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THE 193 K PHASE TRANSITION IN RbCaF_3 : II. CRITICAL NEUTRON SCATTERING

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Résumé. — Des spectres de diffusion inélastique des neutrons, à Q constant, ont été effectués, avec une très bonne résolution, près de la transition de phase $O_h^1 \rightarrow D_{4h}^{18}$ à 193 K dans RbCaF_3 . Nous avons observé un pic central dont l'intensité varie considérablement en fonction de la température, à $\mathbf{q} = \mathbf{q}_R$. Nous avons mesuré les paramètres λ_1 , λ_2 et λ_3 qui caractérisent l'anisotropie des nappes de dispersion près du mode R_{25} à différentes températures. En tenant compte de l'importante anisotropie des facteurs de structure dynamiques des 3 modes issus du mode mou R_{25} , nous avons déterminé les 4 paramètres inconnus (A , ω_∞^2 , Γ , δ^2) de la fonction de réponse utilisée par Shapiro *et al.* dans l'étude de SrTiO_3 en ajustant les courbes calculées aux courbes expérimentales. Nous donnons les courbes de variation de ω_∞^2 et de δ^2 en fonction de la température ; δ^2 décroît quand $(T - T_c)$ croît. Sur la base de nos résultats, nous discutons de la validité de la dépendance en $\mathbf{q}$ et T de la fonction de réponse.

Abstract. — High resolution inelastic neutron scattering constant Q scans have been performed near the 193 K cubic (O_h^1) to tetragonal (D_{4h}^{18}) phase transition in RbCaF_3 . A divergent temperature dependent central peak was observed at $\mathbf{q} = \mathbf{q}_R$. The parameters λ_1 , λ_2 and λ_3 characterizing the anisotropy of the dispersion map in the vicinity of the R_{25} mode have been measured at different temperatures. Taking into account the large anisotropy of the dynamical structure factors of the 3 modes belonging to the R_{25} soft mode, the 4 unknown parameters (A , ω_∞^2 , Γ , δ^2) of the spectral response used by Shapiro *et al.* in SrTiO_3 were determined by fitting the calculated scans with the experimental ones. The temperature dependence of ω_∞^2 and δ^2 is reported ; δ^2 is found to decrease when $(T - T_c)$ increases. The validity of the $\mathbf{q}$ and T dependence of the spectral response function is discussed on the basis of our results.

1. Introduction. — The observation of a temperature dependent central peak centered around $\omega = 0$ in addition to the soft phonon sidebands was first mentioned in 1971 by Riste *et al.* [1] in the study of SrTiO_3 . Since that time this behaviour has been extensively studied, particularly in some perovskite type compounds such as SrTiO_3 [2], LaAlO_3 [3] and KMnF_3 [2]. One of the main problems in the interpretation of this unexpected phenomenon is to detect

whether it is an intrinsic effect or if it is due to impurities [4].

In KMnF_3 , the overdamped nature of the phonons prevented detailed studies. So in the perovskite structure quantitative information is available only for ABO_3 compounds. Therefore, until to-day it has been impossible to compare the central peak behaviour of ABO_3 and AMF_3 perovskite in which the possible defects should be different. The purpose of the present work is twofold : to provide quantitative description of the soft phonon and central peak parameters for an overdamped system, and to study the central peak behaviour in a fluoperovskite compound.

The organization of the present paper is as follows.

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The experimental conditions of the inelastic neutron scattering experiments are described in section 2. In order to minimize the number of fitted parameters in the deconvolution process we have measured the anisotropy of the phonon dispersion surface around the R_{25} mode at different temperatures (section 3). Then, taking into account the strong anisotropy of the dynamical structure factors of the three modes belonging to the R_{25} soft mode, we were able to analyse our data with the same spectral response function as used by Shapiro *et al.* in SrTiO_3 . Finally, in section 4 these results are discussed and compared with those of Shapiro *et al.* for SrTiO_3 .

2. Experimental. — We have grown a single crystal of RbCaF_3 by the Bridgman-Stockbager technique with a temperature gradient of $8^\circ/\text{cm}$ inside the furnace and a vertical displacement of the sample of 15-20 mm per 24 hrs [5]. The crystal obtained had a volume of 2 cm^3 and its mosaic spread was less than $3'$ of arc.

First inelastic neutron scattering measurements were carried out on the H4 spectrometer at the Saclay reactor. Then most of the data were taken on the IN2 thermal-beam three axis spectrometer at the I.L.L. high flux reactor. Incident energies of 15 and 5 meV were used with pyrolytic graphite (002) monochromators. Higher-order contamination was reduced to a negligible level using a pyrolytic graphite filter at the higher energy and a cooled beryllium filter at the lower energy combined with a Ge (111) as analyser. The contribution from the incoherent scattering was measured and subtracted from all the data. The parameters of the resolution ellipsoid were fully determined experimentally, then the collimations were adjusted by fitting the calculated resolution function with the experimental one.

In the classical (*hhl*) scattering plane some interesting modes cannot be observed, so in order to determine the curvatures of the phonon dispersion surface in the vicinity of the R_{25} mode in the R-X, R-M and R- Γ directions, the data were collected in the two scattering planes described in figure 1. The crystal was mounted so that it was possible to pass from one plane to the other by rotating the crystal around a $[311]$ horizontal axis.

The specimen temperature was controlled to within 0.03°K but we could not avoid the occurrence of a small vertical gradient.

3. Results. — **3.1 DISPERSION BRANCHES ALONG THE R-M LINE.** — Room temperature measurements of the low energy branches along the R-M line were performed on the 3-axis spectrometer IN8 (ILL). The experimental points represented on figure 2 are peak positions. Owing to the large damping of the T_2 mode (and T_5 in the neighbourhood of the R point) the peak positions are lower than the corresponding quasi-harmonic frequencies; the change is of the

FIG. 1. — Representation of the two scattering planes in reciprocal space used in this study.

FIG. 2. — Low-energy phonon dispersion curves along the R-M line in RbCaF_3 at 295 K. (All these data are derived from the peak position of the scans.) The solid curves show the calculated dispersion (former paper).

order of 0.2 THz (0.82 meV). The T_2 and T_5 phonon branches are very similar in KMnF_3 and RbCaF_3 . In these two crystals the first branch is nearly flat while the T_5 branch presents a strong curvature.

3.2 PHONON DISPERSION SURFACE AROUND THE R_{25} MODE. — The knowledge of both the dynamical structure factors of the mode (first part of this work) and the resolution function enables us to choose the points of the reciprocal lattice where a phonon of a given symmetry must be intense and well focussed. Taking into account measurements in the P_1 and P_2 scattering planes previously defined, we were able to determine the curvature of the modes A_2 , A_3 , T_2 , T_5 , S_1 , S_2 and S_3 near the R_{25} mode, at different temperatures. From these, we deduced the values of λ_1 , λ_2 , λ_3 and their temperature dependence (Table I).

TABLE I

Experimental values of the λ_i at different temperatures in RbCaF_3

T K	195	201	208	237	254	275	293
λ_1	15	15	14	13	12.5	11	$10.5 \pm 5 \text{ meV}^2 \text{ \AA}^2$
λ_2	895	887	875	820	791	760	$\pm 120 \text{ meV}^2 \text{ \AA}^2$
λ_3	-382	-385	-386	-392	-395	-400	$\pm 100 \text{ meV}^2 \text{ \AA}^2$

The determination of the curvature of the mode is not easy because it is strongly dependent on the position of the R_{25} phonon which is itself dependent on λ_1 , λ_2 and λ_3 so we had to use a self-consistent method. λ_1 , λ_2 and λ_3 measured in this way are somewhat different from the calculated ones (former paper) but we may notice that the measured values are taken at $|\mathbf{q} - \mathbf{q}_R| \simeq 0.1 \mathbf{q}_R$ whereas the calculated values are derived from the limit $(\mathbf{q} - \mathbf{q}_R) \rightarrow \mathbf{0}$. Some scans used for the λ_i determination at $T = 254 \text{ K}$ are shown in figure 3.

FIG. 3. — Typical energy profiles of some phonons used in the experimental determination of λ_1 , λ_2 and λ_3 at 254 K. The black points are measured values; the dotted lines represent the best fitting cross section $(S(\mathbf{q}, \omega) |F_j(\mathbf{Q})|^2)$ which is broadened by instrumental corrections to give the solid lines.

3.3 SOFT PHONON AND CENTRAL PEAK. — High-resolution constant Q scans were made at the $(0.5 - 0.5 1.5)$ R point of the P_1 scattering plane and at the $(1.5 0.5 0.5)$ R point of the P_2 scattering plane. Figure 4 shows a part of these measurements. We may

FIG. 4. — Constant Q scans at the R point of the cubic Brillouin zone at several temperatures showing the narrow divergent central peak superimposed upon the broader overdamped phonon component.

notice that a divergent central peak rises out of the broad overdamped phonon as in KMnF_3 [2]. The linewidth of the observed central peak (FWHM ~ 0.025 to 0.03 THz) is always smaller than the resolution width given by the vanadium (FWHM = 0.04 THz).

We analysed these data with the same spectral response of a soft mode $\begin{pmatrix} \mathbf{q} \\ j \end{pmatrix}$ as used by Shapiro *et al.* for SrTiO_3 [2] :

$$S(\mathbf{q}, \omega) = \frac{k_B T}{\pi} \left[\frac{\Gamma_0}{(\omega_\infty^2(\mathbf{q}, T) - \omega^2)^2 + \omega^2 \Gamma_0^2} + \frac{\delta^2(T)}{\omega_0^2(\mathbf{q}, T) \omega_\infty^2(\mathbf{q}, T)} \frac{\gamma'}{\omega^2 + \gamma'^2} \right]$$

We recognize in the first term the familiar damped harmonic oscillator response where

$$\omega_0^2(\mathbf{q}, T) = \omega_\infty^2(\mathbf{q}, T) - \delta^2(T)$$

is the square of the renormalized mode frequency in the limit $\omega \rightarrow 0$, whereas $\omega_\infty(\mathbf{q}, T)$ is the quasi-harmonic frequency of the mode. The second term represents an extra response of the phonon fluctuations (central peak).

Since the observed energy linewidth of the central peak was always resolution limited, we consider the central peak as a delta function. So we replace $\frac{\gamma'}{\omega^2 + \gamma'^2}$ by $f(\omega)$ with $f(\omega) = 0$ for $\omega \neq 0$ and $f(\omega) = C$ for $\omega = 0$. The constant C was fixed at π by normalization.

On these bases, and provided that the δ^2 parameter is not a function of $\mathbf{q}$ the entire $\mathbf{q}$ dependence of $S(\mathbf{q}, \omega)$ is determined by the $\mathbf{q}$ dependence of the phonon frequency given by

$$\omega_\infty^2(\mathbf{q}, T) = \omega_\infty^2(0, T) + A_f(\mathbf{n}, T) |\boldsymbol{\eta}|^2 \quad \boldsymbol{\eta} = \boldsymbol{\eta}\mathbf{n}$$

where $A_f(\mathbf{n}, T)$ are the eigenvalues of the $\underline{A}(\mathbf{n})$ matrix (defined in the first part of this work) in which λ_1 , λ_2 and λ_3 are temperature dependent (Table I). Both model calculation and experimental determination of the λ_i show that λ_3 is not negligible. So in order to take into account the large anisotropy of the dynamical structure factor around the R_{25} mode, we did not use the simplification outlined by Shapiro *et al.*

Then, for each setting of the spectrometer ($\mathbf{q}_0, \omega$) the neutron intensity can be calculated by analytically performing the convolution of the scattering cross section with the four-dimensional resolution function $R(\mathbf{q} - \mathbf{q}_0, \omega - \omega_0)$ previously discussed in detail by Cooper and Nathans [6] and Dorner [7].

$$I(q_0, \omega_0) = A \iint \sum_{j=1}^3 |F_j(\mathbf{Q})|^2 S\left(\frac{\mathbf{q}}{j}, \omega\right) \times R(\mathbf{q} - \mathbf{q}_0, \omega - \omega_0) d\mathbf{q} d\omega.$$

In this expression, A is a normalization constant and according to Dorner, $R(\mathbf{q} - \mathbf{q}_0, \omega - \omega_0)$ includes the ratio k_f/k_i (k_i and k_f are respectively the initial and final values of the wave vector of the neutrons). In the course of the integration, the dynamical structure factor $F_j(\mathbf{Q})$ was calculated, for each $\mathbf{q}$, by diagonalizing the $\underline{A}(\mathbf{n})$ matrix.

The 4 unknown parameters A , $\omega_\infty^2(0, T)$, Γ_0 and $\delta^2(T)$ were determined by fitting the calculated scans with the experimental ones corrected by subtracting the background and the incoherent scattering. In a first step, A , $\omega_\infty^2(0, T)$ and Γ_0 are determined between 250 K and 300 K, with incident neutron beam of

15 meV, in the domain where no contribution of the central peak was observed. As expected, we obtained values of A and Γ_0 without any significant temperature dependence. Some typical scans are shown in figure 5a. Thus we take :

$$\Gamma_0 = 3.55 \text{ meV}.$$

Then at lower temperature, for the high resolution scans, Γ_0 was fixed and we determined A and $\omega_\infty^2(0, T)$ by fitting the phonon wings of the scans. Finally, once A , $\omega_\infty^2(0, T)$ and Γ_0 are known, $\delta^2(T)$ was calculated from the central peak alone (Fig. 5b).

Figure 6 shows the temperature dependence of δ^2 and ω_∞^2 obtained by this method. The uncertainty in the determination of these parameters is partly due to the fluctuations of the normalization parameter A from its mean value $\langle A \rangle$. From these curves, we conclude that for $T - T_c > 57$ K, δ^2 may be taken as equal to zero. In order to confirm this result, we have done a high resolution constant Q scan at the (0.5 - 0.5 1.5) R point for $T - T_c = 62$ K. As expected, we did not observe any narrow peak around $\omega = 0$ (Fig. 5b).

4. Discussion. — In spite of the fact that the phonon is overdamped for $T - T_c < 70$ K, the method of treating the data described in section 3.3 seems to give reliable results for $T - T_c > 10$ K. As previously observed by Shapiro *et al.* in SrTiO_3 [2], the temperature dependence of $\omega_\infty^2(0, T)$ exhibits two different behaviour patterns. For $T > 250$ K, where no central peak is observed, the temperature dependence of the frequency obeys the following relation

$$\omega_\infty^2(0, T) = a(T - T_0)$$

with $a = 0.13 \pm 0.05 \text{ meV}^2/\text{K}$ and $T_0 = 212 \pm 2 \text{ K}$. In this mean-field region, we may notice that the temperature dependence of RbCaF_3 and KMnF_3 are similar ($a = 0.11 \pm 0.02 \text{ meV}^2/\text{K}$ for KMnF_3) whereas it is somewhat different in SrTiO_3 ($a = 0.19 \text{ meV}^2/\text{K}$ [2]).

On the other hand, $\omega_\infty^2(0, T)$ deviates from a linear temperature behaviour for $T - T_c < 57$ K, in the region where the central peak is observed. So we may conclude that the critical behaviour of $\omega_\infty^2(0, T)$ is strongly related to the occurrence of a central peak.

With respect to the central peak, the main result of our work consists in the temperature dependence of δ^2 which is drastically different from the one obtained in SrTiO_3 by Shapiro *et al.* In fact, our investigations lead us to conclude that this behaviour depends on the way of performing the deconvolution. In our case, when neglecting λ_3 , $\omega_\infty^2(0, T)$ is lowered by about 1 meV^2 and the temperature dependence of δ^2 becomes nearly the same as in SrTiO_3 . It is worth noticing that RbCaF_3 is the first example in which δ^2 decreases when $(T - T_c)$ increases. This type of behaviour was recently predicted theoretically by

Halperin and Varma [4] in considering defects as a cause of the central peak. Nevertheless, the model of Halperin and Varma predicts $\delta^2 \propto 1/T$ whereas the present results indicate a value of δ^2 which decreases much more rapidly with T .

The satisfactory agreement between the calculated scans represented by full lines and the experimental data (Fig. 5) is a good test for the validity of the response function $S(\mathbf{q}, \omega)$ in which the soft mode damping Γ_0 is temperature independent. In order to test the assumption according to which δ^2 is independent of $\mathbf{q}$, we have done several constant $\omega = 0$ scans around the R point in the R-X and R-M directions, at different temperatures. For a given mode j belonging to the R_{25} mode, the $\mathbf{q}$ linewidth of the central component response function is proportional to $|A_j(\mathbf{q}, T)|^{-1/2}$. Owing to the triple degeneracy of the R_{25} soft mode these scans are not easily interpreted. In fact, the scan along R-M ($\mathbf{Q}_R = 1.5 \ 0.5 \ 0.5$), $T = 210 \text{ K}$ is a sum of two contributions :

$$T_2 (\Lambda = 14 \text{ meV}^2 \text{ \AA}^2, |F(\mathbf{Q})|^2 = 1)$$

and

$$T_5 (\Lambda = 875 \text{ meV}^2 \text{ \AA}^2, |F(\mathbf{Q})|^2 = 1)$$

whereas the scan along R-X is a sum of three contributions : $S_1 (\Lambda = 638 \text{ meV}^2 \text{ \AA}^2, |F(\mathbf{Q})|^2 = 0.5)$,

$$S_2 (\Lambda = 875 \text{ meV}^2 \text{ \AA}^2, |F(\mathbf{Q})|^2 = 1)$$

and

$$S_3 (\Lambda = 252 \text{ meV}^2 \text{ \AA}^2, |F(\mathbf{Q})|^2 = 0.5).$$

So, we immediately see that in spite of the weak q dependence of the very low frequency T_2 branch we observe, on the $\omega = 0$ scan in the R-M direction, a narrow peak centered at $\mathbf{q} = \mathbf{q}_R$ due to the contribution of the strongly q dependent T_5 mode. Thus, the q width of these scans cannot be simply related to the q extension of the central peak. As an example cons-

FIG. 5. — Scattered neutron spectra of RbCaF_3 at several temperatures. The full lines represent the fitted scans, the dashed curve is a plot of the spectral response $S(\mathbf{q}_R, \omega)$ and the dotted line represents the level of the room background. All incoherent scattering has been subtracted. a) Soft phonon profiles obtained with $k_1 = 2.672 \text{ \AA}^{-1}$. b) Typical high resolution critical scattering spectra profile.

FIG. 6. — Temperature dependence of ω_0^2 and δ^2 in RbCaF_3 .

tant $\omega = 0$ scans along the R-M line are given in figure 7 for two different temperatures. The dash lines are not obtained from a deconvolution but simply represent the quantity

$$\sum_j S\left(\mathbf{q}_j, 0\right) \left| F_j(\mathbf{Q}) \right|^2$$

where the structure factors are calculated from the model described in the former paper. Moving away from the transition temperature (from $T = 195$ K to $T = 210$ K) the $\mathbf{q}$ width of the central peak is broaden-

FIG. 7. — Scattering at zero energy transfer along a $|001|$ reciprocal rod. The dashed curve is a plot of the cross section

$$\sum_j \left| F_j(\mathbf{Q}) \right|^2 S\left(\mathbf{q}_j, 0\right).$$

ed by the T_2 mode. This change is qualitatively reproduced by the calculated curve but complete quantitative agreement is clearly not obtained by means of this too simple calculation and we are going to deconvolute these scans in order to come to a conclusion about the $\mathbf{q}$ dependence of δ^2 .

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