Soft-modes in displacive transitions

S. Aubry, R. Pick

Classification
Physics Abstracts :
16.70

SOFT-MODES IN DISPLACIVE TRANSITIONS

by S. AUBRY and R. PICK

Service de Physique du Solide et de Résonance Magnétique,
Centre d'Etudes Nucléaires de Saclay, B. P., n° 2, 91, Gif-sur-Yvette

(Reçu le 4 novembre 1970, révisé le 15 février 1971)

Résumé. — On peut classer les transitions de phase displacives qui ne changent pas la maille élémentaire en deux catégories suivant leur paramètre d'ordre ; celui-ci est représenté soit par l'amplitude d'une déformation dans les transitions élastiques, soit par celle du mouvement relatif des atomes dans les transitions optiques. Nous montrons dans ce dernier cas qu'il existe toujours au moins tout un plan de phonons, inactifs en diffusion Raman à haute température, dont la fréquence s'annule à la température critique ; ces modes mous deviennent actifs en diffusion Raman à basse température. Si ces phonons sont actifs en diffusion Raman à haute température, ils induisent une transition élastique comme l'ont montré Miller et Axe : une constante élastique s'annule avant la fréquence optique correspondante. Dans les transitions élastiques qui peuvent être du deuxième ordre d'après la théorie de Landau, nous généralisons la notion de mode mou : il existe au moins une vitesse du son qui s'annule à la température critique. Nous montrons aussi que les modes mous optiques ou élastiques ne sont jamais accompagnés de champ électrique. Cependant, la transition sera ferroélectrique avec une constante diélectrique infinie à la température de transition soit si la fréquence optique est active en absorption infrarouge, soit si la déformation élastique est piézoélectrique. Nous négligeons complètement dans cet article les effets de temps de vie des phonons mous, malgré leur importance évidente dans de telles transitions.

Abstract. — Displacive phase transitions which do not change the size of the unit cell may be classified under two types depending on their order parameter : in the elastic transitions, this is the amplitude of an elastic strain ; it is the amplitude of a relative displacement of the atoms in an optic transition. In this last case, we prove that there always exists at least a whole plane of optical phonons, which are Raman inactive in the high temperature phase, and the frequency of which goes to zero at the transition temperature. These soft modes become Raman active in the low temperature phase. Should these phonons be Raman active in the high temperature phase, they would induce an elastic transition as shown by Miller and Axe : an elastic constant will pass through zero for a still finite frequency of the optical phonon. In the case of an elastic transition, if the Landau theory allows it to be second order, we show by group theory that there always exists at least one sound velocity which passes through zero at the critical temperature. We also prove that the optical or elastic soft mode never carries an electric field with it. Nevertheless the dielectric constant becomes infinite at the transition temperature, and at low temperature is polar, either if the optical soft mode is infrared active or if the elastic mode induces a piezoelectric strain. The damping effect associated with such transitions is not taken into account in this paper.

I. **Introduction.** — Within the framework of the quasi-harmonic theory of phonons, the existence of a relationship between the frequency of optical phonons at the center of the Brillouin zone, on the one hand, and a phase transition on the other has been noticed by various authors [1]. They remarked that the ratio of the low frequency dielectric constant ε_0 to the high frequency dielectric constant ε_∞ is given in two atoms per cell cubic crystals by the Lyddane-Sachs-Teller relation [2]. This relation reads :

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \frac{\omega_L^2}{\omega_T^2}, \qquad (I.1)$$

where ω_L is the longitudinal optical phonon frequency at the center of the Brillouin zone and ω_T that of transverse optical phonons in the same conditions.

If the crystal undergoes a second order phase transition so that ε_0 becomes infinite at a temperature T_c, (I.1) implies that at the same temperature ω_T would be equal to zero.

More generally, let T_c be the temperature at which the crystal undergoes a second order phase transition ; let this transition be such that the low temperature equilibrium positions of the atoms can be described as a displacement of the atoms from their high temperature equilibrium position. In particular, the displacement at $T = T_c$ is proportional to some vector L. If one can, for every temperature, take the amplitude of the projection on L of the displacement of the atoms as an order parameter, this phase transition is said to be displacive. In the above mentioned case, the displacement associated with ω_T could be taken as such a vector L. Equation (I.1) then shows that a phonon exists whose eigenvector may be used as an order parameter and whose eigenvalue goes to zero at the critical temperature, while the other phonons frequencies remain finite. Following Cochran [1c], we shall say that such a transition is accompanied by a soft mode, and, throughout this paper we shall use this expression only for a phonon the eigenvalue of is equal to zero at the critical temperature.

The aim of this paper is to generalize such a result to crystals with an arbitrary number of atoms per cell whatever be its symmetry. We shall maintain ourselves within the framework of the quasi-harmonic theory of phonons i. e. we shall consider an harmonic theory in which the force constants are allowed to vary with temperature in such a way that a displacive second order phase transition takes place at a temperature T_c. We shall prove that when, in such a displacive, transition, the vector L is the same for each cell, there always exists at least one phonon (with a propagating vector $\mathbf{q}$ such as $|q| \to 0$ while remaining parallel to some vector $\mathbf{a}$) the eigenvalue of which goes to zero at the critical temperature. At the same time, we shall show that all the other phonon frequencies remain finite at this temperature. Such a result may be thought to be self evident and has been verified in many particular cases. Nevertheless, its general proof has not been given up to now and is the purpose of this paper.

We shall start by recalling the principal results of the Landau [3] theory of phase transitions, as well as that the phonon theory in insulators. We shall also obtain from the free energy of the crystal the two types of displacive transitions we wish to study here : in the first one, the order parameter is represented by a relative displacement of the atoms within the cell ; in the second one, it is represented by a deformation of the lattice.

In the second part, we shall briefly study the transitions of the first type and prove that, in such a case, an optical phonon frequency always goes to zero at the critical temperature. We shall also discuss under which conditions will the low temperature phase be polar.

The third and fourth parts will be devoted to the displacive phase transitions of the second type. In the third part, we shall give the acoustical phonon equation, the expression of the static dielectric tensor, and we shall discuss the problems which have to be solved in order to prove the existence of a soft mode. Finally, in the last part, we shall show that, if the phase transition is second order, there always exists a sound velocity which goes to zero at the critical temperature. This sound wave will be the soft mode associated with the phase transition.

Let us finally remark that this paper is phenomenological in nature. We shall always admit that a displacive phase transition exists at a certain temperature, but we shall not discuss the microscopic origin of this transition.

II. Survey of the Landau theory and of the phonon equation. — A. THE LANDAU THEORY OF PHASE TRANSITIONS. — Let us recall here the results of the Landau [3] theory of phase transition which we will need later on.

In as second order phase transition, the order parameter η can be taken as the amplitude of a physical quantity L. Landau [3] has shown that :

1) L must transform, under the symmetry operations of the crystal, as an irreducible representation of the symmetry group.

2) This representation cannot be the identity representation.

3) Because the transition is second order, the symmetrized cube of this representation must not contain the identity representation.

Troughout this paper L will be an atomic displacement, and we shall see in parts IV and V that one needs to use the preceeding results in order to prove the existence of soft modes in some displacive transitions.

B. SURVEY OF THE PHENOMENOLOGICAL EQUATIONS OF PHONONS. — We shall briefly recall here the results of the phenomenological theory of phonons.

The phonon spectrum may be obtained by writing that the energy of the system harmonically depends on the position of the atoms and on the mean electric field inside a cell [4], [5], [6]. This energy reads :

$$\Phi = \Phi_0 + \frac{1}{2} \sum_{\substack{\alpha s L \\ \beta s' L'}} \underset{L}{U_s^\alpha} \underset{LL'}{G_{ss'}^{\alpha\beta}} \underset{L'}{U_{s'}^\beta} + \sum_{\substack{\alpha s L \\ \beta L'}} \underset{L}{U_s^\alpha} \underset{LL'}{Z_s^{\alpha\beta}} E_{L'}^\beta - \frac{\varepsilon_0}{2} \sum_{\substack{\alpha L \\ \beta L'}} E_L^\alpha \, \varepsilon_{LL'}^{\alpha\beta} \, E_{L'}^\beta \, . \quad \text{(II.1)}$$

In this expression, $\underset{L}{U_s^\alpha}$ is the displacement, with respect to its equilibrium position, of the atom s which belongs to the cell L in the α direction and E_L^α is the deviation of the mean electric field in the α direction in the cell L. Expression (II.1) must be used when one deals with an insulator ; it remains valid for the case of a metal when one equates to zero two last terms.

By a space Fourier transformation, we can rewrite (II.2) under the from

$$\Phi = \Phi_0 + N \sum_{\mathbf{q} \in BZ} \left[\frac{1}{2} \overline{\mathcal{U}}^*(\mathbf{q}) \, \bar{\bar{\mathcal{G}}}(\mathbf{q}) \, \overline{\mathcal{U}}(\mathbf{q}) + \overline{\mathcal{U}}^*(\mathbf{q}) \times \times \bar{\bar{\mathfrak{Z}}}(\mathbf{q}) \, \bar{\mathcal{E}}(\mathbf{q}) - \frac{\varepsilon_0}{2} \bar{\mathcal{E}}^*(\mathbf{q}) \, \bar{\bar{\varepsilon}}_\infty(\mathbf{q}) \, \bar{\mathcal{E}}(\mathbf{q}) \right] \quad \text{(II.2)}$$

where

$$\overline{\mathcal{U}}(\mathbf{q}) \equiv U_s^\alpha(\mathbf{q}) = \frac{1}{N} \sum_{L} \underset{L}{U_s^\alpha} \, e^{i\mathbf{q}\cdot\mathbf{R}_L^s} \quad \text{(II.3}a\text{)}$$

$$\bar{\mathcal{E}}(\mathbf{q}) \equiv E^{\alpha}(\mathbf{q}) = \frac{1}{N} \sum_{L} E_L^{\alpha} \, e^{i\mathbf{q}.\mathbf{R}_L} \qquad \text{(II.3}b\text{)}$$

$$\bar{\bar{\mathcal{G}}}(\mathbf{q}) \equiv G_{ss'}^{\alpha\beta}(\mathbf{q}) = \sum_{L} G_{\substack{ss'\\LL'}}^{\alpha\beta} \, e^{i\mathbf{q}.(\mathbf{R}_L^s - \mathbf{R}_{L'}^{s})} \qquad \text{(II.4}a\text{)}$$

$$\bar{\bar{\mathcal{Z}}}(\mathbf{q}) \equiv Z_s^{\alpha\beta}(\mathbf{q}) = \sum_{L} Z_{\substack{s\\LL'}}^{\alpha\beta} \, e^{i\mathbf{q}.(\mathbf{R}_L - \mathbf{R}_{L'})} \qquad \text{(II.4}b\text{)}$$

$$\bar{\bar{\mathcal{E}}}_{\infty}(\mathbf{q}) \equiv \varepsilon^{\alpha\beta}(\mathbf{q}) = \sum_{L} \varepsilon_{LL'}^{\alpha\beta} \, e^{i\mathbf{q}.(\mathbf{R}_L - \mathbf{R}_{L'})} \qquad \text{(II.4}c\text{)}$$

N is the number of cells of the crystal ; $\mathbf{R}_L^s$ is the equilibrium position of the atom s in the cell L ; $\mathbf{R}_L$ is the position of the origin of the cell L.

The equations of motion of the atomic displacements simply follow from (II.2) and read :

$$\bar{\bar{\mathcal{M}}} \omega^2 \bar{\mathcal{U}}(\mathbf{q}) = \bar{\bar{\mathcal{G}}}(\mathbf{q}) \bar{\mathcal{U}}(\mathbf{q}) + \bar{\bar{\mathcal{Z}}}(\mathbf{q}) \bar{\mathcal{E}}(\mathbf{q}) , \qquad \text{(II.5)}$$

where

$$\bar{\bar{\mathcal{M}}} \equiv M_s \, \delta_{\alpha\beta} \, \delta_{ss'} .$$

On the other hand, one obtains the electric induction by deriving (II.2) with respect to the electrical field. This yields :

$$\bar{\mathcal{D}}(\mathbf{q}) \equiv \varepsilon_0 \left[\bar{\bar{\varepsilon}}_{\infty}(\mathbf{q}) \bar{\mathcal{E}}(\mathbf{q}) - \frac{1}{\varepsilon_0} \bar{\bar{\mathcal{Z}}}^*(\mathbf{q}) \bar{\mathcal{U}}(\mathbf{q}) \right] . \qquad \text{(II.6)}$$

From (II.5) and (II.6) one obtains the phonon equation of the system as well as the generalized dielectric tensor $\bar{\bar{\varepsilon}}(\mathbf{q}, \omega)$.

If one uses the Maxwell equations in an insulator to relate $\bar{\mathcal{D}}(\mathbf{q})$ to $\bar{\mathcal{E}}(\mathbf{q})$, one may eliminate both quantities between (II.5) and (II.6) [6], [7], which leads to the phonon equation

$$\bar{\bar{\mathcal{T}}}(\mathbf{q}, \omega^2) \bar{\mathcal{V}}(\mathbf{q}) \equiv \left[\bar{\bar{\mathcal{B}}}(\mathbf{q}) + \frac{1}{\varepsilon_0} \times \frac{(\bar{\bar{\mathcal{Y}}}(\mathbf{q}) \hat{q}) ({}^t\hat{q} \bar{\bar{\mathcal{Y}}}^*(\mathbf{q}))}{{}^t\hat{q} \bar{\bar{\varepsilon}}_{\infty}(\mathbf{q}) \hat{q}} - m \bar{\bar{1}} \omega^2(\mathbf{q}) \right] \bar{\mathcal{V}}(\mathbf{q}) = 0 , \qquad \text{(II.7)}$$

where

$$\bar{\bar{\mathcal{Y}}}(\mathbf{q}) \equiv \sqrt{\frac{m}{M_s}} \, Z_s^{\alpha\beta}(\mathbf{q}) \qquad \text{(II.8}a\text{)}$$

$$\bar{\bar{\mathcal{B}}}(\mathbf{q}) \equiv \sqrt{\frac{m}{M_s}} \, G_{ss'}^{\alpha\beta}(\mathbf{q}) \sqrt{\frac{m}{M_{s'}}} \qquad \text{(II.8}b\text{)}$$

$$\bar{\mathcal{V}}(\mathbf{q}) \equiv \sqrt{\frac{M_s}{m}} \, U_s^{\alpha}(\mathbf{q}) \qquad \text{(II.9}a\text{)}$$

$$m = \sum_{s} M_s \qquad \text{(II.9}b\text{)}$$

$$\hat{q} = \frac{\mathbf{q}}{| q |} \qquad \text{(II.10)}$$

and ${}^t\bar{a}$ represents the transpose of some column vector $\bar{a}$.

The phonons which propagate with a vector $\mathbf{q}$ are the solutions of (II.7) and the electric field associated with the atomic displacement is given by

$$\bar{\mathcal{E}}(\mathbf{q}) = -\frac{1}{\varepsilon_0} \hat{q} \frac{({}^t\hat{q} \bar{\bar{\mathcal{Y}}}^*(\mathbf{q}) \bar{\mathcal{V}}(\mathbf{q}))}{{}^t\hat{q} \bar{\bar{\varepsilon}}_{\infty}(\mathbf{q}) \hat{q}} . \qquad \text{(II.11)}$$

On the other hand, the elimination of $\bar{\mathcal{V}}(_\perp)$ between (II.5) and (II.6) yields :

$$\bar{\bar{\varepsilon}}(\mathbf{q}, \omega) = \bar{\bar{\varepsilon}}_{\infty}(\mathbf{q}) + \frac{1}{\varepsilon_0} \bar{\bar{\mathcal{Y}}}^*(\mathbf{q}) \left[\bar{\bar{\mathcal{B}}}(\mathbf{q}) - m \bar{\bar{1}} \omega^2 \right]^{-1} \bar{\bar{\mathcal{Y}}}(\mathbf{q}) . \qquad \text{(II.12)}$$

In order to obtain a simple expression for (II.12), it is convenient [5-7] to use a diagonal representation of the matrix $\bar{\bar{\mathcal{B}}}(\mathbf{q})$. Let us point out that the eigenvalues of $\bar{\bar{\mathcal{B}}}(\mathbf{q})$, $m\omega_{\mu}^2(\mathbf{q})$, represent the frequencies of the phonons of a crystal in which the mean electric field would be zero in every cell. This crystal is called the fictive or shorted crystal, in contradistinction with the free crystal. For the shorted crystal, (II.7) becomes

$$\left[\bar{\bar{\mathcal{B}}}(\mathbf{q}) - m \bar{\bar{1}} \omega^2(\mathbf{q}) \right] \bar{\mathcal{V}}_f(\mathbf{q}) = 0 \qquad \text{(II.13)}$$

and the eigenvector $\bar{\mathcal{V}}_f^{\mu}(\mathbf{q})$ of (II.13) is associated with the eigenvalue $m\omega_{\mu}^2(\mathbf{q})$.

The dielectric tensor can then be written as

$$\varepsilon^{\alpha\beta}(\mathbf{q}, \omega) = \varepsilon_{\infty}^{\alpha\beta}(\mathbf{q}) + \frac{1}{\varepsilon_0} \sum_{\mu=1}^{3n} Y^{*\mu,\alpha}(\mathbf{q}) \times \frac{1}{m[\omega_{\mu}^2(\mathbf{q}) - \omega^2]} Y^{\mu,\beta}(\mathbf{q}) \qquad \text{(II.14)}$$

with

$$Y^{\mu,\alpha}(\mathbf{q}) = \sum_{\beta s} V_{fs}^{*\mu\beta}(\mathbf{q}) \, Y_s^{\beta,\alpha}(\mathbf{q}) , \qquad \text{(II.15)}$$

where n is the number of atoms per cell. In this paper, we shall be interested in the case where $\mathbf{q}$ will be very small and we shall give to μ the values 1,2 and 3 for the acoustical solutions of (II.13), the remaining values being used for its optical solutions.

We shall now study the stability conditions of the crystal and show what relationship exists between a displacive transition and the eigenvalues of the matrix $\bar{\bar{\mathcal{B}}}(\mathbf{q})$.

C. Displacive transition at $\mathbf{q} = 0$. — In section B, we found convenient to derive the phonon equation from the internal energy Φ of the crystal. On the other hand, in the Landau [3] theory one must use the free energy of the crystal. As we restrict ourselves to systems in which the only explicited variables are nuclear displacements and a macroscopic electric field this free energy is given by :

$$F = \Phi + {}^t\bar{\mathcal{E}} \bar{\mathcal{D}} , \qquad \text{(II.16)}$$

where the electric induction $\bar{\mathcal{D}}$ is the partial derivative of $-\Phi$ with respect to the electric field, and its Fourier transform has been given in (II.6).

F must be minimum when the atoms are at their equilibrium position. If we minimize F with respect to $\overline{\mathfrak{D}}$, the minimizing condition can be written as :

$$\bar{\mathcal{E}} = 0\,. \qquad \text{(II.17)}$$

This yields

$$F_{\min} = \tfrac{1}{2}\,{}^{t}\overline{\mathfrak{U}}\,\overline{\overline{\mathfrak{G}}}\,\overline{\mathfrak{U}} \qquad \text{(II.18)}$$

so that (II.18) must be a positive definite form.

Let us now suppose that, when the temperature varies, $\overline{\overline{\mathfrak{G}}}$ has an eigenvalue which passes through zero at T_c and is negative below T_c. Then the crystal undergoes a phase transition at T_c. If $\mathfrak{U}_0$ is the displacement of the atoms corresponding to that eigenvalue, we can take the amplitude of the projection on $\overline{\mathfrak{U}}_0$ of the displacements of the atoms with respect to their equilibrium position as and order parameter.

Let us now restrict ourselves to the case where the relative atomic displacements inside their cell are the same, whatever is the cell. We can write

$$U^{\alpha}_{\substack{s\\L}} = U^{\alpha}_{L} + X^{\alpha}_{s} \qquad \text{(II.19)}$$

where U^{α}_{L} is the displacement of the origin of the cell and X^{α}_{s} is the relative displacement of the s-atom in the α-direction.

Injecting (II.19) in (II.18), we obtain by a classical calculation [4]

$$F_{\min} = \tfrac{1}{2}[\overline{\overline{e}}]\,[\overline{\overline{\overline{\overline{g}}}}]\,[\overline{\overline{e}}] + [\overline{\overline{e}}]\,\overline{\overline{\overline{\mathfrak{G}}}}\,\overline{\mathfrak{X}} + \tfrac{1}{2}\,\overline{\mathfrak{X}}\,\overline{\overline{\mathfrak{G}}}(0)\,\overline{\mathfrak{X}}\,. \qquad \text{(II.20)}$$

In this expression

$[\overline{\overline{e}}] \equiv e^{\alpha\gamma}$ is a strain tensor, which is symmetrical with respect to its two indices.

$[\overline{\overline{\overline{\overline{g}}}}] \equiv g^{\alpha\gamma,\beta\delta}$ has the symmetry of an elastic tensor, i. e. it is symmetric in α, γ and in $(\alpha\gamma)$, $(\beta\delta)$.

$\overline{\overline{\overline{\mathfrak{J}}}} \equiv I^{\alpha\gamma,\beta}_{s}$ has the symmetry of a Raman tensor i. e. it is invariant in the interchange of α with γ.

$[\overline{\overline{\overline{\overline{g}}}}]$ and $\overline{\overline{\overline{\mathfrak{J}}}}$ are linear combinations of, respectively, second and first derivatives of $G^{\alpha\beta}_{ss'}(\mathbf{q})$ for $\mathbf{q} = 0$, and their expressions can be found e. g. in [4].

Let us write :

$$\overline{\mathfrak{V}} \equiv \sqrt{\frac{M_s}{m}}\,X^{\alpha}_{s} \qquad \text{(II.21)}$$

$$\overline{\overline{\overline{\mathfrak{J}}}} \equiv I^{\alpha\alpha,\beta}_{s}\,\sqrt{\frac{M_s}{m}}\,. \qquad \text{(II.22)}$$

If we express the strain tensor $[\overline{\overline{e}}]$ as a six component vector e_i, and project the vector $\overline{\mathfrak{V}}$ on the eigenvectors of the matrix $\overline{\overline{\mathfrak{B}}}(0)$, (II.20) takes the form :

$$F_{\min} = \frac{1}{2}\sum_{i,j=1}^{6} e_i\,g_{ij}\,e_j + \sum_{i=1}^{6}\sum_{\mu=4}^{3n} e_i\,J^{\mu}_{i}\,\tilde{V}^{\mu} + \frac{1}{2}\sum_{\mu=4}^{3n} m\omega^{2}_{\mu}(\tilde{V}^{\mu})^{2} \qquad \text{(II.23)}$$

where

$$\tilde{V}^{\mu} = \sum_{\alpha s} V^{\mu\alpha}_{fs}(0)\,\tilde{V}^{\alpha}_{s} \qquad \text{(II.24)}$$

(In (II.23) the tensors $[\overline{\overline{\overline{\overline{g}}}}]$ and $\overline{\overline{\overline{\mathfrak{J}}}}$ are now written as two index tensors for which we use the same letters).

A displacive phase transition will take place when one of the eigenvalues of (II.23) will be equal to zero. An elementary calculation shows that the determinant of (II.23) may be written as :

$$\Delta = \left|\,[\overline{\overline{b}}]\,\right| \left\{ \prod_{\mu=4}^{3n} m\omega^{2}_{\mu} \right\} \qquad \text{(II.25)}$$

where

$$[\overline{\overline{b}}] \equiv b_{ij} = g_{ij} - \sum_{\mu} \frac{J^{\mu}_{i}\,J^{\mu}_{j}}{m\omega^{2}_{\mu}}\,. \qquad \text{(II.26)}$$

$[\overline{\overline{b}}]$ is the elastic matrix of the crystal, as one may obtain it by minimizing (II.20) with respect to $\overline{\mathfrak{X}}$.

In (II.25) appear two causes of annulation of Δ, and thus of phase transitions. First, an eigenvalue of the elastic matrix $[\overline{\overline{g}}]$ may go to zero. The order parameter is the corresponding strain. These transitions are called elastic ones and, in studying them in part IV and V, we shall show that the corresponding soft mode is an acoustical phonon, the speed of which goes to zero at the critical temperature.

Secondly an ω_μ may go to zero. If the corresponding $\mathfrak{J}^{=\mu}$ is equal to zero by symmetry, Δ also goes to zero at this temperature. In this case the order parameter is the amplitude of a relative atomic displacement. Those are optical transitions, and, in part III, we shall prove that some optical phonons are the corresponding soft modes.

Finally if an ω_μ goes to zero but the corresponding $\mathfrak{J}^{=\mu}$ is not zero, some b_{ii} will tend to minus infinity at the same temperature. Thus, an eigenvalue of $[\overline{\overline{b}}]$ will be equal to zero at an higher temperature, for a still finite value of ω_μ : the transition will again be elastic. As $\overline{\mathfrak{J}}^{\mu}$ has the same symmetry as a Raman tensor, this shows that only Raman inactive frequencies induce optical transitions. As was pointed out by Miller and Axe [8], if a Raman active one tends to zero, an elastic transition will take place, and if this transition is a second order one, the corresponding soft mode will be an acoustical phonon.

III. — **Optical soft mode transitions.** — A. INTRODUCTION. — In this third part, we shall show that, when $\mathbf{q} \to 0$, all the optical phonons of the free crystal which are some solution of (II.7), have frequencies higher than or equal to the smallest optical frequency of the shorted crystal (II.13). The equality condition is always obtained when $\mathbf{q}$ tends to zero while being parallel to a given plane of the reciprocal space; sometimes that last condition can even be relaxed.

This result guarantees that if a Raman inactive optical eigenvalue $m\omega_\mu^2$ ($\mathbf{q} = 0$) of (II.13) tends to zero when T tends to T_c, there always exist some phonons of the free crystal which may be taken as soft modes. We shall finally show that the phase transition will lead to a polar low temperature phase if the frequency ω_μ is infrared active, and to a non polar phase otherwise.

B. Existence of a soft mode. — Let $\bar{\bar{\mathcal{T}}}(\hat{q}, \omega^2)$ be the limit of $\bar{\bar{\mathcal{T}}}(\mathbf{q}, \omega^2)$ when $\mathbf{q}$ goes to zero, $\mathbf{q}$ being parallel to a unit vector $\hat{q}$. We can write equation (II.7) in the space where $\bar{\bar{\mathcal{B}}}(0)$ is diagonal. This yields:

$$\bar{\bar{\mathcal{G}}}(\hat{q}, \omega^2)\,\bar{\mathcal{V}} \equiv \sum_{\mu'=4}^{3n} \left[m(\omega_\mu^2 - \omega^2)\,\delta_{\mu\mu'} + \frac{1}{\varepsilon_0} \times \frac{\bar{Y}^\mu \hat{q}\quad \bar{Y}^{\mu'} \hat{q}}{{}^t\hat{q}\,\varepsilon_\infty\,\hat{q}} \right] V^{\mu'} = 0 \quad \text{(III.1)}$$

where we have written ω_μ^2, $Y^{\mu,\alpha}$, $\varepsilon_\infty^{\alpha\beta}$ and V^μ respectively for $\omega_\mu^2(0)$, $Y^{\mu,\alpha}(0)$, $\varepsilon_\infty^{\alpha\beta}(0)$ and $V^\mu(\hat{q})$. An elementary calculation leads to:

$$|\bar{\bar{\mathcal{G}}}(\hat{q}, \omega^2)| = \frac{1}{\varepsilon_0}\,\frac{1}{{}^t\hat{q}\bar{\bar{\varepsilon}}_\infty\hat{q}} \left\{ \prod_{\mu=4}^{3n} m(\omega_\mu^2 - \omega^2) \right\} \times \left[\varepsilon_0\,{}^t\hat{q}\bar{\bar{\varepsilon}}_\infty\hat{q} + \sum_{\mu=4}^{3n} \frac{(\bar{Y}^\mu \hat{q})^2}{m(\omega_\mu^2 - \omega^2)} \right]. \quad \text{(III.2)}$$

From (III.2) we can easily show than we can always find a direction of $\hat{q}$ such that ω_μ^2 is a solution of equation. Three different cases must be considered.

1) Due to the symmetry of the crystal, $Y^{\mu,\alpha}$ is identical to zero, whatever is α, for a certain mode μ. Then ω_μ^2 is a solution of (III.2) whatever is $\hat{q}$.

2) $Y^{\mu,\alpha}$ differs from zero, and ω_μ^2 appears only once in the product in (III.2). It is then sufficient that $\hat{q}$ is orthogonal to $\mathbf{Y}^\mu$, taken as a vector with cartesian coordinates $Y^{\mu,\alpha}$, to insure that ω_μ^2 is still a solution of (III.2).

3) $Y^{\mu,\alpha}$ differs from zero and ω_μ^2 appears more than once in the product in (III.2). As $(\omega_\mu^2 - \omega^2)$ is a simple pole of the last term of (III.2), ω_μ^2 will always be a solution [9*a*] of (III.2).

This prove our first statement.

Let us now label the frequencies ω_μ so that $\omega_\mu \leqslant \omega_{\mu+1}$, and let us do the same for the solutions $\omega_p(\hat{q})$ of (III.1). As ${}^t\hat{q}\,\bar{\bar{\varepsilon}}_\infty\,\hat{q}$ is always positive, (III.2) implies that, for an arbitrary $\hat{q}$,

$$\omega_\mu^2 \leqslant \omega_p^2(\hat{q}) \leqslant \omega_{\mu+1}^2\,. \quad \text{(III.3)}$$

This shows that all the solutions of (III.2) are larger than or equal to the smallest non zero ω_μ, and it follows from the preceding proof that the equality always holds for some direction $\hat{q}_0$: if $\omega_\mu^{\min} \to 0$ when $T \to T_c$, there exists at least a whole plane of directions $\hat{q}$ such that the phonon propagating with this wave vector is a soft mode.

C. Nature of the transition. Detection by optical techniques. — One could think that those transitions always lead to a non polar low temperature phase because the soft mode are never accompanied by an electric field. Indeed, if $\bar{\mathcal{V}}(\hat{q}_0)$ is an eigenvector of (III.1) and if $\hat{q}_0$ is such that the corresponding eigenvalue is ω_μ, its components $V^\mu(\hat{q}_0)$ satisfy the relation (see III.1)

$$\sum_\alpha \sum_{\mu=4}^{3n} \hat{q}_0^\alpha\, Y^{\mu,\alpha}\, V^\mu(\hat{q}_0) = 0 \quad \text{(III.4)}$$

As the amplitude of the electric field associated with a phonon is proportional to the left handside of (III.4) see (II.11), this field is equal to zero. Nevertheless, the low temperature phase may be polar as can be seen from the expression of the response of the system to an electromagnetic field of frequency ω. One obtains it by taking the $q = 0$ limit of (II.12), ω remaining finite, and this limit is [9].

$$\varepsilon_0^{\alpha\beta}(\omega) = \varepsilon_\infty^{\alpha\beta} + \frac{1}{\varepsilon_0} \sum_{\mu=4}^{3n} Y^{\mu,\alpha} \frac{1}{m(\omega_\mu^2 - \omega^2)} Y^{\mu,\beta}\,. \quad \text{(III.5)}$$

The poles of (III.5) correspond to an infrared absorption, and this one exists when the corresponding $Y^{\mu,\alpha}$ are different from zero.

Thus, if an infrared active frequency goes to zero, at the critical temperature $\varepsilon_0^{\alpha\beta}(0)$ will become infinite, which means that the low temperature phase will be polar. This could be the case e. g. in baryum titanate [10] ([1]). On the contrary if this frequency is infrared inactive, as in the α quartz, β quartz transition [11], [12][(1)], $\varepsilon_0^{\alpha\beta}(0)$ has no singularity at the critical temperature and the low temperature phase is not polar.

All the preceeding results have been obtained by considering the high temperature phase. Another result may be obtained by looking at the transition from the low temperature side. By continuity ω_μ also tends to zero, and the eigenvector $\bar{\mathcal{V}}(\hat{q}_0)$ which corresponds to the eigenvalue $m\omega_\mu^2$ of (III.1) trans-

(1) See also section V.

froms, under the symmetry operations of the low temperature phase, as the identity representation. This representation is Raman active in any point group so that the optical soft mode can always be detected by Raman scattering experiments in that phase.

In summary, in optical second order displacive transitions, there always exists some phonon the frequency of which goes to zero at the critical temperature. Those phonons can always be detected by Raman scattering experiments in the low temperature phase, but never in the high temperature one ; if they can also be detected by infrared absorption, the low temperature phase will be polar. Finally, in this last case, if the frequency of the soft mode is a non degenerate eigenvalue of (II.13), only phonons the wave vectors of which are orthogonal to a given vector are soft modes. Table I contains the list of such cases, the direction of this vector as well as the symmetry of the low temperature phase. In all the other cases, there will always exist a soft mode whatever is the direction $\hat{q}$.

TABLE I

Second order optical displacive transitions with a restricted number of soft modes

We give here the list of the transitions for which the wave vector $\hat{q}$ of the soft modes are not arbitrary in direction. The following table indicates :

in column 1 : the point group of the high symmetry phase ;

in column 2 : the point group of the low symmetry phase ;

in column 3 : the representation of the soft mode ;

in column 4 : the vector $\mathbf{Z}_\mu$ to which the wafe vector $\hat{q}$ of the soft mode is orthogonal.

High symmetry phase	Low symmetry phase	Soft mode	Z_u
—	—	—	—
C^i	C_0	A_u	$\alpha x + \beta y + \gamma z$
C_{2h}	C_2	A_u	z
C_{2h}	C_s	B_u	$\alpha x + \beta y$
D_{2h}	C_{2v}	B_{3u}	x
D_{2h}	C_{2v}	B_{2u}	y
D_{2h}	C_{2v}	B_{1u}	z
D_3	C_3	A_2	z
D_4	C_4	A_2	z
D_4	C_6	A_2	z
D_{3h}	C_{3v}	A_2	z
D_{4h}	C_{4v}	A_{2u}	z
C_{4h}	$C_4{}'$	A^7	z
D_{4h}	C_6	A_{2u}	z
D_{3d}	C_{3v}	A_{2u}	z
D_{4d}	C_{4v}	B_2	z
S_6	C_3	B_u	z

IV. **Elastic phase transitions.** — A. INTRODUCTION. — In part III, we studied phase transitions which could be characterized by a relative displacement of the atoms inside the primitive cell. We showed that they could always be characterized by the annulation of some Raman inactive optical phonon frequency. We wish to study now the same problem when the order parameter is represented by a strain of the crystal. As this problem is complex, we shall simply expose here its principal features. The proof of the existence of acoustical soft modes will be delayed to the last part.

Let b_ν be the eigenvalue of the elastic matrix $[\bar{\bar{b}}]$ (Eq. (II.26)) and $\lfloor e]^\nu$ a corresponding eigenvector

$$\sum_j b_{ij}\, e_j^\nu = b_\nu\, e_i^\nu\,. \tag{IV.1}$$

It follows from Section II.A that a phase transition characterized by $[\bar{e}]^\nu$ will take place at T_c if $[\bar{e}]^\nu$ does not transform as the identity representation of the symmetry group and if b_ν, positive for $T > T_c$, changes its sign at T_c.

Those elastic transitions have been studied by Boccara [13] from the point of view of the Landau theory. He has given a list of those which can be second order transitions ; the others are always first order because the symmetrized cube of the representation of $[\bar{e}]^\nu$ contains the identity representation. We shall need his results in part V but before we can use them, we must recall the form of the equation giving the sound velocity in a crystal.

B. ACOUSTICAL PHONON EQUATION. — The equation giving the speed of sound waves in a free crystal are easily obtained from (II.7) ; in strict analogy with that expression, they read [14]

$$\bar{\bar{\mathfrak{I}}}_0(\hat{q}, v^2)\, \overline{\mathfrak{V}}_0(\hat{q}) \equiv \left[\bar{\bar{\mathfrak{B}}}_0(\hat{q}) + \frac{1}{\varepsilon_0} \times \right.$$
$$\left. \times \frac{[\bar{\bar{\mathfrak{Y}}}_0(\hat{q}).\hat{q}]\,[{}^t\bar{\bar{\mathfrak{Y}}}_0(\hat{q}).\hat{q}]}{{}^t\hat{q}\bar{\bar{\varepsilon}}_0\,\hat{q}} - m\mathbf{1}v(\hat{q})^2\right] \overline{\mathfrak{V}}_0(\hat{q}) = 0 \tag{IV.2}$$

where

$$a) : \bar{\bar{\mathfrak{B}}}_0(\hat{q}) \equiv B_0^{\alpha\beta}(\hat{q}) = \sum_{\gamma,\delta} b^{\alpha\gamma,\beta\delta}\, \hat{q}_\gamma\, \hat{q}_\delta \tag{IV.3}$$

expression in which the elastic tensor $b^{\alpha\gamma,\beta\delta}$ is given by (II.26).

$$b) : \bar{\bar{\mathfrak{Y}}}_0(\hat{q}) \equiv Y_0^{\alpha\beta}(\hat{q}) = \sum_\gamma Y_0^{\alpha\gamma,\beta}\, \hat{q}_\gamma\,, \tag{IV.4}$$

where $\bar{\bar{\bar{\mathfrak{Y}}}}_0 = Y_0^{\alpha\gamma,\beta}$ is a linear combination of piezoelectric coefficients which is symmetrical in the interchange of α and γ.

$$c) : \bar{\bar{\varepsilon}}_0 \equiv \varepsilon_0^{\alpha\beta}(\omega = 0)\,. \tag{IV.5}$$

Similarly, the electric field associated with the sound wave with eigenvector $\mathfrak{V}_0(\hat{q})$ is given by [15]

$$\bar{\varepsilon}_0(\hat{q}) = \frac{1}{\varepsilon_0} \hat{q} \frac{({}^t\hat{q}\bar{\bar{\mathcal{Y}}}_0(\hat{q})\,\bar{\mathcal{V}}_0(\hat{q}))}{{}^t\hat{q}\bar{\bar{\varepsilon}}_0\,\hat{q}} . \qquad \text{(IV.6)}$$

C. Soft mode and elastic phase transition. — The problem we have to solve may now be defined very precisely and is, in every respect, similar to the one we discussed in part III. Let b_ν be an eigenvalue of (IV.1) such that its eigenvector $[\bar{e}]^\nu$ does not transform as the identity representation of the symmetry group of the crystal. Does there always exists a direction $\hat{q}$ such that a sound wave propagating with that wave vector in the free crystal will have a speed of sound related to b_ν by

$$m(v^\mu(\hat{q}))^2 = b_\gamma \qquad \text{(IV.7)}$$

1) We shall prove, in the last part that this property is true if a second order phase transition can effectively take place i. e., if the symmetrized cube of $\bar{e}^\nu$ does not contain the identity representation.

2) We shall also prove that, if b_ν is the smallest eigenvalue of $\bar{\bar{b}}$, the speed of sound has its minimal value when the equality (IV.7) is satisfied.

This sound wave will then represent the soft mode associated with the phase transition due to the annulation of $b_\gamma^{\min}$; as in the second part, we shall see that this soft mode does not carry an electric field with it.

In order to perform these proofs we shall make use, as an intermediate step, of the fact that the two above mentioned properties are always true for the shorted crystal ; for this crystal the acoustical phonon equation simply reads :

$$\sum_\beta \left[B_0^{\alpha\beta}(\hat{q}) - m(v_f(\hat{q}))^2\,\delta_{\alpha\beta}\right] V_f^\beta(\hat{q}) = 0 \,. \qquad \text{(IV.8)}$$

This last expression is obtained by the same technique as the one which leads to (IV.2) if one starts by imposing the macroscopic electrical field to be zero in every cell.

D. Elastic dielectric tensor. — As in the third part, we wish also to know which transitions lead to a polar low temperature phase. In order to find it, let us consider the internal energy of the crystal in the presence of a pure strain and of an electric field. This internal energy reads :

$$\Phi = -\,\bar{\mathfrak{D}}_0 . \bar{\mathcal{E}} + \tfrac{1}{2}\bar{\bar{e}}\,\bar{\bar{\bar{b}}}\,\bar{\bar{e}} + \bar{\bar{e}}\,\bar{\bar{\bar{\mathcal{Y}}}}_0\,\bar{\mathcal{E}} - \tfrac{1}{2}\,\varepsilon_0\,\bar{\mathcal{E}}\bar{\bar{\varepsilon}}_0\,\bar{\mathcal{E}} . \qquad \text{(IV.9)}$$

In (IV.9) $\bar{\mathfrak{D}}_0$ is the spontaneous electric induction of the crystal, which differs from zero if the phase is polar. If one uses, as in part II, the two equations

$$\bar{\mathfrak{D}} = -\left(\frac{\partial\Phi}{\partial\bar{\mathcal{E}}}\right)_{\bar{\bar{e}}} \quad \text{and} \quad \left(\frac{\partial\Phi}{\partial\bar{\bar{e}}}\right)_{\bar{\mathcal{E}}} = 0$$

one obtains the expression of the static dielectric tensor

$$\varepsilon_{\rm st}^{\alpha\beta} = \varepsilon_0^{\alpha\beta} + \sum_{\nu=1}^{6} Y_0^{\nu,\alpha}\frac{1}{b_\nu} Y_0^{\nu,\beta} , \qquad \text{(IV.10)}$$

where

$$Y_0^{\nu,\alpha} = \sum_{i=1}^{6} e_i^\nu\, Y_0^{i,\alpha} \qquad \text{(IV.11)}$$

e_i^ν and b_ν being defined by (IV.1).

The transition characterized by the annulation of b_ν will lead to a divergence of $\bar{\bar{\varepsilon}}_{\rm st}$ and then to a low temperature polar phase if $Y_0^{\nu,\beta}$ is not identical to zero by symmetry. As $Y_0^{\alpha\gamma,\beta}$ is symmetrical with respect to α and γ, the eigenvector must simultaneously transform, under the symmetry operations of the group, as a vector and as a symmetric second rank tensor. In other words, $Y_0^{\nu,\alpha}$ will differ from zero only if e^ν belongs to a representation which can simultaneously be infrared and Raman active. We shall say that such representations are piezoelectric, and only those strainswhich transform as piezoelectric representations lead to low temperature ferroelectric phases.

Remark. — From the Miller and Axe [8] result quoted at the end of Section II.C and the preceding remark, it follows that an optical Raman active phonon induces an elastic transition which has the same nature as that which would have been induced by the optical transition : the low temperature phase is polar if the optical phonon is also infrared active, and non polar in otherwise.

V. Existence of soft modes in an elastic transition.

— A. Introduction. — In this last part, we shall show that a second order elastic transition always carries with it an acoustical phonon with wave vector $\hat{q}_0$ the speed of which is equal to zero.

We have shown in Section IV.C that this result will be the consequence of two more general properties we need now to prove. We shall start by giving the demonstration for the shorted crystal and we shall extend it afterwards to the free crystal.

B. Soft mode in a shorted crystal. — Let $\bar{\mathcal{V}}_f^\mu(\hat{q})$ be a solution of (IV.8) and $v_f^\mu(\hat{q})$ the corresponding sound velocity.

Eq. (IV.8) may be rewritten as :

$$\bar{\mathcal{V}}_f^\mu(\hat{q})\,\bar{\bar{\mathcal{B}}}_0(\hat{q})\,\bar{\mathcal{V}}_f^\mu(\hat{q}) = m v_f^\mu(\hat{q})^2 . \qquad \text{(V.1)}$$

It follows from (IV.2) and from the symmetry properties of the elastic matrix $b^{\gamma,\beta\delta}$ that one can write (V.1) as :

$$\bar{\bar{e}}_f^\mu\,\bar{\bar{\bar{b}}}\,\bar{\bar{e}}_f^\mu = m v_f^\mu(\hat{q})^2 , \qquad \text{(V.2)}$$

where

$$e_f^{\mu,\alpha\beta} \equiv \tfrac{1}{2}(V_f^{\mu,\alpha}(\hat{q})\,\hat{q}^{\beta} + V_f^{\mu,\beta}(\hat{q})\,\hat{q}^{\alpha})\,; \quad (\text{V}.3)$$

$\bar{e}_f^{\mu}$ is then a special strain tensor, the symmetrized product of two vectors ; we shall say that such a deformation is a propagative one.

As $\bar{e}_f^{\mu}$ is a linear combination of the eigenvectors of $\bar{\bar{b}}$, (V.2) shows that

$$b_\nu^{\min} \leqslant m v_f^{\mu}(\hat{q})^2\,, \quad (\text{V}.4)$$

where $b_\nu^{\min}$ is the smallest eigenvalue of $\bar{\bar{b}}$. We shall now prove that if the eigenvectors associated with $b_\nu^{\min}$ may be used to define an order parameter, there exist at least two mutually perpendicular directions $\hat{q}_0$ which are such that the equality sign is effectively obtained in (V.4). This will be enough to show that the phonon μ, $\hat{q}_0$ is a soft mode associated with the elastic transition.

Let then b_ν be an eigenvalue of the 6×6 matrix $\bar{\bar{b}}$. Let us show that, if the corresponding eigenvectors are not invariant under the operations of the symmetry group of the crystal, we can always find in the space spanned by those eigenvectors, a propagative deformation $\bar{e}^{\nu}$. This means that, in developed notations, $\bar{e}^{\nu}$ can be written as

$$e^{\nu,\alpha\beta} = \tfrac{1}{2}(\hat{u}_1^{\alpha}\,\hat{u}_2^{\beta} + \hat{u}_1^{\beta}\,\hat{u}_2^{\alpha})\,. \quad (\text{V}.5)$$

Now, $e^{\nu,\alpha\beta}$ may be considered as a symmetrical matrix and there exists an orthonormal cartesian system of coordinates for which that matrix is diagonal. In those new axes, the solution of equation (V.5) is trivial and leads to a unique solution for the couple $\hat{u}_1$, $\hat{u}_2$ but requires two compatibility conditions :

$$e^{\nu,\alpha\alpha}\,e^{\nu,\beta\beta} < 0 \quad (\text{V}.6a)$$

or cyclic permutation .

$$e^{\nu,\gamma\gamma} = 0 \quad (\text{V}.6b)$$

Also, $\bar{e}^{\nu}$ is orthogonal to all the other eigenspaces of $\bar{\bar{b}}$ and particularly to any linear combination of deformations, which transform as the identity representation. $\bar{e}^{\nu}$ is thus orthogonal to an isotropic dilatation which is such a deformation. In any system of coordinates, that dilatation is represented by the deformation vector (1, 1, 1, 0, 0, 0). Then :

$$e^{\nu,\alpha\alpha} + e^{\nu,\beta\beta} + e^{\nu,\gamma\gamma} = 0\,. \quad (\text{V}.7)$$

(V.7) implies, on the one hand, that $\hat{u}_1$ and $\hat{u}_2$ are mutually perpendicular, on the other, that (V.6*a*) is fulfilled as soon as (V.6*b*) holds.

In order to prove that one can always find an eigenvector $\bar{e}^{\nu}$ corresponding to b_ν, such that the matrix $e^{\nu,\alpha\beta}$ have a zero eigenvalue, one must make use of group theory. This proof is given in Appendix A.

As the matrix $\bar{\bar{b}}$ may have degenerate eigenvalues, one sees that to any eigenvalue b_ν, the eigenvectors of which are not in the identity representation, corresponds at least two mutually perpendicular directions $\hat{q}_0(\hat{q}_0 = \hat{u}_1$ or $\hat{q}_0 = \hat{u}_2)$ such that the equality sign is effectively obtained in (V.4) : there exist at least two soft modes associated with the phase transition characterized by $\bar{e}^{\nu}$.

If the crystal is not piezoelectric either by symmetry (as it is the case for the eleven centered point groups and for the group 0), or because it is metallic, the short and real crystals are one and the same. Then what preceeds is enough to ascertain that in an elastic second order transition, there always exist some sound wave with a velocity equal to zero. Furthermore, from (IV.10) it follows that the low temperature phase will not be polar.

If the crystal is piezoelectric, one must still show that such a sound wave exists also in the free crystal ; this will be done in the following section.

C. Soft mode in a piezoelectric crystal. — Among the two vectors $\hat{u}_1$ and $\hat{u}_2$ obtained in the preceding section, one is the wave vector q_0 of the sound wave, the other a corresponding eigenvector of the shorted crystal. This wave is transverse as the two vectors are perpendicular one to the other. If one uses the same technique which leads from (IV.8) to (V.2) as well as the symmetry properties of $Y^{\alpha\gamma,\beta}$ one sees that one can rewrite (IV.2) as :

$$\bar{e}_0^{\mu}\,\bar{\bar{b}}\bar{e}_0^{\mu} + \frac{1}{\varepsilon_0}\,\frac{(\bar{e}_0^{\mu}\,\bar{\bar{\bar{\mathcal{Y}}}}_0\,\hat{q})^2}{{}^t\hat{q}\bar{\bar{\varepsilon}}_0\,\hat{q}} = m v(\hat{q})^2 \quad (\text{V}.8)$$

where

$$e_0^{\mu,\alpha\beta} = \tfrac{1}{2}\,(V_0^{\mu,\alpha}(\hat{q})\,\hat{q}^{\beta} + V_0^{\mu,\beta}(\hat{q})\,\hat{q}^{\alpha})\,. \quad (\text{V}.9)$$

In (V.9) $\bar{\mathcal{V}}_0(\hat{q})$ is an eigenvector of (IV.2) and $v(\hat{q})$ is the corresponding eigenvalue. If one compares now (V.8) with (V.2), one sees that a propagative deformation will lead to the same sound velocity in the free and shorted crystals and that one can identify $\bar{e}_0^{\mu}$ with $\bar{e}_f^{\mu}$ if and only if

$$\bar{e}_0^{\mu}\,\bar{\bar{\bar{\mathcal{Y}}}}_0\,\hat{q} = 0\,. \quad (\text{V}.10)$$

For this equality to be satisfied in a not fortuitous manner, it is necessary and sufficient that $\hat{q}$ has no projection on the vector which transform under the operations of the symmetry group as $\bar{e}_0^{\mu}$. It is thus sufficient to show that one of the two vectors $\hat{u}_1$ or $\hat{u}_2$ does not belong to the same representation as $\bar{e}_0^{\mu}$.

It is shown in Appendix B that this property is always true if $\bar{e}^{\nu}$ transforms itself as a one dimensional representation (different, of course, of the identity representation). But this property is no longer always true if $\bar{\bar{e}}^{\nu}$ is in a two or three dimension representation. Nevertheless, the only physically interesting cases are those when the transition can be second order i. e. when the symmetrized cube of the representation have no projection on the identity representation. With the help of the Boccara tables mentioned in part IV, where those cases are enumerated, we have checked that, whenever the transition could be a second order one, at least one of the two vectors $\hat{u}$ was indeed not in the same representation as the strain was. In Table II we have given, for the 32 point groups, the vector decomposition of the propagative strains, the representations of both the strain and the corresponding vectors, as well as the order of the transition.

Furthermore, by using the same technique as the one which allowed us to pass from (III.1) to (III.2) one can write

$$| \bar{\bar{\mathfrak{T}}}_0(\hat{q}, v^2) | = \frac{1}{\varepsilon_0} \frac{1}{{}^t\hat{q}\bar{\bar{\varepsilon}}_0 \hat{q}} \left\{ \prod_{\mu=1}^{3} m(v_f^{\mu}(\hat{q})^2 - v(\hat{q})^2) \right\} \times$$

$$\times \left[\varepsilon_0 \, {}^t\hat{q}\bar{\bar{\varepsilon}}_0 \hat{q} + \sum_{\mu=1}^{3} \frac{(\bar{\bar{e}}_f^{\mu} \bar{\bar{\bar{\mathcal{Y}}}}_0 \hat{q})^2}{m(v_f^{\mu}(\hat{q})^2 - v(\hat{q})^2)} \right] . \quad \text{(V.11)}$$

As in part III, this equation shows that the sound velocities in the free crystals, which are the solutions of (V.11), are higher than or equal to those of the shorted crystal, $v_f^{\mu}(\hat{q})$ for the same $\hat{q}$, the equality sign being obtained when (V.10) is fulfilled.

Finally (IV.6) shows that no electric field is associated with the acoustic soft mode of the free crystal as it fulfills (V.10).

That does not bear any relationship with the polar character of the low temperature phase. As has been seen in (IV.11), that phase will be ferroelectric when the strain $\bar{\bar{e}}^{\nu}$ associated with $b_{\nu}^{\min}$ is in a ferroelectric representation, as is the case for K. D. P. [16] (2) for instance.

We have now made clear the perfect parallelism which exists between the two types of displacive transitions at $\mathbf{q} = 0$. The only (and of practical importance) difference is the number of soft modes which are related to a non ferroelectric transition. While all vectors $\hat{q}$ are possible in an optical transition, only two (in general) exist in the elastic ones. This number will generally be reduced when one considers ferroelectric transitions : one plane at least remains for optical transitions, while in the elastic case, there sometimes exists only one such $\hat{q}$.

(2) See also section V.

VI. **Conclusion and final remarks.** — In this paper we have shown that a second order displacive phase transition which does not change the number of atoms per cell always carries with it some phonon soft modes. Those modes may be some Raman inactive optical phonons the frequency of which goes to zero at the critical temperature. They can as well be some acoustical wave the velocity of which goes to zero at this temperature. No electrical field propagates with those soft modes even if the low temperature phase is polar.

Let us point out again that we have obtained those results within the framework of a phenomenological theory of the phonons: we did not try to elucidate the physical origin of the softening. Boccara ans Sarma [17] have shown how the temperature dependent quasi-harmonic theory of phonons could lead to such an effect ; Gillis [18] and Conte [19] computations show that such a mechanism indeed leads to such phase transitions. But other mechanisms need to be invoked e. g. for K. D. P. Nevertheless as has been verified by Brody and Cummins [20] a sound velocity goes to zero at the critical temperature in a direction which is consistent with our analysis of the possible accoustical soft modes in a system with the D_{2d} symmetry.

Let us finally point out that the very existence of second order displacive transitions at $\mathbf{q} = 0$ is nowadays a very controversial subject. For instance, the anharmonic terms in the phonon equation cannot be neglected and they give rise to finite lifetime effects : it is true that no optical soft mode (in the sense we used this concept throughout this paper) has even been detected with a line width which was not large compared to its frequency. Another example is given by the quartz transition which turns out to be a first order one [21] due to mechanisms which have nothing to do with the quasi-harmonic theory of phonons. In this sense it is likely that the examples given in this paper may be questionnable. We have just taken them as cases which would illustrate the points we wanted to make in this paper i. e. what are the consequences of a displacive transition from the point of view of the harmonic lattice dynamics.

APPENDIX A

If b_{ν} is an eigenvalue of the 6×6 elastic matrix $\bar{\bar{b}}$, there corresponds to b_{ν} a certain eigenspace M_{ν} of strain vectors which transforms as a given representation of the symmetry group of the crystal. We shall here prove that, if this representation is not the identity representation, one can always find in this space some strain such that, when written as a 3×3 matrix, one of the three eigenvalues is equal to zero.

We study first the case where M_{ν} is a one dimensional space. Let $\bar{e}^{\nu}$ be a vector of M_{ν}. There exists

TABLE II

Second order displacive transitions with acoustic soft modes

We give here a complete table for all the elastic transitions. They are classified according to the group of their high symmetry phase. The symmetry groups are gathered following the form of their elastic tensor and, for each of them we give the forms of the eigen-strains which induce an elastic transition. For every form, we indicate in the first line :

a) the number of times, this form appears in the elastic matrix ;

b) the order of the transition generated by this strain ;

c) when the representation of the strain $\bar{e}$ is two or three dimensional, the strain is given as a linear combination (with coefficients α, β, γ) of some eigen-strains. In this case, when all the combinations give a propagative strain, we put the symbol A. If, on the contrary, only some of them are propagative, we put the symbol N. A.

The first line is followed by a table in which we indicate :

— in the first column : the group of the high symmetry phase ;

— in the second column : the representation of the strain $\bar{e}$;

— in the third column : the representation of the wave vector $\hat{q}$ of the soft mode ;

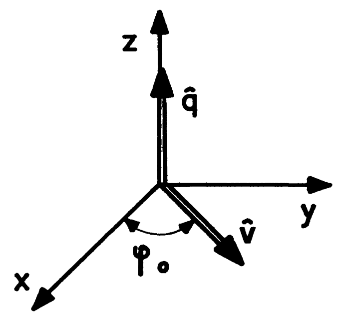
— in the fourth column : the representation of the elongation $\hat{V}$ of the same soft mode ;

— in the fifth column : the representation of the group(s) of the low symmetry phase.

1) *Monoclinic*

$[\bar{e}] = (0\,0\,0\,a\,b\,0)$ 2 2^{th} order

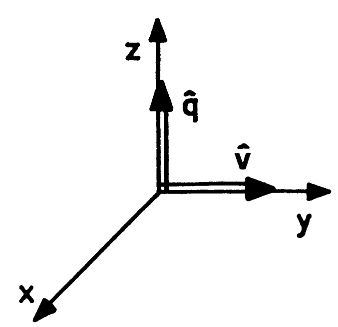
High symmetry phase	$\bar{e}$	$\hat{q}$	$\hat{V}$	Low symmetry phase
C_2	B	A	B	C_0
C_s	A″	A″	A′	C_0
C_{2h}	B_g	A_u	B_u	C_i



2) *Orthorhombic*

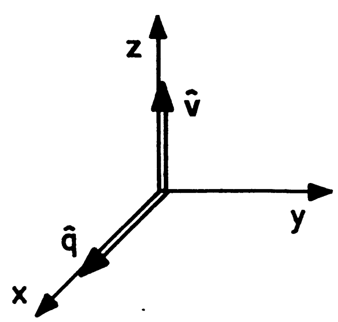
a) $[\bar{e}] = (0\,0\,0\,1\,0\,0)$ 1 2^{th} order

High symmetry phase	$\bar{e}$	$\hat{q}$	$\hat{V}$	Low symmetry phase
D_2	B_3	B_1	B_2	C_2
C_{2v}	B_2	A_1	B_2	C_s
D_{2h}	B_{3g}	B_{1u}	B_{2u}	C_{4h}



b) $[\bar{e}] = (0\,0\,0\,0\,1\,0)$ 1 2^{th} order

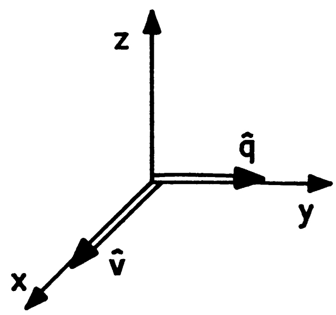
High symmetry phase	$\bar{e}$	$\hat{q}$	$\hat{V}$	Low symmetry phase
D_2	B_2	B_1	B_3	C_2
C_{2v}	B_1	A_1	B_1	C_s
D_{2h}	B_{2g}	B_{3u}	B_{1u}	C_{4h}



c) $[\bar{e}] = (0\,0\,0\,0\,0\,1)$

1 2^{th} order

High symmetry phase	$\bar{e}$	$\hat{q}$	$\hat{V}$	Low symmetry phase
D_2	B_1	B_2	B_3	C_2
C_{2v}	A_2	B_2	B_1	C_2
D_{2h}	B_{1g}	B_{2u}	B_{3u}	C_{4h}

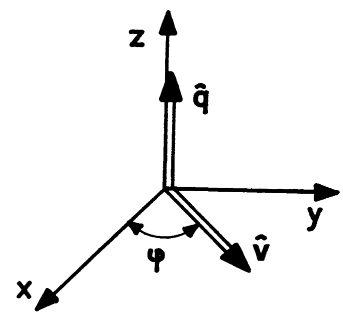


3) *Tetragonal* (First group) : S_4, C_4, C_{4h}

a) $\alpha(0\,0\,0\,1\,0\,0) + \beta(0\,0\,0\,0\,1\,0)$

1 2^{th} order A

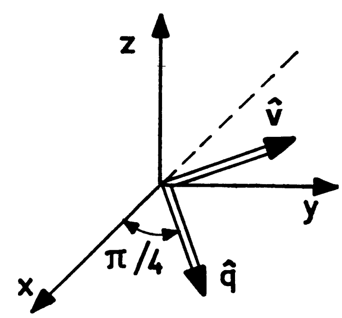
High symmetry phase	$\bar{e}$	$\hat{q}$	$\hat{V}$	Low symmetry phase
S_4	E	A_2	E	C_0
C_4	E	A_1	E	C_0
C_{4h}	E_g	A_u	E_u	C_i



b) (a-a 0 0 0 b)

1 2^{th} order

High symmetry phase	$\bar{e}$	$\hat{q}$	$\hat{V}$	Low symmetry phase
S_4	A_2	E	E	C_2
C_4	A_2	E	E	C_2
C_{4h}	B_g	E_u	E_u	C_{2h}

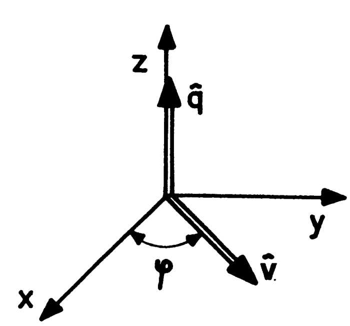


4) *Tetragonal* (Second group) : D_{2d}, D_4, C_{4v}, D_{4h}

a) $\alpha(0\,0\,0\,1\,0\,0) + \beta(0\,0\,0\,0\,1\,0)$

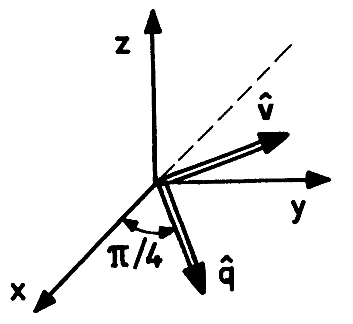
1 2^{th} order A

High symmetry phase	$\bar{e}$	$\hat{q}$	$\hat{V}$	Low symmetry phase
D_{2d}	E	B_2	E	C_s or C_2
D_4	E	A_2	E	C_2
C_{4v}	E	A_1	E	C_s
D_{4h}	E_g	A_{2u}	E_u	C_{2h}



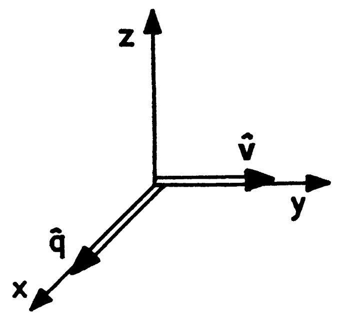
b) (1-1 0 0 0 0) 1 2^{th} order

High symmetry phase	$\bar{e}$	$\hat{q}$	$\hat{V}$	Low symmetry phase
D_{2d}	B_1	E	E	D_2
D_4	B_1	E	E	D_2
C_{4v}	B_1	E	E	C_{2v}
D_{4h}	B_{1g}	E_u	E_u	D_{2h}



c) (0 0 0 0 0 1) 1 2^{th} order

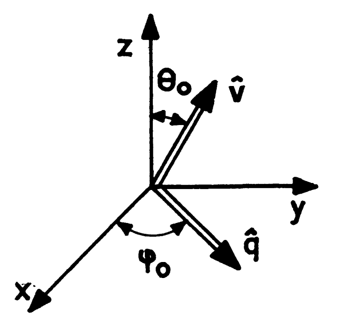
High symmetry phase	$\bar{e}$	$\hat{q}$	$\hat{V}$	Low symmetry phase
D_{2d}	B_2	E	E	C_{2v}
D_4	B_2	E	E	D_2
C_{4v}	B_2	E	E	C_{2v}
D_{4h}	B_{2g}	E_u	E_u	D_{2h}



5) *Trigonal* (First group) C_3 S_6

$\alpha(a - a\,0\,b\,c\,d) + \beta(a' - a'\,0\,b'\,c'\,d')$ 2 1^{st} order N. A.

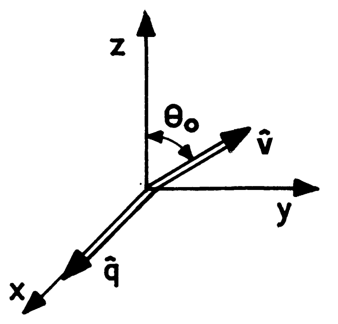
High symmetry phase	$\bar{e}$	$\hat{q}$	$\hat{V}$	Low symmetry phase
C_3	E	E	E $+ A_1$	C_0
S_6	E_{2g}	E_{1u}	$E_{1u} + B_u$	C_i



6) *Trigonal* (Second group) D_3 C_{3v} D_{3d}

$\alpha(a - a\,0\,b\,0\,0) + \beta(0\,0\,0\,0\,b\,a)$ 2 1^{th} order N. A.

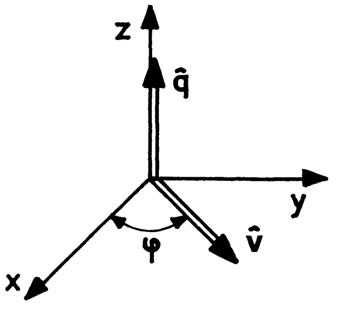
High symmetry phase	$\bar{e}$	$\hat{q}$	$\hat{V}$	Low symmetry phase
D_3	E	E	$E + A_2$	C_2
C_{3v}	E	E	$E + A_1$	C_s
D_{3d}	E_g	E_u	$E + A_{2u}$	C_{2h}



7) *Hexagonal*

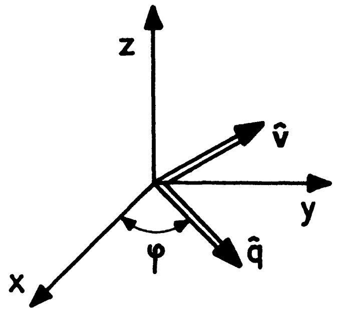
a) $\alpha(0\,0\,0\,1\,0\,0) + \beta(0\,0\,0\,0\,1\,0)$ 1 2^{th} order A

High symmetry phase	$\bar{e}$	$\hat{q}$	$\hat{V}$	Low symmetry phase
D_{3h}	E''	A''	E'	C_0
D_{3h}	E''	A_2''	E'	C_2 or C_s
C_6	E_1	A	E_1	C_0
D_6	E_1	A_2	E_1	C_2
C_{6h}	E_{2g}	A_u	E_{1u}	C_i
C_{6v}	E_1	A_1	E_1	C_i
D_{6h}	E_{1g}	A_{2u}	E_{1u}	C_{2h}



b) $\alpha(0\,0\,0\,0\,0\,1) + \beta(1\,-\,1\,0\,0\,0\,0)$ 1 1 1^{st} order N. A.

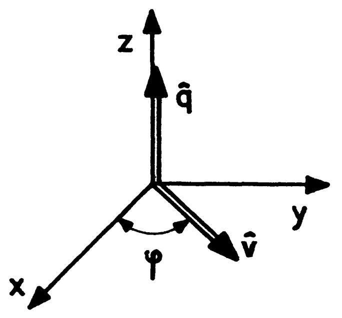
High symmetry phase	$\bar{e}$	$\hat{q}$	$\hat{V}$	Low symmetry phase
C_{3h}	E'	E'	E'	C_s
D_{3h}	E'	E'	E'	C_{2v}
C_6	E_2	E_1	E_1	C_2
D_6	E_2	E_1	E_1	D_2
C_{6h}	E_{2g}	E_{1u}	E_{1u}	C_{2h}
C_{6v}	E_2	E_1	E_1	C_{2v}
D_{6h}	E_{2g}	E_{1u}	E_{1u}	D_{2h}



8) *Cubic*

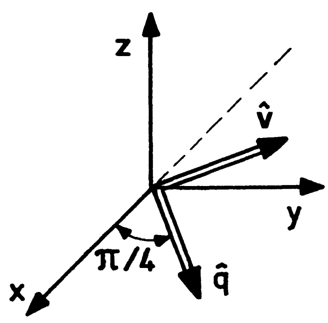
a) $\alpha(0\,0\,0\,1\,0\,0) + \beta(0\,0\,0\,0\,1\,0) + \gamma(0\,0\,0\,0\,0\,1)$ 1 1^{st} order N. A.

High symmetry phase	$\bar{e}$	$\hat{q}$	$\hat{V}$	Low symmetry phase
T	F	F	F	C_2, C_0 or C_3
O	F_2	F_1	F_1	D_3, C_2 or D_2
T_h	F_g	F_u	F_u	C_{2h}, C_i or S_6
T_d	F_2	F_2	F_2	C_{2v}, C_s or C_{3v}
O_h	F_{2g}	F_{1u}	F_{1u}	D_{2h}, C_{2h} or D_{3d}



b) $\alpha(1\,-\,1\,0\,0\,0\,0) + \beta(1\,0\,-\,1\,0\,0\,0)$ 1 1^{st} order N. A

High symmetry phase	$\bar{e}$	$\hat{q}$	$\hat{V}$	Low symmetry phase
T	E	F	F	D_2
O	E	F_1	F_1	D_4 or D_2
T_h	E_g	F_u	F_u	D_{2h}
T_d	E	F_2	F_2	D_{2d} or D_2
O_h	E_g	F_{1u}	F_{1u}	D_{4h} or D_{2h}



at least one operation of the symmetry group which changes $\bar{e}^{\nu}$ in $-\bar{e}^{\nu}$. Let g be this operation and the 3×3 matrix which describes how is transformed by g the cartesian coordinates. If $\bar{\bar{e}}^{\nu}$ is now written as a $3+3$ matrix we have

$$g(\bar{\bar{e}}^{\nu}) = [\Omega(g)]^{-1}\,\bar{\bar{e}}^{\nu}\,\Omega(g) = -\,\bar{\bar{e}}^{\nu}. \qquad (A.1)$$

Taking the determinant of (A.1) yields

$$|\,\Omega(g)^{-1}\,| \times |\,\bar{\bar{e}}^{\nu}\,| \times |\,\Omega(g)\,| = -\,|\,\bar{\bar{e}}^{\nu}\,|. \quad (A.2)$$

As $|\,\Omega(g)\,| = \pm 1$, it follows from (A. 2) that

$$|\,\bar{\bar{e}}_2^{\nu}\,| = 0. \qquad (A.3)$$

Then the matrix $e^{\nu,\alpha\beta}$ has at least one eigenvalue equal to zero and, from (V.7), the trace of the matrix $\bar{\bar{e}}^{\nu}$ is equal to zero. Thus $\bar{\bar{e}}^{\nu}$ has one or all its eigenvalues equal to zero : as the last case is impossible because $e^{\nu,\alpha\beta}$ is not identical to zero, one and only one eigenvalue of $\bar{\bar{e}}^{\nu}$ is equal to zero.

Let us now study the case where M_{ν} is a two or three dimensional space. Let us pick up in this space two linearly independent strains e_1^{ν} and e_2^{ν}. If

$$|\,\bar{\bar{e}}_2^{\nu}\,| = 0 \qquad (A.4)$$

the proof given below (A.3) immediately holds.
If (A.4) is not fullfilled

$$|\,\bar{\bar{e}}_1^{\nu} + \lambda\bar{\bar{e}}_2^{\nu}\,| = 0 \qquad (A.5)$$

is a third degree equation in λ which always has at least, one real solution λ_0. For this value λ_0, the proof given below (A.3) is again valid.

APPENDIX B

Let $\bar{\bar{e}}^{\nu}$ be a strain, eigenvector of the elastic matrix $\bar{\bar{b}}$, which transforms as a one dimensional representation different from the identity. As has been shown in Appendix A, the 3×3 matrix $e^{\nu,\alpha\beta}$ may be written in a particular system of coordinate $(0\ x.y.z)$ as :

$$\bar{\bar{e}}^{\nu} \equiv \begin{vmatrix} \varepsilon^{\nu} & 0 & 0 \\ 0 & -\varepsilon^{\nu} & 0 \\ 0 & 0 & 0 \end{vmatrix}. \qquad (B.1)$$

From (V.2) $\bar{\bar{e}}^{\nu}$ is the symmetrized product of two vectors $\hat{u}_1$ and $\hat{u}_2$ and from (B.1) those vectors are the two bisectors of $\widehat{\mathrm{O}x}$ and $\widehat{\mathrm{O}y}$. All the operations g of the symmetry group are such that $g(\bar{\bar{e}}^{\nu}) = \pm\,\bar{\bar{e}}^{\nu}$. Thus both O$z$ and the zOy plane are invariant under the operations of the group : they form two representations of the group.

If the xOy plane is an irreducible representation, $\hat{u}_1$ and $\hat{u}_2$ which are in this representation, belong to a two dimensional representation while $\bar{\bar{e}}^{\nu}$ belongs to a one dimensional one. $\bar{\bar{e}}^{\nu}$ and $\hat{u}_1$ are in different representations.

If the xOy plane is a reducible representation, let $\hat{a}$ and $\hat{b}$ be the two vectors defining the two one dimensional representations. As there exists an operation g such that $g(\bar{\bar{e}}^{\nu}) = -\,\bar{\bar{e}}^{\nu}$, one easily verifies that its existence implies that $\hat{a}$ and $\hat{b}$ are respectively $\hat{u}_1$ and $\hat{u}_2$. Finally, $\hat{u}_1$ and $\hat{u}_2$ are not in the same representation because that would imply for $\bar{\bar{e}}^{\nu}$ to be in the identity representation which is contracdictory to the hypothesis. Thus $\bar{\bar{e}}^{\nu}$ is certainly in a representation different of at least one of the two vectors $\hat{u}$.

References

[1*a*] FROHLICH (H.), Theory of Dielectrics, Oxford Univ. Press, London, 1949, p. 159.
[1*b*] ANDERSON (P. W.), in : Proceedings of the Conference on the Physics of Dielectiics, Academy of Sciences, Moscow, 1958, p. 290.
[1*c*] COCHRAN (W.), *Phys. Rev. Letters*, 1959, **3**, 412.
[2] LYDANNE (R. H.), SACHS (R. G.) and TELLER (E.), *Phys. Rev.*, 1941, **59**, 673.
[3] LANDAU (L. D.), *J. E. T. P.*, 1937, **7**, 19 ; 1937, **7**, 627, See also.
LANDAU (L. D.) and LIFSHITZ (E. M.), Statistical Physics, Pergamon Press, 1958, Chap. XIV.
[4] BORN (M.) and HUANG (K.), Dynamical theory of crystal lattices, Oxford Press, 1954, Chap. V.
[5] COCHRAN (W.) and COWLEY (R. A.), *J. Phys. Chem. Solids*, 1962, **23**, 447.
[6] PICK (R. M.), *Advances in Physics*, 1970, **19**, 269.
[7] MERTEN (L.), *Z. Naturf.*, 1960, **15A**, 47.
[8] MILLER (P. B.) and AXE (J. D.), *Phys. Rev.*, 1967, **163**, 924.
[9] *a*) MERTEN (L.), *Phys. Stat. Solidi*, 1968, **30**, 449.
b) KUROSAWA (T.), *J. Phys. Soc. of Japan*, 1961, **16**, 1298.
c) BARKER Jr (A. S.), *Phys. Rev.*, 1964, **136A**, 1290.
[10] BALLANTYNE (J. M.), *Phys. Rev.*, 1964, **136A**, 429.
[11] SHAPIRO (S. M.), SHEA (D. C. O.) and CUMMINS (H. Z.), *Phys. Rev. Letters*, 1967, **19**, 361.
SCOTT (J. F.), *Phys. Rev. Letters*, 1968, **21**, 907.
[12] AXE (J. D.) and SHIRANE (G.), *Phys. Rev.*, 1970, **B1**, 342.
[13] BOCCARA (N.), *Annals of Phys.*, 1968, **47**, 40.
[14] LE CORRE (Y.), *J. Phys. Rad.*, 1956, **17**, 1020.
[15] CHAPELLE (J.) and TAUREL (L.), *Comptes Rendus*, 1955, **240**, 743.
[16] MASON (W. P.), *Phys. Rev.*, 1946, **69**, 173.
[17] BOCCARA (N.) and SARMA (G.), *Physics*, 1965, **1**, 219.
[18] GILLIS (N.), *Phys. Rev. Letters*, 1969, **22**, 1251.
[19] CONTE (R.), to be published.
[20] BRODY (E. M.) and CUMMINS (H. Z.), *Phys. Rev. Letters*, 1968, **21**, 1263.
[21] SHAPIRO (S. M.) and COMMINS (M. Z.), in Light Scattering Spectra of Solids, Springer-Verlag. New York, 1969, p. 705.