parameter φ obeys the power law according to the relation:

$$\varphi = A(T_0 - T)^\beta$$

where A, T_0 and the critical exponent β are adjustable parameters. Because of the discontinuity at the phase transition the temperature T_0 obtained by extrapolation to $\varphi = 0$ (broken line) is not equal to the phase transition temperature T_c. The difference between T_0 and T_c is small (about 1 K) and does not depend on pressure. The experimental and calculated values of the present study are collected in table 1.

The changes in the critical exponent β induced by pressure are small; at 0.1 MPa, $\beta = 0.28$, between 350 and 700 MPa, β is equal to about 0.25 and, at 800 MPa, $\beta = 0.23$.
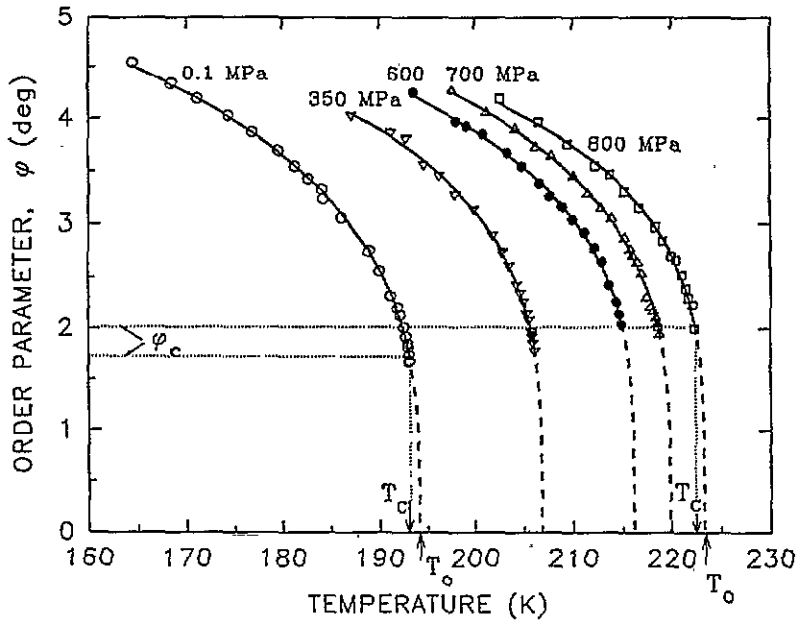
Figure 2. The temperature dependence of the order parameter φ for five values of the hydrostatic pressure in $RbCaF_3:Gd^{3+}-O^{2-}$.

Table 1. The values of the experimental phase transition temperature T_c and the initial values of the order parameter φ_c in $RbCaF_3:Gd^{3+}-O^{2-}$ measured at different values of hydrostatic pressure p. T_0, β and A are the best-fit parameters in the formula $\varphi = A(T_0 - T)^\beta$.

p (MPa)	T_c (K)	φ_c (deg)	T_0 (K)	β	A (deg K^β)
0.1	193.2	1.7	194.2	0.28	1.7
350	206.2	1.8	206.9	0.25	1.9
600	215.0	2.0	216.2	0.25	1.9
700	218.0	1.9	219.8	0.26	1.9
800	222.4	2.0	223.2	0.23	2.1

At the same time, the value of the order parameter at T_c is observed to increase from $\varphi_c = 1.7°$ at 0.1 MPa to $\varphi_c = 2.0°$ at 800 MPa.

Figure 3 shows the dependence of T_c on the hydrostatic pressure up to 800 MPa. In the whole range of pressures the transition temperature varies linearly at the rate $dT_c/dp = (36.5\pm0.3)$ K GPa^{-1}. This value is in accord with the previous EPR measurements (Müller *et al* 1980) but differs from the NMR data (Trokiner and Zanni-Theveneau 1988).

In order to confirm the rise in the discontinuity at the phase transition in $RbCaF_3$ under pressure we performed a study of the temperature variations of the cubic zero-field splitting parameter b_4^0 above T_c at atmospheric pressure and at 700 MPa. At temperatures higher than $T_c + 30$ K, b_4^0 changes with temperature, linearly (dotted lines in figure 4) decreasing at the slope $db_4^0/dT = -5.1 \times 10^{-7}$ cm^{-1} K^{-1}, independent of pressure. The deviation of b_4^0 from the linear dependence near T_c increases when pressure is applied: $\Delta b_4^0 = 0.057 \times 10^{-4}$ cm^{-1} and 0.089×10^{-4} cm^{-1} at 0.1 MPa and 700 MPa, respectively.
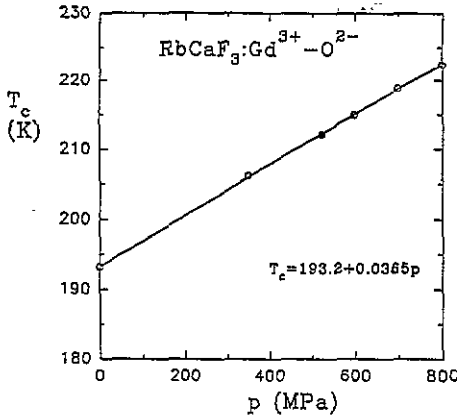
Figure 3. Variation in the transition temperature with pressure in RbCaF₃: ○, from the temperature dependences at constant pressure (see figure 2); ●, from the pressure dependence at constant temperature.
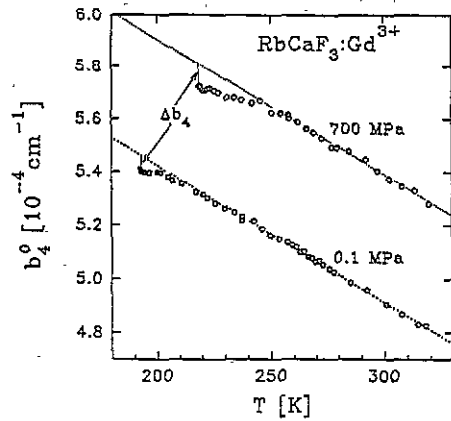
Figure 4. The temperature dependence of the zero-field parameter b_4^0 at atmospheric pressure and at 700 MPa for RbCaF₃:Gd³⁺ in the cubic phase ($\nu = 9.5$ GHz; $H \parallel [100]$).

4. Discussion

4.1. Discontinuity of the phase transition as a function of pressure

From our experimental results, we conclude that the phase transition between 0.1 and 800 MPa maintains its weak first-order character. The discontinuity of the phase transition becomes more pronounced under pressure; the initial value φ_c of the order parameter at T_c increases (figure 2). On the other hand, we observe a reduction in the critical exponent β which amounts to 0.23 ± 0.01 at 800 MPa. This value is lower than the theoretical value near the tricritical point $\beta = 0.25$ (Trokiner and Zanni-Theveneau 1988). Nevertheless, the phase transition at 800 MPa is still of first order.

Our results strongly support the view that the cubic-to-tetragonal phase transition in RbCaF₃, anticipated to be the continuous phase transition according to the mean-field theory, is of first order. It is driven by critical fluctuations; the anisotropic soft-mode behaviour reflects nearly two-dimensional correlated octahedra sheets (100), (010) and (001) which tend to keep the crystal cubic (Natterman 1976). This behaviour is not modified by the hydrostatic pressure which does not break the symmetry, contrary to the effects induced by the uniaxial stress.

4.2. Precursive behaviour of the cubic parameter b_4^0

The deviation of b_4^0 from the linear dependence near T_c, caused by the local rotational fluctuations in the cubic phase, is described by $\Delta b_4^0 = \frac{5}{4} b_4^0 \sin^2(2\Phi)$ (Buzaré *et al* 1980). Φ is the most probable value of the angle of the octahedra rotation representing the fluctuation distribution. This angle calculated at T_c equals 2.6° at normal pressure and 3.2° at 700 MPa, which means that the rotational fluctuations in the cubic phase are larger under pressure. This phenomenon may be related to the disordered high-temperature phase, previously described by Rousseau (1979). The fluorine atoms are pushed out of the Ca–Ca line into four walls in the direction of the diagonals of the faces of the cube formed by the Rb atoms; this can be explained by the negative value of $\frac{1}{2}a - (r_{Ca} + r_F)$. In the high-temperature phase, the fluorine atoms undergo hopping between these four wells. The precursive behaviour of b_4^0

gives evidence of slowing down of the hopping motion. Our results also show increase in the disorder with increasing hydrostatic pressure. This is due to the reduction in the lattice parameter a which gives a larger negative value of $\frac{1}{2}a - (r_{Ca} + r_F)$, and hence a larger displacement of the fluorine atoms from the centre of the cube faces.

4.3. Rigid-sphere model interpretation

The value of T_c in RbCaF$_3$ and its pressure coefficient dT_c/dp result from the rigid-sphere model which was successfully applied to the antifluorite complex A$_2$MX$_6$ and elpasolite A$_2$BMX$_6$ compounds (Krupski 1983, 1989). Now, we apply this model to the description of structural instabilities at T_c for perovskites, in particular to the RbCaF$_3$ crystal. The model assumes free motion of the cation A$^+$, regarded as a rigid sphere, inside the spherical cavity made up of 12 adjacent halogen ions. The phase transition temperature predicted from this model depends on the $n = R_A/R_h$ ratio of the cation radius R_A to the cavity radius $R_h = a\sqrt{2}/2 + R_X$ and is a function of the external pressure p. In particular,

$$T_c = \frac{4\pi R_A^3}{3k} \frac{1-n}{n^3}(p + p_1)$$

with the lattice pressure p_1 (the electrostatic contribution) (Krupski 1983) given by

$$p_1 = \frac{e^2}{12\pi\epsilon_0} \frac{M_a}{a^4}.$$

The Madelung constant M_a, calculated for perovskites using the formula of Simon and Zeller (1974), is given by

$$M_a = 2.035\,36q_A^2 + 7.565\,92q_A q_X + 17.908\,04q_X^2.$$

For RbCaF$_3$ the effective charge q_A of ions A$^+$ and the effective charge q_X of ions F$^-$ are known from the lattice dynamics calculation (Ridou *et al* 1986):

$$q_A = 0.8 \qquad q_X = -0.81.$$

The value of the lattice constant a of the cubic phase should be taken at T_c. The room-temperature value $a = 0.4455$ nm (Ridou *et al* 1986) is extrapolated to T_c using the thermal expansion coefficient $\lambda = 1.68 \times 10^{-5}$ K^{-1} (Rewaj *et al* 1992). Hence, $a_c = 0.4448$ nm.

In the calculation of T_c we enter the Pauling radii corrected for twelvefold coordination (Krupski 1989): $R_X = 0.153$ nm and $R_A = 0.160$ nm. The calculated value of T_c when the external pressure p is neglected equals 192.77 K. This value is in good agreement with the experiment.

In order to calculate the value of dT_c/dp we assume that, firstly, both pressure and temperature affect the lattice constant according to

$$a = a_0(1 + \lambda\,\Delta T - \beta p)$$

and, secondly, the external pressure modifies ionic radii proportionally to the magnitude of the pressure:

$$R_X = R_{X0}(1 - \gamma_X p) \qquad R_A = R_{A0}(1 - \gamma_A p)$$

where a_0, R_{X0} and R_{A0} are the appropriate dimensions at $p = 0$, β is the linear compressibility of the crystal, γ_X and γ_A are the compressibilities of the corresponding ions, and $\Delta T = T_c - T_{C0}$ with T_c and T_{C0} the phase transition temperatures for external pressure p and $p = 0$, respectively.

Because of the thermal vibrations and the free space between the ions, γ_X and γ_A should be less than β. Since it is difficult to estimate the ionic compressibility, we assume that $\gamma_X = \gamma_A = \beta$ and $\beta = 6.6 \times 10^{-6}$ MPa^{-1} for RbCaF₃ (Rewaj *et al* 1992). Taking into account these modifications of the rigid-sphere model we arrive at $dT_c/dp = 40.8$ K GPa^{-1}. The value of dT_c/dp is very sensitive with respect to the values of γ_X and γ_A in comparison with β. For example, if we assume that $\gamma_X = \gamma_A = 0.99\beta$, then $dT_c/dp = 32.6$ K GPa^{-1}. On the other hand, for the rigid lattice ($\beta = 0$ and $\gamma = 0$) we obtain that dT_c/dp is 12 K GPa^{-1}, which is too small when compared with the experimental value of 36.5 K GPa^{-1}. It renders the introduced adjustments of the rigid-sphere model necessary to account for the observed shift in T_c under hydrostatic pressure. Additional calculations of T_c and dT_c/dp for the family of the halogen perovskites will be attempted within the rigid-sphere model, where the different kinds of interaction will be accounted for. It should allow better understanding of the nature of the rotational phase transition in perovskite compounds.

Acknowledgment

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