^{87}Rb nuclear-magnetic-resonance study of the cubic to tetragonal phase transition in $RbCaF_3$

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The static and dynamical phenomena occurring around the structural phase transition at $T_c \simeq 195.90 \pm 0.15$ K in $RbCaF_3$ have been investigated by means of ^{87}Rb Fourier-transform NMR measurements. The second-order shift of the central line due to the static quadrupole perturbation has been related to the electric field gradient arising at the Rb site below T_c and the temperature dependence of the angle of rotation ϕ of the CaF_6 octahedra has been obtained. The ^{87}Rb spin-lattice relaxation rate above T_c has been related to the rotational fluctuations of the octahedra induced by the critical-soft-mode branches, from which information on the symmetry and the anisotropy of the fluctuations are derived. The analysis of the results shows: (i) below $T \simeq 170$ K the temperature dependence of ϕ is well described by the classical mean-field approximation, with critical exponent $\beta = \frac{1}{2}$ and extrapolated transition temperature $T_0 = 220$ K; (ii) above about 170 K a nonclassical critical behavior is evidenced, the apparent critical exponent being not equal to $\frac{1}{3}$, suggesting a possible changeover in the dimensionality of the correlations of the rotations; (iii) the rotational fluctuations appear to be predominantly of R_{25} symmetry but strongly anisotropic, i.e., only slightly correlated in adjacent (100) planes as is consistent with the hypothesis of softening of a large portion of the R-M branch. Order-of-magnitude estimates for the static angle of rotation as well as for the degree of anisotropy of the fluctuations are also obtained and discussed.

I. INTRODUCTION

The cubic-to-tetragonal structural phase transition detected[1] in $RbCaF_3$ has attracted great attention in recent years. Optical birefringence,[1,2] Raman,[2–4] and neutron[5,6] scattering, specific heat,[1,7] EPR,[1,8] and x-ray diffraction[3] studies indicate that the transition involves the condensation of the R_{25} mode $(\pi/a, \pi/a, \pi/a)$, with nonclassical critical region down to about 175 K. For the critical exponent β for the generalized order parameter, i.e., the angle of rotation of the CaF_6 octahedra around a pseudocubic axis, while the expected value $\beta = \frac{1}{3}$ was claimed on the basis of Raman and x-ray diffraction measurements,[3] the birefringence data[2] imply a significant departure, β being close to 0.29. This departure, contrasting also with the value $\beta = 0.36$ and $\beta = 0.32$ found for the similar transitions in $SrTiO_3$,[9,10] and in $KMnF_3$,[11,12] respectively, was supposed[2,5] to be due to large anisotropic fluctuations.

Quadrupole-perturbed NMR spectra and the spin-lattice relaxation driven by the fluctuating part of the quadrupole interaction have been proved to be suitable tools to study static and dynamical phenomena occurring at the structural phase transitions in perovskites.[13] In particular, the second-order shift of the central ($\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition) NMR line due to the arising of a static electric field gradient at the resonant nucleus below T_c has been utilized[11,14] to obtain the temperature dependence of the order parameter. Spin-lattice relaxation-time measurements also have provided[14] valuable information on the symmetry and the anisotropy of the rotational fluctuations induced by the critical-soft-mode branches which drive the phase transitions.

Brief accounts of ^{19}F and ^{87}Rb spin-lattice relaxation measurements[15,16] and of the temperature dependence of the ^{87}Rb quadrupole coupling constant[17] have been reported earlier. In this paper the results of the high-field quadrupole resonance and relaxation measurements for the ^{87}Rb nucleus with high-temperature stability and high-frequency resolution are presented and discussed (Sec. II). From the analysis of the results in the light of the theoretical expressions which connect the quadrupole coupling constant to the order parameter ϕ and the relaxation rate to the amplitude and the decay rate of the rotational fluctuations, interesting information both on the static as well as on the dynamical critical phenomena accompanying the transition are obtained (Sec. III).

II. EXPERIMENTAL DETAILS AND RESULTS

The NMR measurements have been performed at 11 MHz by means of a pulse spectrometer, with Fourier transform (FT) in quadrature detection achieved by means of a Nicolet 1180 data processor system. The quadrature detection, allowing irradiation in resonance, avoided any line-shape distortion and/or broadening, improving the resolution. Furthermore, it was essential for reliable T_1 measurements. Free-induction decays after $\frac{1}{2}\pi$ pulses were averaged over 10^4 accumulations for the line-shift measurements close to T_c and over 10^2 accumulations for the T_1 measurements in the cubic phase. The long-term temperature stability was about 10^{-2} K. The temperature was measured by means of a standardized Pt resistance thermometer with resolution around 10^{-2} K. The temperature gradients at the sample were estimated to be negligible ($\leq 10^{-2}$ K).

The single crystal of $RbCaF_3$ (kindly provided by F. A. Modine, Oak Ridge National Laboratory) was oriented with a cubic axis parallel to the external magnetic field for the T_1 measurements above T_c, while for the line-shift measurements below T_c it was oriented with $\vec{a} \perp \vec{H}_0$ and with $\vec{b}$ axis at approximately 45° from $\vec{H}_0$, in order to improve the resolution (see below).

As a consequence of the rotations of the CaF_6 octahedra below T_c, a nonzero time-averaged electric field gradient (EFG) arises at the Rb site. By expanding the EFG in terms of the atomic displacements of the surrounding atoms induced by the freezing-in of the R_{25} mode, one derives

$$V_{ZZ} = A\phi^2, \quad V_{XX} = V_{YY} = -\tfrac{1}{2} V_{ZZ} , \tag{1}$$

and $\vec{Z} \parallel \vec{c}$, where $\vec{c}$ is the pseudocubic axis around which the octahedra rotate by an angle ϕ. In Eq. (1) A includes the effect of the slight tetragonal distortion of the cell, since the a/c ratio is approximately $a/c \simeq 1 - \frac{1}{2}\phi^2$.

Below the transition temperature the first-order static quadrupole interaction on the Zeeman levels shifts the satellite lines ($\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$ transitions) far from the Larmor frequency ν_L, and they could hardly be detected probably because of strain broadening. The transition temperature was located from the disappearance of the contribution of the satellite transition to the resonance line. A drop of the signal intensity to about 40% was observed. Furthermore, in order to obtain such an intensity, a readjustment of the pulse length maximizing the signal was necessary. A decrease of about 50% was needed in accordance with the density-matrix theory[18] for the pulse response in the presence of quadrupole splitting. The transition temperature was found to be $T_c = 195.9 \pm 0.15$ K, in very good agreement with the temperature at which a cusp was observed in the birefringence measurements,[2] which should mark the transition.[19]

In the second order, the quadrupole interaction induces a shift of the central line ($+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition). For $I = \frac{3}{2}$ the shift is

$$\Delta\nu = -(3\nu_Q/16\nu_L)(1-\cos^2\theta)(9\cos^2\theta - 1) , \tag{2}$$

where $\nu_Q = eQV_{ZZ}/2h$ is the quadrupole coupling constant and θ is the angle between the Z axis and $\vec{H}_0$. Because of the three domains with different orientations of the tetragonal $\vec{c}$ axis, three central lines are observable, in general. According to Eq. (2), for a cry-

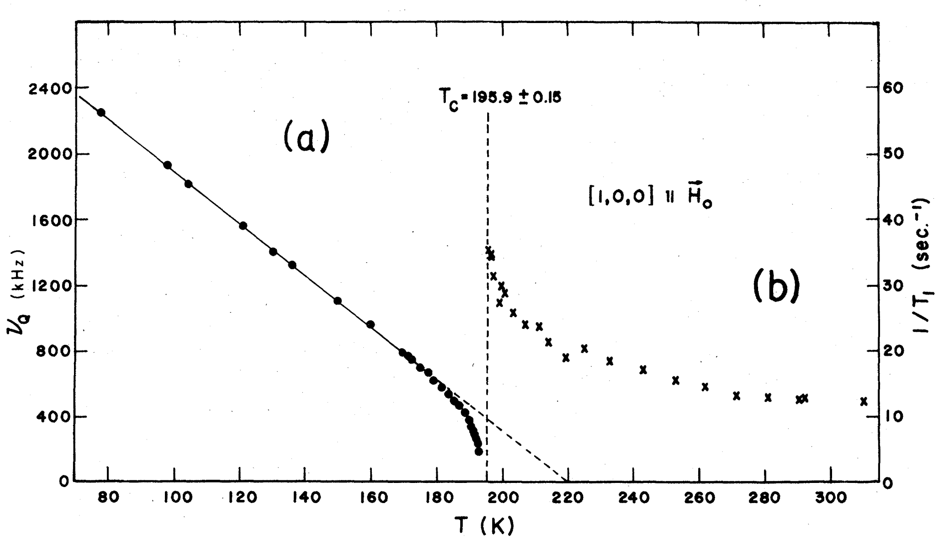

FIG. 1. (a) ^{87}Rb quadrupole coupling constant $\nu_Q = eQV_{zz}/2h$ (●) and (b) spin-lattice relaxation rate (×) in $RbCaF_3$ as a function of temperature.

stal with one pseudocubic axis perpendicular to $\vec{H}_0$ and another at 45°, two lines are observed with intensity ratio 1:2, the frequency separation between the two lines being close to the maximum attainable, namely, 2.75 $(3\nu_Q^2/16\nu_L)$. From this frequency separation the quadrupole coupling constant was derived as a function of temperature. The results are shown in Fig. 1(a). Within the limits of resolutions which could be achieved, the transition appears to be almost second order.

The ^{87}R spin-lattice relaxation measurements[16] have been extended closer to the transition temperature. Standard $\frac{1}{2}\pi$-t-$\frac{1}{2}\pi$ pulse procedure, with FT in quadrature, of the second FID (free-induction-decay) signal was used. The results are shown in Fig. 1(b).

III. DISCUSSION

The measurements of the quadrupole coupling constant ν_Q allow us to extract the temperature dependence of the generalized order parameter ϕ and to estimate its order of magnitude.

In the light of Eq. (1) and Fig. 1(a) one notes that up to about 170 K the angle of rotation is characterized by a classical mean-field (MFA) behavior, with a critical exponent $\beta=0.5$ and an extrapolated transition temperature $T_0 \simeq 220$ K. For $\geqslant 175$ K, i.e., for a reduced temperature $\epsilon=(T_c-T)/T_c \leqslant 10^{-1}$ a departure is observed indicating a nonclassical critical region, with the breakdown of the MFA. An attempt to fit the data in this region according to a law $\nu_Q^{1/2} \propto \phi \propto \epsilon^{1/3}$ puts in evidence a significant departure. As shown in Fig. 2 (a) a better fit is obtained, if for the critical exponent an apparent value $\beta=0.275$ is chosen, close to the value 0.29 as suggested by the birefringence measurements. As we shall see later on, the T_1 measurements in the cubic phase strongly support the hypothesis of anisotropic rotational fluctuations of the CaF_6 octahedra already suggested by a line of soft phonons from M_3 to R_{25} observed by means of neutron scattering. If the correlation between the rotations of the octahedra in adjacent (100) planes are not so strong, a tendency towards the two-dimensional system is present and close to T_c this can induce an apparent β lower than the expected $\frac{1}{3}$. It can be observed that in $NaNbO_3$, for the similar structural transition occurring at 914 K, with strong anisotropic fluctuations,[14] a critical exponent clearly less than 0.33, possibly close to the value 0.125 corresponding to the theoretical prediction for planar Ising models, was obtained.

Taking into account only the nearest-neighbor contribution, in a point-charge approximation, the value of A in Eq. (1) results in

$$A=30e(1-\gamma_\infty)a^{-3} \ ,$$

where γ_∞ is the antishielding factor. Assuming for the quadrupole moment of the ^{87}Rb nucleus $Q=0.13\times10^{-24}$ cm^2 and for γ_∞ the value 51 pertaining to the Rb^+ ion one has

$$\phi=0.15\nu_Q^{1/2} \text{ rad } \ (\nu_Q \text{ in MHz}) \ .$$

Therefore the angle of rotation for $T=77$ K would turn out to be $\simeq 12°$. This value is large compared to 7.4° from x-ray and neutron-diffraction measurements[21] and 7.1° obtained from the V_k-center ESR measurements.[8] It is to be noted that while obtaining the relation $V_{ZZ} \approx A\phi^2 \approx 30ea^{-3}(1-\gamma_\infty)$, the contributions of the neighbors farther from the nearest have been neglected. Including that as well as the tetragonal distortion gives $\phi \simeq 10^0$.

Let us now discuss the ^{87}Rb T_1 measurements. In the cubic phase the Zeeman levels are equally spaced and the condition of a common spin temperature holds. Then one can write

$$T_1^{-1}=A[\mathcal{J}_1(\omega_0)+4\mathcal{J}_2(2\omega_0)] \ , \qquad (3)$$

where

$$A=(2I+3)e^2Q^2/40I^2(2I-1)h^2=e^2Q^2/30h^2$$

and $\mathcal{J}_1$ and $\mathcal{J}_2$ are the spectral densities of the well-known V_1 and V_2 EFG functions. These spectral densities can be evaluated, in the framework of a classical lattice, by expanding the V_{PQ} EFG components in the crystalline frame of reference, as a function of the instantaneous atomic displacements associated with the three critical branches to which the zone-boundary soft modes belong.[22] In the condition of fast motions, one then derives

$$T_1^{-1}=\left(\frac{A}{N}\right)\int d\vec{q}\,\langle|\phi_{\vec{q}}|^2\rangle 2\Gamma_{\vec{q}}^{-1}(\mathcal{A}_{\vec{q}}^{1}+4\mathcal{A}_{\vec{q}}^{2}) \ , \qquad (4)$$

where $\langle|\phi_{\vec{q}}|^2\rangle$ and $\Gamma_{\vec{q}}$ are the mean-square amplitude and the decay rate of the collective rotational fluctuations induced by the soft modes. The expressions for the $\mathcal{A}_{\vec{q}}^{1,2}$ factor for a single crystal oriented with a cubic axis along the external magnetic field give

$$\mathcal{A}_{\vec{q}}^{1}+4\mathcal{A}_{\vec{q}}^{2}=(\tfrac{1}{2}E)[\cos(q_{Bz}+q_z)a+1] \times[51-17(\cos q_x a+\cos q_y a) -13\cos(q_x-q_y)a] \ , \qquad (5)$$

where in a point-charge, nearest-neighbor approximation, E is given by $E=144e^2(1-\gamma_\infty)^2/a^6$. $\vec{q}_B=(\pi/a,\pi/a,q_{Bz})$ is the zone-boundary critical wave vector. Note that for the R_{25} wave vector ($q_{Bz}=\pi/a$, $q_x=q_y=q_z=0$) one has $\mathcal{A}_{\vec{q}}^{1}+4\mathcal{A}_{\vec{q}}^{2}=0$. In the q integration in Eq. (4) we will assume the anisotropic Ornstein-Zernike-type expression

$$\langle|\phi_{\vec{q}}|^2\rangle=\langle|\phi_{\vec{q}_c}|^2\rangle\kappa^2[q^2-(1-\Delta)q_z^2+\kappa^2]^{-1} \ , \qquad (6)$$

where $\kappa=\kappa_0\epsilon^\gamma$ is the inverse correlation length, with the thermodynamical slowing down condition $\Gamma_{\vec{q}} \propto (\langle|\phi_{\vec{q}}|^2\rangle)^{-1}$. The parameter Δ in Eq. (6) takes into account[23] the possible anisotropy in the rotational fluctuations, related to the softening of a large part of the R-M branch at the zone boundary ($\Delta=1$ for pure R_{25} mode, i.e., three-dimensionally correlated rotational fluctuations, and $\Delta=0$ for the limiting case of fluctuations correlated only in a plane, with softening of the whole R-M branch). The capability of Eq. (6) to take into account the anisotropy is also supported by the analogous form for the susceptibility of an anisotropic Heisenberg antiferromagnet.[24]

A straightforward integration in cylindrical coordinates of Eq. (6), taking into account Eqs. (5) and (4), with q starting from the zone boundary, gives the following results. For $\Delta=1$

$$T_1^{-1} = (AE\langle\phi_0^2\rangle\kappa_0^4a^2/6\pi^2\Gamma_0N)\{(5\kappa^3a^2-3\kappa)\arctan(q_m/\kappa) + [2q_m^5a^2+(6-15\kappa^2a^2)q_m^3+(g\kappa^2-15\kappa^4a^2)q_m]/3(q_m^2+\kappa^2)\} \quad (7)$$

For $\Delta \neq 1$, a more complicated expression is obtained for the relaxation rate. For $\Delta \ll 1$ such that the approximation $\arctan\sqrt{\Delta} \simeq \sqrt{\Delta}$ can be made after the integration over the cylindrical coordinate z, the leading term results in

$$T_1^{-1} \simeq (AE\langle\phi_0^2\rangle\kappa_0^4a^2/4\pi^2\Gamma_0)(q_m/\Delta) \times \ln(q_m^2+\kappa^2)/\kappa^2 \ , \quad (8)$$

where the maximum value of the wave vector in the integration is $q_m \simeq 3.55a^{-1}$. ϕ_0 and κ_0 are the quantities in absence of the interactions.

In Fig. 2(b) the temperature behavior of the relaxation rate according to Eqs. (7) and (8) are reported and compared with the experimental results for $RbCaF_3$ and $SrTiO_3$. The comparison clearly evidences that the quite significant difference in the temperature dependence of the relaxation rates can be explained only by assuming for $RbCaF_3$, $\Delta \ll 1$.

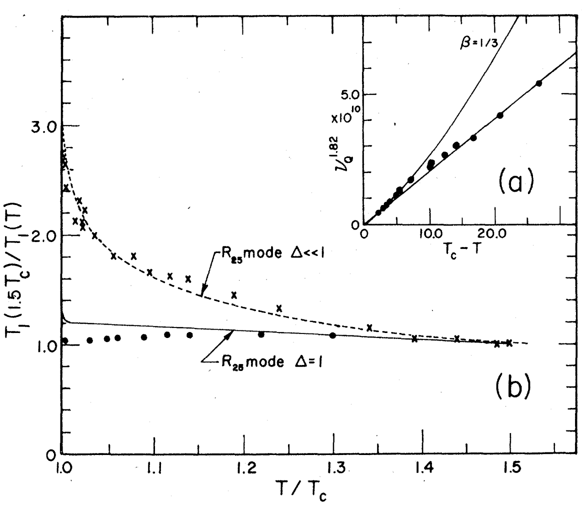

FIG. 2. (a) Comparison of the quadrupole coupling constant ν_Q as a function of T_c-T with the expected behavior for a critical exponent $\beta=0.275$ [as indicated by a least-square fitting of the data in Fig. 1(a)] and for $\beta=\frac{1}{3}$. (b) Temperature behavior of the relaxation rate for a pure R_{25} mode and for softening of a large portion of the R-M branch ($\Delta \ll 1$), normalized to the experimental value at $T=1.5T_c$ according to the Eqs. (7) and (8) in the text and comparison with the experimental results: ($\times$) ^{87}Rb in $RbCaF_3$, present work, and ($\bullet$) ^{87}Sr in $SrTiO_3$, Ref. 20.

As regards the order of magnitude of the absolute values of the relaxation rates, from Eqs. (7) and (8), for $T\simeq 1.2T_c$ one has

$$R = \frac{(T_1^{-1})_{RbCaF_3}}{(T_1^{-1})_{SrTiO_3}} \simeq 6\frac{1}{\Delta}\left(\frac{\phi_0^2}{\Gamma_0}\right)_{RbCaF_3}\Bigg/\left(\frac{\phi_0^2}{\Gamma_0}\right)_{SrTiO_3} \quad (9)$$

(having assumed for $SrTiO_3$ $Q=0.3\times10^{-24}$ cm^2 and $\gamma_\infty=-30$). Since the quantity ϕ_0^2/Γ_0 is expected to be of the same order of magnitude for both crystals, Eq. (9) puts in evidence that the experimental value for the ratio of the ^{87}Rb and ^{87}Sr relaxation rates, namely, $R\simeq 15$ sec^{-1}/0.1 sec^{-1} is justified by a value of $\Delta \ll 1$, typically $\Delta \sim \frac{1}{25}$.

Therefore, both from the temperature dependence of the relaxation rates as well as from their actual values, an independent indication is obtained that in $RbCaF_3$ the rotational fluctuations are strongly anisotropic.

IV. CONCLUSIONS

The ^{87}Rb quadrupole perturbed NMR spectra and the spin-lattice relaxation-time measurements through FT in quadrature detection have been utilized to study the cubic to tetragonal phase transition in $RbCaF_3$. The static electric field gradient at the Rb site extracted from the measurements of the second-order shift of the central line indicates a large value for the angle ϕ of rotation of the CaF_0 octahedra ($\phi \simeq 10°$ at 77 K). The temperature dependence of the order parameter ϕ, in the range 77–170 K, is found to be well described by the MFA with critical exponent $\beta=\frac{1}{2}$ and extrapolated transition temperature $T_0\simeq 220$ K. From about 170 K to the actual transition temperature $T_c=195.9\pm0.15$ K the results show a nonclassical critical behavior of ϕ with the breakdown of MFA. Moreover, in this region, the data could not be explained by a power law of the form $\nu_Q^{1/2} \propto \phi \propto \epsilon^{1/3}$ as would be expected for three-dimensionally correlated rotations induced by the freezing in of the soft mode of R_{25} symmetry and as is approximately observed for similar transitions in $SrTrO_3$,[10] $LaAlO_3$,[25] and $KMnF_3$.[11] A least-square analysis of the data gives an apparent exponent $\beta=0.275$ close to the value $\beta=0.29$ inferred by birefringence measurements. This lower than $\frac{1}{3}$ value of β suggests the presence of two-dimensional correlation of the fluctuations, rotations in adjacent (100) planes being not completely correlated. This hypothesis is further supported by the ^{87}Rb spin-lattice relaxation measurements which indicate strongly anisotropic rotational fluctuations. The relaxation rates in fact have been theoretically related to the rotational fluctuations induced by the critical branch to which the soft modes belong. From the comparison of experimental and theoretical temperature behaviors of ^{87}Rb relaxation with those of $SrTiO_3$ it is concluded that while the predominant symmetry of the rotational fluctuations is R_{25}, they show strong anisotropy, namely, only slightly correlated in adjacent (100) planes. The order of magnitude of the anisotropy parameter has been estimated to be $\frac{1}{25}$.

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