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^{87}Rb NMR study at the cubic to tetragonal phase transition in RbCaF_3

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Résumé. — Le spectre de résonance magnétique nucléaire de ^{87}Rb a été étudié dans un monocristal de RbCaF_3 de part et d'autre de la transition de phase cubique-quadratique à 198 K. Dans la phase cubique (phase haute température) la dépendance en température de l'amplitude de la raie de résonance s'écarte de la loi de Curie ce qui peut être attribué à l'existence de domaines de symétrie quadratique. Dans la phase quadratique (phase basse température) on observe un déplacement de la raie centrale dû à une interaction quadripolaire au second ordre, duquel on peut déduire l'angle de rotation de CaF_6 (paramètre d'ordre). La dépendance en température du paramètre d'ordre est décrite par une loi de puissance d'exposant 0,5 et 0,32 respectivement au-dessous et au-dessus de 150 K. L'amplitude de rotation a été comparée à celles déduites des études radiocristallographiques et de diffraction de neutrons sur poudre.

Abstract. — The ^{87}Rb nuclear magnetic resonance spectrum, in perovskite single crystal of RbCaF_3 , is studied above and below the cubic-to-tetragonal phase transition occurring at 198 K. In the high-temperature cubic phase, the temperature dependence of the resonance line amplitude deviates from the Curie law and this can be attributed to the existence of tetragonal domains. In the low temperature tetragonal phase, a second-order quadrupole shift of the central line is observed, from which the CaF_6 tilt angle (order parameter) is derived. The order parameter temperature dependence is described by a power law with a cross over from exponent 0.5 to exponent 0.32 at 150 K. The tilt angle Φ is compared to the values obtained from X-ray and neutron powder diffraction data.

1. **Introduction.** — Rubidium calcium fluoride has, at room temperature, a cubic perovskite type structure with the space group O_h^1 (Fig. 1a). It undergoes three structural phase transitions, at approximately 198 K, 40 K and 7 K [1]. It has been shown that the 40 to 198 K phase is tetragonal with the space group D_{4h}^{18} and it can be described by tilts of CaF_6 octahedra around the tetragonal axis with alternate rotations in adjacent (001) planes (Fig. 1b). The absolute tilt angle value (Φ) increases when the temperature is lowered from 198 K; it can be regarded as the order parameter. Many experiments [2, 3, 4, 5] have exhibited the first-order character of this transition but with a weak discontinuity of the physical parameters. The lower temperature phases are orthorhombic [6] with first-order transitions [1]. In this paper our attention has

been focussed on the 198 K phase transition, and the relevant cubic and tetragonal phases.

Fig. 1. — a) Cubic cell of RbCaF_3 at room temperature; b) Tetragonal cell. Arrows indicate the tilt angle of CaF_6 octahedra.

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This structural phase transition is similar to those occurring at 105 K and at 186 K in SrTiO_3 [19] and KMnF_3 [20] respectively. The RbCaF_3 transition has been the object of a great number of experimental investigations [1-18], including inelastic neutron scattering studies in cubic phase [7, 8]. In addition to the condensation of the triply-degenerate R_{25} mode, this last technique has shown the occurrence of a central peak. Recently, a tricritical behaviour has been observed by EPR experiments in uniaxially stressed crystal [9].

Useful information could be provided by NMR experiments; for these investigations, rubidium nuclei seem to be the best probes owing to their nuclear quadrupole moments [21]. In the tetragonal phase (contrary to the purely cubic phase), the Rb nuclei experience a quadrupolar interaction which can be measured from the induced NMR line splitting. This provides a measure of the order parameter, as can be deduced from a point charge model. In RbCaF_3 , a NMR study is potentially useful for at least two reasons.

The first reason is to provide information on the exponent which describes the order parameter behaviour. Up to now no agreement has been established [10, 11, 12, 13, 18], specially in the near vicinity of the transition. The second reason is that the tilt amplitude can be compared to the value deduced from direct determination of the position of the ions [18, 6]. Thus RbCaF_3 provides one of the rare cases allowing the point charge approximation to be checked. Moreover, the detection of a phase coexistence in RbCaF_3 could be a confirmation of the order-disorder model proposed to describe transitions of this sort in perovskites [22].

2. Experimental. — The NMR study has been done on ^{87}Rb (nuclear spin $3/2$) instead of ^{85}Rb which is more abundant but less sensitive.

— Measurements were performed using a Varian wide line spectrometer. The pattern consisted of the absorption line derivative recorded at fixed frequency. The temperature was varied by a standard nitrogen flow system and measured with a calibrated copper-constantan thermocouple.

— The sample was a single crystal grown by J. Y. Gesland using Bridgman-Stockbarger method. It consisted of a parallelepiped of

$$7.25 \times 6.04 \times 5.41 \text{ mm}^3$$

with faces parallel to (100), (011) and (0 $\bar{1}1$).

— ^{87}Rb nuclear magnetic resonance was observed in a magnetic field of ~ 1 T corresponding to a radio-frequency of 14.7 MHz.

3. Results. — The crystal was allowed to rotate in such a way that the applied magnetic field $\mathbf{H}_0$ remains always in the (0 $\bar{1}1$) plane. The angle between the

tetragonal axis of this plane and the magnetic field $\mathbf{H}_0$ is denoted Ψ .

3.1 CUBIC PHASE MEASUREMENTS. — In order to check a possible existence of tetragonal domains above the transition temperature, the NMR rubidium line has been studied carefully in the cubic phase to detect any evolution of the characteristic parameters of its profile when the temperature is varied. The occurrence of such domains would lead to the appearance of satellite lines characteristic of a quadrupolar interaction at the rubidium site (and of course a concomitant decrease of the central line intensity).

Fig. 2. — a) Peak to peak amplitude (ΔI) of the absorption line versus temperature in the cubic phase of RbCaF_3 . b) Temperature dependence of $\Delta I \times T$ showing the failure of Curie law for the NMR signal in the cubic phase of RbCaF_3 .

The crystal was oriented with H_0 parallel to the tetragonal axis of the experimental rotating plane (i.e. $\Psi = 0$). The poor signal to noise ratio (less than 4) did not allow us to deduce the second moment of the line. So we focussed our attention on the width and on the amplitude (ΔI) of the line, checking for each temperature that the signal was not saturated. From these results (Fig. 2) it appears that the Curie law for the NMR signal ($\Delta I \sim 1/T$) fails below approximately 210 K. This is more evident from figure 2b where we plotted the temperature dependence of the $\Delta I \times T$. Such a behaviour can be observed in SrTiO₃ (ref. [23], Fig. 2) : the ⁸⁷Sr line intensity decreases below 123 K ($T_c \simeq 105$ K). There is no doubt that a part of the intensity appears in satellite lines arising from quadrupolar interactions, although these lines could not be observed because of their frequency spreading. The origin of these interactions is frequently attributed to strains [24]. However it might be due also to the existence of tetragonal domains. The fact that we observed the same results on powder samples where strains are different increases the probability of the second explanation. It must be pointed out that, in RbCaF₃ as in SrTiO₃, the central peak in the neutron scattering spectrum begins to rise at the same temperature for which the NMR signal begins to decrease [8, 25, 23].

3.2 TETRAGONAL PHASE MEASUREMENTS. — In the tetragonal phase, rubidium ions are no longer in cubic symmetry sites and so they are submitted to static quadrupolar interaction. Due to the point group symmetry of the site ($\bar{4}2m$) the asymmetry parameter η is zero and so the quadrupolar interaction Hamiltonian is represented by

$$\mathcal{H}_Q = \frac{e^2 q Q}{4 I(2I - 1) h} \frac{1}{2} (3 \cos^2 \theta - 1) (3 I_z^2 - I^2). \quad (1)$$

Here θ represents the angle between the magnetic field, H_0 , and the non-degenerate principal axis (i.e. tetragonal axis) of the electric field gradient tensor ; q represents the electric field gradient at the site, Q the electric quadrupole moment of the nucleus and I its nuclear spin moment.

⁸⁷Rb nuclear spin moment is 3/2 and so three NMR lines are expected instead of the single one when the quadrupolar interaction is not present. However a tetragonal domain can arise from each of the three $\langle 100 \rangle$ cubic axes. Hence three such domains are expected, and nine NMR lines. In fact, due to the symmetry of H_0 with respect to the crystal, two of the domains are always equivalent and only six lines would be seen. In spite of this, only two lines were observed corresponding to each of the two types of domain, these lines being the second order shifted central lines. Strains are probably strong enough to wipe out the satellite transitions *via* first-order quadrupolar effect as occurs in KMnF₃ [24] for ³⁹K.

With respect to the experimental angle (Ψ) we have for one of these domains (denoted A) $\theta = \Psi$; for the two others (denoted B) θ is given by

$$\cos^2 \theta = \frac{1 - \cos^2 \Psi}{2}.$$

Thus, in presence of second-order quadrupolar effect, the central line resonance fields for A and B domains are

$$H_A = H_Z + H'_A = H_Z - 4 CH_Q (1 - \cos^2 \Psi) \times (1 - 9 \cos^2 \Psi) \quad (2)$$

$$H_B = H_Z + H'_B = H_Z + CH_Q (1 + \cos^2 \Psi) \times (7 - 9 \cos^2 \Psi). \quad (3)$$

Here H_Z is the resonance field without quadrupolar interaction, $H_Q = 2 \pi \nu_Q / \gamma$ where γ represents the gyromagnetic ratio of the nucleus and $\nu_Q = e^2 Q q / 2 h$ the quadrupolar coupling constant $C = 3 \nu_Q / 64 \nu_L$, where ν_L is the Larmor frequency.

The Ψ dependence of this shift is plotted figure 3.

Fig. 3. — Rotation patterns of the second order shifted central lines for A domains (dashed line) and B domains (solid line) in the tetragonal phase of RbCaF₃ obtained from expressions (2) and (3).

The distance between the two observed lines : $\Delta H' = H_A - H_B$ is given from (2) and (3),

$$\Delta H' = - CH_Q (3 \cos^2 \Psi - 1) (9 \cos^2 \Psi - 11). \quad (4)$$

As one can see in figure 4 the experimental rotation pattern $\Delta H' = f(\Psi)$ is in very good agreement with the above formula.

Far below the transition temperature (T_c), ν_Q measurements *versus* temperature were performed at $\Psi = 90^\circ$, the largest splitting giving the best accuracy. However, in the near vicinity of T_c , the two lines were no longer resolved. Hence we obtained a single crystal consisting of one B domain. To do this, we crossed $T_c = 198$ K very slowly (i.e. over several hours). We deduced ν_Q from the resonance line shift

Fig. 4. — Angular dependence of the distance $\Delta H'$ of the two central lines. Full circles represent experimental results at $T = 138$ K. The solid line is calculated from equation (4) where CH_Q is obtained from the experimental result at $\Psi = 90^\circ$, $T = 138$ K.

occurring when we rotate the crystal (Fig. 3). However in this way the uncertainty in ν_Q is increased.

The temperature dependence of ν_Q is plotted figure 5. The fast variation close to the transition does not allow us to observe the discontinuity expected for the first-order transition.

Fig. 5. — Temperature dependence of the ^{87}Rb quadrupolar coupling constant in the tetragonal phase of RbCaF_3 . The straight line fits the experimental results below 150 K and crosses the temperature axis at 230 K. A typical error bar is shown in the corner.

4. Discussion. — The quadrupole coupling constant ν_Q is proportional to the electric field gradient q which depends on the positions of ions surrounding the observed nucleus. A point charge approximation enables the theoretical computation according to the relationship

$$eq = (1 - \gamma_\infty) \frac{e}{4\pi\epsilon_0} \sum_i Z_i \left(\frac{1}{r_i^3} - \frac{3z_i^2}{r_i^5} \right) \quad (5)$$

where Z_i represents the electric charge number of the ion labeled i ($Z_i = -1, +1, +2$ for fluorine, rubidium and calcium ions respectively).

x_i, y_i, z_i represent the coordinates of these ions ($r_i = (x_i^2 + y_i^2 + z_i^2)^{1/2}$) and γ_∞ the antishielding factor.

Taking into account the nearest-neighbour contribution alone (i.e. 12 fluorine and 8 calcium ions) and assuming alternate rotation of CaF_6 octahedra as our only hypotheses, we obtained

$$q = \frac{1 - \gamma_\infty}{4\pi\epsilon_0 a^3} \left(80.61(\text{tg } \Phi)^2 - 15.87 \frac{c - a}{a} \right) \quad (6)$$

where c and a represent the pseudo-cubic subcell parameters and Φ the CaF_6 tilt angle.

In order to evaluate the contribution of the more-distant ions, the computation has been extended to second neighbours (i.e. 26 rubidium, 36 fluorine and 8 calcium ions). We find

$$q = \frac{1 - \gamma_\infty}{4\pi\epsilon_0 a^3} \left(81.28(\text{tg } \Phi)^2 + 0.67 \frac{c - a}{a} \right) \quad (7)$$

and concerning ν_Q we are led to :

$$\nu_Q = 17400 \frac{Q(1 - \gamma_\infty)}{a^3} \times \left(80.61(\text{tg } \Phi)^2 - 15.87 \frac{c - a}{a} \right) \quad (8)$$

in the first approximation and

$$\nu_Q = 17400 \frac{Q(1 - \gamma_\infty)}{a^3} \times \left(81.28(\text{tg } \Phi)^2 + 0.67 \frac{c - a}{a} \right) \quad (9)$$

in the second approximation where Q is expressed in barns and a in angströms.

The contribution of the third and fourth-order terms in Φ and $(c - a)/a$ has been shown to be negligible. Using the experimental values of ν_Q , computation has been possible in each of these two approximations. The a and c parameters were deduced from X-ray experiments : Q was taken to be 0.135 [26] and $1 - \gamma_\infty$ to be 51 [27]. Results are reported on figure 6. In order to show the validity of the point charge model we have also plotted on this picture the values obtained from direct neutron measurements of the ion position [6]. As can be seen the two results are in good agreement ; it is interesting to note the slight improvement brought when second neighbours are taken into account. The deviation to the real value of Φ at very low temperature can be due to the great distortion which no longer allows us to omit further ions and higher-order terms. The antishielding factor is probably also affected by the great anisotropy of the neigh-

Fig. 6. — Temperature dependence of the tilt angle Φ of CaF_6 octahedra in the tetragonal phase of RbCaF_3 obtained from : present NMR data in the nearest-neighbour approximation (dotted line) and next nearest-neighbour approximation (dot-and-dash line); neutron scattering determination of ion positions (squares) according to ref. [6]; EPR data using $\text{Gd}^{3+}\text{-O}^{2-}$ probe [28] (full circles); the classical displacive model applied to X-ray measurements [14] (dashed line); the order-disorder model [22] (solid line).

bouring rubidium ions. As a comparison, the tilt angle amplitude deduced from EPR experiments [28, 15], has also been plotted on figure 6.

In spite of the first-order character of this transition, due to the weak discontinuity of the order parameter, it is interesting to fit the temperature dependence of Φ with a power law ε^β (with $\varepsilon = (T_c - T)/T_c$). Close to the transition $(c - a)/a$ is very small compared to the $(\text{tg } \Phi)^2$ term, so the Φ dependence of ν_Q is simplified. In this case, assuming also $\text{tg } \Phi = \Phi$, equation (5) can be written :

$$\Phi \simeq 3 \times 10^{-3} \sqrt{\nu_Q} \quad (10)$$

where ν_Q is expressed in kHz and Φ in radians. Thus we obtain

$$\nu_Q \propto \varepsilon^{2\beta}. \quad (11)$$

— Below ~ 150 K it can be seen (Fig. 5) that ν_Q is nearly a linear function of T and so

$$\Phi \propto \varepsilon^{0.5} \quad (12)$$

with $T'_c \sim 230$ K.

— Above ~ 150 K a least square refinement yields to $2\beta = 0.64 \pm 0.02$ and $T_c = (198.0 \pm 0.5)$ K.

To check the validity of this law, we drew $(\nu_Q)^{1/0.64}$ versus T on figure 7. Hence we have

$$\Phi \propto \varepsilon^{0.32} \quad (13)$$

in the range where $\varepsilon < 0.2$.

Fig. 7. — Temperature dependence of $(\nu_Q)^{1/0.64}$ above 150 K in RbCaF_3 .

This behaviour is similar to the one occurring in KMnF_3 [24]. It has not been possible to find the dependence very close to the transition.

It may be seen from figure 6 that the tilt angles deduced from NMR are much larger than those inferred from X-ray data [29] using the classical displacive description proposed ref. [14], where

$$\frac{3}{2} \Phi^2 \simeq \frac{c - a}{a}. \quad (14)$$

A better evaluation of the tilt angles from the cell parameters is obtained when the transition is described by the disordered model proposed by M. Rousseau [22], which introduces in the cubic phase domains of tetragonal symmetry with finite lifetime. Notice that the decrease in intensity of the NMR line when approaching the transition in the cubic phase may be attributed to this dynamical disorder. The order of magnitude of the relative displacements of fluorine and oxygen ions in fluoroperovskites and SrTiO_3 respectively, indicates that RbCaF_3 , with its large tilt angles, is one of the most suitable compounds to test the validity of Rousseau's model. To achieve this goal, measurements of the spin, spin-lattice relaxation time are in progress.

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