The 193 k phase transition in RbCaf₃: I lattice dynamics

M Rousseau, J. Nouet, R. Almairac

► To cite this version:

M Rousseau, J. Nouet, R. Almairac. The 193 k phase transition in RbCaf₃: I lattice dynamics. Journal de Physique, 1977, 38 (11), pp.1423-1428. 10.1051/jphys:0197700380110142300 . jpa-00208714

HAL Id: jpa-00208714

<https://hal.science/jpa-00208714>

Submitted on 1 Jan 1977

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
 63.20 — 64.70K

THE 193 K PHASE TRANSITION IN RbCaF_3 : I LATTICE DYNAMICS

M. ROUSSEAU and J. NOUET

Laboratoire de Physique de l'Etat Condensé (*), Faculté des Sciences, 72017 Le Mans Cedex, France

R. ALMAIRAC (**)

Institut Max Von Laue-Paul Langevin, Cedex n° 156, 38042 Grenoble, France

(Reçu le 3 mai 1977, accepté le 12 juillet 1977)

Résumé. — Le carré de la fréquence du phonon mou R_{25} a été calculé en fonction des constantes de force interatomiques d'un modèle à ions rigides. Nous donnons les expressions analytiques des paramètres λ_1 , λ_2 et λ_3 qui caractérisent l'anisotropie des courbes de dispersion des phonons autour du mode R_{25} . Les courbes de dispersion des phonons de basse énergie que nous avons calculées sont comparées avec les données expérimentales existantes. Tous ces résultats sont discutés en terme de rotation des octaèdres CaF_6 .

Abstract. — The squared frequency of the R_{25} soft mode is calculated as a function of the interatomic force constants of a rigid ion model. Analytical expressions of the parameters λ_1 , λ_2 and λ_3 characterizing the anisotropy of the dispersion surface near the R_{25} mode are given. The calculated low frequency dispersion branches are compared with the available experimental data. All these results are discussed in terms of CaF_6 octahedron rotations.

1. Introduction. — Much experimental and theoretical work has been devoted to solid-solid phase transitions and special attention has been paid to the so-called *central peak*. Presently, this behaviour is still an exciting subject for research since no completely satisfactory theory has been proposed. The perovskite structure with its well known central peak in SrTiO_3 [1], KMnF_3 [1] and LaAlO_3 [2] is very fruitful in this domain. In fact, the perovskite structure is certainly the simplest structure in which this unexpected behaviour has been observed. Therefore we have focused our attention on the fluoperovskites of general formula AMF_3 [3] and specially ACaF_3 where A is a monovalent ion. In this sequence of compounds, CsCaF_3 is still cubic at 4 K [4], RbCaF_3 undergoes a transition from a cubic (O_h^1) to a tetragonal (D_{4h}^{18}) space group at 193 K [5-9] and KCaF_3 is already distorted from the cubic symmetry at room temperature [10]. Some raw data were published previously and show unambiguously the coexistence of a central peak and a soft phonon near the 193 K phase transition in RbCaF_3 [11]. The aim of this paper is to present the results of the model used in the prepara-

tion and the interpretation of the experiments described in the second part of this work.

In this hardly polarizable compound, the rigid ion model described in section 2 gives a satisfactory description of the low frequency modes involved in the cubic to tetragonal phase transition. Furthermore, the expression of the squared frequency of the soft mode calculated in section 3 allows us to improve the physical understanding of the soft mode. In section 4 we give an analytical formulation of the parameters λ_1 , λ_2 and λ_3 which characterize the phonon dispersion map around the R_{25} mode and we study the effects of λ_3 on the anisotropy of the structure factor of these modes around the R point of the cubic Brillouin zone. Finally all these results are discussed in terms of octahedron rotations in section 5.

2. Model of force constants. — The intention of this model was to prepare for the inelastic neutron scattering experiments by calculating the dynamical structure factors in order to choose for each scan, the most appropriate point in the reciprocal lattice. So, we have used a rigid ion model.

Axially symmetric short range interactions, classically defined by A_i and B_i [12], are considered to act between calcium and fluorine nearest neighbours (index 2). On the other hand, the alkali-halide type

(*) Equipe de recherche associée au C.N.R.S. n° 682.

(**) Present address : Groupe de Dynamique des Phases Condensées (Laboratoire Associé au C.N.R.S. n° 233), place Eugène-Bataillon 34060 Montpellier Cedex, France.

interactions Rb-F and F-F, referred to respectively by the indexes 1 and 3, are assumed to derive from Born Mayer central potentials. So, as it has been currently found [13-14] for such interactions we take :

$$\frac{A_1}{B_1} = \frac{A_3}{B_3} = -10.$$

In the perovskite structure (Fig. 1), since every ion is located at a center of symmetry, the polarizabilities do not affect the elastic constants and we introduce the C_{ij} explicitly in the model

$$\begin{aligned} C_{11} &= \frac{e^2}{rv} \left[\frac{1}{8} (2A_1 + 2B_1 + A_2 + 2A_3 + 2B_3) + F_{11}(Z_A, Z_M, Z_F) \right] \\ C_{12} &= \frac{e^2}{rv} \left[\frac{1}{8} (A_1 - 5B_1 - B_2 + A_3 - 5B_3) + F_{12}(Z_A, Z_M, Z_F) \right] \\ C_{44} &= \frac{e^2}{rv} \left[\frac{1}{8} (A_1 + 3B_1 + B_2 + A_3 + 3B_3) + F_{44}(Z_A, Z_M, Z_F) \right]. \end{aligned}$$

The electrostatic contributions F_{ij} were calculated by Cowley [12] Z_A , Z_M and Z_F are respectively the ionic charges of A, M and F atoms ; r is half the lattice parameter and v the volume of the unit cell ($v = 8r^3$).

FIG. 1. — Cubic perovskite crystal structure.

With the previous relations, we may express A_1 , A_2 and B_2 in terms of C_{11} , C_{12} , C_{44} , $\alpha = A_1/A_3$, Z_A and Z_M . The elastic constants are known experimentally [4] and the last three parameters have to be fitted (Z_F was fixed by charge neutrality).

The fitting was carried out for the three transverse infrared-active optical modes and for the lowest

FIG. 2. — Calculated dispersion curves of RbCaF_3 at room temperature. The modes are labelled according to a choice of origin at the Rb atom. The Raman frequencies are taken from reference [7]; the data measured at Saclay and Grenoble are from the second part of this work. The fitting was carried out for the three transverse infrared-active optical modes and for the lower zone boundary modes (< 10 meV) of the X, M and R points. The calculated Raman frequencies are taken from the R zone boundary modes which become Raman active under T_c when the R point becomes a Γ point.

zone boundary modes in the [001], [110] and [111] directions. As shown in figure 2, in spite of the simplicity of the model, we obtain a good agreement even for the optical zone boundary mode which becomes Raman active below T_c.

3. The soft mode. — In order to understand the temperature dependence of the soft mode, it will be desirable to evaluate explicitly the frequency of the soft mode in terms of the interatomic force constant parameters. From a general point of view, for a wave vector **q**, the squared frequency of a given mode *j* can be defined by the following relation :

$$\omega^2 \left(\begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right) e_\alpha \left(\begin{smallmatrix} k \\ j \end{smallmatrix} \middle| \begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right) = \sum_{k'\beta} D_{\alpha\beta} \left(\begin{smallmatrix} k \\ k' \end{smallmatrix} \middle| \begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right) e_\beta \left(\begin{smallmatrix} k' \\ j \end{smallmatrix} \middle| \begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right) \quad (1)$$

where the $e_\alpha \left(\begin{smallmatrix} k \\ j \end{smallmatrix} \middle| \begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right)$ are the components of the $\left| e \left(\begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right) \right\rangle$ column eigenvectors of the dynamical matrix $\underline{D}(\mathbf{q})$. In these notations, the components $U_\alpha(lk)$ of the displacement of the *k*th atom in the *l*th unit cell for the mode $\left(\begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right)$ are defined by

$$U_\alpha(lk) = \frac{e_\alpha \left(\begin{smallmatrix} k \\ j \end{smallmatrix} \middle| \begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right)}{\sqrt{M_k}} e^{i\mathbf{q}\cdot\mathbf{x}(lk)}$$

and the elements of the dynamical matrix are classically [15] given by :

$$D_{\alpha\beta} \left(\begin{smallmatrix} k \\ k' \end{smallmatrix} \middle| \begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right) = (M_k M_{k'})^{-1/2} \times \\ \times \sum_{l'} \Phi_{\alpha\beta} \left(\begin{smallmatrix} 0 & k \\ l' & k' \end{smallmatrix} \right) e^{i\mathbf{q}\cdot[\mathbf{x}(l'k') - \mathbf{x}(0k)]}.$$

In matrixial notation we can write (1) in the form :

$$\omega^2 \left(\begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right) \left| e \left(\begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right) \right\rangle = \underline{D}(\mathbf{q}) \left| e \left(\begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right) \right\rangle.$$

Generally it is practically impossible to evaluate explicitly the eigenvalues $\omega^2 \left(\begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right)$ in terms of the $D_{\alpha\beta} \left(\begin{smallmatrix} k \\ k' \end{smallmatrix} \middle| \begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right)$, unless we know beforehand the eigenvectors. In this case, let us multiply both sides of the last equation by the $\left\langle e \left(\begin{smallmatrix} \mathbf{q} \\ j \right) \right|$ row vector of components $e_\alpha^* \left(\begin{smallmatrix} k \\ j \end{smallmatrix} \middle| \begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right)$. According to the orthogonality of the eigenvectors, we get

$$\omega^2 \left(\begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right) = \left\langle e \left(\begin{smallmatrix} \mathbf{q} \\ j \right) \middle| \underline{D}(\mathbf{q}) \middle| e \left(\begin{smallmatrix} \mathbf{q} \\ j \end{smallmatrix} \right) \right\rangle. \quad (2)$$

In our case, symmetry considerations give us the eigenvectors of the soft mode in terms of MF₆ octahedra rotations around $\langle 100 \rangle$ axes. Let us call $\omega_\infty^2(\mathbf{q}_R)$ the squared frequency of the triply degenerate R₂₅ soft mode and $\left| e \left(\begin{smallmatrix} \mathbf{q}_R \\ x \end{smallmatrix} \right) \right\rangle, \left| e \left(\begin{smallmatrix} \mathbf{q}_R \\ y \end{smallmatrix} \right) \right\rangle, \left| e \left(\begin{smallmatrix} \mathbf{q}_R \\ z \end{smallmatrix} \right) \right\rangle$ the eigenvectors representing MF₆ octahedra rotations around the *x*, *y* and *z* fourfold axes respectively :

$$\omega^2(\mathbf{q}_R) = \omega^2 \left(\begin{smallmatrix} \mathbf{q}_R \\ x \end{smallmatrix} \right) = \omega^2 \left(\begin{smallmatrix} \mathbf{q}_R \\ y \end{smallmatrix} \right) = \omega^2 \left(\begin{smallmatrix} \mathbf{q}_R \\ z \end{smallmatrix} \right).$$

Thus, according to (2), we immediately obtain the squared frequency of the soft mode in terms of force constant parameters

$$\omega_\infty^2(\mathbf{q}_R) = \frac{e^2}{M_F v} \underbrace{[A_1 + B_1 + B_2 + 4 B_3 - 3.50 - 14.461 Z_F^2 + 5.779 Z_A Z_F - 13.596 Z_M Z_F]}_{3.695} \quad (3)$$

With the fitted parameters, we see that the short-range contribution is negative whereas the long-range contribution is positive. Then a 6 % variation in the short-range forces, which strongly depend on the lattice parameter, can lead $\omega_\infty^2(\mathbf{q}_R)$ to zero. This result is consistent with the analysis performed by Cowley (1964) who mentioned that for SrTiO₃ *the experimentally observed changes in the frequencies of this normal mode could be obtained by changing the parameters of the shell models only slightly* [12].

In the same way, let us consider the flat T₂ low frequency mode of the R-M line for which the eigenvector is represented by octahedron rotations around the *z* axis. According to the relation (2) we can calculate the frequency of this mode at the M point of the cubic Brillouin zone

$$\omega_\infty^2(\mathbf{q}_M) = \frac{e^2}{M_F v} [A_1 + B_1 + B_2 + 4 B_3 - 14.383 Z_F^2 + 5.779 Z_A Z_F - 13.596 Z_M Z_F]. \quad (4)$$

From (3) and (4) we get

$$\omega_\infty^2(\mathbf{q}_M) = \omega_\infty^2(\mathbf{q}_R) + \frac{e^2}{M_F v} \times 0.078 Z_F^2. \quad (5)$$

This last relation leads us to conclude that in a rigid ion model the frequency of the T₂ low frequency mode is always lower at the R point than at the M point. Thus, neglecting electronic polarizabilities, the cubic to tetragonal phase transitions associated with octahedron rotations must be due to soft modes at the R point of the cubic Brillouin zone. Effectively no such phase transitions caused by soft modes at the M point of the cubic Brillouin zone have been observed in the hardly polarizable fluoperovskites whereas it occurs in NaNbO₃ [16].

TABLE I

Eigenvalues $\Lambda_j(\mathbf{n})$ and eigenvector components of the $\underline{A}(\mathbf{n})$ matrix for the modes belonging to the R_{25} soft mode

$\mathbf{q} - \mathbf{q}_R$	Mode	Degeneracy	Eigenvector components	$\Lambda_j(\mathbf{n})$
[00 ξ]	T_2	1	(001)	λ_1
	T_5	2	(100), (010)	λ_2
	S_1	1	$\left(\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}} 0\right)$	$\frac{\lambda_1 + \lambda_2 - \lambda_3}{2}$
[$\xi\xi 0$]	S_2	1	(001)	λ_2
	S_3	1	$\left(\frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} 0\right)$	$\frac{\lambda_1 + \lambda_2 + \lambda_3}{2}$
	A_2	1	$\left(\frac{1}{\sqrt{3}} \frac{1}{\sqrt{3}} \frac{1}{\sqrt{3}}\right)$	$\frac{\lambda_1 + 2\lambda_2 + 2\lambda_3}{3}$
[$\xi\xi\xi$]	A_3	2	$\perp$ to $\left(\frac{1}{\sqrt{3}} \frac{1}{\sqrt{3}} \frac{1}{\sqrt{3}}\right)$	$\frac{\lambda_1 + 2\lambda_2 - \lambda_3}{3}$

4. Phonon dispersion surface around the R_{25} mode.

— Following Gesi *et al.* [17], in the neighbourhood of the triply degenerate R_{25} mode, the eigenvectors of the modes can be approximated by linear combination of octahedron rotations (Table I) and the dispersion relation may be written as :

$$\omega_\infty^2 \begin{pmatrix} \eta \\ j \end{pmatrix} = \omega_\infty^2(\mathbf{0}) + \Lambda_j(\mathbf{n}) |\boldsymbol{\eta}|^2 \quad (6)$$

where $\mathbf{n}$ is a unit vector in the direction of $\boldsymbol{\eta} = \mathbf{q} - \mathbf{q}_R$ and $\Lambda_j(\mathbf{n})$ are the eigenvalues of the following matrix defined with $\left| e \begin{pmatrix} \mathbf{q}_R \\ x \end{pmatrix} \right\rangle, \left| e \begin{pmatrix} \mathbf{q}_R \\ y \end{pmatrix} \right\rangle, \left| e \begin{pmatrix} \mathbf{q}_R \\ z \end{pmatrix} \right\rangle$ as basis vectors

$$\underline{A}(\mathbf{n}) = \begin{bmatrix} \lambda_2 + (\lambda_1 - \lambda_2) n_x^2 & \lambda_3 n_x n_y & \lambda_3 n_x n_z \\ \lambda_3 n_x n_y & \lambda_2 + (\lambda_1 - \lambda_2) n_y^2 & \lambda_3 n_y n_z \\ \lambda_3 n_x n_z & \lambda_3 n_y n_z & \lambda_2 + (\lambda_1 - \lambda_2) n_z^2 \end{bmatrix}$$

Then, the phonon dispersion map around the R_{25} mode is fully specified by λ_1 , λ_2 and λ_3 . In order to express these 3 parameters in terms of interatomic force constants, let us expand the dynamical matrix $\underline{D}(\mathbf{q})$ and the eigenvectors of the modes belonging to R_{25} as a power series in η^2 .

$$\underline{D}(\mathbf{q}) = \underline{D}(\mathbf{0}) + \eta^2 \underline{D}_1(\mathbf{n}) + \dots$$

$$\left| e \begin{pmatrix} \mathbf{q} \\ j \end{pmatrix} \right\rangle = \left| e \begin{pmatrix} \mathbf{0} \\ j \end{pmatrix} \right\rangle + \eta^2 |e_j\rangle + \dots$$

where $|e_j\rangle$ is assumed to be a linear combination of $\left| e \begin{pmatrix} \mathbf{0} \\ i \end{pmatrix} \right\rangle$ with $i \neq j$ and $\left| e \begin{pmatrix} \mathbf{0} \\ j \end{pmatrix} \right\rangle$ is the eigenvector of the mode $\begin{pmatrix} \mathbf{q} \\ j \end{pmatrix}$ in the limit $\mathbf{q} \rightarrow \mathbf{q}_R$. According to table I, taking the S_1 mode as an example, one can express the eigenvector of this mode by

$$\frac{1}{\sqrt{2}} \left| e \begin{pmatrix} \mathbf{q}_R \\ x \end{pmatrix} \right\rangle - \frac{1}{\sqrt{2}} \left| e \begin{pmatrix} \mathbf{q}_R \\ y \end{pmatrix} \right\rangle.$$

When substituting the expanded terms $\underline{D}(\mathbf{q})$ and $\left| e \begin{pmatrix} \mathbf{q} \\ j \end{pmatrix} \right\rangle$ in relation (2), to first order in η^2 we get :

$$\omega^2 \begin{pmatrix} \mathbf{q} \\ j \end{pmatrix} = \frac{\langle e \begin{pmatrix} \mathbf{q} \\ j \end{pmatrix} | \underline{D}(\mathbf{q}) | e \begin{pmatrix} \mathbf{q} \\ j \end{pmatrix} \rangle}{\langle e \begin{pmatrix} \mathbf{q} \\ j \end{pmatrix} | e \begin{pmatrix} \mathbf{q} \\ j \end{pmatrix} \rangle} = \omega^2 \begin{pmatrix} \mathbf{0} \\ j \end{pmatrix} + \eta^2 \langle e \begin{pmatrix} \mathbf{0} \\ j \end{pmatrix} | \underline{D}_1(\mathbf{n}) | e \begin{pmatrix} \mathbf{0} \\ j \end{pmatrix} \rangle + \dots$$

This relation is identical to (6) with

$$A_j(\mathbf{n}) = \left\langle e^{(\mathbf{0})}_j \left| \underline{D}_1(\mathbf{n}) \right| e^{(\mathbf{0})}_j \right\rangle.$$

Then, with the help of table I we obtain :

$$\begin{cases} \lambda_1 = \frac{e^2 r^2}{M_F v} \times (0.073 \pm 0.005) Z_F^2 \\ \lambda_2 = \frac{e^2 r^2}{M_F v} \left[\frac{A_3 - B_3}{2} + (5.177 \pm 0.005) Z_F^2 \right] \\ \lambda_3 = \frac{e^2 r^2}{M_F v} [B_3 - (2.388 \pm 0.005) Z_F^2] \end{cases} \quad (7)$$

So, with the fitted parameters we get

$$\begin{cases} \lambda_1 = 6.7 \text{ meV}^2 \text{ \AA}^2 \\ \lambda_2 = 901 \text{ meV}^2 \text{ \AA}^2 \\ \lambda_3 = -297 \text{ meV}^2 \text{ \AA}^2. \end{cases}$$

Once $\lambda_1, \lambda_2, \lambda_3$ are known, we can calculate in any direction $\mathbf{n}$ around the R_{25} point, the eigenvalues and the eigenvectors of $\underline{A}(\mathbf{n})$ giving respectively $A_j(\mathbf{n})$ and $|e^{(\mathbf{q})}_j\rangle$, from which we can easily calculate the inelastic structure factor of the $\begin{pmatrix} \mathbf{q} \\ j \end{pmatrix}$ mode defined by

$$F_j(\mathbf{Q}) = \sum_k b_k^{\text{coh}} e^{-i2\pi\tau \cdot \mathbf{x}_k} \frac{\mathbf{Q} \cdot \mathbf{e}^{(\mathbf{k})}_j}{\sqrt{M_k}}$$

where the Debye-Waller factor is taken as a constant ; $\mathbf{Q}$ is the momentum transfer ($\mathbf{Q} = 2\pi\tau + \mathbf{q}$).

Figure 3 shows an example of the calculated angular dependence of A_j and $|F_j(\mathbf{Q})|^2$ for the lowest energy phonon around the (1.5 0.5 2.5) R point in RbCaF₃. Owing to the triple degeneracy of the R_{25} phonon, in the vicinity of the R point, the sum of the squared structure factors of the three modes is constant but each $|F_j(\mathbf{Q})|^2$ is very anisotropic.

FIG. 3. — Polar representation a) of the calculated angular dependence of the curvature $\lambda_j(\mathbf{n})$ of the dispersion surfaces b) of the calculated structure factor $|F_j(\mathbf{Q} + \mathbf{n})|^2_{\mathbf{n} \rightarrow 0}$, for the lowest energy phonons around the (1.5 0.5 2.5) R point in RbCaF₃. An anti-crossing point is observed in the [111] direction. In fact, the dotted line must stay below the full line because no crossing of these two phonon maps is allowed between the [110] direction and the [100] or [010] directions.

5. Discussion. — The physical meaning of the parameters λ_1, λ_2 and λ_3 becomes clear when we interpret the phonon dispersion map around the R_{25} mode in terms of octahedron rotations. Figure 4a shows the following. The triply degenerate R_{25} mode corresponds to perfectly correlated octahedron rotation around $\langle 100 \rangle$ axes so that two opposite vertices of an octahedron move exactly in phase opposition (same amplitude, opposite direction). Near $\mathbf{q} = \mathbf{q}_R$ the motion of the fluorine atoms is similar but the phase shift is such that two opposite atoms of an octahedron do not have the same amplitude. Hence the octahedra are distorted. These deformations are characterized by variations of the F-F distance between the F ions of an octahedron. So, it is not surprising that only A_3, B_3 and Z_F appear in the expressions of λ_1, λ_2 and λ_3 (relations (7)).

Let us illustrate this behaviour with the T_2 and T_3 branches of the R-M line near the R_{25} mode. On the R-M line (0.5, 0.5, ξ), the shift of phase due to the displacement from the R point arises only in the z direction. So, for the T_2 mode which corresponds to octahedron rotation around the z axis, the octahedra are not distorted (Fig. 4c) and consequently only the long range forces are affected. This explains the small value of λ_1 in relation to the weak coupling between

FIG. 4. — Displacements of the fluorine atoms for the R_{25} mode at $\mathbf{q} = \mathbf{q}_R$ (a). For $(\mathbf{q} - \mathbf{q}_R) = (00\xi)$, the change of phase occurs in the [001] direction so the fluorine octahedra are distorted in the T_3 mode (b) whereas they are not in the T_2 mode (c).

the planes. On the other hand, for the twofold degenerate T_5 mode which consists of octahedron rotation around x and y axes, the shift of phase in the (100) and (010) planes induces deformations of the octahedra (Fig. 4b) leading to a high value for λ_2 . So, we may conclude that λ_1 characterizes the coupling between adjacent planes, λ_2 the coupling inside a plane and λ_3 the variations of the coupling out of these two directions.

The experimental values of λ_1 , λ_2 and λ_3 obtained with SrTiO_3 , KMnF_3 and RbCaF_3 are recorded in table II. We may notice that λ_1 and λ_2 have almost the same value in the two fluoperovskites in agreement with our model in which the λ_i depend only on the F-F interactions. As shown in table I, λ_3 is always given by a linear combination of λ_1 and λ_2 ; consequently, owing to the uncertainty in its experimental determination, one should not pay too much attention to the radically different values given for RbCaF_3 and KMnF_3 . However the relative position of the A_2 and A_3 modes, which could not be obtained in the scattering planes used by Gesi *et al.*, allows us to conclude that λ_3 is negative. According to our model, this result implies that B_3 is negative as in other fluorine compounds such as MgF_2 for example [14]. The situation seems to be drastically different in SrTiO_3 where the different shell models proposed by Cowley (1964) and Stirling (1972) give generally $B_3 > 0$.

In the elaboration of the model, since the Cauchy relation was not exactly verified ($C_{12}/C_{44} = 1.14$) we assumed that the Ca-F interactions were not spherically symmetric but axially symmetric. Let us

TABLE II

*Experimental values of the λ_i
for 3 perovskite compounds*

λ_i ($\text{meV}^2 \text{\AA}^2$)	SrTiO_3			kMnF_3		RbCaF_3 (see 2nd part of this work)
—	[19]	[1]	[17]	[1]	[17]	—
λ_1	137 ± 34	—	300	—	~ 10	10 ± 5
λ_2	3 500 ± 460	—	3 200	—	710	720 ± 120
λ_3	from -200 to 420	—	—	—	~ 100	-405 ± 100

ignore this restriction and represent all the interactions by Born Mayer central potentials. It is then possible to expand the short range contribution of $\omega_\infty^2(\mathbf{q}_R)$ in terms of the lattice parameter. With the fitted parameters we obtain :

$$\frac{d\omega_\infty^2(\mathbf{q}_R)}{dr} \simeq 290 \text{ meV}^2/\text{\AA}.$$

This result indicates that the squared frequency of the R_{25} mode decreases when the lattice parameter decreases. So we may forecast a softening of this mode under the action of a hydrostatic pressure or on cooling down. According to (5) we may forecast the same behaviour for the T_2 mode all along the R-M line. Therefore, we plan to undertake neutron scattering experiments under hydrostatic pressure in order to separate the thermal expansion contribution from the self energy contribution [18] in the temperature dependence of the soft mode.

References

- [1] SHAPIRO, S. M., AXE, J. D., SHIRANE, G. and RISTE, T., *Phys. Rev. B* **6** (1972) 4332.
- [2] KJEMS, J. K., SHIRANE, G., MÜLLER, K. A. and SCHEEL, H. J., *Phys. Rev. B* **8** (1973) 1119.
- [3] ROUSSEAU, M., GESLAND, J. Y., JULLIARD, J., NOUET, J., ZAREMBOWITCH, J. and ZAREMBOWITCH, A., *Phys. Rev. B* **12** (1975) 1579.
- [4] RIDOU, C., Thèse, Le Mans (1977).
- [5] MODINE, F. A., SONDER, E., UNRUH, W. P., FINCH, C. B. and WESTBROOK, R. D., *Phys. Rev. B* **10** (1974) 1623.
- [6] BATES, J. B., MAJOR, R. W., MODINE, F. A., *Solid state Commun.* **17** (1975) 1347;
KAMITAKAHARA, W. A. and ROTTER, C. A., *Solid state Commun.* **17** (1975) 1350.
- [7] RIDOU, C., ROUSSEAU, M., GESLAND, J. Y. and NOUET, J., *Ferroelectrics* **12** (1976) 199;
RUSHWORTH, A. J. and RYAN, J. F., *Solid state Commun.* **18** (1976) 1239.
- [8] HO, J. C. and UNRUH, W. P., *Phys. Rev. B* **13** (1976) 447.
- [9] ROUSSEAU, J. J., ROUSSEAU, M. and FAYET, J. C., *Phys. Status Solidi (b)* **73** (1976) 625.
- [10] HALLIBURTON, L. E. and SONDER, E., *Solid State Commun.* **21** (1977) 445.
- [11] GESLAND, J. Y. (to be published).
- [12] ROUSSEAU, M., NOUET, J., ALMAIRAC, R. and HENNION, B., *J. Physique Lett.* **37** (1976) L. 33.
- [13] COWLEY, R. A., *Phys. Rev.* **134** (1964) 981.
- [14] NAMJOSHI, K. V., MITRA, S. S. and VETELINO, J. F., *Phys. Rev. B* **3** (1970) 4398.
- [15] ALMAIRAC, R., Thèse I.L.L., Grenoble (1975).
- [16] MARADUDIN, A. A., *Solid state Phys. Suppl.* **3**, Eds F. Seitz, D. Turnbull and H. Ehrenreich (New York Acad. Press) 1967.
- [17] DENOYER, F., Thèse Orsay (1977), and references therein.
- [18] GESI, K., AXE, J. D., SHIRANE, G. and LINZ, A., *Phys. Rev. B* **5** (1972) 1933.
- [19] COWLEY, R. A., *Lattice dynamics* Ed. R. F. Wallis (Per-gamon Press) 1965.
- [20] STIRLING, W. G., *J. Phys. C* **5** (1972) 2711.