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External Vibrations in Complex Crystals

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The study of dispersion relations for external modes in molecular and complex ionic crystals is reviewed. The concept of external modes is introduced, so that the formal theory may be developed along the lines of standard Born–von Kármán formalism. The studies reported thus far in the literature are then surveyed against the background of the formal theory. The role of macroscopic electric fields in relation to external modes is next discussed, and the work of Kellermann is generalized to obtain Coulomb coefficients connected with external modes in complex ionic crystals. Finally, the group-theoretical aspects are considered, and the recent work of Maradudin and Vosko is extended to cover the external modes. A detailed illustrative example is also provided.

CONTENTS

I. INTRODUCTION

The study of vibrations of atoms in crystals has been approached from various angles. Broadly speaking, we can identify two schools of thought. On the one hand, there were those who were interested in studying the details of the interatomic forces and confined their attention to crystals with relatively simple structures and with a small number of atoms in the primitive unit cell. In this way, they could concentrate on the basic physics of interatomic forces, keeping to the barest minimum the complications arising out of the degrees of freedom of the problem. Such efforts have been amply rewarded, and thanks to a good interplay between theory and experiment, progress has been made to the extent that the dynamics of at least the crystals of simple structures may be discussed on the basis of a detailed quantum mechanical description of the electrons (Martin, 1968, 1969; Gliss and Bilz, 1968; Toya, 1958; other relevant references may be found in Joshi and Rajagopal, 1968). On the other hand, there were others (mainly molecular physicists and spectroscopists) who were interested in crystals containing well-bound molecules and ions, notwithstanding the fact that such crystals generally tend to have complicated structures and a large number of atoms in the primitive cell. The studies of this school were directed primarily towards understanding the dynamics of molecules and ions in crystalline environment as opposed to their behavior in free conditions. Experimental information came mainly from spectroscopic investigations, and the data were often analyzed using the picture of an individual molecule interacting with its environment rather than in terms of cooperative vibrations of all atoms in the crystal, as discussed by the other school.

It is clearly unsatisfactory to have such radically different kinds of theoretical descriptions for different types of crystals. It turns out that the dynamics of all categories of crystals, irrespective of their structure, can in fact be discussed using the same formalism, viz., the Born–von Kármán formalism (Born and von Kármán, 1912; Born and Huang, 1954, frequently abbreviated hereafter as BH), used extensively by the first school. In this, one assigns three degrees of freedom to every atom in the crystal, sets up the equations of motion, and then solves them to obtain the vibrational displacements of atoms. There are, however, serious limitations in applying the formalism in practice to complicated crystals of the type which generally interest molecular physicists. In the first place, there is the

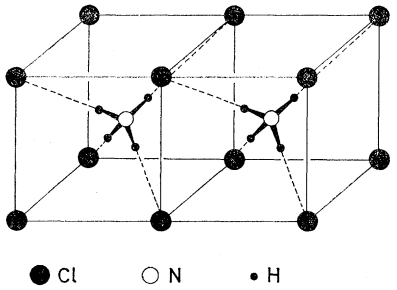

FIG. 1. Structure of NH_4Cl in the ordered (CsCl) phase.

computational difficulty arising from the large number of degrees of freedom per unit cell. Secondly, the physical picture of molecules executing motions as a whole like translational oscillations, rotational oscillation or librations, etc., is completely lost and can be constructed only retrospectively after numerical solutions for the displacements are available.

Fortunately, there exists yet another approach for complex crystals, which combines the best of both worlds. In this, one identifies *a priori* the well-bound molecules and polyatomic clusters like ionic radicals (frequently referred to hereinafter simply as "molecular groups") in the crystal and treats them as rigid bodies capable not only of translation but also of rotation. Coupling is then allowed for between all the various units in the crystal, i.e., the various atoms which have individual identity (if there are any such atoms in the crystal) as well as the molecular groups, and the effects of crystal periodicity are taken into account in the same way as in the Born–von Kármán formalism. One thus obtains the so-called *external modes* which involve not only the vibrations of the single atoms but also the rigid-body motions of the molecular groups. The effects of nonrigidity of the molecules or ionic clusters may be examined separately, once again allowing for coupling between different units and for crystal periodicity. This leads to the *internal modes*. In this language, the spectroscopic experiments mentioned earlier study special cases of internal and external modes.

Although these concepts have existed in the literature for a long time, the mathematical framework, especially for the study of external modes, was not fully developed, and for many years these ideas were used merely for the arithmetrical enumeration of the number of external and internal modes associated with a given crystal. As regards the external and internal modes, the former generally have lower frequencies and are more interesting since they strongly depend on intermolecular forces. In recent years, a beginning has been made in the detailed study of external modes, both theoretical and experimental, and this article will survey these developments emphasizing the theoretical aspects. Additionally, clarifications will be offered concerning several points which do not seem to have received sufficient attention so far. Our discussion will cover not only molecular crystals like hexamine, naphthalene, etc., in which all the molecules are identical, but also inorganic crystals like NH_4Cl, $CaWO_4$, and $LiClO_4 \cdot 3H_2O$, etc., in which one may identify both individual ions as well as well-bound molecules and ionic clusters. We shall use the term "complex crystals" to cover comprehensively all these different categories.

The formal theory of external modes closely follows standard Born–von Kármán theory in many respects. An elementary account of the latter is nowadays an integral part of all solid state texts (see for example, Kittel, 1966; Ziman, 1965; Seitz, 1940) and we shall suppose that the reader is familiar with the basic concepts. More detailed accounts may be found in the review articles by Blackman (1955), Cochran (1963), Leibfried (1955), Cochran and Cowley (1968), and in the monographs by Born and Huang (1954), Maradudin, Montroll, and Weiss (1963) (abbreviated MMW), and Ludwig (1967).

Before embarking on the formal theory of external modes, it is useful to consider the qualitative aspects of treating the dynamics in terms of internal and external modes vis-a-vis the standard Born–von Kármán approach. This is best done with a specific example, and the crystal we shall consider is NH_4Cl.

Figure 1 shows a portion of the NH_4Cl lattice.[1] The primitive unit cell is cubic and contains one molecule of NH_4Cl, i.e., six atoms, resulting in 18 degrees of freedom. In the conventional Born–von Kármán scheme, therefore, there will be 18 branches to the phonon dispersion relations.

In the external-mode approach, on the other hand, one views the primitive unit cell as containing a Cl^- ion and one rigidly bound NH_4^+ ion, with a total of nine degrees of freedom, six of which correspond to the translational degrees of freedom of the Cl^- and NH_4^+ ions, and the remaining three to the rotational degrees of freedom of the NH_4^+ ion. The dispersion relations obtained on this basis will have only nine branches called *external branches*, as opposed to the 18 branches in the conventional formulation.

The external-mode approach thus focuses attention on only part of the problem, and clearly some informa-

TABLE I. Frequencies of the NH_4^+ ion.

Vibration	Isolated ion[a] (cm^{-1})	In crystal (cm^{-1})
ν_1 (nondegenerate)	3033	3048[b]
ν_2 (doubly degenerate)	1685	1683[c]
ν_3 (triply degenerate)	3134	3086[c]
ν_4 (triply degenerate)	1397	1402[c]

[a] Herzberg (1945).
[b] Krishnan (1947).
[c] Wagner and Hornig (1950).

[1] NH_4Cl has several phases. Figure 1 corresponds to the ordered phase (often called the CsCl phase) which exists below 242.2°K.

tion is lost in reducing the degrees of freedom and attempting a simplification. The degrees of freedom suppressed are those in which the different atoms of the NH_4^+ ion move relative to each other, while preserving, however, the center of mass of the ion. Such motions are referred to as internal vibrations, and in the isolated NH_4^+ ion these nine vibrations manifest as four distinct frequencies of which some are degenerate. These frequencies have been measured for the ion in solution, and are listed in the second column of Table I. They are fairly large compared to the usual scale of vibrational frequencies in crystals and reflect the strong binding of the N–H bond. (For comparison, the highest frequency in NaI is ~ 200 cm^{-1}.)

In crystalline NH_4Cl, the internal vibrations of the different ammonium ions are coupled and are propagated as waves, resulting in nine *internal branches*. The third column of Table I shows some of the frequencies in NH_4Cl measured in spectroscopic experiments. These pick out mainly the $\mathbf{q}=0$ modes, i.e., the modes of zero wave vector, and the near equality of the frequencies listed with those of the isolated ion indicates that these modes correspond essentially to internal vibrations of the ammonium ion. Further, we see that the frequencies are barely altered by the crystalline environment. This in turn suggests that in NH_4Cl the forces within the NH_4^+ ion are much stronger than the NH_4^+–NH_4^+, NH_4^+–Cl^-, and Cl^-–Cl^- forces. In view of this weak interionic coupling relative to the intraionic forces in NH_4^+, one also expects the internal vibration branches to be relatively flat and dispersionless. Thus the fact that nine branches out of a total of 18 have virtually the same frequencies as those for an isolated ion shows that nothing much will be lost if we suppress these branches altogether. This is precisely what we do in the external-mode approach to the dynamics of complex crystals.

Generalizing the example of NH_4Cl, we may say that whenever well-bound groups of atoms can be identified, it is advantageous to regard them as rigid, and thereby simplify the problem. The basic physical criterion for viewing a group as well bound is that the forces coupling atoms within the group should be much stronger than those coupling the atoms of the group to the remaining atoms in the crystal. Experimental evidence for the existence of such a situation include

(i) close similarity in the vibrational frequencies of the isolated group and those of the group in the crystal (e.g., as in Table I);

(ii) large differences between the scale of frequencies associated with internal vibrations of bound groups and those involving other types of motion. In the case of NH_4Cl, for example, it is known experimentally that the largest frequency not involving internal vibrations is ~ 390 cm^{-1}, which is to be compared with the value of ~ 1400 cm^{-1} for the lowest internal vibration frequency.

Thus the existence of two different scales of forces and consequently of two different domains of frequencies enables us (at least to a good first approximation) to view them separately and in isolation of each other. We could suppress the internal degrees of freedom of the various clusters and study the waves set up by the coupling of the rigid-body displacements, both linear and angular (where appropriate), of the different groups. This leads to the external branches of the phonon spectrum of the crystal, and often these are physically the most interesting ones. Should the need arise, we could examine separately the effects of nonrigidity. This may be done by first considering the internal vibrations of one cluster and then allowing for the coupling of vibrations in different clusters, thereby obtaining the internal branches of the phonon dispersion curves (Davydov, 1962). Such branches will generally be rather flat owing to the relative weakness of intermolecular forces as compared to intraionic or intramolecular forces. The analysis could, if necessary, be carried even further by allowing for coupling between the external and internal modes via some perturbation scheme, recovering at this point more or less complete identification with the Born–von Kármán approach where no such compartmentalization is made.

In general, if a complex crystal has μ atoms which have individual identity, and ν nonlinear relatively well-bound clusters in the primitive unit cell, then there will be $(3\mu+6\nu)$ external branches.[2] Three of these will be the so-called acoustic branches and will tend to zero frequency as $\mathbf{q}\rightarrow 0$. The remaining $(3\mu+6\nu)-3$ external branches behave like optic branches in that they tend to finite frequencies as $\mathbf{q}\rightarrow 0$. If n be the total number of atoms in the primitive cell, then it follows that the number of internal branches equals $3n-(3\mu+6\nu)$. These also will have the character of optic branches.

Our attention in this article will be confined to the external modes, and in the following sections we shall discuss their various aspects. In Sec. II we develop a Born–von Kármán-type formalism for external modes. This is followed by a review in Sec. III of the studies reported thus far (both experimental and theoretical) concerning dispersion relations for external modes in complex crystals. The effects of electric fields set up by the vibrations are examined in Sec. IV, while the group-theoretical aspects are discussed in Sec. V. The concluding section presents a summary. It must be mentioned that sometimes the standard Born–von Kármán treatment is given a molecular twist by expressing the interatomic forces in terms of bond stretching, bond bending, torsion, etc. The dynamics of diamond (Musgrave and Pople, 1962; McMurray *et al.*, 1967), polyethylene (Tasumi and Shimanouchi, 1965), and crystalline HCl (Trevino *et al.*, 1968) have been treated in this fashion. In our version of introducing a

[2] This number will be modified if there are linear molecules present since linear molecules have only five external degrees of freedom as opposed to six for nonlinear molecules.

molecular picture, some degrees of freedom are completely suppressed unlike the cases just mentioned.

II. FORMAL THEORY

A. Dynamics in the Fixed Frame

In this section we shall discuss the formal aspects of the dynamics of external vibrations in complex crystals in the harmonic approximation, using appropriate extensions of the traditional Born–von Kármán approach to lattice dynamics.

We begin by supposing that the primitive unit cell contains

(I) μ single atoms or ions labeled by the index κ ranging from 1 to μ, and

(II) ν well-bound molecular groups labeled $\kappa=(\mu+1), \cdots, (\mu+\nu)$.

For simplicity, we shall assume the polyatomic clusters to be nonlinear so that they have six external degrees of freedom each. A linear molecule has only five degrees of freedom since two coordinates alone are sufficient to specify its orientation, making one of the rotational degrees of freedom redundant. We shall refer to both types of entities I and II as vibrating units. The crystal thus has $(\mu+\nu)$ sublattices[3] containing both single ions and molecular groups and has $(3\mu+6\nu)$ degrees of freedom per unit cell.

The next step is to write down the vibrational Hamiltonian for the external vibrations. This requires a convention for the specification of the displacement components. Several choices are possible, two particularly useful ones being the following: In the first the displacements, both linear and angular, are referred to a set of Cartesian axes fixed to the crystal. This frame of reference will frequently be referred to hereinafter as the "fixed frame." While the Cartesian axes can be chosen arbitrarily with respect to the crystallographic axes, it is convenient and useful to make the choice in conformity with some accepted convention say, as recommended by the Standards Committee of IRE (1949) or as given in the *International Tables of X-ray Crystallography* (Londsdale, 1952). Alternatively, the displacements of each vibrating unit may be referred to a set of local axes oriented so as to coincide with the principal axes of the moment-of-inertia tensor of the concerned unit. This system of axes will be referred to as the "principal-axes frame." Both systems have their own usefulness. For the present, we shall consider the dynamics with the displacements specified in the fixed frame. This formulation is useful especially if one wants to go to the long-wavelength limit and explore the connection with elasticity theory. It is also convenient for developing analytic expressions for the contributions to the dynamical equations arising from Coulomb interactions in ionic crystals (Sec. IV).

The displacements (both linear and angular) in which we are interested are small displacements. By this we mean that the linear displacements of the units from their respective equilibrium positions are small compared to typical interunit distances. Similarly the angular displacements will be supposed to be essentially infinitesimal so that they can be represented by vectors along the axes of rotation having magnitudes equal to those of the rotations. Further, the direction of such a vector is along that of the advancement of a right-handed screw (e.g., a counterclockwise rotation by $\delta\phi$ about the Z axis will be represented by a vector of appropriate length along the Z axis).

Both linear and angular displacements are thus represented by vectors. There is, however, an important difference in their transformation properties under inversion. Whereas vectors corresponding to linear displacements change sign under inversion, those corresponding to angular displacements do not. The former are called ordinary or polar vectors, and the latter as pseudo- or axial vectors. It can be shown (Goldstein, 1953) that under an orthogonal transformation S-like rotation, reflection, roto-reflection, etc., an axial vector $\mathbf{u}^r$ transforms as

$$\begin{aligned} \mathbf{u}^r \rightarrow \mathbf{u}'^r &= \mathbf{S}\mathbf{u}^r \quad \text{if } \mathbf{S} \text{ is a proper rotation} \\ &= -\mathbf{S}\mathbf{u}^r \quad \text{if } \mathbf{S} \text{ is an improper rotation,} \end{aligned} \tag{II.A.1a}$$

where an improper rotation implies a compound operation involving a pure rotation and inversion. Since the determinant of $\mathbf{S}$ is ± 1 according as $\mathbf{S}$ is a proper or improper rotation, (II.A.1a) is frequently written

$$\mathbf{u}'^r = |\,\mathbf{S}\,|\,\mathbf{S}\mathbf{u}^r. \tag{II.A.1b}$$

A.1 Vibration Hamiltonian

Let $\mathbf{X}(l\kappa k)$ denote the equilibrium position of the kth atom in the κth unit in the lth cell. $\mathbf{X}(l\kappa k)$ can be written as

$$\mathbf{X}(l\kappa k) = \mathbf{X}(l) + \mathbf{X}(\kappa) + \mathbf{X}(k), \tag{II.A.2}$$

where $\mathbf{X}(k)$ represents the equilibrium position of the atom k with respect to the center of the mass of the unit κ; $\mathbf{X}(\kappa)$ is the equilibrium position of the center of mass of κ with respect to the cell l, and $\mathbf{X}(l)$ is the position vector of the cell concerned. For type I units, $\mathbf{X}(k)=0$, and clearly

$$\mathbf{X}(l\kappa k) \rightarrow \mathbf{X}(l\kappa).$$

The linear and angular displacements will be denoted, respectively, by $\mathbf{u}^t(l\kappa)$ and $\mathbf{u}^r(l\kappa)$, the superscripts emphasizing their character explicitly.

The kinetic energy T of the crystal is given by

[3] Usually each sublattice site is thought of as being occupied by only one atom. We generalize the concept by supposing that the sites are occupied by vibrating units defined above.

(treating vibrating units of type II as rigid bodies)

$$T=\tfrac{1}{2}\sum_{l}\sum_{\kappa=1}^{\mu+\nu}\sum_{\alpha=x,y,z} m_\kappa[\dot{u}_\alpha{}^t(l\kappa)]^2+\tfrac{1}{2}\sum_{l}\sum_{\kappa=(\mu+1)}^{(\mu+\nu)}\sum_{\alpha,\beta=x,y,z}\mathcal{I}_{\alpha\beta}(\kappa)\dot{u}_\alpha{}^r(l\kappa)\dot{u}_\beta{}^r(l\kappa) \tag{II.A.3a}$$

$$=\tfrac{1}{2}\sum_{l}\sum_{\kappa=1}^{\mu+\nu} m_\kappa[\dot{\mathbf{u}}^t(l\kappa)\cdot\dot{\mathbf{u}}^t(l\kappa)]+\tfrac{1}{2}\sum_{l}\sum_{\kappa=(\mu+1)}^{(\mu+\nu)}\dot{\mathbf{u}}^r(l\kappa)\cdot\mathcal{I}(\kappa)\cdot\dot{\mathbf{u}}^r(l\kappa), \tag{II.A.3b}$$

using tensor notation. Here m_κ is the mass of the κth unit, and $\mathcal{I}_{\alpha\beta}(\kappa)$ the $\alpha\beta$th element of the moment-of-inertia tensor. The dots on top denote differentiation with respect to time.

Since the displacements are considered to be small,[4] the potential energy Φ can be expanded in a Taylor series in the displacements as follows:

$$\begin{aligned}\Phi&=\Phi_0+\Phi_1+\Phi_2+\cdots\\&=\Phi_0+\{\sum_{l}\sum_{\kappa=1}^{(\mu+\nu)}\sum_{\alpha}\phi_\alpha{}^t(l\kappa)u_\alpha{}^t(l\kappa)+\sum_{l}\sum_{\kappa=(\mu+1)}^{(\mu+\nu)}\sum_{\alpha}\phi_\alpha{}^r(l\kappa)u_\alpha{}^r(l\kappa)\}\\&\quad+\tfrac{1}{2}\{\sum_{ll'}\sum_{\kappa=1}^{(\mu+\nu)}\sum_{\kappa'=1}^{(\mu+\nu)}\sum_{\alpha\beta}\phi_{\alpha\beta}{}^{tt}(l\kappa;l'\kappa')u_\alpha{}^t(l\kappa)u_\beta{}^t(l'\kappa')+\sum_{ll'}\sum_{\kappa=1}^{(\mu+\nu)}\sum_{\kappa'=(\mu+1)}^{(\mu+\nu)}\sum_{\alpha\beta}\phi_{\alpha\beta}{}^{tr}(l\kappa;l'\kappa')u_\alpha{}^t(l\kappa)u_\beta{}^r(l'\kappa')\\&\quad+\sum_{ll'}\sum_{\kappa=(\mu+1)}^{(\mu+\nu)}\sum_{\kappa'=1}^{(\mu+\nu)}\sum_{\alpha\beta}\phi_{\alpha\beta}{}^{rt}(l\kappa;l'\kappa')u_\alpha{}^r(l\kappa)u_\beta{}^t(l'\kappa')+\sum_{ll'}\sum_{\kappa=(\mu+1)}^{(\mu+\nu)}\sum_{\kappa'=(\mu+1)}^{(\mu+\nu)}\sum_{\alpha\beta}\phi_{\alpha\beta}{}^{rr}(l\kappa;l'\kappa')u_\alpha{}^r(l\kappa)u_\beta{}^r(l'\kappa')\}\\&\quad+\text{higher-order terms.}\end{aligned} \tag{II.A.4}$$

The leading term Φ_0 represents the energy in the equilibrium configuration, and the coefficients $\phi_\alpha{}^t(l\kappa)$, etc., are given by the derivatives of the potential energy in the equilibrium configuration as follows:

$$\phi_\alpha{}^i(l\kappa)=\partial\Phi/\partial u_\alpha{}^i(l\kappa)\,|_0, \qquad i=t,r; \tag{II.A.5a}$$

$$\phi_{\alpha\beta}{}^{ii'}(l\kappa;l'\kappa')=\partial^2\Phi/\partial u_\alpha{}^i(l\kappa)\,\partial u_\beta{}^{i'}(l'\kappa')\,|_0, \qquad i,i'=t,r, \text{ etc.} \tag{II.A.5b}$$

The symbol $|_0$ signifies that the derivatives are to be evaluated with all vibrating units in their respective equilibrium positions. Since we have assumed the displacements to be small, we may terminate the series at the second-order term Φ_2. This, as we shall see later, will lead to harmonic vibrations, and for this reason the approximation is called the harmonic approximation. The coefficients $\phi_\alpha{}^t(l\kappa)$ and $\phi_\alpha{}^r(l\kappa)$ represent the force and torque, respectively, on the unit $(l\kappa)$ in the undistorted crystal, and must obviously vanish since the configuration corresponds to equilibrium. The potential energy in the harmonic approximation is thus given by

$$\Phi\approx\Phi_0+\Phi_2. \tag{II.A.6}$$

It is now a simple matter to formulate the equations of motion from the Hamiltonian

$$H=T+\Phi_0+\Phi_2. \tag{II.A.7}$$

[4] In practical applications, it is important to ensure that this requirement is met within the crystal under investigation. In many crystals with weak binding, the molecules exhibit relatively large amplitude rotational motions, and in such cases it is meaningless to consider a small amplitude treatment as above. A notable example is solid hydrogen in which the molecules exhibit very nearly a free rotation spectrum. This requires quite different methods. See van Kranendonk and Sears (1966).

Before doing so, however, it is necessary to consider some of the properties of the quantities $\phi_{\alpha\beta}{}^{ii'}(l\kappa;l'\kappa')$ which have the significance of force constants (this will be seen explicitly after formulating the equations of motion).

A.2 Properties of Force Constants

(i) Due to the translational symmetry of the lattice, we have

$$\phi_{\alpha\beta}{}^{ii'}(l\kappa;l'\kappa')=\phi_{\alpha\beta}{}^{ii'}(l+L,\kappa;l'+L,\kappa'). \tag{II.A.8a}$$

In particular,

$$\begin{aligned}\phi_{\alpha\beta}{}^{ii'}(l\kappa;l'\kappa')&=\phi_{\alpha\beta}{}^{ii'}(l-l',\kappa;0\kappa')\\&=\phi_{\alpha\beta}{}^{ii'}(0\kappa;l'-l,\kappa').\end{aligned} \tag{II.A.8b}$$

(ii) Making the reasonable assumption that the potential function Φ is well behaved, we find that the force constants have the permutation symmetry

$$\phi_{\alpha\beta}{}^{ii'}(l\kappa;l'\kappa')=\phi_{\beta\alpha}{}^{i'i}(l'\kappa';l\kappa) \tag{II.A.9}$$

since the order of differentiation in (II.A.5b) is immaterial.

(iii) Crystalline symmetry bestows important properties on the force constants. Let $\mathcal{S}_m=\{\mathbf{S}\mid\mathbf{V}(S)+\mathbf{X}(m)\}$ denote an operation of the space group of the crystal, i.e., an operation which carries the crystal into coincidence with itself. Here $\mathbf{S}$ is the rotational part and corresponds to either a proper or an improper rotation. $\mathbf{X}(m)$ is a lattice translation, and $\mathbf{V}(S)$ a fractional translation which depends on the nature of the crystal and $\mathbf{S}$. In crystals belonging to symmorphic space groups, for example, $\mathbf{V}(S)$ is always zero. In crystals

containing glide and screw operations, $\mathbf{V}(S)$ is nonzero for some space group elements.

Let us suppose that under the action of $\mathcal{S}_m$ the vibrating unit at $\mathbf{X}(l\kappa)$ is carried to the one at $\mathbf{X}(LK)$. (Clearly the units in the Kth sublattice must be chemically identical to those in the sublattice κ). We then have

$$\mathcal{S}_m\mathbf{X}(l\kappa)=\mathbf{X}(LK)$$
$$=\mathsf{S}\mathbf{X}(l\kappa)+\mathbf{V}(S)+\mathbf{X}(m). \quad \text{(II.A.10)}$$

Let $\mathbf{u}^i(l\kappa)$ and $\mathbf{u}^{i'}(l'\kappa')$ denote the displacements of the $(l\kappa)$th and $(l'\kappa')$th units, respectively. The deformation energy associated with this particular pair is

$$\tfrac{1}{2}\sum_{\alpha,\beta}\phi_{\alpha\beta}{}^{ii'}(l\kappa;l'\kappa')u_\alpha{}^i(l\kappa)u_\beta{}^{i'}(l'\kappa'). \quad \text{(II.A.11a)}$$

Suppose now that under $\mathcal{S}_m$, the units $(l\kappa)$ and $(l'\kappa')$ are carried over to (LK) and $(L'K')$, respectively. The displacements $\mathbf{u}^i(l\kappa)$ and $\mathbf{u}^{i'}(l'\kappa')$ will be carried over to these sites as

$$C^i(S)\mathsf{S}\mathbf{u}^i(l\kappa) \quad \text{and} \quad C^{i'}(S)\mathsf{S}\mathbf{u}^{i'}(l'\kappa'),$$

where

$$C^i(S)=1 \quad \text{for} \quad i=t$$
$$=|\,\mathsf{S}\,| \quad \text{for} \quad i=r. \quad \text{(II.A.12)}$$

The potential energy associated with the pair (LK) and $(L'K')$ in the transformed configuration is

$$\tfrac{1}{2}\sum_{\alpha,\beta}\sum_{\mu,\nu}\phi_{\mu\nu}{}^{ii'}(LK;L'K')S_{\mu\alpha}u_\alpha{}^i(l\kappa)C^i(S)$$
$$\times S_{\nu\beta}u_\beta{}^{i'}(l'\kappa')C^{i'}(S). \quad \text{(II.A.11b)}$$

Clearly this must equal (II.A.11a), whence

$$\phi_{\alpha\beta}{}^{ii'}(l\kappa;l'\kappa')=\sum_{\mu\nu}C^i(S)S_{\mu\alpha}\phi_{\mu\nu}{}^{ii'}(LK;L'K')$$
$$\times S_{\nu\beta}C^{i'}(S), \quad \text{(II.A.13a)}$$

or more compactly,

$$\boldsymbol{\phi}^{ii'}(l\kappa;l'\kappa')=C^i(S)\mathsf{S}^{\mathrm{tr}}\boldsymbol{\phi}^{ii'}(LK;L'K')\mathsf{S}C^{i'}(S), \quad \text{(II.A.13b)}$$

where tr denotes transpose. Observe in passing that due to the connection between the vibrating units at $(l\kappa)$ and (LK) via $\mathcal{S}_m$, a relationship also exists between their moment-of-inertia tensors. Proceeding as above, and comparing the rotational kinetic energy

$$\tfrac{1}{2}\sum_{\alpha,\beta}\mathcal{I}_{\alpha\beta}(\kappa)\dot{u}_\alpha{}^r(l\kappa)\dot{u}_\beta{}^r(l\kappa)$$

before transformation, with the energy

$$\tfrac{1}{2}\sum_{\mu,\nu}\mathcal{I}_{\mu\nu}(K)\dot{u}_\mu{}^r(LK)\dot{u}_\nu{}^r(LK)$$
$$=\tfrac{1}{2}\sum_{\mu,\nu}\sum_{\alpha,\beta}C^r(S)S_{\mu\alpha}\dot{u}_\alpha{}^r(l\kappa)\mathcal{I}_{\mu\nu}(K)S_{\nu\beta}\dot{u}_\beta{}^r(l\kappa)C^r(S)$$

after transformation, we obtain, remembering

$$[C^i(S)]^2=1,$$
$$\mathcal{I}(\kappa)=\mathsf{S}^{\mathrm{tr}}\mathcal{I}(K)\mathsf{S}. \quad \text{(II.A.14a)}$$

A similar exercise involving the translational kinetic energy yields

$$m_\kappa=m_K, \quad \text{(II.A.14b)}$$

a result which is intuitively obvious.

In addition to the properties discussed above, there are other constraints on the force constants, due to the invariance of the potential energy under infinitesimal translation and rotation of the crystal as a whole. These are best discussed after we have set up the equations of motion.

A.3 Equations of Motion

The equations of motions will be derived from (II.A.7) using a classical approach, the transition to quantum mechanics being indicated later. Using Hamilton's equations, we directly obtain

$$m_\kappa\ddot{u}_\alpha{}^t(l\kappa)=\text{linear force along } \alpha \text{ on } (l\kappa)$$
$$=-\Big(\sum_{l'}\sum_{\kappa'}\sum_{\beta}\phi_{\alpha\beta}{}^{tt}(l\kappa;l'\kappa')u_\beta{}^t(l'\kappa')$$
$$+\sum_{l'}\sum_{\kappa'\in\mathrm{II}}\sum_{\beta}\phi_{\alpha\beta}{}^{tr}(l\kappa;l'\kappa')u_\beta{}^r(l'\kappa')\Big), \quad \text{for all } l,\ \kappa, \text{ and } \alpha, \quad \text{(II.A.15a)}$$

$$\mathcal{I}_{\alpha\alpha}(\kappa)\ddot{u}_\alpha{}^r(l\kappa)=\text{torque about } \alpha \text{ on } (l\kappa)$$
$$=-\Big(\sum_{l'}\sum_{\kappa'}\sum_{\beta}\phi_{\alpha\beta}{}^{rt}(l\kappa;l'\kappa')u_\beta{}^t(l'\kappa')+\sum_{l'}\sum_{\kappa'\in\mathrm{II}}\sum_{\beta}\phi_{\alpha\beta}{}^{rr}(l\kappa;l'\kappa')u_\beta{}^r(l'\kappa')$$
$$+\sum_{\beta\neq\alpha}\mathcal{I}_{\alpha\beta}(\kappa)\ddot{u}_\beta{}^r(l\kappa)\Big), \quad \text{(II.A.15b)}$$

for all l and α, and κ restricted to type II units.

In the above equations as well as in all subsequent ones, it will be assumed that the summations over the sublattice index κ' runs over both types I and II, i.e., from 1 to $(\mu+\nu)$ except when indicated as $\kappa'\in$ II, in which case the range of κ' is restricted to $(\mu+1)\cdots(\mu+\nu)$.

Equation (II.A.15) is similar to the corresponding equation in standard lattice dynamics with one important additional feature, viz., we have here equations of motion for angular displacements also. Further, due to the coupling between linear and angular displacements via the constants $\phi_{\alpha\beta}{}^{tr}$ and $\phi_{\alpha\beta}{}^{rt}$, the vibrational motions will in general be composed of both linear as well as angular oscillations (also called torsional oscillations or librations).

In special cases, however, the admixture may be small and even zero. It is also worth drawing attention to the presence of off-diagonal terms in the moment of inertia in (II.A.15b). This is a consequence of the fact that the moment-of-inertia tensor of a rigid body with respect to an arbitrary set of axes has, in general, off-diagonal elements. One of the advantages of the principal-axes formulation to be discussed later is that the off-diagonal terms $g_{\alpha\beta}(\kappa)$ $(\alpha \neq \beta)$ are absent.

From (II.A.15a) we see that $\phi_{\alpha\beta}{}^{tt}(l\kappa; l'\kappa')$ represents the negative of the linear force on $(l\kappa)$ along the α direction due to unit linear displacement of $(l'\kappa')$ along β direction; likewise, $\phi_{\alpha\beta}{}^{rt}(l\kappa; l'\kappa')$ is the negative of the torque about the α direction on $(l\kappa)$, exerted by unit linear displacement of $(l'\kappa')$ along β. Similar meanings can be given to $\phi_{\alpha\beta}{}^{tr}$ and $\phi_{\alpha\beta}{}^{rr}$. It is useful to note that $\phi_{\alpha\beta}{}^{tt}$, $(\phi_{\alpha\beta}{}^{tr}, \phi_{\alpha\beta}{}^{rt})$, and $\phi_{\alpha\beta}{}^{rr}$ all have different dimensions.

A.4 Sum Rules

We are now ready to consider the constraints arising from the invariance of the potential energy under infinitesimal translation and rotation. Suppose first that the crystal is given a uniform infinitesimal translation ϵ_β, say, i.e., $\mathbf{u}^r(l\kappa) \equiv 0$ for $\kappa \in \text{II}$, and $u_\alpha{}^t(l\kappa) = \epsilon_\beta \delta_{\alpha\beta}$, for all l and κ. Such a translation produces no restoring forces on any vibrating unit, and from (II.A.15a) we therefore have[5]

$$0 = \Big(\sum_{l'} \sum_{\kappa'} \phi_{\alpha\beta}{}^{tt}(l\kappa; l'\kappa')\Big)\epsilon_\beta,$$

or, since ϵ_β is arbitrary,

$$\sum_{l'} \sum_{\kappa'} \phi_{\alpha\beta}{}^{tt}(l\kappa; l'\kappa') = \sum_{l'} \sum_{\kappa'} \phi_{\alpha\beta}{}^{tt}(0\kappa; l'\kappa') = 0, \qquad \text{for all } \alpha, \beta, \text{ and } \kappa. \tag{II.A.16}$$

Similarly, from (II.A.15b) we have

$$\sum_{l'} \sum_{\kappa'} \phi_{\alpha\beta}{}^{rt}(0\kappa; l'\kappa') = 0, \qquad \text{for all } \alpha, \beta, \text{ and } \kappa \in \text{II}. \tag{II.A.17a}$$

Using (II.A.8) and (II.A.9) we also have

$$\sum_{l'} \sum_{\kappa'} \phi_{\alpha\beta}{}^{tr}(0\kappa'; l'\kappa) = 0, \qquad \text{for all } \alpha \text{ and } \beta, \text{ and } \kappa \in \text{II}. \tag{II.A.17b}$$

Next let us suppose that the crystal as a whole is subjected to an infinitesimal rotation $\boldsymbol{\theta}$ about the origin. As a result, the centers of mass will undergo displacements $\boldsymbol{\theta} \times \mathbf{X}(l\kappa)$, and in addition, all vibrating units of type II will themselves be rotated through $\boldsymbol{\theta}$. For purposes of illustration let us suppose that the rotation is about the x axis. The center-of-mass displacement of the $(l\kappa)$th unit is then given by $(0, -\theta_x X_z(l\kappa), \theta_x X_y(l\kappa))$. Remembering that rotation of the crystal as a whole does not produce a restoring force on any vibrating unit, we obtain from (II.A.15a)

$$0 = \theta_x \Big\{ \sum_{l'} \sum_{\kappa'} \big[\phi_{\alpha z}{}^{tt}(0\kappa; l'\kappa') X_y(l'\kappa') - \phi_{\alpha y}{}^{tt}(0\kappa; l'\kappa') X_z(l'\kappa')\big] + \sum_{l'} \sum_{\kappa' \epsilon \text{II}} \phi_{\alpha x}{}^{tr}(0\kappa; l'\kappa') \Big\}.$$

Since θ_x is arbitrary, the quantity within the braces must vanish. The result is readily generalized to give[6]

$$\sum_{l'} \sum_{\kappa'} \big[\phi_{\alpha\delta}{}^{tt}(0\kappa; l'\kappa') X_\gamma(l'\kappa') - \phi_{\alpha\gamma}{}^{tt}(0\kappa; l'\kappa') X_\delta(l'\kappa')\big] + \sum_{l'} \sum_{\kappa' \epsilon \text{II}} \phi_{\alpha\beta}{}^{tr}(0\kappa; l'\kappa') = 0. \tag{II.A.18}$$

This holds for all values of κ. The indices α and β can be x, y, or z. However, for a given value of β, (β, γ, δ) are cyclic order of x, y, z as in the example discussed above.

In a similar fashion, we obtain from (II.A.15b)

$$\sum_{l'} \sum_{\kappa'} \big[\phi_{\alpha\delta}{}^{rt}(0\kappa; l'\kappa') X_\gamma(l'\kappa') - \phi_{\alpha\gamma}{}^{rt}(0\kappa; l'\kappa') X_\delta(l'\kappa')\big] + \sum_{l'} \sum_{\kappa' \epsilon \text{II}} \phi_{\alpha\beta}{}^{rr}(0\kappa; l'\kappa') = 0,$$

$$\alpha, \beta = x, y, z; \qquad (\beta, \gamma, \delta) \text{ cyclic order of } (x, y, z); \qquad \kappa \in \text{II}. \tag{II.A.19}$$

The sum rules (II.A.16)–(II.A.19) are important in practical work, especially in the determination of the "self" force constants $\phi_{\alpha\beta}{}^{ii'}(0\kappa; 0\kappa)$.

A.5 Solution of the Equations of Motion

We return to the equations of motion (II.A.15), and guided by the periodicity of the crystal, try the wavelike solutions

$$u_\alpha{}^i(l\kappa) = U_\alpha{}^i(\kappa \mid \mathbf{q}) \exp\{i[\mathbf{q} \cdot \mathbf{X}(l) - \omega(\mathbf{q})t]\}. \tag{II.A.20}$$

[5] A less restrictive sum rule can be obtained by considering the invariance of the energy as such, rather than the force equations as above. In that case one obtains

$$\sum_{l\kappa} \sum_{l'\kappa'} \phi_{\alpha\beta}{}^{tt}(l\kappa; l'\kappa') = 0.$$

See also MMW, p. 7.

[6] In standard lattice dynamics, it is well known (see, for example, Lax, 1965) that the corresponding sum rule does not exhaust all the consequences of rotational invariance. There are in fact other constraints that the force constants have to fulfill, known as Born–Huang conditions, which also arise from rotational invariance (Lax, 1965). The analogous constraints in the case of complex crystals do not appear to have been explored fully. [See, however, Deprez and Fouret (1966) and Parlinski (1968).]

Observe that while $U_\alpha{}^t(\kappa \mid \mathbf{q})$ has the dimensions of length, $U_\alpha{}^r(\kappa \mid \mathbf{q})$ is dimensionless. On substituting the above solution in (II.A.15), we obtain

$$\omega^2(\mathbf{q}) m_\kappa U_\alpha{}^t(\kappa \mid \mathbf{q}) = \sum_{\kappa'} \sum_{\beta} B_{\alpha\beta}{}^{tt}(\mathbf{q}, \kappa\kappa') U_\beta{}^t(\kappa' \mid \mathbf{q}) + \sum_{\kappa' \epsilon \mathrm{II}} \sum_{\beta} B_{\alpha\beta}{}^{tr}(\mathbf{q}, \kappa\kappa') U_\beta{}^r(\kappa' \mid \mathbf{q}), \quad \text{for all } \alpha \text{ and } \kappa, \quad \text{(II.A.21a)}$$

$$\omega^2(\mathbf{q}) g_{\alpha\alpha}(\kappa) U_\alpha{}^r(\kappa \mid \mathbf{q}) = \sum_{\kappa'} \sum_{\beta} B_{\alpha\beta}{}^{rt}(\mathbf{q}, \kappa\kappa') U_\beta{}^t(\kappa' \mid \mathbf{q}) + \sum_{\kappa' \epsilon \mathrm{II}} \sum_{\beta} B_{\alpha\beta}{}^{rr}(\mathbf{q}, \kappa\kappa') U_\beta{}^r(\kappa' \mid \mathbf{q}) - \omega^2(\mathbf{q}) \sum_{\beta \neq \alpha} g_{\alpha\beta}(\kappa) U_\beta{}^r(\kappa \mid \mathbf{q}), \quad \text{for all } \alpha \text{ and } \kappa \in \mathrm{II}, \quad \text{(II.A.21b)}$$

in which

$$B_{\alpha\beta}{}^{ii'}(\mathbf{q}, \kappa\kappa') = \sum_{l'} \phi_{\alpha\beta}{}^{ii'}(0\kappa; l'\kappa') \exp[i\mathbf{q}\cdot\mathbf{X}(l')]. \quad \text{(II.A.22)}$$

The simultaneous equations (II.A.21) in the wave amplitudes can be written in matrix notation as

$$\omega^2(\mathbf{q})\, \mathsf{m}\mathbf{U}(\mathbf{q}) = \mathsf{B}(\mathbf{q})\mathbf{U}(\mathbf{q}), \quad \text{(II.A.23)}$$

where m and $\mathsf{B}(\mathbf{q})$ are $(3\mu+6\nu)$-dimensional square matrices, while $\mathbf{U}(\mathbf{q})$ is a column matrix with $(3\mu+6\nu)$ elements. Depending on one's preferences, the matrices could be arranged in various ways, one possible scheme being

$$\mathsf{B}(\mathbf{q}) = \begin{bmatrix} \mathsf{B}^{tt}(\mathbf{q}, 11) & \cdots & \mathsf{B}^{tt}(\mathbf{q}, 1\mu) & \mathsf{B}^{tt}(\mathbf{q}, 1(\mu+1)) & \mathsf{B}^{tr}(\mathbf{q}, 1(\mu+1)) & \cdots & \mathsf{B}^{tr}(\mathbf{q}, 1(\mu+\nu)) \\ \cdots & & & & & & \\ \mathsf{B}^{tt}(\mathbf{q}, \mu 1) & \cdots & \mathsf{B}^{tt}(\mathbf{q}, \mu\mu) & \mathsf{B}^{tt}(\mathbf{q}, \mu(\mu+1)) & \mathsf{B}^{tr}(\mathbf{q}, \mu(\mu+1)) & \cdots & \mathsf{B}^{tr}(\mathbf{q}, \mu(\mu+\nu)) \\ \mathsf{B}^{tt}(\mathbf{q}, (\mu+1)1) & \cdots & \mathsf{B}^{tt}(\mathbf{q}, (\mu+1)\mu) & \mathsf{B}^{tt}(\mathbf{q}, (\mu+1)(\mu+1)) & & \cdots & \mathsf{B}^{tr}(\mathbf{q}, (\mu+1)(\mu+\nu)) \\ \cdots & & & & & & \\ \mathsf{B}^{rt}(\mathbf{q}, (\mu+\nu)1) & \cdots & \mathsf{B}^{rt}(\mathbf{q}, (\mu+\nu)\mu) & \mathsf{B}^{rt}(\mathbf{q}, (\mu+\nu)(\mu+1)) & & \cdots & \mathsf{B}^{rr}(\mathbf{q}, (\mu+\nu)(\mu+\nu)) \end{bmatrix}. \quad \text{(II.A.24)}$$

Each submatrix above is a 3×3 matrix with elements as in (II.A.22). The matrix m can be built up in a similar fashion out of the submatrices $\mathsf{m}^{ii'}(\kappa\kappa')$. In this case, all submatrices except those along the leading diagonal are null matrices. The diagonal submatrices are given by

$$\mathsf{m}^{tt}(\kappa\kappa) = m_\kappa \mathsf{1}_3 \quad \text{(for all } \kappa), \quad \text{(II.A.25a)}$$

$$\mathsf{m}^{rr}(\kappa\kappa) = \mathsf{g}(\kappa) \quad (\kappa \in \mathrm{II}). \quad \text{(II.A.25b)}$$

where $\mathsf{1}_3$ is the three-dimensional unit matrix. Also, we have

$$\mathbf{U}(\mathbf{q}) = \begin{bmatrix} U_x{}^t(\kappa=1 \mid \mathbf{q}) \\ U_y{}^t(\kappa=1 \mid \mathbf{q}) \\ U_z{}^t(\kappa=1 \mid \mathbf{q}) \\ \vdots \\ U_z{}^t(\kappa=\mu \mid \mathbf{q}) \\ \\ U_x{}^t(\kappa=\mu+1 \mid \mathbf{q}) \\ U_y{}^t(\kappa=\mu+1 \mid \mathbf{q}) \\ U_z{}^t(\kappa=\mu+1 \mid \mathbf{q}) \\ U_x{}^r(\kappa=\mu+1 \mid \mathbf{q}) \\ \vdots \\ U_z{}^r(\kappa=\mu+\nu \mid \mathbf{q}) \end{bmatrix}. \quad \text{(II.A.26)}$$

Equation (II.A.23) is the eigenvalue equation for the present problem, and is to be compared with the corresponding equation

$$\mathsf{D}(\mathbf{q})\mathbf{U}(\mathbf{q}) = \omega^2(\mathbf{q})\mathbf{U}(\mathbf{q}), \quad \text{(II.A.27)}$$

$$D_{\alpha\beta}(\mathbf{q}, kk') = \sum_{l'} (m_k m_{k'})^{-1/2} \times \phi_{\alpha\beta}(0k; l'k') \exp[i\mathbf{q}\cdot\mathbf{X}(l')] \quad \text{(II.A.28)}$$

in standard Born–von Kármán treatment. The important difference is the appearance of the matrix m in (II.A.23) in contrast to (II.A.27). Such a matrix is absent in the latter due to the use of mass-weighted displacements. A corresponding formulation of the present problem is not possible in the fixed frame due to the presence of off-diagonal elements $g_{\alpha\beta}(\kappa)$.

The eigenvalues $\omega_j{}^2(\mathbf{q})$ $[j=1, 2, \cdots, (3\mu+6\nu)]$ of (II.A.23) are obtained by solving the determinental equation

$$|\mathsf{B}(\mathbf{q}) - \omega^2(\mathbf{q})\,\mathsf{m}| = 0, \quad \text{(II.A.29)}$$

which follows from the requirement that the wave amplitudes $\mathbf{U}(\kappa \mid \mathbf{q})$ have nontrivial solutions.

Now $\mathsf{B}(\mathbf{q})$ is Hermitian, i.e.,

$$B_{\alpha\beta}{}^{ii'}(\mathbf{q}, \kappa\kappa') = [B_{\beta\alpha}{}^{i'i}(\mathbf{q}, \kappa'\kappa)]^*. \quad \text{(II.A.30)}$$

This follows readily from the property (II.A.9) of the force constants. Furthermore, m is real symmetric, i.e.,

$$m_{\alpha\beta}{}^{ii'}(\kappa\kappa') = m_{\beta\alpha}{}^{i'i}(\kappa'\kappa).$$

This is evident from the fact that

$$m_{\alpha\beta}{}^{ii'}(\kappa\kappa') = m_{\alpha\beta}{}^{ii}(\kappa\kappa)\delta_{ii'}\delta(\kappa, \kappa'), \qquad \text{(II.A.31a)}$$

with

$$m_{\alpha\beta}{}^{ii}(\kappa\kappa) = m_\kappa\delta_{\alpha\beta} \qquad i=t, \text{ for all } \kappa,$$
$$= \mathcal{I}_{\alpha\beta}(\kappa) \qquad i=r, \text{ for } \kappa\in \text{II}. \qquad \text{(II.A.31b)}$$

In view of these properties of $\mathbf{B}(\mathbf{q})$ and $\mathbf{m}$ and the fact that $\mathbf{m}$ is positive definite, it can be shown that the eigenvalues $\omega_j^2(\mathbf{q})$ are real. See also Appendix I.) Furthermore, for stable crystals (our prime concern here), $\omega_j^2(\mathbf{q})$ is positive. This imposes some restrictions on the force constants which we shall assume to hold.

Once the eigenvalues $\omega_j^2(\mathbf{q})$ are known, the associated (complex) wave amplitudes $\mathbf{U}(\mathbf{q}j)$ can be solved for by introducing the value of $\omega_j^2(\mathbf{q})$ in (II.A.21) and (II.A.23), subject to the usual limitations of homogeneous equations (Margenau and Murphy, 1956). A normalization condition is subsequently imposed to obtain a normalized eigenvector, but this is applied not on $\mathbf{U}(\mathbf{q}j)$ but on a related quantity. The details are: Introduce first a quantity $e_\alpha{}^i(\kappa \mid \mathbf{q}j)$ via the relation

$$U_\alpha{}^i(\kappa \mid \mathbf{q}j) = a(\mathbf{q}j)e_\alpha{}^i(\kappa \mid \mathbf{q}j), \qquad \text{(II.A.32)}$$

such that $a(\mathbf{q}j)$ has the dimensions of length. This means that whereas $\mathbf{e}^t$ is dimensionless, $\mathbf{e}^r$ has the dimensions of inverse length. It is obvious that the column matrix $\mathbf{e}(\mathbf{q}j)$ with components $e_\alpha{}^i(\kappa \mid \mathbf{q}j)$ is an eigenvector belonging to the eigenvalue $\omega_j^2(\mathbf{q})$ just as $\mathbf{U}(\mathbf{q}j)$ is. The normalization constraint is now imposed on $\mathbf{e}(\mathbf{q}j)$ rather than on $\mathbf{U}(\mathbf{q}j)$ and is chosen as

$$\mathbf{e}^+(\mathbf{q}j)\mathbf{m}\mathbf{e}(\mathbf{q}j) = \text{const.} \qquad \text{(II.A.33a)}$$

In view of the remarks just made concerning the dimensions of $e_\alpha{}^i(\kappa \mid \mathbf{q}j)$, it is clear that the left-hand side of (II.A.33a) has the dimensions of mass. The constant on the right-hand side is therefore conveniently chosen as M, the mass of the primitive unit cell. In component form, (II.A.33a) reads

$$\sum_{\alpha\beta\kappa i} e_\alpha{}^{i*}(\kappa \mid \mathbf{q}j)m_{\alpha\beta}{}^{ii}(\kappa\kappa)e_\beta{}^i(\kappa \mid \mathbf{q}j) = M. \qquad \text{(II.A.33b)}$$

As in standard lattice dynamics, the eigenvectors $\mathbf{e}(\mathbf{q}j)$ corresponding to different j values can be chosen to be orthogonal but in a slightly different sense, i.e., we can construct $\mathbf{e}(\mathbf{q}j)$'s such that

$$\mathbf{e}^+(\mathbf{q}j)\mathbf{m}e(\mathbf{q}j') = 0 \qquad j\neq j'. \qquad \text{(II.A.34)}$$

Equations (II.A.33) and (II.A.34) can be combined into

$$\sum_{\alpha\beta\kappa i} e_\alpha{}^{i*}(\kappa \mid \mathbf{q}j)m_{\alpha\beta}{}^{ii}(\kappa\kappa)e_\beta{}^i(\kappa \mid \mathbf{q}j') = M\delta_{jj'}. \qquad \text{(II.A.35)}$$

By introducing a $(3\mu+6\nu)$-dimensional matrix $\mathbf{e}(\mathbf{q})$ defined by

$$\mathbf{e}(\mathbf{q}) = [\mathbf{e}(\mathbf{q}, 1), \mathbf{e}(\mathbf{q}, 2)\cdots\mathbf{e}(\mathbf{q}, 3\mu+6\nu)], \qquad \text{(II.A.36)}$$

(II.A.35) can be succinctly written as

$$\mathbf{e}^+(\mathbf{q})\,\mathbf{m}\mathbf{e}(\mathbf{q}) = M\mathbf{1}_{(3\mu+6\nu)}, \qquad \text{(II.A.37)}$$

which is to be compared with the unitarity condition

$$\mathbf{e}^+(\mathbf{q})\mathbf{e}(\mathbf{q}) = \mathbf{e}(\mathbf{q})\mathbf{e}^+(\mathbf{q}) = \mathbf{1}_{3n} \qquad \text{(II.A.38)}$$

of standard lattice dynamics. In other words, the eigenvectors of the present problem are not orthonormal in the same sense as the eigenvectors of conventional lattice dynamics. The reason for this is linked to the generalized nature of our problem as compared to the usual one [cf. Eqs. (II.A.23) and (II.A.27)]; further comments on this are offered in Appendix I.

In view of (II.A.37), we obtain from (II.A.23)

$$\mathbf{e}^+(\mathbf{q})\mathbf{B}(\mathbf{q})\mathbf{e}(q) = M\mathbf{\Omega}(\mathbf{q}), \qquad \text{(II.A.39)}$$

where $\mathbf{\Omega}(\mathbf{q})$ is a diagonal matrix with elements

$$\Omega_{ij}(\mathbf{q}) = \omega_j^2(\mathbf{q})\delta_{ij}. \qquad \text{(II.A.40)}$$

The matrix $\mathbf{e}(\mathbf{q})$ thus brings both $\mathbf{m}$ and $\mathbf{B}(\mathbf{q})$ into diagonal form.

A.6 Most General Solution for Displacement

We have so far been concerned with finding the frequencies and eigenvectors corresponding to a given wave vector $\mathbf{q}$. The next question to be considered is the allowed values of $\mathbf{q}$. The enumeration of these permitted values is done exactly as in standard lattice dynamics by starting with a crystal containing N cells and then subjecting it to the periodic boundary conditions. This leads to N allowed (distinct) values for $\mathbf{q}$ which are distributed evenly in the first Brillouin zone with a density of $[Nv/(2\pi)^3]$, where v is the volume of the primitive cell.

The most general solution for the displacement $u_\alpha{}^i(l\kappa)$ is obtained by superposing the solution for all the allowed values of $\mathbf{q}$ as below:

$$u_\alpha{}^i(l\kappa) = N^{-1/2}\sum_{\mathbf{q}}\sum_j e_\alpha{}^i(\kappa \mid \mathbf{q}j)\,\exp[i\mathbf{q}\cdot\mathbf{X}(l)]a(\mathbf{q}j)\,\exp[-i\omega_j(\mathbf{q})t]$$
$$= N^{-1/2}\sum_{\mathbf{q}}\sum_j e_\alpha{}^i(\kappa \mid \mathbf{q}j)\,\exp[i\mathbf{q}\cdot\mathbf{X}(l)]A(\mathbf{q}j). \qquad \text{(II.A.41)}$$

Here, the summation over $\mathbf{q}$ ranges over the first Brillouin zone. The quantity $A(\mathbf{q}j)$ describes the time-dependent amplitude contributed by the $(\mathbf{q}j)$th mode. The factor $N^{-1/2}$ has been added for convenience. It must be pointed out that corresponding to each eigenvalue $\omega_j^2(\mathbf{q})$, there are two possible solutions $\pm\omega_j(\mathbf{q})$ for the frequency, and correspondingly two plane-wave solutions of the form

$$\exp\{i[\mathbf{q}\cdot\mathbf{X}(l)-\omega_j(\mathbf{q})t]\} \quad \text{and} \quad \exp\{i[\mathbf{q}\cdot\mathbf{X}(l)+\omega_j(\mathbf{q})t]\}.$$

However, the plane wave corresponding to $(\mathbf{q}, -\omega_j(\mathbf{q}))$ is equivalent to that for $(-\mathbf{q}, +\omega_j(-\mathbf{q}))$ so that, in

building up the most general solution, it is sufficient to restrict attention to the positive values of frequency alone, as we have done in (II.A.41).

Now the displacements $u_\alpha{}^i(l\kappa)$ are real. This places an important constraint on the complex amplitude factor $A(\mathbf{q}j)$. Let us first write (II.A.41) as

$$u_\alpha{}^i(l\kappa)=N^{-1/2}\sum_{\mathbf{q}>0}\sum_j\{e_\alpha{}^i(\kappa\mid\mathbf{q}j)\exp[i\mathbf{q}\cdot\mathbf{X}(l)]A(\mathbf{q}j)+e_\alpha{}^i(\kappa\mid-\mathbf{q}j)\exp[-i\mathbf{q}\cdot\mathbf{X}(l)]A(-\mathbf{q}j)\},\quad\text{(II.A.42a)}$$

where $\mathbf{q}>0$ signifies that $\mathbf{q}$ is now permitted to range over only one-half of the Brillouin zone. Taking the complex conjugate of (II.A.42a), we obtain

$$[u_\alpha{}^i(l\kappa)]^*=N^{-1/2}\sum_{\mathbf{q}>0}\sum_j\{e_\alpha{}^{i*}(\kappa\mid\mathbf{q}j)\exp[-i\mathbf{q}\cdot\mathbf{X}(l)]A^*(\mathbf{q}j)+e_\alpha{}^{i*}(\kappa\mid-\mathbf{q}j)\exp[i\mathbf{q}\cdot\mathbf{X}(l)]A^*(-\mathbf{q}j)\}.\quad\text{(II.A.42b)}$$

At this point we use the property

$$\mathbf{e}(-\mathbf{q}j)=\mathbf{e}^*(\mathbf{q}j)$$

(this will be referred to again shortly) which is well known in standard lattice dynamics and which applies in our case also. This enables us to write (II.A.42b) as

$$[u_\alpha{}^i(l\kappa)]^*=N^{-1/2}\sum_{\mathbf{q}>0}\sum_j\{e_\alpha{}^i(\kappa\mid-\mathbf{q}j)\exp[-i\mathbf{q}\cdot\mathbf{X}(l)]A^*(\mathbf{q}j)+e_\alpha{}^i(\kappa\mid\mathbf{q}j)\exp[i\mathbf{q}\cdot\mathbf{X}(l)]A^*(-\mathbf{q}j)\}.\quad\text{(II.A.42c)}$$

Remembering $[u_\alpha{}^i(l\kappa)]^*=u_\alpha{}^i(l\kappa)$, we obtain on comparing (II.A.42c) with (II.A.42a)

$$A(-\mathbf{q}j)=A^*(\mathbf{q}j).\quad\text{(II.A.43)}$$

The relation (II.A.41) may be inverted to express $A(\mathbf{q}j)$ in terms of the $u_\alpha{}^i(l\kappa)$'s. Multiplying both sides by $N^{-1/2}\exp[-i\mathbf{q}'\cdot\mathbf{X}(l)]e_\beta{}^{i*}(\kappa\mid\mathbf{q}'j')m_{\beta\alpha}{}^{ii}(\kappa\kappa)$ and summing over l, κ, β, α, and i, we obtain

$$N^{-1/2}\sum_{l\kappa\beta\alpha i}e_\beta{}^{i*}(\kappa\mid\mathbf{q}'j')\exp[-i\mathbf{q}'\cdot\mathbf{X}(l)]m_{\beta\alpha}{}^{ii}(\kappa\kappa)u_\alpha{}^i(l\kappa)=N^{-1}\sum_{\mathbf{q}j}A(\mathbf{q}j)\{\sum_l\exp[i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{X}(l)]\}$$
$$\times\sum_{\kappa\alpha\beta i}e_\beta{}^{i*}(\kappa\mid\mathbf{q}'j')m_{\beta\alpha}{}^{ii}(\kappa\kappa)e_\alpha{}^i(\kappa\mid\mathbf{q}j).\quad\text{(II.A.44)}$$

Using the theorem (BH, p. 296)

$$\sum_l\exp[i\mathbf{Q}\cdot\mathbf{X}(l)]=N\Delta(\mathbf{Q}),\quad\text{(II.A.45a)}$$

where

$$\Delta(\mathbf{Q})=1\quad\text{if}\quad\mathbf{Q}=\mathbf{G}$$
$$=0\quad\text{if}\quad\mathbf{Q}\neq\mathbf{G},\quad\text{(II.A.45b)}$$

and $\mathbf{G}$ is a vector of the reciprocal lattice,[7] and remembering further that $\mathbf{q}$, $\mathbf{q}'$ in (II.A.44) are confined to the first Brillouin zone, the right-hand side of (II.A.44) simplifies to

$$\sum_{\mathbf{q}j}A(\mathbf{q}j)\delta_{\mathbf{q}\mathbf{q}'}\sum_{\kappa\alpha\beta i}e_\beta{}^{i*}(\kappa\mid\mathbf{q}'j')m_{\beta\alpha}{}^{ii}(\kappa\kappa)e_\alpha{}^i(\kappa\mid\mathbf{q}j)=A(\mathbf{q}'j')M\qquad[\text{using (II.A.35)}].$$

We thus obtain (remembering that α, β are dummy indices)

$$A(\mathbf{q}j)=(1/MN^{1/2})\sum_{l\kappa\alpha\beta i}e_\alpha{}^{i*}(\kappa\mid\mathbf{q}j)\exp[-i\mathbf{q}\cdot\mathbf{X}(l)]m_{\alpha\beta}{}^{ii}(\kappa\kappa)u_\beta{}^i(l\kappa),\quad\text{(II.A.46a)}$$

$$=(1/MN^{1/2})\sum_l\exp[-i\mathbf{q}\cdot\mathbf{X}(l)]\{\sum_\kappa e_\alpha{}^{i*}(\kappa\mid\mathbf{q}j)m_\kappa u_\alpha{}^i(l\kappa)+\sum_{\kappa\in\mathrm{II}}\sum_{\alpha,\beta}e_\alpha{}^{r*}(\kappa\mid\mathbf{q}j)\vartheta_{\alpha\beta}(\kappa)u_\beta{}^r(l\kappa)\}.\quad\text{(II.A.46b)}$$

A.7 Properties in Reciprocal Space

The properties of $\mathbf{B}(\mathbf{q})$, $\omega_j{}^2(\mathbf{q})$, and $\mathbf{e}(\mathbf{q}j)$ in reciprocal space are the same as in ordinary Born–von Kármán theory (Born and Huang, 1954; Maradudin and Vosko, 1968). Thus we have

(i) $\mathbf{B}(\mathbf{q})=\mathbf{B}(\mathbf{q}+\mathbf{G})$, (II.A.47a)

(ii) $\mathbf{B}(\mathbf{q})=\mathbf{B}^*(-\mathbf{q})$, (II.A.47b)

(iii) $\omega_j{}^2(\mathbf{q})=\omega_j{}^2(\mathbf{q}+\mathbf{G})$, (II.A.47c)

(iv) $\omega_j{}^2(\mathbf{q})=\omega_j{}^2(-\mathbf{q})$, (II.A.47d)

(v) $\mathbf{e}(\mathbf{q}j)=\mathbf{e}(\mathbf{q}+\mathbf{G}j)$, (II.A.47e)

(vi) $\mathbf{e}(\mathbf{q}j)=\mathbf{e}^*(-\mathbf{q}j)$. (II.A.47f)

In writing the last relation, we have followed a phase convention due to Born and Huang (BH, p. 298). In addition to the symmetries discussed above, there are others related to the rotational symmetry of the crystal. These will be mentioned in Sec. V while dealing with the group-theoretical aspects.

A.8 Frequency Distribution

The frequency distribution is an important quantity in the discussion of several properties of the crystal, for

[7] Our definition of $\mathbf{G}$ is such that it has built into it a 2π factor, i.e., $\mathbf{G}\cdot\mathbf{x}(l)=2\pi\times$integer.

example, thermodynamic properties. The frequency distribution associated with external modes is defined as

$$g(\omega)=[N(3\mu+6\nu)]^{-1}\sum_{\mathbf{q}}\sum_{j}\delta(\omega-\omega_j(\mathbf{q})). \quad \text{(II.A.48a)}$$

The factor $[N(3\mu+6\nu)]^{-1}$ guarantees the normalization

$$\int g(\omega)\,d\omega=1.$$

An alternate expression for $g(\omega)$ [8] is

$$g(\omega)=\frac{v}{(3\mu+6\nu)}\frac{1}{(2\pi)^3}\sum_{j}\int\frac{dS}{|\operatorname{grad}\omega_j(\mathbf{q})|}, \quad \text{(II.A.48b)}$$

where the integration is over the surface of constant frequency $S=\omega$. The second form for $g(\omega)$ is easily derived from the first (see, for example, MMW, p. 61).

For many purposes, it is convenient to think of $g(\omega)$ as being made up of a translational part and a librational part. Such a break up can be achieved by the following definitions:

$$g^t(\omega)=[1/NM(3\mu+6\nu)]\times\sum_{\mathbf{q}}\sum_{j}\Big[\sum_{\alpha\kappa}e_\alpha^{t*}(\kappa\mid\mathbf{q}j)m_\kappa e_\alpha{}^t(\kappa\mid\mathbf{q}j)\Big]\times\delta(\omega-\omega_j(\mathbf{q})); \quad \text{(II.A.49a)}$$

$$g^r(\omega)=[1/NM(3\mu+6\nu)]\times\sum_{\mathbf{q}}\sum_{j}\Big[\sum_{\alpha\beta\kappa}e_\alpha^{r*}(\kappa\mid\mathbf{q}j)\mathcal{I}_{\alpha\beta}(\kappa)e_\beta{}^r(\kappa\mid\mathbf{q}j)\Big]\times\delta(\omega-\omega_j(\mathbf{q})). \quad \text{(II.A.49b)}$$

The orthogonality condition (II.A.35) automatically ensures that

$$g(\omega)=g^t(\omega)+g^r(\omega). \quad \text{(II.A.50)}$$

As is evident from the definitions in (II.A.49a) and (II.A.49b), the amplitude factors serve to project out the translational and librational components, respectively. If, for example, a given mode $(\mathbf{q}j)$ is wholly librational, then $\mathbf{e}^t(\kappa\mid\mathbf{q}j)=0$ for all κ, and hence the contribution from that mode to $g^t(\omega)$ will automatically be zero.

A.9 Normal Coordinates and Transition to Quantum Mechanics

Up to this point, our discussion of the dynamical problem has been essentially classical. We now consider briefly the transition to quantum mechanics. As is well known, the quantum aspects of an oscillator are confined to its amplitude, which in the present instance means the quantity $A(\mathbf{q}j)$. To discuss the quantum aspects of external modes, therefore, we must first express the Hamiltonian in terms of $A(\mathbf{q}j)$'s.

From (II.A.3) and (II.A.4) the vibrational Hamiltonian (suppressing Φ_0 as it merely provides a baseline) is given by

$$H=T+\Phi_2=\sum_{l}\sum_{\kappa}\sum_{i}[(d\tilde{\mathbf{u}}^i/dt)(l\kappa)\,\mathbf{m}^{ii}(\kappa\kappa)\dot{\mathbf{u}}^i(l\kappa)]+\tfrac{1}{2}\sum_{ll'}\sum_{\kappa\kappa'}\sum_{ii'}[\tilde{\mathbf{u}}^i(l\kappa)\boldsymbol{\phi}^{ii'}(l\kappa;l'\kappa')\mathbf{u}^{i'}(l'\kappa')].$$

In writing the above expression, we have, in the interests of compactness, employed matrix notation. Thus $\tilde{\mathbf{u}}^i(l\kappa)$ is the row matrix $[u_x{}^i(l\kappa), u_y{}^i(l\kappa), u_z{}^i(l\kappa)]$, etc. Using the expansion (II.A.41) and subsequently employing the orthogonality property (II.A.35), it is straightforward to show that H transforms to

$$H=\tfrac{1}{2}M\sum_{\mathbf{q}j}\dot{A}^*(\mathbf{q}j)\dot{A}(\mathbf{q}j)+\tfrac{1}{2}M\sum_{\mathbf{q}j}\omega_j^2(\mathbf{q})A^*(\mathbf{q}j)A(\mathbf{q}j). \quad \text{(II.A.51)}$$

In terms of the $A(\mathbf{q}j)$'s, the Hamiltonian has no cross terms and is the sum of Hamiltonians of simple harmonic oscillators of square frequencies $\omega_j^2(\mathbf{q})$. The $A(\mathbf{q}j)$'s are thus the normal coordinates of the problem.

In a quantum mechanical picture, the $A(\mathbf{q}j)$'s are regarded as operators, and $A^*(\mathbf{q}j)$ signifies the Hermitian adjoint of $A(\mathbf{q}j)$ rather than its complex conjugate as it does in the classical case. Define now annihilation and creation operators $a_{\mathbf{q}j}$ and $a_{\mathbf{q}j}{}^+$ related to $\dot{A}(\mathbf{q}j)$ and $A(\mathbf{q}j)$ by

$$A(\mathbf{q}j)=[\hbar/2M\omega_j(\mathbf{q})]^{1/2}(a_{\mathbf{q}j}+a_{-\mathbf{q}j}{}^+), \quad \text{(II.A.52a)}$$

$$\dot{A}(\mathbf{q}j)=(1/i)[\hbar\omega_j(\mathbf{q})/2M]^{1/2}(a_{\mathbf{q}j}-a_{-\mathbf{q}j}{}^+), \quad \text{(II.A.52b)}$$

with $a_{\mathbf{q}j}$ and $a_{\mathbf{q}j}{}^+$ satisfying the commutation relations

$$[a_{\mathbf{q}j}, a_{\mathbf{q}'j'}]=[a_{\mathbf{q}j}{}^+, a_{\mathbf{q}'j'}{}^+]=0, \quad \text{(II.A.53)}$$

$$[a_{\mathbf{q}j}, a_{\mathbf{q}'j'}{}^+]=\delta_{jj'}\delta_{\mathbf{q}\mathbf{q}'}. \quad \text{(II.A.54)}$$

From this point onwards, the discussion concerning matrix elements, thermal averages, etc., can be taken *in toto* from existing literature (e.g., Maradudin, Montroll, and Weiss, 1963), and does not require repetition here.

A.10 Force Constants for External Modes in Terms of Born–von Karman Constants

The force constants $\phi_{\alpha\beta}{}^{ii'}(l\kappa;l'\kappa')$ have been treated up to this point merely as formal quantities. Ideally, one would like to compute their values from a suitably constructed potential function Φ for the crystal via (II.A.5). In practical work, however, they are often treated as parameters to be determined from experimental data. Nevertheless, in the case of molecular crystals at least, attempts have been made to evaluate them on the basis of suitable phenomenological potentials connecting atoms located in different molecules. In this context, it is desirable to write formal expressions for $\phi_{\alpha\beta}{}^{ii'}(l\kappa;l'\kappa')$ in terms of the conventional Born–von Kármán constants $\phi_{\alpha\beta}(l\kappa k;l'\kappa'k')$. Such a connection is not easy to establish in the case in which molecules are

[8] Numerical techniques for evaluating $g(\omega)$ (Gilat and Dolling, 1964; Gilat and Raubenheimer, 1966; Raubenheimer and Gilat, 1967) and the singularities exhibited by it (van Hove, 1953; Philipps, 1956; Maradudin, Montroll, and Weiss, 1963) have been widely discussed in the context of standard Born–von Karman theory. The consideration of these papers are, however, quite general and apply in full to the $g(\omega)$ of the present problem. The interested reader should consult the references cited for further details.

regarded as nonrigid. In the case of rigid molecules, however, the relevant formulas are easily derived.

Let us first write the potential function for the crystal as

$$\Phi(\cdots, \mathbf{X}(l\kappa k)+\mathbf{u}(l\kappa k), \cdots), \qquad \text{(II.A.55)}$$

where $\mathbf{u}(l\kappa k)$ denotes the displacement from the equilibrium position $\mathbf{X}(l\kappa k)$ of the kth atom in the κth unit in the lth cell. In the rigid-body approximation, we can write $\mathbf{u}(l\kappa k)$ as the sum of the displacements produced by the center-of-mass translations and by the rotations, i.e.,

$$u_\alpha(l\kappa k) = u_\alpha{}^t(l\kappa) + [\mathbf{u}^r(l\kappa) \times \mathbf{X}(k)]_\alpha. \qquad \text{(II.A.56)}$$

The components of the cross product are most conveniently expressed through the use of the Levi-Civita symbol $\epsilon_{\alpha\beta\gamma}$ which is defined as follows:

$\epsilon_{\alpha\beta\gamma}=0$ if any two of the Cartesian indices α, β, γ are equal;
$=1$ if (α, β, γ) corresponds to a cyclic order of (x, y, z);
$=-1$ if (α, β, γ) corresponds to a noncyclic order of (x, y, z).

Thus, for example, we have

$$\epsilon_{xxy}=0, \qquad \epsilon_{yzx}=1, \qquad \epsilon_{xzy}=-1.$$

When this notation is used, we then have

$$[\mathbf{u}^r(l\kappa) \times \mathbf{X}(k)]_\alpha = \sum_{\mu\nu} \epsilon_{\alpha\mu\nu} u_\mu{}^r(l\kappa) X_\nu(k). \qquad \text{(II.A.57)}$$

In the potential function, when (II.A.57) is used, the second-order term Φ_2 can be expressed as

$$\begin{aligned}
\Phi_2 &= \tfrac{1}{2} \sum_{ll'} \sum_{\kappa\kappa'} \sum_{kk'} \sum_{\alpha\beta} \phi_{\alpha\beta}(l\kappa k; l'\kappa' k') u_\alpha(l\kappa k) u_\beta(l'\kappa' k') \\
&= \tfrac{1}{2} \sum_{ll'} \sum_{\kappa\kappa'} \sum_{kk'} \sum_{\alpha\beta} \phi_{\alpha\beta}(l\kappa k; l'\kappa' k') \{u_\alpha{}^t(l\kappa) + \sum_{\mu\nu} \epsilon_{\alpha\mu\nu} u_\mu{}^r(l\kappa) X_\nu(k)\} \{u_\beta{}^t(l'\kappa') + \sum_{\gamma\delta} \epsilon_{\beta\gamma\delta} u_\gamma{}^r(l'\kappa') X_\delta(k')\} \\
&= \tfrac{1}{2} \sum_{ll'} \sum_{\kappa\kappa'} \sum_{\alpha\beta} \Big[\{\sum_{kk'} \phi_{\alpha\beta}(l\kappa k; l'\kappa' k')\} u_\alpha{}^t(l\kappa) u_\beta{}^t(l'\kappa') \\
&\quad + \{\sum_{kk'} \sum_{\gamma\delta} \phi_{\alpha\gamma}(l\kappa k; l'\kappa' k') \epsilon_{\gamma\beta\delta} X_\delta(k')\} u_\alpha{}^t(l\kappa) u_\beta{}^r(l'\kappa') + \{\sum_{kk'} \sum_{\mu\nu} \phi_{\mu\beta}(l\kappa k; l'\kappa' k') \epsilon_{\mu\alpha\nu} X_\nu(k)\} u_\alpha{}^r(l\kappa) u_\beta{}^t(l'\kappa') \\
&\quad + \{\sum_{kk'} \sum_{\mu\nu} \sum_{\gamma\delta} \phi_{\mu\gamma}(l\kappa k; l'\kappa' k') \epsilon_{\gamma\beta\delta} \epsilon_{\mu\alpha\nu} X_\delta(k') X_\nu(k) u_\alpha{}^r(l\kappa) u_\beta{}^r(l'\kappa')\Big].
\end{aligned}$$

In writing the last step, we have manipulated the dummy indices so that the rigid-body displacement components are indexed by α and β. Comparing the above expression with the second-order term in (II.A.4), we obtain

$$\phi_{\alpha\beta}{}^{tt}(l\kappa; l'\kappa') = \sum_{kk'} \phi_{\alpha\beta}(l\kappa k; l'\kappa' k'); \qquad \text{(II.A.58a)}$$

$$\phi_{\alpha\beta}{}^{tr}(l\kappa; l'\kappa') = \sum_{kk'} \sum_{\gamma\delta} \phi_{\alpha\gamma}(l\kappa k; l'\kappa' k') \epsilon_{\gamma\beta\delta} X_\delta(k'); \qquad \text{(II.A.58b)}$$

$$\phi_{\alpha\beta}{}^{rt}(l\kappa; l'\kappa') = \sum_{kk'} \sum_{\mu\nu} \phi_{\mu\beta}(l\kappa k; l'\kappa' k') \epsilon_{\mu\alpha\nu} X_\nu(k); \qquad \text{(II.A.58c)}$$

$$\phi_{\alpha\beta}{}^{rr}(l\kappa; l'\kappa') = \sum_{kk'} \sum_{\mu\nu} \sum_{\gamma\delta} \phi_{\mu\gamma}(l\kappa k; l'\kappa' k') \epsilon_{\gamma\beta\delta} \epsilon_{\mu\alpha\nu} X_\nu(k) X_\delta(k'). \qquad \text{(II.A.58d)}$$

If the Born–von Kármán force constants $\phi_{\alpha\beta}(l\kappa k; l'\kappa' k')$ are known, as from a knowledge of the potential for the atom pair $(l\kappa k - l'\kappa' k')$, the force constants required for external-mode computations can be obtained from the above formulas.

A.11 Linear Molecules

We have pointed out earlier that linear molecules have only two rotational degrees of freedom. Consequently, if λ of the ν molecular groups in the unit cell are linear, then there will be only $(3\mu+6\nu-\lambda)$ external branches. In computing these using the fixed-frame formulation, one must eliminate the redundant coordinates.

Let $u_x{}^r$, $u_y{}^r$, and $u_z{}^r$ denote the components of the angular displacement of a linear molecule in the crystal with respect to a set of axes xyz parallel to the fixed frame. We now choose a set of axes $x'y'z'$ such that the z' axis is along the length of the molecule. With respect to the new axes, only the x' and y' component of $\mathbf{u}^r$ will be nonvanishing. The component along z' will be zero since a molecule does not have a rotational degree of freedom about its axis. In other words, if $u_x{}^{r,p}$, $u_y{}^{r,p}$, and $u_z{}^{r,p}$ denote the new components of $\mathbf{u}^r$, then $u_z{}^{r,p}=0$. Let us formally denote the transformation

$$(u_x{}^r, u_y{}^r, u_z{}^r) \rightarrow (u_x{}^{r,p}, u_y{}^{r,p}, u_z{}^{r,p})$$

by the matrix equation

$$\begin{bmatrix} u_x{}^{r,p} \\ u_y{}^{r,p} \\ 0 \end{bmatrix} = \mathsf{A} \begin{bmatrix} u_x{}^r \\ u_y{}^r \\ u_z{}^r \end{bmatrix},$$

where A represents the orthogonal transformation of axes $(xyz) \rightarrow (x'y'z')$. It is easily seen that

$$u_z{}^r = -(A_{31} u_x{}^r + A_{32} u_y{}^r)/A_{33}.$$

This gives the expression for one of the rotational components in terms of the remaining two. Using this, all redundant coordinates may be systematically eliminated from the expressions for kinetic and potential energy before the equation of motion is formulated.

B. Dynamics in the Principal Axes Frame

A convenient alternate formulation for the dynamics of complex crystals can be made by expressing the displacements of the vibrating units with respect to the principal axes of the moment-of-inertia tensors of the corresponding units. One of the advantages of this approach is that the moment-of-inertia tensor $\mathcal{I}^P(\kappa)$ (the superscript P makes explicit the fact that we are dealing with the principal-axes frame) has a diagonal form, i.e., $\mathcal{I}_{\alpha\beta}{}^P(\kappa)=\delta_{\alpha\beta}\mathcal{I}_{\alpha\alpha}{}^P(\kappa)$, and this makes the dynamical equations somewhat simpler. In particular, there are automatically only two rotational coordinates associated with linear molecules, and consequently there is no need to eliminate redundant coordinates as in the fixed-frame formulation. Also, the eigenvalue problem can be transformed into the standard form quite conveniently.

Some molecular groups (e.g., H_2O) have different inertia components about the three principal axes, and consequently the principal axes are uniquely fixed relative to the molecule. Such groups are referred to as *asymmetric tops* in molecular physics. Some ions like CO_3^{--} have two of the principal moments-of-inertia components equal. For such groups, often called *symmetric tops*, only one of the three principal axes is unique, and the other two may be chosen at will. In the case of *spherical tops* (e.g., NH_4^+ ion), all the three principal moments are equal, and the inertia ellipsoid is therefore a sphere (Goldstein, 1953). Any set of three mutually perpendicular axes therefore qualifies as the principal axes of the inertia tensor.

Let us now locate at the center of mass of each vibrating unit, a set of orthogonal axes such that they coincide with the principal axes of the moment-of-inertia tensor, with the additional qualification that whenever there is degeneracy in the values of the principal inertia components, the axes are to be chosen to suit convenience. Thus the axes of all spherical-top units are chosen to be mutually parallel, and further parallel to a Cartesian frame suitably chosen relative to the crystallographic axes. In the case of the individual atoms, these being point masses, the local axes can be chosen as we like, and once again it is desirable to have them all parallel to a Cartesian frame tied to the crystal. In many crystals, it is possible to choose the principal-axes frame such that it coincides with the fixed frame. One example is NH_4Cl, in which such a possibility arises because the NH_4^+ ion is a spherical top. Another example is $NaNO_2$, which is an orthorhombic crystal. In this case, even though the NO_2^- ion is an asymmetric top, it happens that its principal axes are parallel to the crystallographic axes, and this simplifies matters. In general, however, the two frames are distinct as, for example, in naphthalene and $LiClO_4\cdot 3H_2O$.

On referring the displacements to the principal-axes frame, the kinetic and potential energies assume the form

$$T=\tfrac{1}{2}\sum_{l}\sum_{\kappa}\sum_{\alpha} m_\kappa[\dot{u}_\alpha{}^{t,P}(l\kappa)]^2 + \tfrac{1}{2}\sum_{l}\sum_{\kappa\in II}\sum_{\alpha}\mathcal{I}_{\alpha\alpha}{}^P(\kappa)[\dot{u}_\alpha{}^{r,P}(l\kappa)]^2 \quad \text{(II.B.1a)}$$

$$\Phi_2=\tfrac{1}{2}\sum_{ll'}\sum_{\kappa\kappa'}\sum_{\alpha\beta}\sum_{ii'}\phi_{\alpha\beta}{}^{ii',P}(l\kappa;l'\kappa')u_\alpha{}^{i,P}(l\kappa)u_\beta{}^{i',P}(l'\kappa'). \quad \text{(II.B.1b)}$$

In attributing physical meanings to the force constants $\phi_{\alpha\beta}{}^{ii',P}(l\kappa;l'\kappa')$, we must be careful to remember that the displacements are now referred to the principal axes. Thus $\phi_{\alpha\beta}{}^{tr,P}(l\kappa;l'\kappa')$ would be the negative of the linear force on $(l\kappa)$ along the α direction of the principal axes of $(l\kappa)$, due to unit anticlockwise rotation of $(l'\kappa')$ about the β direction of the principal axes of $(l'\kappa')$.

Let $\mathsf{A}(\kappa)$ be the orthogonal transformation which transforms a set of axes on a vibrating unit of the κth sublattice located parallel to the fixed frame, to the principal axes of the unit concerned. We shall discuss later the exact specification of $\mathsf{A}(\kappa)$ although we might note that for $\kappa\in I$ we can (and do) make the choice

$$\mathsf{A}(\kappa)=\mathsf{1}_3,$$

where $\mathsf{1}_3$ is the three-dimensional unit matrix. Using the transformation $\mathsf{A}(\kappa)$, we can write

$$u_\alpha{}^{i,P}(l\kappa)=\sum_\beta A_{\alpha\beta}(\kappa)u_\beta{}^i(l\kappa), \quad \text{(II.B.2a)}$$

with the inverse relation

$$u_\alpha{}^i(l\kappa)=\sum_\beta A_{\beta\alpha}(\kappa)u_\beta{}^{i,P}(l\kappa), \quad \text{(II.B.2b)}$$

since $\mathsf{A}(\kappa)$ is orthogonal.

Using (II.B.2), we can write

$$\begin{aligned}\tfrac{1}{2}\sum_{l\kappa\alpha\beta}&\dot{u}_\alpha{}^r(l\kappa)\mathcal{I}_{\alpha\beta}(\kappa)\dot{u}_\beta{}^r(l\kappa)\\ &=\tfrac{1}{2}\sum_{l\kappa\alpha\beta}\Big[\sum_\gamma A_{\gamma\alpha}(\kappa)\dot{u}_\gamma{}^{r,P}(l\kappa)\Big]\mathcal{I}_{\alpha\beta}(\kappa)\times\Big[\sum_\delta A_{\delta\beta}(\kappa)\dot{u}_\delta{}^{r,P}(l\kappa)\Big]\\ &=\tfrac{1}{2}\sum_{l\kappa\gamma\delta}\Big\{\sum_{\alpha\beta}A_{\gamma\alpha}(\kappa)\mathcal{I}_{\alpha\beta}(\kappa)A_{\delta\beta}(\kappa)\Big\}\times\dot{u}_\gamma{}^{r,P}(l\kappa)\dot{u}_\delta{}^{r,P}(l\kappa).\end{aligned}$$

Comparing this with the corresponding term in (II.A.3a), we see that

$$\mathcal{I}_{\gamma\gamma}{}^P(\kappa)\delta_{\gamma\delta}=\sum_{\alpha\beta}A_{\gamma\alpha}(\kappa)\mathcal{I}_{\alpha\beta}(\kappa)A_{\delta\beta}(\kappa), \quad \text{(II.B.3a)}$$

or

$$\mathcal{I}^P(\kappa)=\mathsf{A}(\kappa)\,\mathcal{I}(\kappa)\,\mathsf{A}^{tr}(\kappa). \quad \text{(II.B.3b)}$$

In a similar fashion, it is easy to establish that

$$\phi_{\alpha\beta}{}^{ii',P}(l\kappa;l'\kappa')=\sum_{\gamma\delta}A_{\alpha\gamma}(\kappa)\phi_{\gamma\delta}{}^{ii'}(l\kappa;l'\kappa')A_{\beta\delta}(\kappa'), \quad \text{(II.B.4a)}$$

or more compactly,

$$\boldsymbol{\phi}^{ii',P}(l\kappa;l'\kappa')=\mathbf{A}(\kappa)\boldsymbol{\phi}^{ii'}(l\kappa;l'\kappa')\mathbf{A}^{\mathrm{tr}}(\kappa'). \quad \text{(II.B.4b)}$$

The force constants again exhibit translation and permutation symmetry, i.e.,

$$\boldsymbol{\phi}^{ii',P}(l\kappa;l'\kappa')=\boldsymbol{\phi}^{ii',P}(l+L,\kappa;l'+L,\kappa'), \quad \text{(II.B.5a)}$$

$$\phi_{\alpha\beta}{}^{ii',P}(l\kappa;l'\kappa')=\phi_{\beta\alpha}{}^{i'i,P}(l'\kappa';l\kappa). \quad \text{(II.B.5b)}$$

The discussion of the transformation of $\boldsymbol{\phi}^{ii',P}$ under space-group operations requires some care because the orthogonal transformation $\mathbf{S}$ in a typical space-group operation $\{\mathbf{S}\mid\mathbf{V}(S)+\mathbf{X}(m)\}$ is referred to a set of axes fixed in relation to the entire crystal, whereas the force constants now under consideration pertain to displacements referred to the principal-axes frame.

Using (II.B.4b) on both sides of (II.A.13b), we have

$$\mathbf{A}^{\mathrm{tr}}(\kappa)\boldsymbol{\phi}^{ii',P}(l\kappa;l'\kappa')\mathbf{A}(\kappa')$$
$$=C^i(S)\mathbf{S}^{\mathrm{tr}}\mathbf{A}^{\mathrm{tr}}(K)\boldsymbol{\phi}^{ii',P}(LK;L'K')\mathbf{A}(K')\mathbf{S}C^{i'}(S).$$

Therefore, it follows that

$$\boldsymbol{\phi}^{ii',P}(l\kappa;l'\kappa')=C^i(S)\,(\mathbf{A}(\kappa)\mathbf{S}^{\mathrm{tr}}\mathbf{A}^{\mathrm{tr}}(K))\boldsymbol{\phi}^{ii',P}(LK;L'K')\times(\mathbf{A}(K')\mathbf{S}\mathbf{A}^{\mathrm{tr}}(\kappa'))C^{i'}(S)$$
$$=C^i(S)\mathbf{s}^{\mathrm{tr}}(\kappa,K)\boldsymbol{\phi}^{ii',P}(LK;L'K')\times\mathbf{s}(\kappa';K')C^{i'}(S), \quad \text{(II.B.6)}$$

where

$$\mathbf{s}(\kappa,K)=\mathbf{A}(K)\mathbf{S}\mathbf{A}^{\mathrm{tr}}(\kappa);$$
$$\mathbf{s}(\kappa',K')=\mathbf{A}(K')\mathbf{S}\mathbf{A}^{\mathrm{tr}}(\kappa'). \quad \text{(II.B.7)}$$

Since both $\mathbf{A}$ and $\mathbf{S}$ are orthogonal matrices, it follows that the 3×3 matrices $\mathbf{s}$ defined above are also orthogonal. We thus see from (II.B.6) that in discussing the transformation properties of force constants in the principal-axes frame, we must use the modified transformation $\mathbf{s}$ rather than $\mathbf{S}$ itself. An inspection of above formulas shows that what $\mathbf{s}$ does is to first transform the force constants into the fixed frame. The transformation $\mathbf{S}$ is then applied, and finally the force constants are restored to the principal-axes frame. Observe that for type I units, $\mathbf{s}\equiv\mathbf{S}$.

The same matrix $\mathbf{s}$ also serves to specify the transformation of the moment-of-inertia tensors and we have, analogous to (II.A.14a)

$$\mathcal{I}^P(\kappa)=\mathbf{s}^{\mathrm{tr}}(\kappa,K)\,\mathcal{I}^P(K)\,\mathbf{s}(\kappa,K). \quad \text{(II.B.8)}$$

The sum rules obeyed by the present force constants are easily deduced from (II.A.16)–(II.A.19) using the transformations given above.

Consider, for example, the expression

$$\sum_{l'}\sum_{\kappa'}\phi_{\alpha\beta}{}^{tt}(l\kappa;l'\kappa')=0. \quad \text{(II.A.16)}$$

Using (II.B.4), we can write it as

$$\sum_{l'}\sum_{\kappa'}\sum_{\mu\nu}A_{\mu\alpha}(\kappa)\phi_{\mu\nu}{}^{tt,P}(l\kappa;l'\kappa')A_{\nu\beta}(\kappa')=0.$$

Multiplying by $A_{\lambda\alpha}(\kappa)$ and summing over α, we obtain, remembering $\mathbf{A}$ is orthogonal,

$$\sum_{l'}\sum_{\kappa'}\sum_{\mu\nu}\delta_{\lambda\mu}\phi_{\mu\nu}{}^{tt,P}(l\kappa;l'\kappa')A_{\nu\beta}(\kappa')=0,$$

or

$$\sum_{l'}\sum_{\kappa'}\Big[\sum_{\nu}\phi_{\alpha\nu}{}^{tt,P}(l\kappa;l'\kappa')A_{\nu\beta}(\kappa')\Big]=0, \quad \text{(II.B.9)}$$

in which the index λ is replaced by α. Comparing (II.B.9) with (II.A.16), we see that the transition to the principal-axes frame results in the replacement

$$\phi_{\alpha\beta}{}^{tt}(l\kappa;l'\kappa')\rightarrow\sum_{\nu}\phi_{\alpha\nu}{}^{tt,P}(l\kappa;l'\kappa')A_{\nu\beta}(\kappa')$$

as far as the sum rule is concerned. Equation (II.B.9) holds for all α, β, and κ. In the same fashion, we obtain from (II.A.17a), (II.A.18), and (II.A.19), respectively,

$$\sum_{l'}\sum_{\kappa'}\Big[\sum_{\nu}\phi_{\alpha\nu}{}^{rt,P}(l\kappa;l'\kappa')A_{\nu\beta}(\kappa')\Big]=0; \quad \text{(II.B.10)}$$

$$\sum_{l'}\sum_{\kappa'}\Big[\Big\{\sum_{\nu}\phi_{\alpha\nu}{}^{tt,P}(0\kappa;l'\kappa')A_{\nu\delta}(\kappa')\Big\}X_\gamma(l'\kappa')-\Big\{\sum_{\nu}\phi_{\alpha\nu}{}^{tt,P}(0\kappa;l'\kappa')A_{\nu\gamma}(\kappa')\Big\}X_\delta(l'\kappa')\Big]$$
$$+\sum_{l'}\sum_{\kappa'\in\mathrm{II}}\Big[\sum_{\nu}\phi_{\alpha\nu}{}^{tr,P}(0\kappa;l'\kappa')A_{\nu\beta}(\kappa')\Big]=0; \quad \text{(II.B.11)}$$

$$\sum_{l'}\sum_{\kappa'}\Big[\Big\{\sum_{\nu}\phi_{\alpha\nu}{}^{rt,P}(0\kappa;l'\kappa')A_{\nu\delta}(\kappa')\Big\}X_\gamma(l'\kappa')-\Big\{\sum_{\nu}\phi_{\alpha\nu}{}^{rt,P}(0\kappa;l'\kappa')A_{\nu\gamma}(\kappa')\Big\}X_\delta(l'\kappa')\Big]$$
$$+\sum_{l'}\sum_{\kappa'\in\mathrm{II}}\Big[\sum_{\nu}\phi_{\alpha\nu}{}^{rr,P}(0\kappa;l'\kappa')A_{\nu\beta}(\kappa')\Big]=0. \quad \text{(II.B.12)}$$

Here (β,γ,δ) are cyclic order of x, y, and z as before (note that they all pertain to κ').

At this stage, we must specify the explicit form of $\mathbf{A}(\kappa)$. Let XYZ represent a set of axes located on some vibrating unit and oriented parallel to the fixed frame, and let $X'''Y'''Z'''$ represent the frame coinciding with the principal axes of the moment of inertia of that unit. (See Fig. 2. Both systems are right-handed.)

Given two sets of orthogonal axes, it is possible to go from one to the other via three operations involving the so-called Eulerian angles (ξ,η,ζ). The procedure is as follows:

(1) Perform a counterclockwise rotation through ξ about the Z axis carrying XYZ to $X'Y'Z'$ as illustrated in Fig. 2(a).

(2) Next perform a counterclockwise rotation through η about the X' axis, going over thereby to $X''Y''Z''$ as shown in Fig. 2(b).

(3) Finally rotate through ζ about the Z'' axis arriving thus at $X'''Y'''Z'''$ as indicated in Fig. 2(c).

The matrix A characterizing the transformation $XYZ \rightarrow X'''Y'''Z'''$ can be constructed by considering each of the above transformations individually and then compounding them.

Thus, we find

$$\mathsf{A}=\begin{pmatrix}\cos\zeta & \sin\zeta & 0\\ -\sin\zeta & \cos\zeta & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}1 & 0 & 0\\ 0 & \cos\eta & \sin\eta\\ 0 & -\sin\eta & \cos\eta\end{pmatrix}\begin{pmatrix}\cos\xi & \sin\xi & 0\\ -\sin\xi & \cos\xi & 0\\ 0 & 0 & 1\end{pmatrix}$$

$$=\begin{bmatrix}\cos\zeta\cos\xi-\cos\eta\sin\xi\sin\zeta & \cos\zeta\sin\xi+\cos\eta\cos\xi\sin\zeta & \sin\zeta\sin\eta\\ -\sin\zeta\cos\xi-\cos\eta\sin\xi\cos\zeta & -\sin\zeta\sin\xi+\cos\eta\cos\xi\cos\zeta & \cos\zeta\sin\eta\\ \sin\eta\sin\xi & -\sin\eta\cos\xi & \cos\eta\end{bmatrix}. \quad \text{(II.B.13)}$$

Let us now write down the equations of motion. From (II.B.1) these are found to be

$$m_\kappa \ddot{u}_\alpha{}^{t,P}(l\kappa) = -\Big[\sum_{l'}\sum_{\kappa'}\sum_{\beta}\phi_{\alpha\beta}{}^{tt,P}(l\kappa;\, l'\kappa')u_\beta{}^{t,P}(l'\kappa') + \sum_{l'}\sum_{\kappa'\epsilon II}\sum_{\beta}\phi_{\alpha\beta}{}^{tr,P}(l\kappa;\, l'\kappa')u_\beta{}^{r,P}(l'\kappa')\Big], \quad \text{for all } l,\ \kappa, \text{ and } \alpha, \quad \text{(II.B.14a)}$$

and

$$\mathcal{I}_{\alpha\alpha}{}^{P}(\kappa)\ddot{u}_\alpha{}^{r,P}(l\kappa) = -\Big[\sum_{l'}\sum_{\kappa'}\sum_{\beta}\phi_{\alpha\beta}{}^{rt,P}(l\kappa;\, l'\kappa')u_\beta{}^{t,P}(l'\kappa') + \sum_{l'}\sum_{\kappa'\epsilon II}\sum_{\beta}\phi_{\alpha\beta}{}^{rr,P}(l\kappa;\, l'\kappa')u_\beta{}^{r,P}(l'\kappa')\Big], \quad \text{for all } l \text{ and } \alpha, \text{ and } \kappa\in II. \quad \text{(II.B.14b)}$$

The absence of the off-diagonal term in the moment of inertia in (II.B.14b), in contrast to its presence in (II.A.15b), is a consequence of the fact that $\mathcal{I}^P(\kappa)$ is diagonal.

The sum rules quoted in (II.B.9)–(II.B.12) can be deduced from the above equations also, and it is a useful exercise to do so.

By trying wavelike solutions of the form

$$u_\alpha{}^{i,P}(l\kappa) = U_\alpha{}^{i,P}(\kappa \mid \mathbf{q})\ \exp\{i[\mathbf{q}\cdot\mathbf{X}(l)-\omega(\mathbf{q})t]\}, \quad \text{(II.B.15)}$$

we obtain the following simultaneous equations in the wave amplitudes:

$$\omega^2(\mathbf{q})m_\kappa U_\alpha{}^{t,P}(\kappa \mid \mathbf{q}) = \sum_{\kappa'}\sum_{\beta}B_{\alpha\beta}{}^{tt,P}(\mathbf{q},\, \kappa\kappa')U_\beta{}^{t,P}(\kappa' \mid \mathbf{q}) + \sum_{\kappa'\epsilon II}\sum_{\beta}B_{\alpha\beta}{}^{tr,P}(\mathbf{q},\, \kappa\kappa')U_\beta{}^{r,P}(\kappa' \mid \mathbf{q}), \quad \text{for all } \alpha \text{ and } \kappa; \quad \text{(II.B.16a)}$$

$$\omega^2(\mathbf{q})\mathcal{I}_{\alpha\alpha}{}^{P}(\kappa)U_\alpha{}^{r,P}(\kappa \mid \mathbf{q}) = \sum_{\kappa'}\sum_{\beta}B_{\alpha\beta}{}^{rt,P}(\mathbf{q},\, \kappa\kappa')U_\beta{}^{t,P}(\kappa' \mid \mathbf{q}) + \sum_{\kappa'\epsilon II}\sum_{\beta}B_{\alpha\beta}{}^{rr,P}(\mathbf{q},\, \kappa\kappa')U_\beta{}^{r,P}(\kappa' \mid \mathbf{q}), \quad \text{for all } \alpha, \text{ and } \kappa\in II. \quad \text{(II.B.16b)}$$

In the above equations, we have

$$B_{\alpha\beta}{}^{ii',P}(\mathbf{q},\, \kappa\kappa') = \sum_{l'}\phi_{\alpha\beta}{}^{ii',P}(0\kappa;\, l'\kappa')\ \exp\big[i\mathbf{q}\cdot\mathbf{X}(l')\big]. \quad \text{(II.B.17)}$$

The components of the vectors $\mathbf{q}$ and $\mathbf{X}(l)$, as indeed also the equilibrium positions and $\mathbf{X}(k)$, can be specified as we choose. For convenience, these are always referred to Cartesian axes tied suitably to the crystallographic axes. It is the *displacements* from equilibrium positions which are specified with respect to the principal axes.

Due to the result (II.B.4), it readily follows that

$$\mathsf{B}^{ii',P}(\mathbf{q},\, \kappa\kappa') = \mathsf{A}(\kappa)\mathsf{B}^{ii'}(\mathbf{q},\, \kappa\kappa')\mathsf{A}^{\mathrm{tr}}(\kappa'). \quad \text{(II.B.18)}$$

As before, we can write the simultaneous equations (II.B.16) in matrix form as

$$\omega^2(\mathbf{q})\,\mathsf{m}^P\mathbf{U}^P(\mathbf{q}) = \mathsf{B}^P(\mathbf{q})\,\mathbf{U}^P(\mathbf{q}), \quad \text{(II.B.19)}$$

where all the quantities (except the frequency) have been superscripted to distinguish them from their counterparts in (II.A.23). The structures of $\mathsf{B}^P(\mathbf{q})$ and $\mathbf{U}^P(\mathbf{q})$ are the same as in (II.A.24) and (II.A.26).

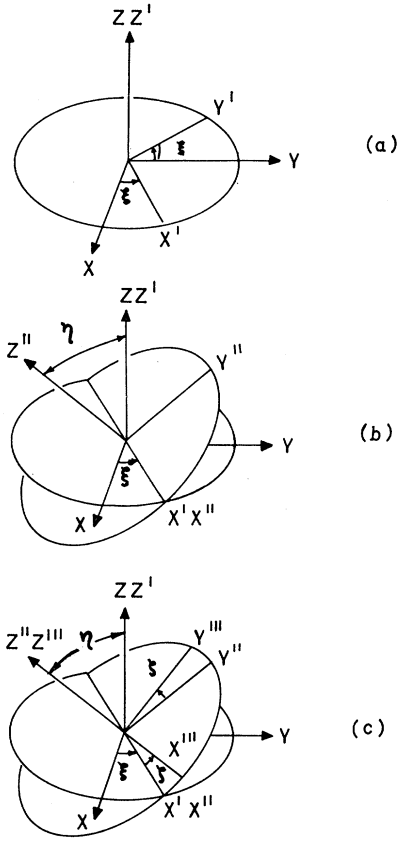

FIG. 2. Operations involved in the transformation of axes $(XYZ)\rightarrow(X'''Y'''Z''')$. The transformation involves three stages, each characterized by one of the Eulerian angles.

However, $\mathbf{m}^P$ is diagonal, in contrast to (II.A.25). Its elements are given by

$$m_{\alpha\beta}^{ii',P}(\kappa\kappa') = \delta_{ii'}\delta_{\alpha\beta}\delta(\kappa,\kappa')m_\kappa \quad \text{if } i=t$$
$$= \delta_{ii'}\delta_{\alpha\beta}\delta(\kappa,\kappa')g_{\alpha\alpha}^P(\kappa) \quad \text{if } i=r. \quad \text{(II.B.20)}$$

The eigenvalues $\omega_j^2(\mathbf{q})$ are obtained this time from the determinantal equation

$$|\,\mathbf{B}^P(\mathbf{q}) - \omega^2(\mathbf{q})\,\mathbf{m}^P\,| = 0. \quad \text{(II.B.21)}$$

It is easily established that the solutions $\{\omega_j^2(\mathbf{q})\}$, $j=1, 2\cdots(3\mu+6\nu)$ are the same as those obtained from (II.A.29) as indeed they must be.

The components $e_\alpha^{i,P}(\kappa\,|\,\mathbf{q}j)$ of the normalized eigenvector $\mathbf{e}^P(\mathbf{q}j)$ can be chosen to satisfy the condition

$$\sum_{\alpha\kappa i} e_\alpha^{i,P*}(\kappa\,|\,\mathbf{q}j)m_{\alpha\alpha}^{ii,P}(\kappa\kappa)e_\alpha^{i,P}(\kappa\,|\,\mathbf{q}j') = M\delta_{jj'}, \quad \text{(II.B.22)}$$

with M being, as before, the mass of the primitive unit cell.

The properties of $\mathbf{B}^P(\mathbf{q})$ and $\mathbf{e}^{i,P}(\kappa\,|\,\mathbf{q}j)$ arising from the translational symmetry of the reciprocal lattice are the same as in (II.A.47). The transition to quantum mechanics is also essentially the same as that given earlier and does not require repetition.

The principal-axes representation is readily amenable to a formulation in which the eigenvalue problem assumes the same form as in (II.A.27) and permits the eigenvectors to be chosen orthonormal. All this requires is to choose as trial solutions

$$u_\alpha^{t,P}(l\kappa) = (m_\kappa)^{-1/2}V_\alpha^{t,P}(\kappa\,|\,\mathbf{q}) \times\exp\{i[\mathbf{q}\cdot\mathbf{X}(l)-\omega(\mathbf{q})t]\},$$
$$u_\alpha^{r,P}(l\kappa) = (g_{\alpha\alpha}(\kappa))^{-1/2}V_\alpha^{r,P}(\kappa\,|\,\mathbf{q}) \times\exp\{i[\mathbf{q}\cdot\mathbf{X}(l)-\omega(\mathbf{q})t]\}, \quad \text{(II.B.23)}$$

instead of (II.B.15). The dynamical matrix in this case is given by

$$D_{\alpha\beta}^{ii',P}(\mathbf{q},\kappa\kappa') = \{m_{\alpha\alpha}^{ii,P}(\kappa\kappa)m_{\beta\beta}^{i'i',P}(\kappa'\kappa')\}^{-1/2} \times B_{\alpha\beta}^{ii',P}(\mathbf{q},\kappa\kappa'), \quad \text{(II.B.24)}$$

[cf. (II.A.27)]. The eigenvectors $\mathbf{E}^P(\mathbf{q}j)$ of $\mathbf{D}^P(\mathbf{q})$ can be chosen to satisfy the orthogonality and completeness relations

$$\sum_{\alpha\kappa i} E_\alpha^{i,P*}(\kappa\,|\,\mathbf{q}j)E_\alpha^{i,P}(\kappa\,|\,\mathbf{q}j') = \delta_{jj'}, \quad \text{(II.B.25a)}$$

$$\sum_j E_\alpha^{i,P*}(\kappa\,|\,\mathbf{q}j)E_\beta^{i',P}(\kappa'\,|\,\mathbf{q}j) = \delta_{\alpha\beta}\delta_{ii'}\delta(\kappa,\kappa'). \quad \text{(II.B.25b)}$$

This concludes the study of the formal theory of external modes in complex crystals.

III. REVIEW OF THEORETICAL AND EXPERIMENTAL WORK ON DISPERSION RELATIONS FOR EXTERNAL MODES

A. General

We have earlier pointed out that, although the concept of viewing the vibrational motions of atoms in complex crystals in terms of external and internal vibrations has existed for a long time, serious attempts to quantify the concepts and make detailed numerical calculations have been made only during the last few years. Simple models to delineate the basic ideas have, however, been proposed from time to time. The earliest reference we could find is the work of Frenkel (1935; 1946), who investigated the angular oscillations of identical dipoles in a linear chain, in connection with his studies on orientation order in dipolar crystals. Frenkel solved the problem by using cyclic boundary conditions and concluded that the "rotational part of the heat motion can be described as a superposition of 'rotation–oscillation' waves, which are quite analogous to the 'optical' waves of the Born–Karman theory in the case of an ionic lattice." Later, guided by Frenkel's work, Ancelme and Porfireva (1949) examined the dynamics of linear chains of molecules containing one and two molecules per unit cell, taking into account

the translational as well as rotational degrees of freedom. Two cases were studied, viz., without and with coupling between the translational and rotational motions. About the same time, Raskin, Sechkarev, and Skripov (1949) discussed the dynamics of a one-dimensional chain containing two identical dumbbell-type diatomic molecules per unit cell. The two molecules were assumed to be related to each other by (i) mirror plane or (ii) screw axes or (iii) center of symmetry. The $q=0$ frequencies for all the cases were computed assuming nearest-neighbor interactions, the aim being to provide a theoretical basis for understanding the role of librations in relation to Raman spectra. Later, Skripov (1949) extended some of these considerations to three-dimensional crystals. In 1957, the problem was considered afresh by Asano and Tomishima (1957a, 1957b, 1957c). These authors were interested in such complex inorganic crystals as sulphates, phosphates, etc. To begin with, Asano and Tomishima (1957a) formulate the problem for three-dimensional crystals by writing down formal expressions for the kinetic and potential energies in terms of linear and angular displacements. They then indicate how the equations of motion may be obtained. The treatment is rather sketchy (for example, the consequences of translational and rotational invariance are not mentioned) and restricted to crystals containing radicals whose principal axes can be chosen at will, like the sulphates, phosphates, etc., in which these authors were primarily interested. Asano and Tomishima have also explored some one-dimensional models by way of illustrating the concept of librational and translational waves, their mixing, etc.

About this time, Sandor (1962) became interested in the problem from the point of understanding the contribution of the external vibrations to the diffuse spots seen in x-ray scattering, and reinvestigated a few one-dimensional models since he saw objections in the analysis of Asano and Tomishima. Sandor deduced the dispersion curves for his models employing essentially an extension of the methods commonly used in the discussion of the Born–von Kármán problem for one-dimensional chains (Kittel, 1966). It is interesting to rederive Sandor's results as a special case of the general formulation given in Sec. II and this is done below.

Sandor considers a one-dimensional chain made up of identical ring-type molecules each consisting of six close-packed spherical atoms as illustrated in Fig. 3. There is thus only one molecule per cell, and for purposes of describing this chain the sublattice index κ may be dropped. In one of the models he discusses, each molecule is permitted to make only translational motions perpendicular to the chain and in the plane of the molecule, i.e., along the X direction, and rotations about an axis passing through the molecular center and normal to the plane of the molecule, i.e., about the Z direction. With these restrictions, the equations of motion (II.A.15) simplify to

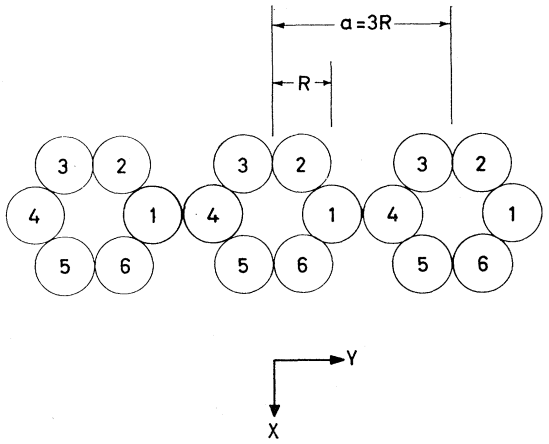

FIG. 3. One-dimensional monomolecular chain of ring-type molecules. The atoms are imagined to be spheres of diameter R. The intermolecular spacing is $a=3R$. The X and Y axes are as shown, while the Z axis is normal to the plane of the paper and coming out of it.

$$M\ddot{u}_x{}^t(l) = -\Big(\sum_{l'} \phi_{xx}{}^{tt}(l;l')u_x{}^t(l') + \sum_{l'} \phi_{xz}{}^{tr}(l;l')u_z{}^r(l')\Big); \quad \text{(III.A.1a)}$$

$$\mathcal{I}_{zz}\ddot{u}_z{}^r(l) = -\Big(\sum_{l'} \phi_{zx}{}^{rt}(l;l')u_x{}^t(l') + \sum_{l'} \phi_{zz}{}^{rr}(l;l')u_z{}^r(l')\Big). \quad \text{(III.A.1b)}$$

Substitution of wavelike solutions

$$u_x{}^t(l) = U_x{}^t(q)\,\exp\left[i(qla-\omega t)\right],$$
$$u_z{}^r(l) = U_z{}^r(q)\,\exp\left[i(qla-\omega t)\right], \quad \text{(III.A.2)}$$

yields the equations

$$\left[B_{xx}{}^{tt}(q)-M\omega^2\right]U_x{}^t(q)+B_{xz}{}^{tr}(q)\,U_z{}^r(q)=0,$$
$$B_{zx}{}^{rt}(q)\,U_x{}^t(q)+\left[B_{zz}{}^{rr}(q)-\mathcal{I}_{zz}\omega^2\right]U_z{}^r(q)=0, \quad \text{(III.A.3)}$$

where

$$B_{xx}{}^{tt}(q) = \sum_{l'} \phi_{xx}{}^{tt}(0;l')\,\exp\,(iql'a), \quad \text{etc.}$$

To proceed further, we follow Sandor and assume that only the interactions between nearest-neighbor molecules are important. This means that in order to evaluate the elements of the dynamical matrix, we need to know only the following force constants:

$$\phi_{xx}{}^{tt}(0;l'), \quad \phi_{xz}{}^{tr}(0;l'),$$
$$\phi_{zx}{}^{rt}(0;l'), \quad \phi_{zz}{}^{rr}(0;l'),$$
$$l'=-1,\,0,\,1.$$

Sandor further supposes that there is a central force F^c with force constant C_1 acting between the centers of neighboring molecules, and a noncentral force F^{nc} with force constant C_2 acting between the centers of nearest atoms of neighboring molecules, i.e., between

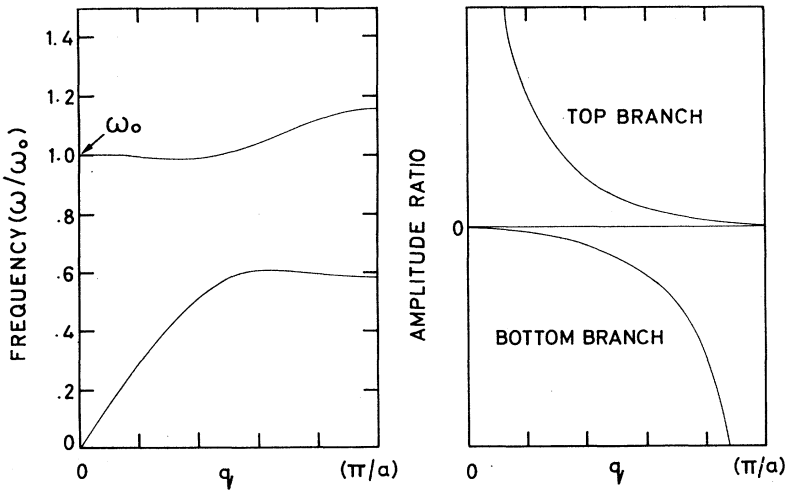

FIG. 4. Left-hand side shows plot of the dispersion relations for the one-dimensional chain of Fig. 3 based on the model discussed in the text. The frequencies are given in units of the $q=0$ optic frequency ω_0. The calculations are for $(C_1/C_2)=1$. On the right is plotted the ratio of the amplitude of the librational part to the translational part. Observe that for $q=0$, the top branch is purely librational, while for q corresponding to the zone boundary, the mode is translational. The converse is true of the bottom branch. For intermediate values, there is an admixture. [After Sandor (1962).]

the atom with index 1 in one molecule, and the atom with index 4 in the neighboring molecule (see Fig. 3). The force F^c depends only on the linear displacements of neighboring molecules, while the noncentral force F^{nc} depends also on their angular displacements relative to the equilibrium position. These assumptions are somewhat in the spirit of taking the intermolecular potential to consist of a central part and an angular part (Hirschfelder *et al.*, 1954). The need for taking into account explicitly a central part in intermolecular interactions has also been pointed out by Craig (1968).

It is clear from above that whereas $\phi_{xx}{}^{tt}(0;1)$ has contributions from both kind of forces, $\phi_{xz}{}^{tr}(0;1)$, $\phi_{zx}{}^{rt}(0;1)$, and $\phi_{zz}{}^{rr}(0;1)$ have contributions from noncentral forces alone, since rotations do not change the distance between the centers of molecules. This noncentral component can be evaluated by an application of the formulas given in Sec. II.A since it arises from the interaction between atoms located in different molecules.

Consider first $\phi_{xx}{}^{tt}(0;1)$. Using (II.A.58a), we have

$$\phi_{xx}{}^{tt}(0;1)=\text{central component}+\text{noncentral component}$$
$$=-C_1+\sum_{k\in 0}\sum_{k'\in 1}\phi_{xx}(0k;1k')$$
$$\approx -C_1+\phi_{xx}(01;14). \qquad \text{(III.A.4a)}$$

Sandor writes this quantity as $-(C_1+C_2)$, which shows that the noncentral force constant C_2 is related to the atomic force constant by

$$C_2=-\phi_{xx}(01;14).$$

To obtain the remaining force constants, we note that these involve only noncentral components, and that they are contributed solely by the atomic pairs of the (1–4) type. Thus, from (II.A.58b), we obtain

$$\phi_{xz}{}^{tr}(0;1)=\phi_{xx}(01;14)R$$
$$=-C_2R, \qquad \text{(III.A.4b)}$$

and

$$\phi_{zx}{}^{rt}(0;1)=C_2R, \qquad \text{(III.A.4c)}$$
$$\phi_{zz}{}^{rr}(0;1)=C_2R^2; \qquad \text{(III.A.4d)}$$

as well as

$$\phi_{xx}{}^{tt}(0;-1)=-(C_1+C_2), \qquad \text{(III.A.5a)}$$
$$\phi_{xz}{}^{tr}(0;-1)=C_2R, \qquad \text{(III.A.5b)}$$
$$\phi_{zx}{}^{rt}(0;-1)=-C_2R, \qquad \text{(III.A.5c)}$$
$$\phi_{zz}{}^{rr}(0;-1)=C_2R^2. \qquad \text{(III.A.5d)}$$

These last results can also be obtained by invoking the inversion symmetry of the crystal.

We are now left with only the "self" terms $\phi_{xx}{}^{tt}(0;0)$, etc. These are easily obtained from the sum rules (II.A.16)–(II.A.19). Thus, from (II.A.16), we have

$$\phi_{xx}{}^{tt}(0;0)=-\{\phi_{xx}{}^{tt}(0;1)+\phi_{xx}{}^{tt}(0;-1)\}$$
$$=2(C_1+C_2), \qquad \text{(III.A.6a)}$$
$$\phi_{xz}{}^{tr}(0;0)=0, \qquad \text{(III.A.6b)}$$
$$\phi_{zx}{}^{rt}(0;0)=0, \qquad \text{(III.A.6c)}$$
$$\phi_{zz}{}^{rr}(0;0)=-\{\phi_{zz}{}^{rr}(0;1)+\phi_{zz}{}^{rr}(0;-1)\}$$
$$+\{\phi_{zx}{}^{rt}(0;1)a-\phi_{zx}{}^{rt}(0;-1)a\}$$
$$=4C_2R^2, \qquad \text{(III.A.6d)}$$

remembering that $a=3R$. Using these expressions for the force constants, the elements of the dynamical matrix become

$$B_{xx}{}^{tt}(q)=2(C_1+C_2)[1-\cos(aq)],$$
$$B_{xz}{}^{tr}(q)=-2iC_2R\sin(aq),$$
$$B_{zx}{}^{rt}(q)=2iC_2R\sin(aq),$$
$$B_{zz}{}^{rr}(q)=2C_2R^2[2+\cos(aq)]. \qquad \text{(III.A.7)}$$

The secular determinant therefore is

$$\begin{vmatrix} 4(C_1+C_2)\sin^2\tfrac{1}{2}(aq)-M\omega^2 & -2iC_2R\sin(aq) \\ 2iC_2R\sin(aq) & 2C_2R^2[1+2\cos^2\tfrac{1}{2}(aq)]-\vartheta_{zz}\omega^2 \end{vmatrix} = 0 \qquad \text{(III.A.8)}$$

in agreement with Sandor's results. The essential difference in our derivation is that we make explicit use of the sum rules, for evaluating the "self" force constants, in contrast to Sandor, who employed indirect arguments to ensure that his equations of motion were rotationally invariant. By examining the solutions of (III.A.8) for various cases, Sandor demonstrated that the dispersion curves for the model under consideration have two branches, and that, in general, the motions are of a mixed character. These features are illustrated in Fig. 4.

As already indicated, one-dimensional models of this kind are mainly of pedagogical value, and play a role similar to the one-dimensional atomic chains considered in connection with the Born–von Kármán theory. Several other models may be found in a paper by Hahn and Biem (1963) and in a recent monograph by Ludwig (1967).

The years 1963 and 1964 saw a major qualitative change in the approach of physicists to the problem of external vibrations. Models were constructed for the first time for real three-dimensional crystals, and even numerical results were presented. Since then, there have been several advances in the theoretical development of the subject, and spurred by these, experimentalists also have paid increasing attention to the study of dispersion relations for external modes. These developments are reviewed below.

For the sake of completeness, we must record that brief reviews of the formal theory may be found in the articles by Janik (1968) and Walmsley (1968) and in Ludwig's monograph (1967). Janik considers a crystal with a total of $3n$ degrees of freedom per unit cell and then discusses their separation into internal and external modes. This is analogous to the separation in molecular physics of the degrees of freedom of a molecule into the internal (vibrational) and external degrees of freedom (Wilson *et al.*, 1955). The problem is quite involved, and Janik does not explore it in detail. Ludwig (1967), however, takes cognizance of the problem. Janik also does not clarify the points to be observed if the principal axes of the molecular groups cannot be chosen parallel to the crystal-fixed axes. This is presumably because he is interested in crystals like NH_4Cl, where the principal axes can be chosen at will. Walmsley (1968) is interested mainly in molecular crystals, and formulates the theory by considering all linear displacements in the fixed frame and angular displacements in the principal-axes frame. Passing mention must also be made of the work of Brot (1965), who considered librational waves in a cubic lattice of linear molecules and the resulting frequency spectrum, and of the work of Deprez and Fouret (1966), who investigated the long-wavelength modes in relation to elasticity theories. It is also worth remarking that the quanta of librations are sometimes referred to as librons, torsons, etc., by analogy with the word phonon. It is our view that such nomenclature, though attractive, is not desirable, since in general there is admixture between the translational and librational components.

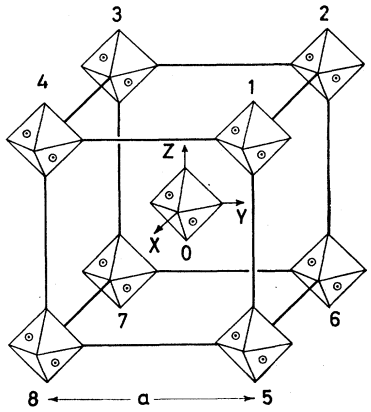

FIG. 5. Cubic unit cell of HMT. The octahedral objects symbolize the HMT molecules of symmetry T_d. [After Cochran and Pawley (1964).]

We shall presently survey the work reported thus far on theoretical and experimental studies of dispersion relations for external modes in complex crystals.

B. Hexamethylenetetramine

We shall begin our review with hexamethylenetetramine $[(CH_2)_6N_4]$ (also abbreviated as hexamine and HMT) in view of the fact that this is one of the most extensively studied substances, both experimentally and theoretically, as well as being the first one for which detailed calculations for external modes were reported (Biem, 1963; Cochran and Pawley, 1964). Also, this crystal provides a convenient example with which to illustrate the formal theory of Sec. II; and we shall discuss it in some detail.

HMT is a molecular crystal and belongs to the space group T_d^3 with the underlying point group T_d. The cubic unit cell contains two molecules, and is illustrated in Fig. 5. If we collapse the molecules to points, the structure reduces to a bcc lattice, the space group of which is O_h^9. The same space group obtains if the molecule has inversion symmetry, which in fact it does not.

The primitive unit cell is chosen as in the case of the bcc lattice (Kittel, 1966) and contains only one molecule. The reciprocal lattice has the fcc structure, and the Brillouin zone is as illustrated in Fig. 6.

Following Cochran and Pawley (1964) and Biem (1963), we shall now set up the force constant matrices assuming that interactions are negligible beyond the second neighbors. Now each molecule has eight first

neighbors at a distance of $(\sqrt{3}/2)a$ and six second neighbors at a distance of a, where a is the lattice constant. The labeling of these neighbors and their coordinates is summarized in Table II.

Before proceeding further, we observe that HMT is a spherical-top molecule. The principal axes can therefore be chosen at will, which means that the fixed frame can also be used as the principal-axes frame.

Let us now write the force constant matrix for the molecular pair (0–1) as

$$\boldsymbol{\phi}(000; l_1l_2l_3)\rightarrow\boldsymbol{\phi}(000; 111)$$

$$=\begin{bmatrix}\boldsymbol{\phi}^{tt}(000;111) & \boldsymbol{\phi}^{tr}(000;111)\\ \boldsymbol{\phi}^{rt}(000;111) & \boldsymbol{\phi}^{rr}(000;111)\end{bmatrix}$$

$$=\begin{bmatrix} XX^{tt} & XY^{tt} & XZ^{tt} & XX^{tr} & XY^{tr} & XZ^{tr}\\ YX^{tt} & YY^{tt} & YZ^{tt} & YX^{tr} & YY^{tr} & YZ^{tr}\\ ZX^{tt} & ZY^{tt} & ZZ^{tt} & ZX^{tr} & ZY^{tr} & ZZ^{tr}\\ XX^{rt} & XY^{rt} & XZ^{rt} & XX^{rr} & XY^{rr} & XZ^{rr}\\ YX^{rt} & YY^{rt} & YZ^{rt} & YX^{rr} & YY^{rr} & YZ^{rr}\\ ZX^{rt} & ZY^{rt} & ZZ^{rt} & ZX^{rr} & ZY^{rr} & ZZ^{rr}\end{bmatrix}. \quad \text{(III.B.1)}$$

The indices l_1, l_2, l_3 denote the components of the lattice vector $\mathbf{X}(l)$ along the basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$. We wish to explore the restrictions, if any, on the force constants imposed by crystal symmetry. Basically this involves a systematic application of (II.A.13). In particular, what we need to examine are the effects of operations which leave the bond (0–1) invariant. In the present case, of the 24 operations belonging to the point group T_d of the crystal, a 120° counterclockwise rotation about the [111] direction ($\mathbf{C}_3[111]$), a clockwise rotation by the same angle about the same direction ($\mathbf{C}_3^{-1}[111]$), and a reflection in the $(1\bar{1}0)$ plane [$\boldsymbol{\sigma}(1\bar{1}0)$] leave the bond (0–1) undisturbed.

Consider first the effect of $\mathbf{C}_3[111]$. We have, using (II.A.13)

$$\boldsymbol{\phi}(000;111)=\begin{bmatrix}\mathbf{C}_3[111] & 0\\ 0 & \mathbf{C}_3[111]\end{bmatrix}\times\boldsymbol{\phi}(000;111)\begin{bmatrix}\mathbf{C}_3^{tr}[111] & 0\\ 0 & \mathbf{C}_3^{tr}[111]\end{bmatrix}, \quad \text{(III.B.2)}$$

with

$$\mathbf{C}_3[111]=\begin{bmatrix}0&0&1\\1&0&0\\0&1&0\end{bmatrix}.$$

Here we are writing the transformation of 6×6 matrices by combining the transformation rules for 3×3 matrices given previously and taking note of the fact that $\mathbf{C}_3[111]$ is a proper rotation. On simplifying the right-hand side and comparing it with the left-hand side, we obtain

$$XX^{tt}=YY^{tt}=ZZ^{tt};$$
$$XY^{tt}=YZ^{tt}=ZX^{tt};$$
$$XZ^{tt}=YX^{tt}=ZY^{tt};$$
$$XX^{rr}=YY^{rr}=ZZ^{rr};$$
$$XY^{rr}=YZ^{rr}=ZX^{rr};$$
$$XZ^{rr}=YX^{rr}=ZY^{rr};$$
$$XX^{tr}=YY^{tr}=ZZ^{tr};$$
$$XY^{tr}=YZ^{tr}=ZX^{tr};$$
$$XZ^{tr}=YX^{tr}=ZY^{tr};$$
$$XX^{rt}=YY^{rt}=ZZ^{rt};$$
$$XY^{rt}=YZ^{rt}=ZX^{rt};$$
$$XZ^{rt}=YX^{rt}=ZY^{rt}.$$

Next we consider the effect of $\boldsymbol{\sigma}(1\bar{1}0)$. Since reflection is an improper rotation, care is required in discussing the force constant transformation. Using (II.A.13) with due regard to the negative signs contributed by factors of type $C^i(S)$, we have

$$\boldsymbol{\phi}(000;111)=\begin{bmatrix}\boldsymbol{\sigma}(1\bar{1}0) & 0\\ 0 & -\boldsymbol{\sigma}(1\bar{1}0)\end{bmatrix}\times\boldsymbol{\phi}(000;111)\begin{bmatrix}\boldsymbol{\sigma}^{tr}(1\bar{1}0) & 0\\ 0 & -\boldsymbol{\sigma}^{tr}(1\bar{1}0)\end{bmatrix},$$

$$\boldsymbol{\sigma}(1\bar{1}0)=\begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix}.$$

Upon simplification this leads to the additional relations

$$XY^{tt}=XZ^{tt}, \qquad XY^{rr}=XZ^{rr},$$
$$XY^{rt}=-XZ^{rt}, \qquad XY^{tr}=-XZ^{tr},$$
$$XX^{tr}=XX^{rt}=0.$$

The symmetry $\mathbf{C}_3^{-1}[111]$ does not produce any further

simplification. We may thus write

$$\phi(000;\,111) = -\begin{bmatrix} \lambda & \omega & \omega & 0 & -\epsilon & \epsilon \\ \omega & \lambda & \omega & \epsilon & 0 & -\epsilon \\ \omega & \omega & \lambda & -\epsilon & \epsilon & 0 \\ 0 & -\theta & \theta & \psi & \delta & \delta \\ \theta & 0 & -\theta & \delta & \psi & \delta \\ -\theta & \theta & 0 & \delta & \delta & \psi \end{bmatrix}. \quad \text{(III.B.3)}$$

A negative sign has been pulled out on the right-hand side for convenience. [See also remarks around Eq. (II.A.15).] We see from above that the first-neighbor interactions corresponding to the pair (0–1) involve six independent constants.

The force constant matrix for the pair (0–7) follows immediately from (III.B.3) since the bond (0–7) is identical to the bond (1–0), apart from a lattice translation. We therefore have, using (II.A.9),

$$\phi(000;\,-1-1-1) = \phi^{tr}(000;\,111). \quad \text{(III.B.4)}$$

The force constant matrices for the remaining first neighbors of the central molecule 0 can be written from those given above, by using in (II.A.13) appropriate transformations which transform the (0–1) or (0–7) pair to the pair concerned. For example, the force constants for the (0–3) pair are given by

$$\phi(000;\,-100) = \begin{bmatrix} C_2[001] & 0 \\ 0 & C_2[001] \end{bmatrix} \times \phi(000;\,111) \begin{bmatrix} C_2^{tr}[001] & 0 \\ 0 & C_2^{tr}[001] \end{bmatrix}, \quad \text{(III.B.5)}$$

where $C_2[001]$ corresponds to a 180° rotation about the z axis and is represented by

$$C_2[001] = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Simplifying the right-hand side of (III.B.5) yields

$$\phi(000;\,-100) = -\begin{bmatrix} \lambda & \omega & -\omega & 0 & -\epsilon & -\epsilon \\ \omega & \lambda & -\omega & \epsilon & 0 & \epsilon \\ -\omega & -\omega & \lambda & \epsilon & -\epsilon & 0 \\ 0 & -\theta & -\theta & \psi & \delta & -\delta \\ \theta & 0 & \theta & \delta & \psi & -\delta \\ \theta & -\theta & 0 & -\delta & -\delta & \psi \end{bmatrix}. \quad \text{(III.B.6)}$$

The force constant matrices for all the eight first neighbors obtained in this manner are summarized in Table III. The matrices for the second neighbors are deduced in a similar fashion and are listed in Table IV (see also, Dolling and Powell, 1970). We thus see that a

TABLE II. Coordinates of the first- and second-neighbor molecules of the molecule at the origin in HMT. The integers l_1, l_2, l_3 denote the components of $\mathbf{X}(l)$ along the basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, where $\mathbf{a}_1 = (a/2)(\mathbf{i}+\mathbf{j}-\mathbf{k})$, $\mathbf{a}_2 = (a/2)(\mathbf{i}-\mathbf{j}+\mathbf{k})$, and $\mathbf{a}_3 = (a/2)(-\mathbf{i}+\mathbf{j}+\mathbf{k})$. Molecules (1–8) constitute the first neighbors, and (9–14), the second neighbors.

Molecule No.	Cartesian coordinates	(l_1, l_2, l_3)
1	$a(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	(1, 1, 1)
2	$a(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	(0, 0, 1)
3	$a(-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$	(−1, 0, 0)
4	$a(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$	(0, 1, 0)
5	$a(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	(1, 0, 0)
6	$a(-\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$	(0, −1, 0)
7	$a(-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2})$	(−1, −1, −1)
8	$a(\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2})$	(0, 0, −1)
9	$a(1, 0, 0)$	(1, 1, 0)
10	$a(0, 1, 0)$	(1, 0, 1)
11	$a(-1, 0, 0)$	(−1, −1, 0)
12	$a(0, -1, 0)$	(−1, 0, −1)
13	$a(0, 0, 1)$	(0, 1, 1)
14	$a(0, 0, -1)$	(0, −1, −1)

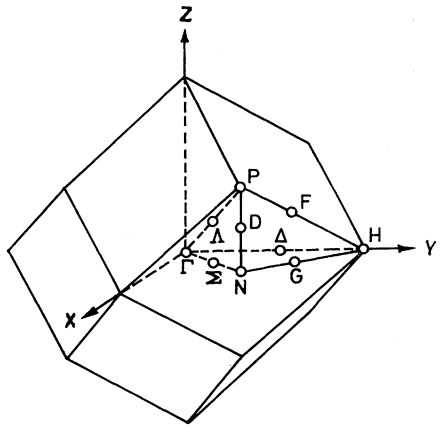

FIG. 6. Brillouin zone for HMT. The labeling of symmetry points and directions follows standard practice in solid state physics.

TABLE III. Force constant matrices for the first neighbors in HMT.

Molecular pair	Force constant matrix
(0–1)	$-\begin{bmatrix} \lambda & \omega & \omega & 0 & -\epsilon & \epsilon \\ \omega & \lambda & \omega & \epsilon & 0 & -\epsilon \\ \omega & \omega & \lambda & -\epsilon & \epsilon & 0 \\ 0 & -\theta & \theta & \psi & \delta & \delta \\ \theta & 0 & -\theta & \delta & \psi & \delta \\ -\theta & \theta & 0 & \delta & \delta & \psi \end{bmatrix}$
(0–2)	$-\begin{bmatrix} \lambda & -\omega & -\omega & 0 & -\theta & \theta \\ -\omega & \lambda & \omega & \theta & 0 & \theta \\ -\omega & \omega & \lambda & -\theta & -\theta & 0 \\ 0 & -\epsilon & \epsilon & \psi & -\delta & -\delta \\ \epsilon & 0 & \epsilon & -\delta & \psi & \delta \\ -\epsilon & -\epsilon & 0 & -\delta & \delta & \psi \end{bmatrix}$
(0–3)	$-\begin{bmatrix} \lambda & \omega & -\omega & 0 & -\epsilon & -\epsilon \\ \omega & \lambda & -\omega & \epsilon & 0 & \epsilon \\ -\omega & -\omega & \lambda & \epsilon & -\epsilon & 0 \\ 0 & -\theta & -\theta & \psi & \delta & -\delta \\ \theta & 0 & \theta & \delta & \psi & -\delta \\ \theta & -\theta & 0 & -\delta & -\delta & \psi \end{bmatrix}$
(0–4)	$-\begin{bmatrix} \lambda & -\omega & \omega & 0 & -\theta & -\theta \\ -\omega & \lambda & -\omega & \theta & 0 & -\theta \\ \omega & -\omega & \lambda & \theta & 0 & \theta \\ 0 & -\epsilon & -\epsilon & \psi & -\delta & \delta \\ \epsilon & 0 & -\epsilon & -\delta & \psi & -\delta \\ \epsilon & \epsilon & 0 & \delta & -\delta & \psi \end{bmatrix}$
(0–5)	$-\begin{bmatrix} \lambda & \omega & -\omega & 0 & \theta & \theta \\ \omega & \lambda & -\omega & -\theta & 0 & -\theta \\ -\omega & -\omega & \lambda & -\theta & \theta & 0 \\ 0 & \epsilon & \epsilon & \psi & \delta & -\delta \\ -\epsilon & 0 & -\epsilon & \delta & \psi & -\delta \\ -\epsilon & \epsilon & 0 & -\delta & -\delta & \psi \end{bmatrix}$
(0–6)	$-\begin{bmatrix} \lambda & -\omega & \omega & 0 & \epsilon & \epsilon \\ -\omega & \lambda & -\omega & -\epsilon & 0 & \epsilon \\ \omega & -\omega & \lambda & -\epsilon & -\epsilon & 0 \\ 0 & \theta & \theta & \psi & -\delta & \delta \\ -\theta & 0 & \theta & -\delta & \psi & -\delta \\ -\theta & -\theta & 0 & \delta & -\delta & \psi \end{bmatrix}$
(0–7)	$-\begin{bmatrix} \lambda & \omega & \omega & 0 & \theta & -\theta \\ \omega & \lambda & \omega & -\theta & 0 & \theta \\ \omega & \omega & \lambda & \theta & -\theta & 0 \\ 0 & \epsilon & -\epsilon & \psi & \delta & \delta \\ -\epsilon & 0 & \epsilon & \delta & \psi & \delta \\ \epsilon & -\epsilon & 0 & \delta & \delta & \psi \end{bmatrix}$
(0–8)	$-\begin{bmatrix} \lambda & -\omega & -\omega & 0 & \epsilon & -\epsilon \\ -\omega & \lambda & \omega & -\epsilon & 0 & -\epsilon \\ -\omega & \omega & \lambda & \epsilon & \epsilon & 0 \\ 0 & \theta & -\theta & \psi & -\delta & -\delta \\ -\theta & 0 & -\theta & -\delta & \psi & \delta \\ \theta & \theta & 0 & -\delta & \delta & \psi \end{bmatrix}$

TABLE IV. Force constant matrices for the second neighbors in HMT.

Molecular pair	Force constant matrix
(0–9)	$-\begin{bmatrix} \zeta & 0 & 0 & 0 & 0 & 0 \\ 0 & \rho & 0 & 0 & \mu & \nu \\ 0 & 0 & \rho & 0 & -\nu & -\mu \\ 0 & 0 & 0 & \xi & 0 & 0 \\ 0 & \mu & \nu & 0 & \eta & 0 \\ 0 & -\nu & -\mu & 0 & 0 & \eta \end{bmatrix}$
(0–10)	$-\begin{bmatrix} \rho & 0 & 0 & -\mu & 0 & -\nu \\ 0 & \zeta & 0 & 0 & 0 & 0 \\ 0 & 0 & \rho & \nu & 0 & \mu \\ -\mu & 0 & -\nu & \eta & 0 & 0 \\ 0 & 0 & 0 & 0 & \xi & 0 \\ \nu & 0 & \mu & 0 & 0 & \eta \end{bmatrix}$
(0–11)	$-\begin{bmatrix} \zeta & 0 & 0 & 0 & 0 & 0 \\ 0 & \rho & 0 & 0 & \mu & -\nu \\ 0 & 0 & \rho & 0 & \nu & -\mu \\ 0 & 0 & 0 & \xi & 0 & 0 \\ 0 & \mu & -\nu & 0 & \eta & 0 \\ 0 & \nu & -\mu & 0 & 0 & \eta \end{bmatrix}$
(0–12)	$-\begin{bmatrix} \rho & 0 & 0 & -\mu & 0 & \nu \\ 0 & \zeta & 0 & 0 & 0 & 0 \\ 0 & 0 & \rho & -\nu & 0 & \mu \\ -\mu & 0 & \nu & \eta & 0 & 0 \\ 0 & 0 & 0 & 0 & \xi & 0 \\ -\nu & 0 & \mu & 0 & 0 & \eta \end{bmatrix}$
(0–13)	$-\begin{bmatrix} \rho & 0 & 0 & \mu & \nu & 0 \\ 0 & \rho & 0 & -\nu & -\mu & 0 \\ 0 & 0 & \zeta & 0 & 0 & 0 \\ \mu & \nu & 0 & \eta & 0 & 0 \\ -\nu & -\mu & 0 & 0 & \eta & 0 \\ 0 & 0 & 0 & 0 & 0 & \xi \end{bmatrix}$
(0–14)	$-\begin{bmatrix} \rho & 0 & 0 & \mu & -\nu & 0 \\ 0 & \rho & 0 & \nu & -\mu & 0 \\ 0 & 0 & \zeta & 0 & 0 & 0 \\ \mu & -\nu & 0 & \eta & 0 & 0 \\ \nu & -\mu & 0 & 0 & \eta & 0 \\ 0 & 0 & 0 & 0 & 0 & \xi \end{bmatrix}$

two-neighbor general force constant model for hexamine involves 12 independent parameters, 6 for each set of neighbors.

All the force constant matrices except the "self" terms $\Phi^{ii'}(000;000)$ are now known. The latter are determined by a systematic application of the sum rules (II.A.16)–(II.A.19). Thus, from (II.A.16) we get

$$\Phi^{tt}(000;000)=A1_3, \qquad A=(8\lambda+2\zeta+4\rho). \quad \text{(III.B.7)}$$

From (II.A.17a) we have

$$\Phi^{rt}(000;000)=-\sum_{l'}{}' \Phi^{rt}(0;l'),$$

where the prime on the l' summation implies the exclusion of $l'=0$. This expression, when evaluated using Tables III and IV, leads to

$$\Phi^{rt}(000;000)=\Phi^{tr}(000;000)=0_3, \quad \text{(III.B.8)}$$

where 0_3 is the three-dimensional null matrix. Similarly, application of (II.A.19) yields

$$\Phi^{rr}(000;000)=B1_3,$$
$$B=(8\psi+4\eta+2\xi)+4(\theta+\epsilon)a-4\nu a. \quad \text{(III.B.9)}$$

The elements $B_{\alpha\beta}{}^{ii'}(\mathbf{q})$ of the dynamical matrix can now be evaluated in a straightforward manner by

performing the Fourier sum in (II.A.22). The results are given below:

$$B_{\alpha\alpha}{}^{tt}(\mathbf{q})=8\lambda\{1-\cos[\tfrac{1}{2}(aq_\alpha)]\cos[\tfrac{1}{2}(aq_\beta)]\cos[\tfrac{1}{2}(aq_\gamma)]\}+2\zeta\{1-\cos(aq_\alpha)\}+2\rho\{2-\cos(aq_\beta)-\cos(aq_\gamma)\},$$

$$B_{\alpha\beta}{}^{tt}(\mathbf{q})=8\omega\sin[\tfrac{1}{2}(aq_\alpha)]\sin[\tfrac{1}{2}(aq_\beta)]\cos[\tfrac{1}{2}(aq_\gamma)],$$

$$B_{\alpha\alpha}{}^{rr}(\mathbf{q})=8\psi\{1-\cos[\tfrac{1}{2}(aq_\alpha)]\cos[\tfrac{1}{2}(aq_\beta)]\cos[\tfrac{1}{2}(aq_\gamma)]\}$$
$$+2\xi\{1-\cos(aq_\alpha)\}+2\eta\{2-\cos(aq_\beta)-\cos(aq_\gamma)\}+4(\theta+\epsilon)a-4\nu a,$$

$$B_{\alpha\beta}{}^{rr}(\mathbf{q})=8\delta\sin[\tfrac{1}{2}(aq_\alpha)]\sin[\tfrac{1}{2}(aq_\beta)]\cos[\tfrac{1}{2}(aq_\gamma)],\qquad \alpha=x,\ y,\text{ or }z;\qquad \alpha\neq\beta\neq\gamma.$$

Further, we have

$$B_{\alpha\alpha}{}^{tr}(\mathbf{q})=2\mu\{\cos(aq_\beta)-\cos(aq_\gamma)\},\qquad (\alpha,\beta,\gamma)\text{ cyclic order of }(x,y,z);$$

$$B_{xy}{}^{tr}(\mathbf{q})=4i(\epsilon+\theta)\cos[\tfrac{1}{2}(aq_x)]\cos[\tfrac{1}{2}(aq_y)]\sin[\tfrac{1}{2}(aq_z)]$$
$$-2i\nu\sin(aq_z)+4(\theta-\epsilon)\sin[\tfrac{1}{2}(aq_x)]\sin[\tfrac{1}{2}(aq_y)]\cos[\tfrac{1}{2}(aq_z)],$$

$$B_{xz}{}^{tr}(\mathbf{q})=-4i(\epsilon+\theta)\cos[\tfrac{1}{2}(aq_x)]\sin[\tfrac{1}{2}(aq_y)]\cos[\tfrac{1}{2}(aq_z)]$$
$$+2i\nu\sin(aq_y)+4(\epsilon-\theta)\sin[\tfrac{1}{2}(aq_x)]\cos[\tfrac{1}{2}(aq_y)]\sin[\tfrac{1}{2}(aq_z)],$$

$$B_{yz}{}^{tr}(\mathbf{q})=4i(\epsilon+\theta)\sin[\tfrac{1}{2}(aq_x)]\cos[\tfrac{1}{2}(aq_y)]\cos[\tfrac{1}{2}(aq_z)]$$
$$-2i\nu\sin(aq_x)+4(\theta-\epsilon)\cos[\tfrac{1}{2}(aq_x)]\sin[\tfrac{1}{2}(aq_y)]\sin[\tfrac{1}{2}(aq_z)],$$

$$B_{yx}{}^{tr}(\mathbf{q})=-B_{xy}{}^{tr}(\mathbf{q}),\qquad B_{zx}{}^{tr}(\mathbf{q})=-B_{xz}{}^{tr}(\mathbf{q}),\qquad B_{zy}{}^{tr}(\mathbf{q})=-B_{yz}{}^{tr}(\mathbf{q}).\qquad\text{(III.B.10)}$$

The remaining elements are of the type $B_{\alpha\beta}{}^{rt}(\mathbf{q})$ and can be readily written from those given above using the Hermitian symmetry

$$B_{\alpha\beta}{}^{ii'}(\mathbf{q})=B_{\beta\alpha}{}^{i'i*}(\mathbf{q}).$$

$\mathbf{B}(\mathbf{q})$ for hexamine is thus a six-dimensional matrix which when diagonalized will yield six eigenvalues $\omega_j{}^2(\mathbf{q})$ ($j=1, 2, \cdots, 6$). It is worth remarking that along symmetry directions, $\mathbf{B}(\mathbf{q})$ can be brought into a block diagonal form. For example, along [100], the secular determinant can be factorized to obtain the following simplified equations:

$$B_{xx}{}^{tt}(\mathbf{q})-M\omega^2(\mathbf{q})=0,$$

$$\begin{vmatrix} B_{yy}{}^{tt}(\mathbf{q})-M\omega^2(\mathbf{q}) & B_{yy}{}^{tr}(\mathbf{q})+B_{yz}{}^{tr}(\mathbf{q}) \\ B_{yy}{}^{tr}(\mathbf{q})-B_{yz}{}^{tr}(\mathbf{q}) & B_{yy}{}^{rr}(\mathbf{q})-I\omega^2(\mathbf{q}) \end{vmatrix}=0,$$

$$\begin{vmatrix} B_{yy}{}^{tt}(\mathbf{q})-M\omega^2(\mathbf{q}) & B_{yy}{}^{tr}(\mathbf{q})-B_{yz}{}^{tr}(\mathbf{q}) \\ B_{yy}{}^{tr}(\mathbf{q})+B_{yz}{}^{tr}(\mathbf{q}) & B_{yy}{}^{rr}(\mathbf{q})-I\omega^2(\mathbf{q}) \end{vmatrix}=0,$$

$$B_{xx}{}^{rr}(\mathbf{q})-I\omega^2(\mathbf{q})=0,\qquad\text{(III.B.11)}$$

with M being the mass of the molecule, and I the moment of inertia. The possibility of such a factorization is related to the symmetry properties of the crystal, and a further discussion of this topic is reserved for Sec. V.

The preceding discussion illustrates the general mechanics for determining the structure of the force constant matrices and subsequent evaluation of the elements of the dynamical matrix. To proceed further and compute numerically the dispersion relations, it is necessary to know the values of the force constants. Several approaches are possible in this respect, and the various calculations for hexamine and its deuterated analog (DHMT) reported in the literature provide examples.

The earliest numerical work on HMT is due to Cochran and Pawley (1964), who constructed a two-neighbor model for the dynamics. In their calculations, the values of the force constants were deduced from the then available experimental data. As this was rather meager, Cochran and Pawley made the simplifying assumption that the molecule, and therefore the crystal, has inversion symmetry. This reduced the number of independent force constants from 12 to 10. An additional equilibrium constraint reduced the number to eight with four parameters for each of the two sets of neighbors. Even this was in excess of the then available experimental information, viz., the values of the elastic constants c_{11}, c_{12}, and c_{44} (Haussühl, 1958), and the $\mathbf{q}=0$ optic frequency. The latter is purely

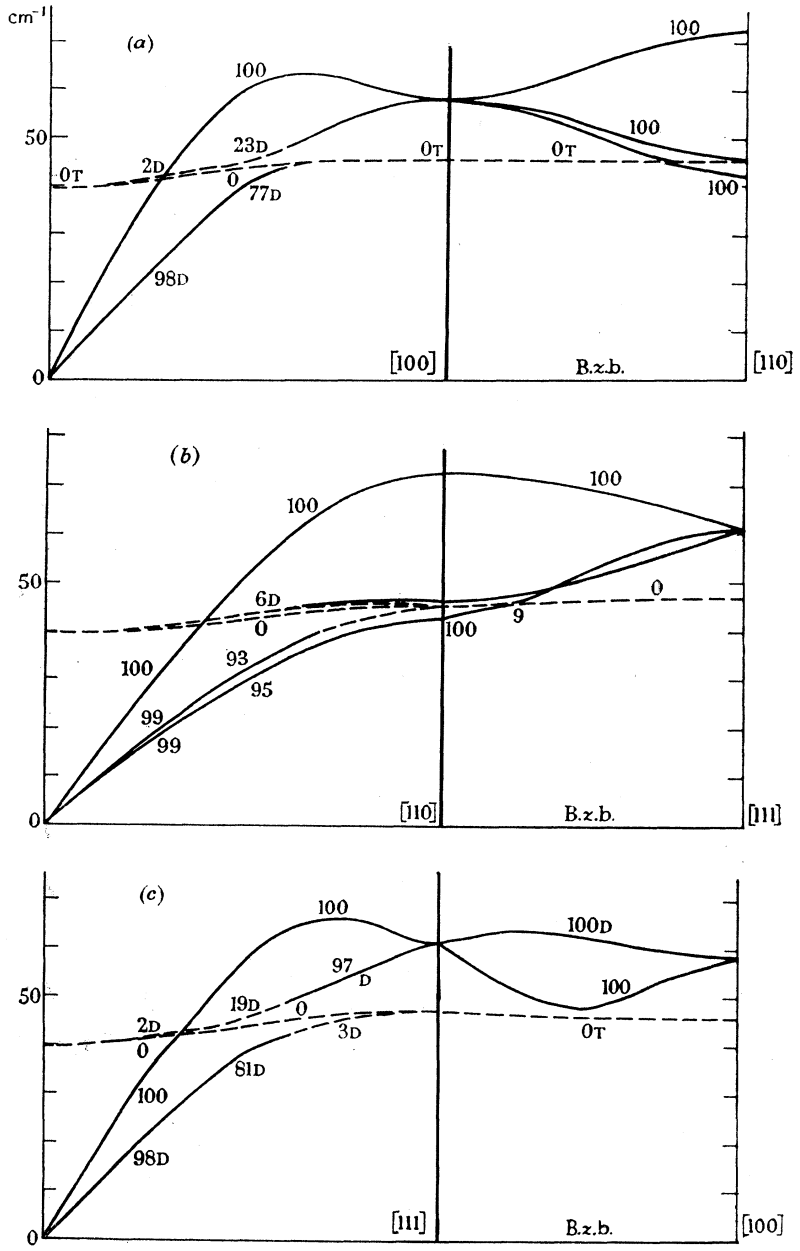

FIG. 7. Dispersion curves for HMT along the three principal directions. (a) [000] to [100] to [110]; (b) [000] to [110] to [111]; (c) [000] to [111] to [100]. The numbers give the percentage translational character of the mode. Predominantly librational modes have broken lines. *D* and *T* denote doubly and triply degenerate modes. [After Cochran and Pawley (1964).]

rotational in character, and an estimate of its value was available from a second-order Raman spectrum (Couture-Mathieu *et al.*, 1951) and a second-order infrared absorption spectrum (Cheutin and Mathieu, 1956). [The $\mathbf{q}=0$ mode is inactive in first-order optical spectra.] With only four pieces of information available, it is obvious that only four out of the eight constants of the model can be determined. The remaining ones were therefore related to the four primary constants by special assumptions tailored to the problem.

The dispersion relations calculated by Cochran and Pawley in this fashion are displayed in Fig. 7. As expected, there are six branches; some are predominantly translational in character, while others are predominantly librational in character. Furthermore, in some regions where crossing between two types of branches occurs, the modes are not pure as illustrated in the figure. A noteworthy feature is that the predominantly librational branches are relatively flat. Also worth observing is the fact that the librational frequency lies *within* the spectrum of translational frequencies.

Most of the other models constructed to describe the dynamics of HMT and DHMT are based on recent experimental results, and so it is appropriate at this point to briefly review the experimental situation.

One of the earliest experimental investigations of the dynamics of hexamine is due to Ramachandran and

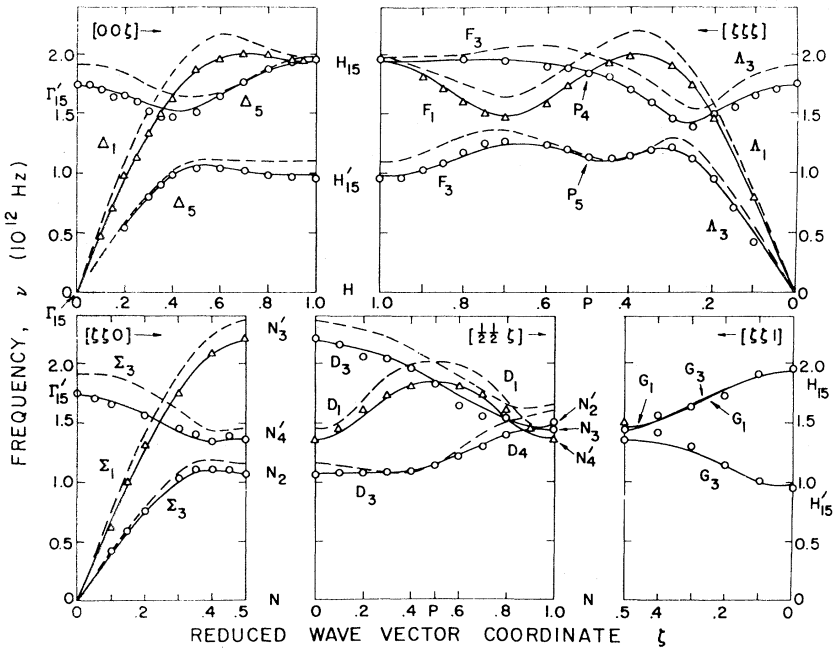

FIG. 8. Dispersion curves for DHMT. The points denote the experimental data corresponding to 298°K, and the solid curves are a least-squares fit to these based on a five-parameter model discussed in the text. The dashed curves represent a fit to similar results obtained at 100°K and are based on the eight-parameter Cochran–Pawley model. They are included to give an idea of the temperature dependence of the various modes. The branches not observed in the experiments are not shown. The labels are group theoretic symbols. [After Dolling and Powell (1970).]

Wooster (1951), who, by a study of diffuse x-ray spots, deduced the velocities of long-wavelength acoustic modes and thereby the elastic constants. Later, Amoros and Amoros (1968) extended their work by mapping completely the acoustic branches along the symmetry directions, once again using the x-ray diffuse scattering method (Cochran, 1963; Cochran, 1966; Smith, 1966). In this, one deduces the phonon frequencies from an absolute measurement of the intensity associated with diffuse scattering, after corrections for Compton scattering and multiphonon processes. Owing to the difficulty of making these corrections accurately, the dispersion relations obtained by this method often contain large errors.

Recently, Powell (1968) and Dolling and Powell (1970) have carried out detailed studies of the dispersion relations in DHMT using the technique of coherent neutron inelastic scattering (Dolling and Woods, 1965; Brockhouse, 1964, 1966). A deuterated sample was used in place of normal HMT to render easier the observation of coherently scattered events. In the case of normal HMT, the large incoherent scattering amplitude of hydrogen makes this a difficult task. Incidentally, the determination of the dispersion relations by neutron scattering methods is direct, unlike in the x-ray method.

Figure 8 shows the latest results of Dolling and Powell. Here the circles and triangles indicate the experimental data corresponding to 298°K. The dashed line represents a fit to similar data obtained at 100°K and is included to give an indication of the temperature dependence of the various modes. These results have been analyzed in terms of variety of force constant models, all derivable from the basic 12-parameter two-neighbor model. Dolling and Powell find that the best fit is obtained as expected, with the most general model with its full complement of 12 parameters. Good fits for both temperatures were also obtained with the eight-parameter Cochran–Pawley model. It turned out that three of the eight parameters had rather small values. The Cochran–Pawley model was therefore modified by setting these three parameters equal to zero *ab initio*, and the resulting model also yielded a good fit. However, a four-parameter model derived from the Cochran–Pawley model by setting all second-neighbor constants equal to zero gave a very poor fit, demonstrating the importance of second-neighbor forces in hexamine.

One unexpected feature of all the models was that even the mixed modes were very nearly pure in character at least in the symmetry directions. Another interesting feature concerns the crossing of the Σ_1 acoustic and Σ_3 optic branches in the [110] direction. This occurs in all models which assume that the HMT molecule has inversion symmetry, i.e., the crystal has the space group O_h^9. If, however, the true space group, viz., T_d^3, is used as in the general 12-parameter model, the two branches do not cross. Rather, there is a "splitting apart" which occurs because the two branches concerned carry the same group-theoretical label and are therefore extremely unlikely to cross (Warren, 1968). Thus if the assumption of a centrosymmetric molecule is indeed a poor one, then it should be possible to detect the splitting. The presently available experimental results are not definitive on this point (Dolling, 1970).

Dolling and Powell have also computed, using the best-fit values for the eight-parameter Cochran–Pawley model, the frequency distribution $g(\omega)$ by means of a numerical technique due to Gilat and

Raubenheimer (1966). Their results for 100°K are shown in Fig. 9. If the plausible assumption is made that the replacement of deuterium by hydrogen atoms does not significantly change the intermolecular forces, then the frequency distribution for HMT can be calculated using the same model as for DHMT by simply changing the molecular mass and moment of inertia. The result of this calculation is the solid curve (in Fig. 9) which has a very similar shape to the DHMT curve and is simply shifted to higher frequencies with respect to it. Similar calculations have also been reported for HMT at 298°K, together with the individual contributions $g^t(\omega)$ and $g^r(\omega)$ from the translational and librational parts, respectively. It is found that whereas $g^t(\omega)$ extends all the way from 0 to $\sim 2.3\times 10^{12}$ Hz, $g^r(\omega)$ spans a relatively narrower range from $\sim 0.9\times 10^{12}$ Hz to $\sim 1.9\times 10^{12}$ Hz, with a prominent peak around 1.2×10^{12} Hz (40 cm^{-1}).

The calculated frequency spectrum for normal HMT at 100°K has been used by Dolling and Powell to compute the temperature variation of the heat capacity C_v and the Debye temperature Θ, and the results are shown in Fig. 10. The figure also displays the measured heat capacity C_p (Chang and Westrum, 1960). The disagreement between theory and experiment at higher temperatures is believed to be due mainly to the contributions from the internal modes which are ignored in the external-mode approximation. Additionally, at lower temperatures, the calculated C_v is systematically larger than the experimental C_p. Dolling and Powell suggest that the discrepancy probably arises from the use of a frequency distribution corresponding to 100°K for the calculation of low temperature specific heats, rather than a distribution appropriate to the temperature concerned. This is supported by the observed strong temperature dependence of many of the modes (see Fig. 8).

It is interesting to compare the results of Dolling and Powell with the calculations of Cochran and Pawley given in Fig. 7. The most significant differences concern the behavior of the librational branches. Consider, for example, the Σ_3 optic branch in DHMT along [110] (see Fig. 8). This branch is almost wholly librational in character and shows considerable dispersion. One expects therefore, on the basis of arguments given earlier, a similar behavior in HMT which is in contrast to the findings of Cochran and Pawley. Furthermore, the $\mathbf{q}=0$ librational frequency of HMT at 298°K as derived from the corresponding DHMT frequency by scaling by the moment of inertia has a value of ~ 63 cm^{-1} ($\sim 1.88\times 10^{12}$ Hz), as opposed to the value of 40 cm^{-1} derived from two-phonon optical data which was used by Cochran and Pawley. Now in two-phonon optical spectra (both Raman and infrared) one sees effectively a combined density of states (Burstein, 1965). In the case of hexamine, the combination from which the librational frequency was deduced involved a libration mode (L) of wave vector $\mathbf{q}$ and an intramolecular mode (I) of equal and opposite wave vector. On the reasonable assumption that the intramolecular modes have very little dispersion, one would expect the ($I+L$) combination band to reflect primarily the frequency distribution of the librational modes. The latter, as already noted, has a peak at 40 cm^{-1} which arises from phonons away from the zone center. To ascribe the value of 40 cm^{-1}, deduced from the combination band peak, to the $\mathbf{q}=0$ mode is therefore in error. It is the use of this incorrect value in the Cochran–Pawley calculations which resulted in features substantially different from those observed in subsequent experiments. This underscores the need for caution in the extraction of single-phonon critical frequencies from two-phonon optical data.

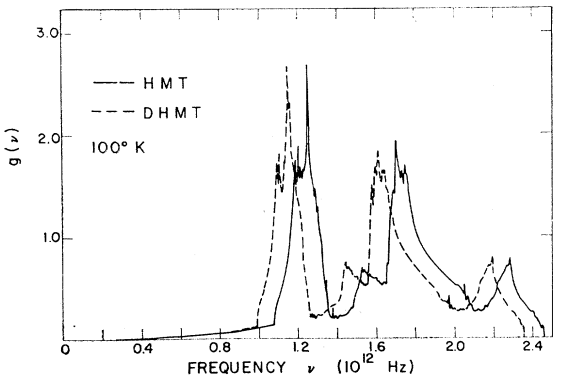

FIG. 9. Frequency distribution functions for external modes in HMT (solid curve) and DHMT (dashed curve) at 100°K computed from the eight-parameter model. [After Dolling and Powell (1970).]

The results for DHMT have been reanalyzed by Rafizadeh and Yip (1970) using a model that has some interesting features. The essential idea underlying their model is that the interaction between a given pair (l, l') of molecules can be visualized as if acting between two effective centers whose positions with respect to the centers of mass of the molecules are given by $\mathbf{R}(l)$ and $\mathbf{R}(l')$, respectively. If the interaction between these effective centers is described by a 3×3 force constant tensor as one would if there were atoms located at these points, then the 36 elements of the force constant matrix $\boldsymbol{\phi}(l, l')$ can be expressed entirely in terms of the components of $\mathbf{R}(l)$ and $\mathbf{R}(l')$ and the nine "atomic" force constants referred to above, using Eqs. (II.A.58). In other words, there is a reduction factor of (36/15) in the number of independent force constants, not taking into account the effects of symmetry.

Physically, the vectors $\mathbf{R}(l)$ and $\mathbf{R}(l')$ may be thought of as denoting (or at least relating to) the positions of the atomic pair dominant in producing the interaction between the molecules l and l'. It will be recalled that a situation like this was encountered in the Sandor model, wherein the (noncentral) interaction between adjacent molecules was attributed entirely to the atomic pair which were in contact in the equilibrium crystal. As one would expect, the vector $\mathbf{R}(l)$ is not unique to the molecule l. Rather it depends on the

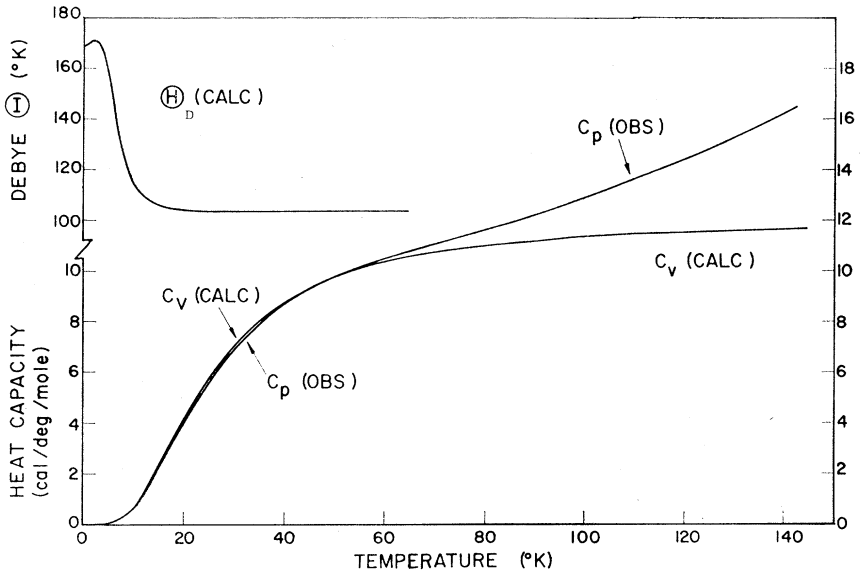

FIG. 10. Heat capacity of HMT: C_p, observed by Chang and Westrum (1960); C_v, computed from the results of the previous figure. The computed variation of the Debye temperature is also shown. [After Dolling and Powell (1970).]

molecule l' with which l is interacting. Thus, Rafizadeh and Yip find that for the molecular pair (0–1), $\mathbf{R}(0)$ has components

$$R_x(0)=R_y(0)=R_z(0)=R/\sqrt{3} \quad \text{(say)},$$

while $\mathbf{R}(1)$ has components

$$R_x(1)=R_y(1)=R_z(1)=-R/\sqrt{3}.$$

Similarly, for the pair (0–9)

$$R_y(0)=R_z(0)=R_y(9)=R_z(9)=0,$$
$$R_x(0)=-R_x(9)=R' \quad \text{(say)}.$$

Using such an approach, Rafizadeh and Yip were able to construct a model with second-neighbor interactions, which involves only six independent parameters including R and R', unlike the Cochran–Pawley model which had 10 parameters (before applying the equilibrium constraint). Using the five triply degenerate frequencies at zone center, [100] zone boundary, and [111] zone boundary measured by Powell, the parameters of the model were determined in terms of R. The latter was then varied to obtain a fit with Powell's data. The values of R and R' deduced are 2.76 and 3.47 A, respectively. It is interesting to observe that these are smaller than half the first and second neighbor separation, i.e., $R<\sqrt{3}a/4$ and $R'<a/2$ ($a\simeq 7$ Å).

The main virtue of the Rafizadeh–Yip model is that it offers a means of reducing the number of independent parameters. This is of value when one is trying to compute dispersion relations based on limited experimental data.

An even further reduction of parameters is possible by explicitly identifying the atomic pair or pairs dominant in providing the forces between a given pair of molecules and subsequently expressing the relevant interatomic constants $\phi_{\alpha\beta}(l\kappa k; l'\kappa' k')$ in terms of a suitably assumed form for the atomic pair potential. Thus if one supposes that the potential has a form $V(r)$ which depends only on the separation between the atoms, then the interatomic force constants can be expressed as (Wolfram *et al.*, 1963)

$$\phi_{\alpha\beta}(l\kappa k; l'\kappa' k')=(r_\alpha r_\beta/r^2)(A-B)+\delta_{\alpha\beta}B, \quad \text{(III.B.12)}$$

where

$$A=(\partial^2 V/\partial r^2), \quad \text{(III.B.13a)}$$
$$B=(1/r)(\partial V/\partial r), \quad \text{(III.B.13b)}$$

and

$$r=|\mathbf{X}(l\kappa k)-\mathbf{X}(l'\kappa' k')|. \quad \text{(III.B.13c)}$$

We thus see that the intermolecular force constants $\phi_{\alpha\beta}{}^{ii'}(l\kappa; l'\kappa')$ can be expressed via (II.A.58) in terms of the derivatives A and B of the pair atomic potential, provided the potential is a function of the separation between the atoms involved. Such a scheme has been successfully employed by Dolling (1970) in the case of DHMT. Assuming that the most important bonds in DHMT are the shortest D–D bonds of length 2.72 Å connecting the origin and the second-neighbor molecules, and the shortest D–N bonds of length 2.88 Å connecting the origin and first-neighbor molecules, a four-parameter model was constructed using Eqs. (II.A.58), (III.B.12), and (III.B.13) which fitted the data quite well. A similar model has also been employed by Powell and Sandor (1970) to analyze their data on x-ray diffuse scattering from normal HMT.

The foregoing discussion gives an idea not only of the amount of work which has been done on hexamine but also of the various types of force constant models usually employed.

C. Naphthalene and Anthracene

Naphthalene and anthracene are aromatic molecules built up from benzene rings. Figure 11 shows the primitive unit cell of crystalline naphthalene. The

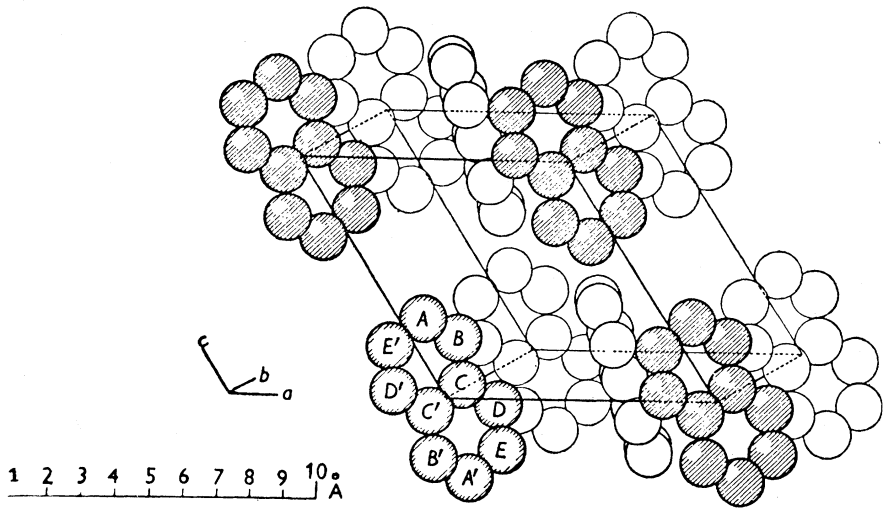

FIG. 11. Unit cell of naphthalene. [After J. M. Robertson, *Organic Crystals and Molecules* (Cornell U. P., Ithaca, N. Y., 1953).]

crystal is monoclinic and belongs to the space group C_{2h}^5. The structure of anthracene is similar. The dynamics of these crystals has attracted attention for a long time, particularly from the point of view of understanding the thermal parameters associated with x-ray diffraction (Cruickshank 1956a, 1958). Recently, Pawley (1967) has computed the dispersion relations for these crystals using the external-mode approximation. These calculations have some interesting features not present in the hexamine work discussed earlier. Firstly, the molecules are asymmetric tops. Secondly, the principal axes of the two molecules in the primitive unit cell are oriented differently, and for these reasons Pawley found it convenient to work in the principal-axes frame rather than in the fixed frame. In addition, the force constants were not left as parameters to be determined from auxiliary data but were computed using the semiempirical potential functions for interactions between nonbonded atoms as given by Kitaigorodski (1966). These potentials have the general form

$$V(r) = -A/r^6 + B \exp(-\alpha r),$$

where A, B, and α are constants whose values depend on the atom pair involved in the interaction. Note that this potential involves atoms located in *different* molecules. Using the values of the constants as given by Kitaigorodski for C–C, C–H, and H–H interactions, Pawley computed the various force constants numerically in a computer. In evaluating the force constants using such potential functions, it must be remembered that basically the force constant is a second derivative of the crystal potential Φ evaluated about *the equilibrium configuration*. One must ensure therefore, that the structure that one ascribes to the crystal is consistent with the minimum of Φ based on the two-body functions under consideration. In his work, Pawley found it necessary to rotate the molecules slightly from the configuration deduced by crystal structure investigations (Cruickshank 1956b, 1957a, 1957b) so as to ensure that there were no resultant couples on them. Having obtained the equilibrium configuration, the force constants were obtained by giving various kinds of displacements to the molecules and computing numerically the forces produced thereby. For example, to obtain $\phi_{\alpha\beta}{}^{tr}(l\kappa; l'\kappa')$, the molecule $(l'\kappa')$ is given a suitable rotation $\Delta\theta_\beta$ from the equilibrium orientation, and the force produced on $(l\kappa)$ along the α direction is calculated. This force component divided by $\Delta\theta_\beta$ gives the desired force constant. Care must be taken over the choice of increments used in the numerical differentiation. Pawley found that 10^{-4} Å and 3×10^{-4} rad were the most suitable increments in displacements and angles, respectively. It must be pointed out that Pawley's procedure is essentially equivalent to using our Eqs. (II.A.58), with the derivatives involved in the Born–von Karman constants, evaluated in the equilibrium configuration.

Figure 12 shows Pawley's results for the [010] direction, which is the only symmetry direction for a monoclinic crystal. An interesting outcome of the calculations is that the $\mathbf{q}=0$ librations do not take place about the principal axes as had been previously assumed (Rousset, 1947). Rather, the axes of librations are considerably rotated with respect to the principal axes, especially for the low-frequency antisymmetric modes.

As a sequel to the calculation, Pawley and Yeats (1969) have recently attempted to measure the dispersion relations in deuterated naphthalene, using the technique of coherent neutron scattering. As yet, the results are too preliminary and meager to draw firm conclusions.

Some results for deuterated anthracene have recently been obtained by Lutz and Halg (1970), and these are shown in Fig. 13. Comparison with calculations similar to those of Pawley's shows general agreement between experiment and theory. The disagreement becomes worse at higher frequencies, indicative of the breakdown of the rigid-molecule approximation. This is not unexpected in view of the fact that some of the

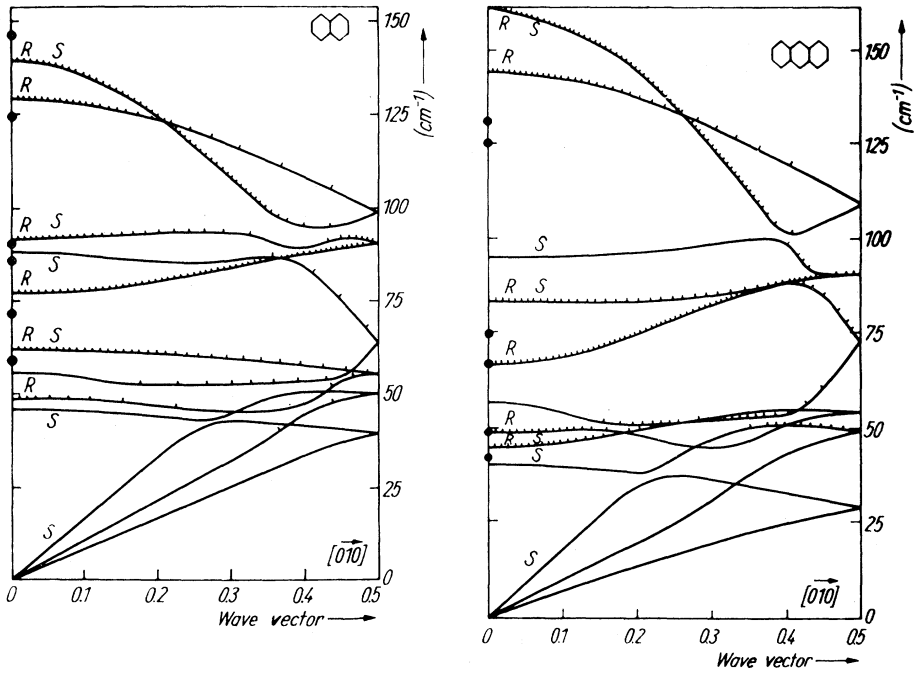

FIG. 12. Calculated dispersion curves for naphthalene (left) and anthracene (right), along the [010] direction. *S* indicates a symmetric mode. *R* shows rotational character. ●, refers to Raman measurements. [After Pawley (1967).]

internal vibrations have a frequency as low as ~100 cm^{-1}. Indeed, Pawley and Cyvin (1970) have recently demonstrated by explicit calculations in the case of naphthalene that such a modification of external-mode frequencies does occur due to the nonrigidity of the molecule.

D. Adamantane

Adamantane $[(CH_2)_6(CH)_4]$ is a molecular crystal like hexamine. Recent measurements indicate that above 208°K it has a cubic fcc structure, while below that temperature, a tetragonal structure is stable. The dynamics of this substance has been studied experimentally using slow-neutron scattering by Stockmeyer and Stiller (1968). The scattering is predominantly from hydrogen, and being incoherent, the measured spectra yield essentially the frequency distribution weighted by the amplitude of the hydrogen atoms (Boutin and Yip, 1969). By way of providing a comparison with the observed data, Stockmeyer and Stiller have computed dispersion relations and frequency spectra for both phases. It must be pointed out that adamantane in the high-temperature phase is a plastic crystal, and it is known that the molecule makes hindered rotations between equivalent configurations. These being of large amplitude, the rotational motions cannot be completely described within the framework of the harmonic approximation. A model which takes account of both small amplitude librations and large amplitude reorientational motions is therefore necessary, as has been pointed out by Stockmeyer and Stiller (1968) and by Dolling (1970). Very recently, the Chalk River group has initiated the experimental study of dispersion relations in deuterated adamantane (Dolling, 1970). Detailed results are yet to be reported, but it is clear even from the preliminary measurements that fresh thinking is called for when large amplitude rotational motions are involved as in plastic crystals.

E. Urea

Deprez and Fouret (1964) have worked out the formal theory of external modes in urea $[CO(NH_2)_2]$, which belongs to the space group V_d^3. There are two molecules per primitive unit cell, and force constant matrices have been set up as far as second neighbors.

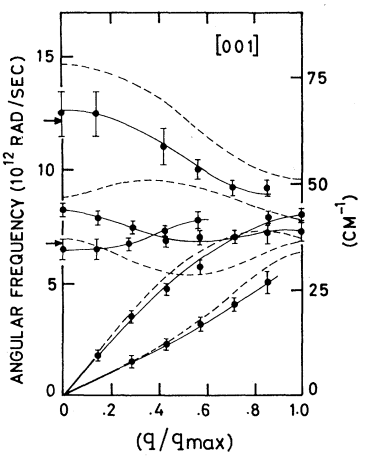

FIG. 13. Dispersion curves for deuterated anthracene along [001] direction. The dots denote experimental points, and the solid lines are guides to the eye. The dashed lines represent calculations similar to those of Pawley (previous figure). The arrows indicate the Raman frequencies deduced from the measured values for normal anthracene (Suzuki *et al.*, 1968) after appropriate scaling. The heavy lines through the origin are based on elastic constants for deuterated anthracene derived from the values for normal anthracene (Afaneseva *et al.*, 1967; Huntington *et al.*, 1969) after scaling. [After Lutz and Halg (1970).]

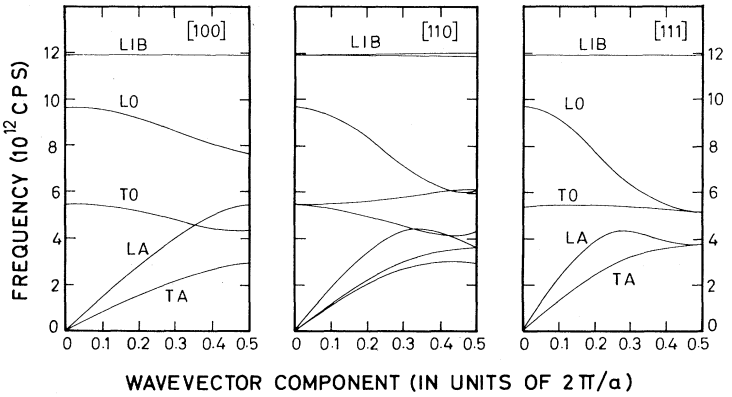

FIG. 14. Dispersion relations for NH_4Cl in the ordered phase. [After Parlinski (1969).]

Also expressions are given for the $\mathbf{q}=0$ frequencies and the frequencies for wave propagation along the four-fold axis, which is the direction of maximum symmetry. No numerical results are presented.

F. NH_4Cl

The dynamics of NH_4Cl has attracted considerable interest for a number of years, particularly in relation to its well-known phase transition at 242°K. Several experimental studies, both optical and neutron, were made and from these a knowledge of the $\mathbf{q}=0$ translational optic frequency and the librational frequency of the NH_4^+ ion is available. Around 1968 and 1969, Parlinski (1968, 1969) undertook detailed numerical calculation of the dispersion relations appropriate to the ordered state (see Fig. 1). The crystal was regarded as made up of Cl^- ions and well-bound NH_4^+ ions (which, remember, are spherical tops), and each ion was supposed to interact with its neighbors via both electrostatic and short-range phenomenological potentials, leading to two contributions to the dynamical matrix $\mathbf{B}(\mathbf{q})$. The treatment of the electrostatic part is discussed in the following section. The short-range part was treated in a manner similar to that discussed in the hexamine example, in terms of parametrized force constants. Interactions were included up to the third neighbors, and all this resulted in 18 parameters. The only experimental results available at that time were the elastic constants C_{11}, C_{12}, and C_{44} (Garland and Renard, 1966), and the $\mathbf{q}=0$ translational optic frequency and the librational frequency (Wagner and Hornig, 1950; Krishnan, 1948; Woods *et al.*, 1961; Venkataraman *et al.*, 1966; Bajorek *et al.*, 1965). Extra assumptions were therefore made to reduce the number of independent constants to five, and from the parameter values deduced from the above information, the dispersion relations were computed for the symmetry directions. The results are shown in Fig. 14 and are very similar to those published for CsCl type crystals (e.g., Cowley and Okazaki, 1967), apart from the appearance of a very flat torsional branch which is well above the translational band of frequencies, unlike HMT. The frequency distribution curves based on this model are shown in Fig. 15, where a prominent peak is seen due to the librational branch.

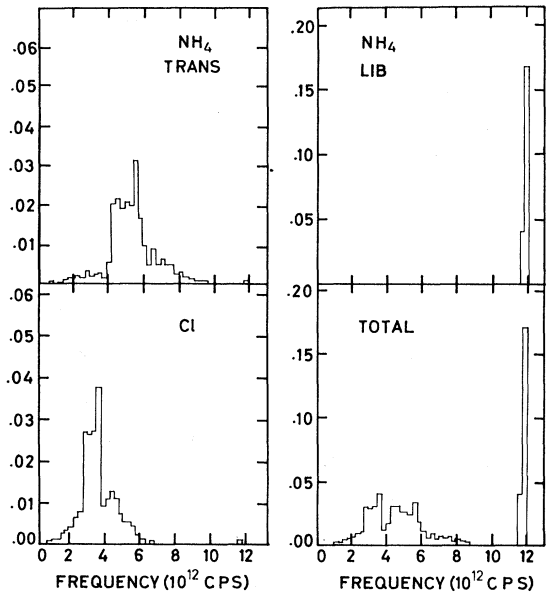

FIG. 15. Partial and total frequency distributions for NH_4Cl. Observe that the frequency spectrum of Cl^- motions is somewhat lower than the band for NH_4^- translations. This arises from the fact that Cl^- is heavier than NH_4^+. Also note that there is a small contribution from Cl^- and NH_4^+ translations at the frequency corresponding to the librational mode, indicative of weak translational–rotational coupling. [After Parlinski (1969).]

Not to be left behind, experimentalists also have studied the dispersion relations in ammonium chloride. Two independent measurements have been reported up to now. In the first of these, Smith *et al.* (1969) have investigated the dispersion relations in NH_4Cl. These experiments represent a tour-de-force in view of the difficulty of observing the coherently scattered events from NH_4Cl, which is predominantly an incoherent scatterer owing to the large incoherent scattering amplitude of hydrogen. The latest results of Smith *et al.* are displayed in Fig. 16, where the various curves are merely guides to the eye. The measured dispersion curves agree with those computed by Parlinski as to over-all shape. There are, however, some quantitative differences. For example, the

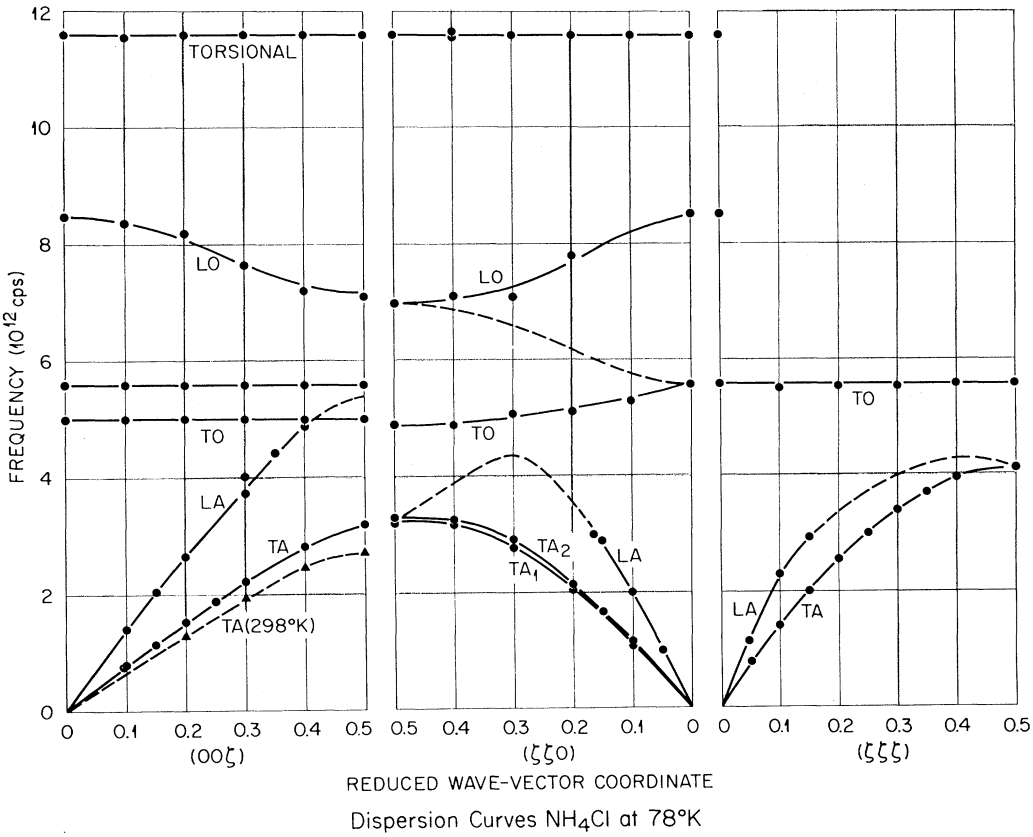

FIG. 16. Preliminary dispersion curves for NH_4Cl at 78°K. The various curves shown in the figure are guides to the eye. The apparent two TO branches seen in the [100] direction are actually due to the superposition of the peaks in the scattered neutron spectrum arising from coherent and incoherent scattering processes. As yet, the dispersion of the TO branch in this direction has not been completely determined. [After H. G. Smith (private communication).]

measured *LO* frequencies along [100] are systematically lower than the computed ones. This is reminiscent of the situation in alkali halides where the rigid-ion model always predicts *LO* frequencies higher than the measured ones (Woods *et al.*, 1960). Several other differences may be noted on comparing Figs. 14 and 16.

Teh *et al.* (1969; 1970) have made measurements on ND_4Cl to overcome the difficulty associated with incoherent scattering background produced by hydrogen, and their results are shown in Fig. 17. The dotted lines in the figure are guides to the eye, drawn through the experimental points. The measured curves for ND_4Cl are similar in all essential respects to those computed by Parlinski for NH_4Cl (shown in Fig. 17 as solid lines) although there are some differences in the actual values of the frequencies. These are to be expected in view of the difference between the two crystals. In particular, the librational frequency is found to be 8.3×10^{12} cps in agreement with earlier optical (Wagner and Hornig, 1950) and neutron experiments on powder samples (Venkataraman *et al.*, 1966). This is to be contrasted with the value of 11.7×10^{12} cps observed in NH_4Cl. The difference arises from the fact that the moment of inertia of the NH_4^+ ion is smaller by a factor of 2 as compared to that for the ND_4^+ ion. Teh and Brockhouse (1970) have compared their results with Parlinski's model as adapted for the deuterated crystal and find that while the qualitative features of the experimental results are well predicted, quantitative agreement is poor particularly in the case of *LO* modes, reminiscent of the situation in NH_4Cl. The results of Teh and Brockhouse have also been analyzed by Cowley (1970). Interestingly, rather than use an external-mode approach, Cowley has taken all the 18 degrees of freedom per cell into account and has calculated the dynamics using the shell model (Woods *et al.*, 1960; Cowley *et al.*, 1963) which takes account of the polarizabilities of the ions. The results for the nine lowest branches (viz., the external branches) agree well with the measurements of Teh and Brockhouse and demonstrate the need for considering polarization effects which were ignored by Parlinski. Similar calculations were also done for NH_4Cl by Cowley and they compare favorably with the measurements of Smith *et al.*

G. $NaNO_2$

$NaNO_2$ has been investigated extensively due to its unusual dielectric properties. In its low-temperature (<163°C) phase, it is ferroelectric with a structure as illustrated in Fig. 18. Between 163 and 164.5°C, it

exhibits an antiferroelectric phase in which the average electric dipole moment along the b axis oscillates as one moves along the a direction. The period of oscillation is temperature dependent and incommensurate with the a lattice period. Above 164.5°C, the NO_2^- dipole moments are directed equally and randomly along the $+$ and $-b$ direction, the material being paraelectric. In view of the connection between ferroelectricity and lattice dynamics (Cochran, 1960; 1961), it is not surprising that the phonon spectrum of $NaNO_2$ has received attention.

From Fig. 18, we observe that the primitive unit cell contains two ions, NO_2^- at (0, 0, 0) and Na^+ at $(b/2, 0, 0)$. There are therefore nine external degrees of freedom per cell, and consequently nine external branches to the phonon spectrum. Some of these have been mapped (Sakurai *et al.*, 1967; Dolling, 1968; Sakurai *et al.*, 1970) using neutron scattering techniques; the results are displayed in Fig. 19.

To analyze the data, Sakurai *et al.* (1970) assume that the crystal consists of Na^+ and nondeformable NO_2^- ions which interact via both Coulomb and short-range forces, and thence compute the external-mode frequencies. The evaluation of the Coulomb contribution to the dynamical matrix is discussed in Sec. IV. As far as the short-range part is concerned, interactions were included up to five neighbors with additional simplifying assumptions. The resulting force constants were treated as adjustable, and the fit achieved is shown by the solid lines in Fig. 19.

H. Concluding Remarks

From the foregoing survey, the reader can see that not only is the formalism for doing Born–von Kármán type calculations for external modes by now well established, but also that numerical results which are

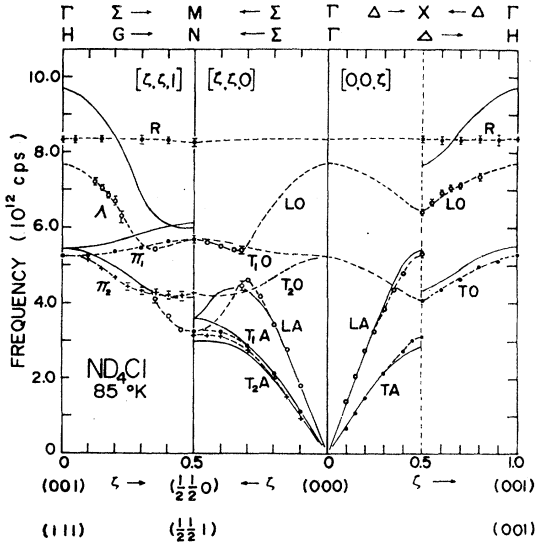

FIG. 17. Dispersion relations for ND_4Cl at 85°K. The dashed lines are guides to the eye. The solid lines are the calculations for NH_4Cl by Parlinski (1969). [After Teh *et al.* (1969).]

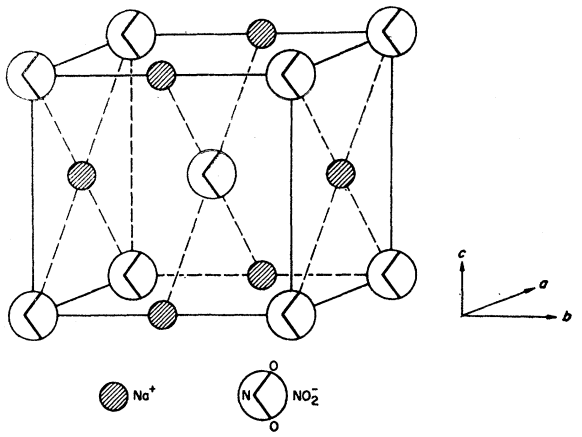

FIG. 18. Unit cell of $NaNO_2$. [After Dolling (1968).]

beginning to be reported have in turn provided impetus to experimentalists to make detailed measurements. Up to now, only crystals with relatively simple structures have been investigated, and quite understandably so. In spite of this, the number of force constants to be handled has always turned out to be fairly large. This is inconvenient, especially if the force constants are to be treated as adjustable parameters. In the case of molecular crystals, the use of model potential functions for the nonbonded interactions enables one to overcome the difficulty of parameter proliferation. For other types of crystals, however, the difficulty remains, since one does know how to describe quantitatively the short-range interactions between the various units, owing to the complicated nature of the bonding. At present all that one can hope for is simplifying assumptions (e.g., as in the Dolling model for $NaNO_2$ or the Rafizadeh–Yip model for HMT) which will reduce the number of independent parameters. It remains to be seen whether potential functions for bonded interactions can be developed with the same degree of success as for the nonbonded interactions.

IV. ELECTRIC FIELD EFFECTS

A. Role and Importance of Electric Field Effects

A number of complex crystals are ionic or partially ionic in nature. In such crystals, owing to the Coulomb interactions between the ions, a macroscopic electric field is set up which produces important modifications in the behavior of those long-wavelength modes which carry a net dipole moment (also often called infrared-active modes).[9] Such effects are well known in the case of simple diatomic crystals but their role in the case of

[9] Group theory provides a convenient and simple means of determining whether a mode is infrared active or not. The method is to first carry out a group-theoretical classification of the $q=0$ modes (see Sec. V). Of these, those which exhibit the same transformation properties as x, y, and z are infrared active. Character tables given in the literature (e.g., Wilson, Decius, and Cross, 1954; Heine, 1960) frequently identify the representations corresponding to x, y, and z, and this facilitates a quick identification of the infrared-active modes.

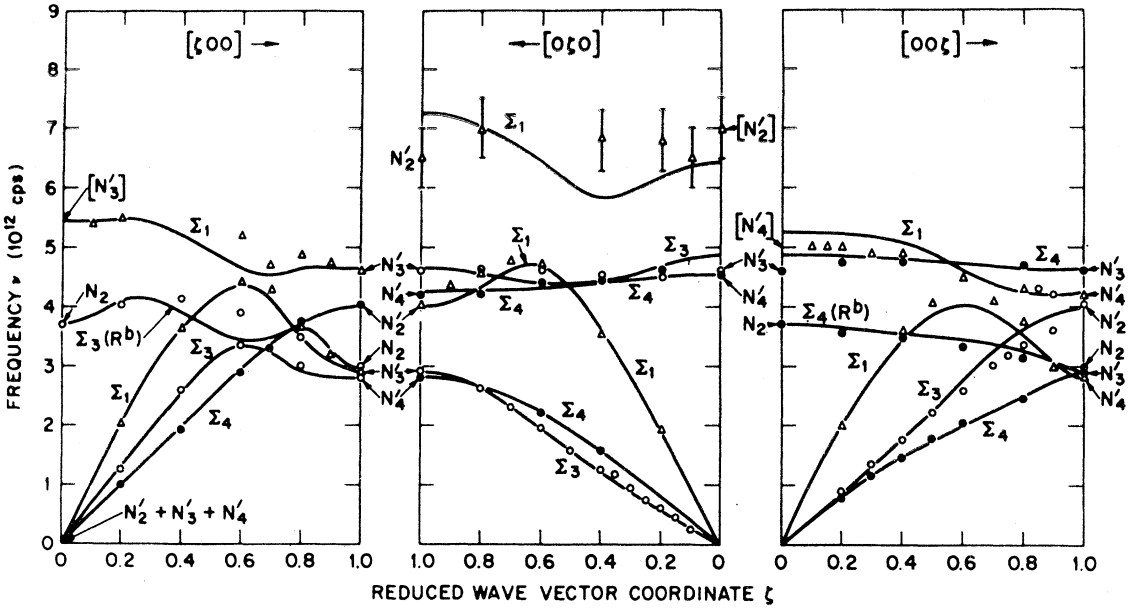

FIG. 19. Dispersion curves for $NaNO_2$ at 296°K. The solid curves are based on a model discussed in text. [After Dolling (1968).]

complex crystals has not been widely appreciated even though experimental evidence for them has existed for a long time. For this reason, we shall devote the present section to a comprehensive discussion of this topic.

It is helpful to begin by briefly recapitulating the role of the macroscopic electric field in some simple crystals. Figure 20 shows a schematic plot of dispersion relations for a cubic diatomic ionic crystal like NaCl, CsCl, or ZnS (sphalerite), which has two ions in the primitive unit cell. The feature of current interest is the difference in frequency between the $\mathbf{q}=0$ longitudinal and transverse optic modes. This split, it is well known (BH, Chap. II), is due to the long-range electrostatic field arising from the Coulomb interactions between the ions. If the two atoms are identical, then there is no residual charge on them and consequently no macroscopic field, and in this case the two modes become degenerate (e.g., in diamond). Another feature of the splitting in cubic (ionic) crystals is that the limiting frequencies for the optic branches are the same for all directions of $\mathbf{q}$ (see Fig. 20).

Figure 21 shows schematic plots of the dispersion relations for a cubic crystal with the CaF_2 structure, which also has two types of ions but a total of three atoms in the primitive unit cell. Here, only one set of optic modes (identified by dots) have dipole moments associated with them, and these alone exhibit a splitting. Once again, on account of cubic symmetry, the limiting frequencies of the infrared-active modes are direction independent.

Similar effects are known to occur in the case of noncubic crystals also. There are, however, additional features arising from crystalline anisotropy. The wurtzite-type crystals (ZnO, CdS, etc.) provide a convenient example. These are hexagonal and have four

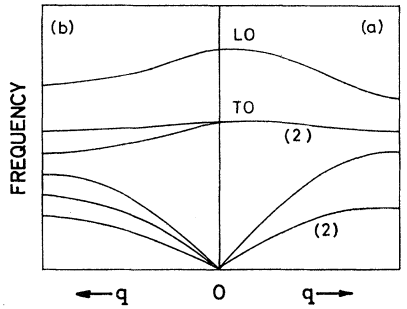

FIG. 20. Schematic drawing of the dispersion curves in the electrostatic approximation for a cubic diatomic crystal like NaCl. (a) shows the curves along a symmetry direction like [100], the numbers in parentheses denoting the degeneracy. (b) shows the curves along an off-symmetry direction. LO and TO refer to longitudinal optic and transverse optic, respectively. Observe that the $\mathbf{q}=0$ limiting frequencies are the same when approached from various directions.

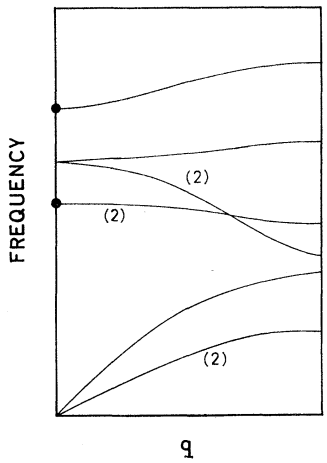

FIG. 21. Schematic drawing of the dispersion curves in the electrostatic approximation for a CaF_2-type crystal along the [100] direction. The numbers in parentheses indicate the degeneracies. The $\mathbf{q}=0$ modes identified by dots carry dipole moments.

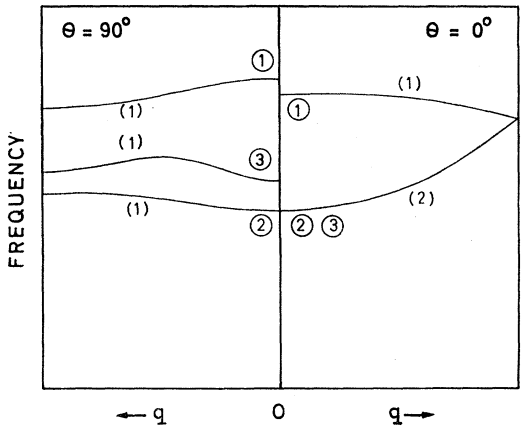

FIG. 22. Schematic plots in the electrostatic approximation of the dispersion curves for a wurtzite-type crystal. Only the branches whose limiting frequencies are infrared active are shown. $\theta=0°$ corresponds to wave propagation along the c axis, while $\theta=90°$ corresponds to wave propagation in a typical direction in the basal plane. The numbers in parentheses denote as usual the degeneracies. The curves sketched are based on results for CdS (c/a<ideal) published in the literature. Observe the anisotropic effects in the limiting frequencies, and the removal of degeneracy for the pair (②, ③) for $\theta=90°$ case. In the mode ①, the atomic displacements are parallel to the c axis, while in modes ② and ③ they are in the basal plane. In hexagonal ZnS (c/a>ideal), the relative values at $\mathbf{q}=0$ for the modes ① and (②, ③) will be reversed.

atoms in the primitive unit cell. There are consequently 12 branches to the phonon dispersion curves. Of these, only three exhibit effects associated with macroscopic electric fields. Figure 22 shows schematic plots of these branches along the c direction ($\theta=0°$) and for $\mathbf{q}$ normal to the c-axis ($\theta=90°$). Two effects can be observed: one is the anisotropy in the limiting frequencies, and another is that for $\theta=90°$, there is a splitting at $\mathbf{q}=0$ for the mode which appears as doubly degenerate in the $\theta=0°$ case. The angular variation of these frequencies (identified simply as ①, ②, and ③) is sketched in Fig. 23(a). If the macroscopic fields were absent, then the behavior would be as in Fig. 23(b). It must be pointed out that in all the above discussion, $\mathbf{q}=0$ implies a vibrational wavelength large compared to the unit cell dimensions but small compared to the physical dimensions of the crystal.

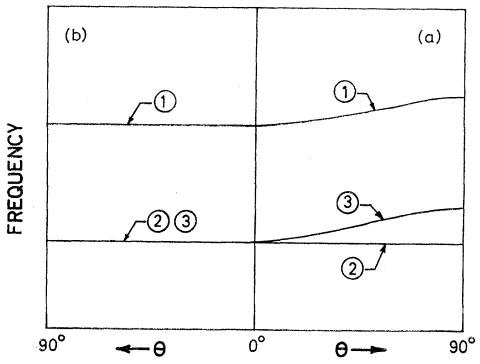

FIG. 23. Schematic drawing of the angular dependence of the limiting frequency of the infrared-active mode in wurtzite-type crystal. The curves are appropriate to a crystal with (c/a) <ideal (e.g., CdS). (a) shows the θ dependence with macroscopic field effects included. (b) shows the θ dependence in the absence of the field.

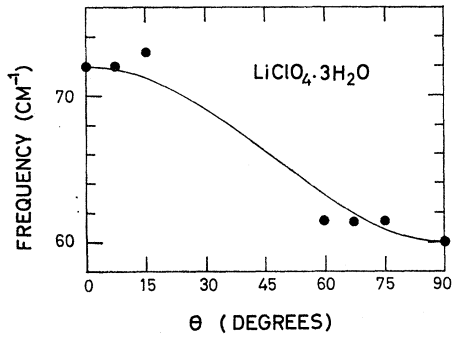

FIG. 24. Angular dependence of one of the low-frequency modes in $LiClO_4 \cdot 3H_2O$. The solid curve is the theoretically expected variation. Based on the data of Mathieu *et al.* (1952).

In the case of uniaxial crystals, in addition to the phenomena just discussed, there are also important features connected with changes in the polarization vector as a function of θ. These are dictated by two factors with opposing effects, viz., crystalline anisotropy and the electrostatic field.[10] A full discussion on this subject may be found in a review article by Loudon (1964). We might note, however, that in crystals in which anisotropy dominates, the polarization vectors are essentially along or perpendicular to the c axis. This is true for all values of θ provided $\mathbf{q}$ is small and approaches 0.

Electric field effects similar to those just considered are also exhibited in complex crystals of ionic or partially ionic character, both in the case of external as well as internal modes that carry dipole moments. Evidence for these have been reported by spectroscopists for a number of years, and Figs. 24 and 25 provide two early examples due to the French group (Mathieu *et al.*, 1952). In Fig. 24 is illustrated the angular dependence of one of the low-frequency infrared-active modes in $LiClO_4 \cdot 3H_2O$, which is a uniaxial crystal belonging to the space group C_{6v}^4. The mode under

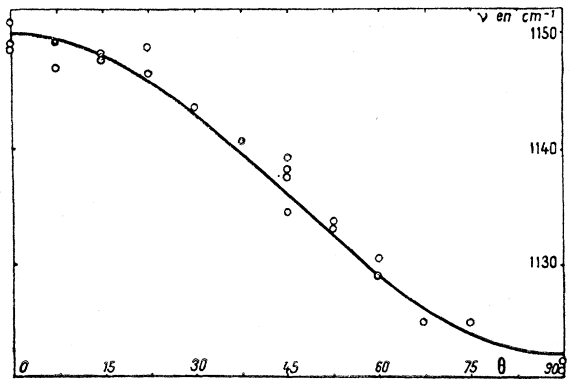

FIG. 25. Angular dependence of one of the high-frequency modes in $LiClO_4 \cdot 3H_2O$. [After Mathieu *et al.* (1952).]

[10] In wurtzite-type crystals, electrostatic field is the dominating factor.

consideration is nondegenerate and translational in character, the displacements of the ions being along the c axis. Figure 25 illustrates similar anisotropy observed in the case of one of the high-frequency modes, presumably corresponding to an internal vibration of the ClO_4^- ion. A few other cases of anisotropic behavior have also been reported, notably by the French group who have done pioneering work in this field.[11]

In what follows, we shall restrict our attention to external modes alone. In general, we can make the qualitative observation that external modes which carry a dipole moment will exhibit effects similar to those discussed above. In cubic crystals, such modes, which in the absence of macroscopic field effects would have been triply degenerate, will be split into a doubly degenerate mode and a nondegenerate mode. For example, in NH_4Cl, the translational optic modes corresponding to $\mathbf{q}=0$ carry a dipole moment and are split the same way as in CsCl. The torsional mode, on the other hand, is not infrared active and does not manifest such a behavior.

In the case of uniaxial crystals, angular variation as well as splitting as discussed in Figs. 22 and 23 are expected both for the translational and librational modes, subject of course to their having dipole moments. In most (complex) uniaxial crystals, the (c/a) ratio is large so that crystalline anisotropy dominates over electrostatic forces and primarily controls the polarization vectors. This results in $\mathbf{e}^t$ and $\mathbf{e}^r$ being either parallel or perpendicular to the c axis in the $\mathbf{q}\to 0$ limit, quite independent of θ.

One example of anisotropy in frequency associated with external modes in uniaxial crystals has already been cited in Fig. 24, which illustrates the effect for a translational mode. We have been unable to find in the literature a similar angular dependence study of the librational modes in uniaxial crystals although the limiting frequencies for $\theta=0°$ and $\theta=90°$ have been reported in a few cases. For instance, it is known from the work of Barker (1964) on $CaWO_4$ that the infrared-active librational modes in that crystal are doubly degenerate and have a frequency of 202 cm^{-1} when viewed along the c axis, while perpendicular to the c axis they are split and have a frequency difference of $\sim$46 cm^{-1}. (Recall Figs. 22 and 23.)

Similar effects are also expected in crystals having lower symmetry. Tramer (1959), for example, reports that the $\mathbf{q}=0$ librational frequency in room temperature $NaNO_2$ is angle dependent and that it varies in the range 150–170 cm^{-1}. Full details of the variation are, however, not given.

In general, experimental work concerning effects produced by electric fields is somewhat meager and it is hoped that increased attention will be paid to it in the near future.

Our immediate question is how to reproduce such effects by theoretical calculations. Basically the problem is one of taking proper account of Coulomb interactions in the crystal. The treatment of this problem in the conventional Born–von Kármán framework has been discussed in detail in the literature (Kellerman, 1940; BH, Chap. V). The analogous problem for external modes in complex crystals has been discussed only partially and needs some clarifications. These are offered in the following subsections.

B. Extension of Kellerman's Work

Let us suppose that interatomic forces in the crystal can be divided into a purely electrostatic part plus a short-range part. The dynamical matrix will correspondingly have two contributions, and we are at present interested in developing analytical expressions for that arising from the Coulomb interactions among the ions. This will be done in the fixed frame first since the algebra is simpler. Later we shall consider the transformation to the principal-axes frame. The basic difficulty in evaluating the electrostatic contribution arises from the long-range character of the Coulomb potential. Fortunately, however, methods exist which make the problem tractable.

To start with, we shall assume that the charge distribution consists of a set of point charges located at the nuclear sites $\mathbf{r}(l\kappa k)$. Denote by $Z(\kappa k)e$ ($e=+4.802\times 10^{-10}$ esu) the charge on the kth atom in the κth unit. The Coulomb part $\phi_{\alpha\beta}{}^{c,ii'}(l\kappa;l'\kappa')$ of the force constant associated with the units $(l\kappa)$ and $(l'\kappa')$ can be written using (II.A.58), with $\phi_{\alpha\beta}{}^{c}(l\kappa k;l'\kappa'k')$, the force constant due to Coulomb interactions between the atomic pair $(l\kappa k-l'\kappa'k')$, being given by

$$\phi_{\alpha\beta}{}^{c}(l\kappa k;l'\kappa'k')=e^2Z(\kappa k)Z(\kappa'k')\{\delta_{\alpha\beta}/|\mathbf{X}|^3-3X_\alpha X_\beta/|\mathbf{X}|^5\},\qquad \mathbf{X}=\mathbf{X}(l'\kappa'k')-\mathbf{X}(l\kappa k),\qquad (l\kappa k\neq l'\kappa'k'). \quad \text{(IV.B.1)}$$

This result follows from the more general one applicable to interatomic potentials of the form $V(r)$, namely

$$\phi_{\alpha\beta}(l\kappa k;l'\kappa'k')=-\partial^2V(r)/\partial r_\alpha\partial r_\beta\,|_{\mathbf{r}=\mathbf{X}(l'\kappa'k')-\mathbf{X}(l\kappa k)}.$$

We thus obtain the following expressions for $\phi_{\alpha\beta}{}^{c,ii'}(l\kappa;l'\kappa')$:

(1)
$$\phi_{\alpha\beta}{}^{c,tt}(l\kappa;l'\kappa')=\sum_{k\in\kappa}\sum_{k'\in\kappa'}\phi_{\alpha\beta}{}^{c}(l\kappa k;l'\kappa'k'). \quad \text{(IV.B.2)}$$

The notation $k\in\kappa$ signifies that k runs over all atoms in the molecular group κ. A similar meaning applies to the

[11] References pertaining to this subject may be found in the article by London (1964).

symbol $k' \in \kappa'$:

$$\phi_{\alpha\beta}{}^{c,tr}(l\kappa; l'\kappa') = \sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa'} \sum_{\sigma\rho} \phi_{\alpha\sigma}{}^{c}(l\kappa k; l'\kappa' k') \epsilon_{\sigma\beta\rho} X_\rho(k'), \tag{2, IV.B.3}$$

$$\phi_{\alpha\beta}{}^{c,rt}(l\kappa; l'\kappa') = \sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa'} \sum_{\mu\nu} \phi_{\mu\beta}{}^{c}(l\kappa k; l'\kappa' k') \epsilon_{\mu\alpha\nu} X_\nu(k); \tag{3, IV.B.4}$$

$$\phi_{\alpha\beta}{}^{c,rr}(l\kappa; l'\kappa') = \sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa'} \sum_{\mu\nu} \sum_{\sigma\rho} \phi_{\mu\sigma}{}^{c}(l\kappa k; l'\kappa' k') \epsilon_{\sigma\beta\rho} \epsilon_{\mu\alpha\nu} X_\nu(k) X_\rho(k'). \tag{4, IV.B.5}$$

In all the above expressions, $\phi_{\alpha\beta}{}^{c}(l\kappa k; l'\kappa' k')$ is as in Eq. (IV.B.1).

To obtain $B_{\alpha\beta}{}^{c,ii'}(\mathbf{q}, \kappa\kappa')$ we must substitute the above expressions into (II.A.22) and perform the lattice sum. It is here that the difficulty associated with the long-range nature of the Coulomb potential manifests itself. However, thanks to Ewald (1917, 1921) and Kellerman (1940), the hurdle is surmountable.

Using Kellerman's results as summarized in Appendix II [see Eq. (AII.4)], we can now write the Coulombic contributions $B_{\alpha\beta}{}^{c,ii'}(\mathbf{q}, \kappa\kappa')$ to the dynamical equations. Thus, we obtain

$$\begin{aligned} B_{\alpha\beta}{}^{c,tt}(\mathbf{q}, \kappa\kappa') &= \sum_{l'} \phi_{\alpha\beta}{}^{c,tt}(0\kappa; l'\kappa') \exp[i\mathbf{q}\cdot\mathbf{X}(l')] \\ &= \sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa'} \sum_{l'} \phi_{\alpha\beta}{}^{c}(0\kappa k; l'\kappa' k') \exp[i\mathbf{q}\cdot\mathbf{X}(l')] \\ &= e^2 \sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa'} Z(\kappa k) Z(\kappa' k') \{4\mathfrak{G}_{\alpha\beta}(\mathbf{q}, \mathbf{X}(\kappa k) - \mathbf{X}(\kappa' k')) - \mathfrak{C}_{\alpha\beta}(\mathbf{q}, \mathbf{X}(\kappa k) - \mathbf{X}(\kappa' k'))\}, \end{aligned}$$

$$\alpha, \beta = x, y, z; \qquad \kappa, \kappa' = 1, 2, \cdots, (\mu+\nu) \quad (\kappa \neq \kappa'), \tag{IV.B.6}$$

where the quantities $\mathfrak{G}_{\alpha\beta}$ and $\mathfrak{C}_{\alpha\beta}$ are defined in Eqs. (AII.5) and (AII.6), respectively.

The series corresponding to $\mathfrak{G}_{\alpha\beta}$ and $\mathfrak{C}_{\alpha\beta}$ can be made rapidly convergent by a suitable choice of the parameter η occurring in the series (see equations cited above). Care must be exercised in evaluating $B_{\alpha\beta}{}^{c,tt}(\mathbf{q}, \kappa\kappa')$ for the $\mathbf{q}=0$ case. This is necessitated by the $\mathbf{G}=0$ term in $\mathfrak{G}_{\alpha\beta}$ which has the form

$$(q_\alpha q_\beta / |\mathbf{q}|^2)(\pi/v) \exp(-q^2/4\eta^2) \exp\{i\mathbf{q}\cdot[\mathbf{X}(\kappa k) - \mathbf{X}(\kappa' k')]\}. \tag{IV.B.7}$$

The factor $q_\alpha q_\beta / |\mathbf{q}|^2$ has no unique limit, and the limiting value depends entirely on the direction by which the point $\mathbf{q}=0$ is approached. For this reason, while making calculations corresponding to $\mathbf{q}=0$, $B_{\alpha\beta}{}^{c,tt}$ (and also the other similar elements of the dynamical matrix) is evaluated by a limiting procedure, the limit being taken along the direction of interest. It is this dependence of the limit on the direction of $\mathbf{q}$ which leads to the various effects discussed qualitatively earlier.

For some purposes, it is convenient to write $B_{\alpha\beta}{}^{c,tt}(\mathbf{q}, \kappa\kappa')$ as

$$B_{\alpha\beta}{}^{c,tt}(\mathbf{q}, \kappa\kappa') = \bar{B}_{\alpha\beta}{}^{c,tt}(\mathbf{q}, \kappa\kappa') + (4\pi/v)(q_\alpha q_\beta / |\mathbf{q}|^2) e^2 \sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa'} Z(\kappa k) Z(\kappa' k'), \tag{IV.B.8}$$

where the leading term in the reciprocal space series for $\bar{B}_{\alpha\beta}{}^{c,tt}(\mathbf{q}, \kappa\kappa')$ has the form

$$-e^2 \sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa'} Z(\kappa k) Z(\kappa' k') (4\pi/v) (1 - \exp(-q^2/4\eta^2) \exp\{i\mathbf{q}\cdot[\mathbf{X}(\kappa k) - \mathbf{X}(\kappa' k')]\}) (q_\alpha q_\beta / |\mathbf{q}|^2).$$

This, observe, is regular at $\mathbf{q}=0$. A similar decomposition of other Coulombic contributions into one part that is regular in $\mathbf{q}$ and another that is not, is also possible. The usefulness of such a separation will become apparent later.

Next let us consider $B_{\alpha\beta}{}^{c,tr}(\mathbf{q}, \kappa\kappa')$. Proceeding as above, we have

$$\begin{aligned} B_{\alpha\beta}{}^{c,tr}(\mathbf{q}, \kappa\kappa') &= \sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa'} \sum_{\sigma\rho} \{\sum_{l'} \phi_{\alpha\sigma}{}^{c}(0\kappa k; l'\kappa' k') \exp[i\mathbf{q}\cdot\mathbf{X}(l')]\} \epsilon_{\sigma\beta\rho} X_\rho(k') \\ &= e^2 \sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa'} \sum_{\sigma\rho} Z(\kappa k) Z(\kappa' k') \epsilon_{\sigma\beta\rho} X_\rho(k') \{4\mathfrak{G}_{\alpha\sigma}(\mathbf{q}, \mathbf{X}(\kappa k) - \mathbf{X}(\kappa' k')) - \mathfrak{C}_{\alpha\sigma}(\mathbf{q}, \mathbf{X}(\kappa k) - \mathbf{X}(\kappa' k'))\}, \end{aligned}$$

$$\alpha, \beta = x, y, z; \quad \kappa = 1, 2, \cdots, (\mu+\nu); \quad \kappa' \in \text{II} \quad (\kappa \neq \kappa'); \tag{IV.B.9}$$

and

$$B_{\alpha\beta}{}^{c,rt}(\mathbf{q}, \kappa\kappa') = e^2 \sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa'} \sum_{\mu\nu} Z(\kappa k) Z(\kappa' k') \epsilon_{\mu\alpha\nu} X_\nu(k) \{4\mathfrak{G}_{\mu\beta}(\mathbf{q}, \mathbf{X}(\kappa k) - \mathbf{X}(\kappa' k')) - \mathfrak{C}_{\mu\beta}(\mathbf{q}, \mathbf{X}(\kappa k) - (\kappa' k'))\},$$

$$\alpha, \beta = x, y, z; \quad \kappa \in \text{II}; \quad \kappa' = 1, 2, \cdots, (\mu+\nu); \quad (\kappa \neq \kappa'); \tag{IV.B.10}$$

$$\begin{aligned} B_{\alpha\beta}{}^{c,rr}(\mathbf{q}, \kappa\kappa') = e^2 \sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa'} \sum_{\mu\nu} \sum_{\sigma\rho} Z(\kappa k) Z(\kappa' k') \epsilon_{\sigma\beta\rho} \epsilon_{\mu\alpha\nu} X_\nu(k) X_\rho(k') \\ \times \{4\mathfrak{G}_{\mu\sigma}(\mathbf{q}, \mathbf{X}(\kappa k) - \mathbf{X}(\kappa' k')) - \mathfrak{C}_{\mu\sigma}(\mathbf{q}, \mathbf{X}(\kappa k) - \mathbf{X}(\kappa' k'))\}, \end{aligned}$$

$$\alpha, \beta = x, y, z; \quad \kappa \in \text{II}; \quad \kappa' \in \text{II} \quad (\kappa \neq \kappa'). \tag{IV.B.11}$$

Let us now turn our attention to the case $\kappa=\kappa'$. Following the practice in conventional lattice dynamics, we shall assume that Coulombic and any other type of short-range forces that may be present in the crystal are additive, and that the force constants due to them therefore separately fulfill the sum rules (II.A.16)–(II.A.19).

Thus, considering first $B_{\alpha\beta}{}^{c,tt}(\mathbf{q}, \kappa\kappa)$, we have

$$B_{\alpha\beta}{}^{c,tt}(\mathbf{q}, \kappa\kappa) = \sum_{l'\neq 0} \phi_{\alpha\beta}{}^{c,tt}(0\kappa; l'\kappa) \exp\left[i\mathbf{q}\cdot\mathbf{X}(l')\right] + \phi_{\alpha\beta}{}^{c,tt}(0\kappa; 0\kappa)$$

$$= \sum_{l'\neq 0} \phi_{\alpha\beta}{}^{c,tt}(0\kappa; l'\kappa) \exp\left[i\mathbf{q}\cdot\mathbf{X}(l')\right] - \sum_{l'\neq 0} \phi_{\alpha\beta}{}^{c,tt}(0\kappa; l'\kappa) - \sum_{l'} \sum_{\kappa'(\neq\kappa)} \phi_{\alpha\beta}{}^{c,tt}(0\kappa; l'\kappa'), \quad \text{(IV.B.12)}$$

on using (II.A.16). If we formally add the infinity

$$e^2 \sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa} Z(\kappa k) Z(\kappa k') \{\delta_{\alpha\beta}/|\mathbf{X}|^3 - 3X_\alpha X_\beta/|\mathbf{X}|^5\}_{\mathbf{X}=\mathbf{X}(k')-\mathbf{X}(k)}$$

to the first term on the right-hand side of Eq. (IV.B.12) and subtract it from the second, we get

$$B_{\alpha\beta}{}^{c,tt}(\mathbf{q}, \kappa\kappa) = e^2 \sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa} Z(\kappa k) Z(\kappa k') \Big[\sum_{l'} \{\delta_{\alpha\beta}/|\mathbf{X}|^3 - 3X_\alpha X_\beta/|\mathbf{X}|^5\}_{\mathbf{X}=\mathbf{X}(l')-\mathbf{X}(k)+\mathbf{X}(k')} \exp\left[i\mathbf{q}\cdot\mathbf{X}(l')\right]$$

$$- \sum_{l'} \{\delta_{\alpha\beta}/|\mathbf{X}|^3 - 3X_\alpha X_\beta/|\mathbf{X}|^5\}_{\mathbf{X}=\mathbf{X}(l')-\mathbf{X}(k)+\mathbf{X}(k')}\Big] - \sum_{\kappa'(\neq\kappa)} \sum_{l'} \phi_{\alpha\beta}{}^{c,tt}(0\kappa; l'\kappa'). \quad \text{(IV.B.13)}$$

On recalling the results of Appendix II and further employing the convenient notation $B_{\alpha\beta}{}^{c,tt}(\mathbf{q}\equiv 0, \kappa\kappa')$ for the quantity

$$\sum_{l'} \phi_{\alpha\beta}{}^{c,tt}(0\kappa; l'\kappa'),$$

we obtain

$$B_{\alpha\beta}{}^{c,tt}(\mathbf{q}, \kappa\kappa) = e^2 \sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa} Z(\kappa k) Z(\kappa k') \{4[\mathfrak{B}_{\alpha\beta}(\mathbf{q}, \mathbf{X}(k)-\mathbf{X}(k')) - \mathfrak{B}_{\alpha\beta}(\mathbf{q}\equiv 0, \mathbf{X}(k)-\mathbf{X}(k'))]$$

$$- [\mathfrak{C}_{\alpha\beta}(\mathbf{q}, \mathbf{X}(k)-\mathbf{X}(k')) - \mathfrak{C}_{\alpha\beta}(\mathbf{q}\equiv 0, \mathbf{X}(k)-\mathbf{X}(k'))]\} - \sum_{\kappa'(\neq\kappa)} B_{\alpha\beta}{}^{c,tt}(\mathbf{q}\equiv 0, \kappa\kappa'),$$

$$\alpha, \beta = x, y, z; \quad \kappa = 1, 2, \cdots, (\mu+\nu). \quad \text{(IV.B.14)}$$

This expression requires several comments. Firstly, when $k=k'$, the leading terms in the series for $\mathfrak{C}_{\alpha\beta}(\mathbf{q}, 0)$ and $\mathfrak{C}_{\alpha\beta}(\mathbf{q}\equiv 0, 0)$, (i.e., the $l'=0$) terms in Eq. (AII.6) are ill-defined. Fortunately, however, they occur with opposite signs and hence cancel each other. This means that in practical calculations these terms may be safely omitted.

Next consider the leading term in the series for

$$4\mathfrak{B}_{\alpha\beta}(\mathbf{q}\equiv 0, \mathbf{X}(k)-\mathbf{X}(k')).$$

This has the form

$$\sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa} (4\pi/v)(G_\alpha G_\beta/|\mathbf{G}|^2)_{\mathbf{G}\equiv 0} Z(\kappa k) Z(\kappa k')$$

which clearly is ill-defined. It turns out, however, that

$$\sum_{\kappa'(\neq\kappa)} B_{\alpha\beta}{}^{c,tt}(\mathbf{q}\equiv 0, \kappa\kappa') = e^2 \sum_{\kappa'(\neq\kappa)} \sum_{k\epsilon\kappa} \sum_{k'\epsilon\kappa'} Z(\kappa k) Z(\kappa' k') \{4\mathfrak{B}_{\alpha\beta}(\mathbf{q}\equiv 0, \mathbf{X}(\kappa k)-\mathbf{X}(\kappa' k')) - \mathfrak{C}_{\alpha\beta}(\mathbf{q}\equiv 0, \mathbf{X}(\kappa k)-\mathbf{X}(\kappa' k'))\},$$

[see Eq. (IV.B.6)] also contributes several ill-defined terms of the same sign, and together they add up to zero. This is because their sum is multiplied among other things by

$$\Big[\sum_{\kappa} \sum_{k\epsilon\kappa} Z(\kappa k) e\Big],$$

and this quantity vanishes on account of the over-all charge neutrality of the primitive cell.

Thus, in the numerical evaluation of (IV.B.14), we can (i) ignore the ill-defined real-space terms occurring in the series expansion for $\mathfrak{C}_{\alpha\beta}$, and (ii) ignore all ill-defined terms in the series for $\mathfrak{B}_{\alpha\beta}$. The former is possible due to the cancellation of two terms with opposite signs, while the latter is connected with the fact that the sum of such terms is multiplied by total charge of the unit cell which always vanishes.

Similar considerations will apply to the expressions to be given below. In these cases also, the ill-defined terms both in real space as well as reciprocal space series can be omitted during practical calculations for the same reasons as above.

When we return to the calculation of the remaining elements of the Coulombic part of the dynamical matrix, we

have, using the same line of reasoning as employed in arriving at (IV.B.14),

$$B_{\alpha\beta}^{c,rt}(\mathbf{q},\kappa\kappa)=\sum_{l'(\neq 0)}\phi_{\alpha\beta}^{c,rt}(0\kappa;l'\kappa)\exp\left[i\mathbf{q}\cdot\mathbf{X}(l')\right]-\sum_{l'(\neq 0)}\phi_{\alpha\beta}^{c,rt}(0\kappa;l'\kappa)-\sum_{\kappa'(\neq\kappa)}\sum_{l'}\phi_{\alpha\beta}^{c,rt}(0\kappa;l'\kappa')$$
$$=e^2\sum_{k\epsilon\kappa}\sum_{k'\epsilon\kappa}\sum_{\mu\nu}Z(\kappa k)Z(\kappa k')\sum_{l'}\{\exp\left[i\mathbf{q}\cdot\mathbf{X}(l')\right]-1\}\epsilon_{\mu\alpha\nu}X_\nu(k)\{\delta_{\mu\beta}/|(\mathbf{X})|^3-3X_\mu X_\beta/|\,\mathbf{X}\,|^5\}_{\mathbf{X}=\mathbf{X}(l')-\mathbf{X}(k)+\mathbf{X}(k')}$$
$$-\sum_{\kappa'(\neq\kappa)}B_{\alpha\beta}^{c,rt}(\mathbf{q}\equiv 0,\kappa\kappa')$$
$$=e^2\sum_{k\epsilon\kappa}\sum_{k'\epsilon\kappa}\sum_{\mu\nu}Z(\kappa k)Z(\kappa k')\epsilon_{\mu\alpha\nu}X_\nu(k)\{4[\mathfrak{B}_{\mu\beta}(\mathbf{q},\mathbf{X}(k)-\mathbf{X}(k'))-\mathfrak{B}_{\mu\beta}(\mathbf{q}\equiv 0,\mathbf{X}(k)-\mathbf{X}(k'))]$$
$$-[\mathfrak{C}_{\mu\beta}(\mathbf{q},\mathbf{X}(k)-\mathbf{X}(k'))-\mathfrak{C}_{\mu\beta}(\mathbf{q}\equiv 0,\mathbf{X}(k)-\mathbf{X}(k'))]\}-\sum_{\kappa'(\neq\kappa)}B_{\alpha\beta}^{c,rt}(\mathbf{q}\equiv 0,\kappa\kappa'),$$
$$\alpha,\beta=x,y,z;\quad\kappa\in\mathrm{II};\qquad\text{(IV.B.15)}$$

and also

$$B_{\alpha\beta}^{c,tr}(\mathbf{q},\kappa\kappa)=e^2\sum_{k\epsilon\kappa}\sum_{k'\epsilon\kappa}\sum_{\sigma\rho}Z(\kappa k)Z(\kappa k')\epsilon_{\sigma\beta\rho}X_\rho(k')\{4[\mathfrak{B}_{\alpha\sigma}(\mathbf{q},\mathbf{X}(k)-\mathbf{X}(k'))-\mathfrak{B}_{\alpha\sigma}(\mathbf{q}\equiv 0,\mathbf{X}(k)-\mathbf{X}(k'))]$$
$$-[\mathfrak{C}_{\alpha\sigma}(\mathbf{q},\mathbf{X}(k)-\mathbf{X}(k'))-\mathfrak{C}_{\alpha\sigma}(\mathbf{q}\equiv 0,\mathbf{X}(k)-\mathbf{X}(k'))]\}-\sum_{\kappa'(\neq\kappa)}B_{\alpha\beta}^{c,tr}(\mathbf{q}\equiv 0,\kappa'\kappa),$$
$$\alpha,\beta=x,y,z;\quad\kappa\in\mathrm{II}.\qquad\text{(IV.B.16)}$$

Finally, let us consider $B_{\alpha\beta}^{c,rr}(\mathbf{q},\kappa\kappa)$ for which we obtain

$$B_{\alpha\beta}^{c,rr}(\mathbf{q},\kappa\kappa)=\sum_{l'}\phi_{\alpha\beta}^{c,rr}(0\kappa;l'\kappa)\exp\left[i\mathbf{q}\cdot\mathbf{X}(l')\right]$$
$$=\sum_{l'(\neq 0)}\phi_{\alpha\beta}^{c,rr}(0\kappa;l'\kappa)\exp\left[i\mathbf{q}\cdot\mathbf{X}(l')\right]-\sum_{l'(\neq 0)}\phi_{\alpha\beta}^{c,rr}(0\kappa;l'\kappa)-\sum_{l'}\sum_{\kappa'\epsilon\mathrm{II}(\neq\kappa)}\phi_{\alpha\beta}^{c,rr}(0\kappa;l'\kappa')$$
$$+\sum_{l'}\sum_{\kappa'}\{\phi_{\alpha\gamma}^{c,rt}(0\kappa;l'\kappa')X_\delta(l'\kappa')-\phi_{\alpha\delta}^{c,rt}(0\kappa;l'\kappa')X_\gamma(l'\kappa')\},\qquad\alpha,\beta=x,y,z;\quad\kappa\in\mathrm{II}.\qquad\text{(IV.B.17)}$$

As earlier [see (II.A.19)], the indices β, γ, δ are cyclic, order of x, y, z. We now rewrite the last term as

$$\sum_{l'}\sum_{\kappa'}\{\phi_{\alpha\gamma}^{c,rt}(0\kappa;l'\kappa')X_\delta(l')-\phi_{\alpha\delta}^{c,rt}(0\kappa;l'\kappa')X_\gamma(l')\}+\sum_{l'}\sum_{\kappa'}\{\phi_{\alpha\gamma}^{c,rt}(0\kappa;l'\kappa')X_\delta(\kappa')-\phi_{\alpha\delta}^{c,rt}(0\kappa;l'\kappa')X_\gamma(\kappa')\}$$
$$=-i\sum_{\kappa'}\{[(\partial/\partial q_\delta)B_{\alpha\gamma}^{c,rt}(\mathbf{q},\kappa\kappa')]_{\mathbf{q}\equiv 0}-[(\partial/\partial q_\gamma)B_{\alpha\delta}^{c,rt}(\mathbf{q},\kappa\kappa')]_{\mathbf{q}\equiv 0}\}$$
$$+\sum_{l'}\sum_{\kappa'(\neq\kappa)}\{\phi_{\alpha\gamma}^{c,rt}(0\kappa;l'\kappa')X_\delta(\kappa')-\phi_{\alpha\delta}^{c,rt}(0\kappa;l'\kappa')X_\gamma(\kappa')\}$$
$$+\sum_{l'}\{\phi_{\alpha\gamma}^{c,rt}(0\kappa;l'\kappa)X_\delta(\kappa)-\phi_{\alpha\delta}^{c,rt}(0\kappa;l'\kappa)X_\gamma(\kappa)\}$$
$$=-i\sum_{\kappa'}\{[(\partial/\partial q_\delta)B_{\alpha\gamma}^{c,rt}(\mathbf{q},\kappa\kappa')]_{\mathbf{q}\equiv 0}-[(\partial/\partial q_\gamma)B_{\alpha\delta}^{c,rt}(\mathbf{q},\kappa\kappa')]_{\mathbf{q}\equiv 0}\}$$
$$+\sum_{l'}\sum_{\kappa'(\neq\kappa)}\{\phi_{\alpha\gamma}^{c,rt}(0\kappa;l'\kappa')[X_\delta(\kappa')-X_\delta(\kappa)]-\phi_{\alpha\delta}^{c,rt}(0\kappa;l'\kappa')[X_\gamma(\kappa')-X_\gamma(\kappa)]\}.\qquad\text{(IV.B.18)}$$

Questions may be raised about irregular terms in

$$\sum_{\kappa'}[(\partial/\partial q_\delta)B_{\alpha\gamma}^{c,rt}(\mathbf{q},\kappa\kappa')]_{\mathbf{q}\equiv 0},\quad\text{etc.},$$

in above expression. Fortunately, however, charge neutrality comes to the rescue as before, and the quantity may be evaluated without any difficulty. Carrying out some simplifications to the result in (IV.B.18) similar to those employed in arriving at (IV.B.14), we obtain eventually

$$B_{\alpha\beta}^{c,rr}(\mathbf{q},\kappa\kappa)=e^2\sum_{k\epsilon\kappa}\sum_{k'\epsilon\kappa}\sum_{\mu\nu\sigma\rho}Z(\kappa k)Z(\kappa k')\epsilon_{\mu\alpha\nu}\epsilon_{\sigma\beta\rho}X_\nu(k)X_\rho(k')$$
$$\times\{4[\mathfrak{B}_{\mu\sigma}(\mathbf{q},\mathbf{X}(k)-\mathbf{X}(k'))-\mathfrak{B}_{\mu\sigma}(\mathbf{q}\equiv 0,\mathbf{X}(k)-\mathbf{X}(k'))]-[\mathfrak{C}_{\mu\sigma}(\mathbf{q},\mathbf{X}(k)-\mathbf{X}(k'))-\mathfrak{C}_{\mu\sigma}(\mathbf{q}\equiv 0,\mathbf{X}(k)-\mathbf{X}(k'))]\}$$
$$-\sum_{\kappa'\epsilon\mathrm{II}(\neq\kappa)}B_{\alpha\beta}^{c,rr}(\mathbf{q}\equiv 0,\kappa\kappa')-i\sum_{\kappa'}\sum_{\mu\nu}[(\partial/\partial q_\nu)B_{\alpha\mu}^{c,rt}(\mathbf{q},\kappa\kappa')]_{\mathbf{q}\equiv 0}\epsilon_{\beta\mu\nu}$$
$$+\sum_{\kappa'(\neq\kappa)}\sum_{\mu\nu}\{B_{\alpha\mu}^{c,rt}(\mathbf{q}\equiv 0,\kappa\kappa')\epsilon_{\beta\mu\nu}[X_\nu(\kappa')-X_\nu(\kappa)]\},\qquad\alpha,\beta=x,y,z;\quad\kappa\in\mathrm{II}.\qquad\text{(IV.B.19)}$$

The above expressions for $B_{\alpha\beta}^{c,ii'}(\mathbf{q},\kappa\kappa')$ may be programmed for numerical evaluation in a computer, and values corresponding to any given crystal may be obtained. The value of η is chosen such that both the real-space and reciprocal-space series are rapidly convergent. If the dynamical matrix is required in the principal-axes frame,

then, having computed $\mathbf{B}^{c,ii'}(\mathbf{q}, \kappa\kappa')$ as described above, the matrix corresponding to the principal-axes frame may be obtained via the transformation (II.B.18). In passing we may note that if the units κ and κ' are just individual atoms, then only the term $\mathbf{B}^{c,tt}$ is nonvanishing. The others become identically equal to zero owing to the fact that $\mathbf{X}(k)=\mathbf{X}(k')=0$. Also the expression for $\mathbf{B}^{c,tt}$ becomes the conventional expression as given, for example, in the book by Born and Huang (1954), after, of course, allowance for the differences in phase factors.

C. Macroscopic Fields Associated with External Modes

We shall now exhibit explicitly the role of macroscopic field in influencing the dynamics. Our approach will be similar to that of Born and Huang (BH, Chap. V), who have discussed the corresponding problem in standard lattice dynamics. From (II.A.21) we have

$$\sum_{\kappa'}\sum_{\beta}\sum_{i'} B_{\alpha\beta}{}^{ii'}(\mathbf{q}, \kappa\kappa')e_\beta{}^{i'}(\kappa' \mid \mathbf{q}j)=\omega_j{}^2(\mathbf{q})\sum_{\gamma} m_{\alpha\gamma}{}^{ii}(\kappa\kappa)e_\gamma{}^{i}(\kappa \mid \mathbf{q}j), \qquad (i=t,r), \tag{IV.C.1}$$

with $B_{\alpha\beta}{}^{ii'}(\mathbf{q}, \kappa\kappa')=B_{\alpha\beta}{}^{c,ii'}(\mathbf{q}, \kappa\kappa')+$short-range contributions. We know from the earlier discussion that $B_{\alpha\beta}{}^{c,ii'}$ has a part that is not regular at $\mathbf{q}=0$, which, however, may be separated in the manner of (IV.B.8). We may thus write $B_{\alpha\beta}{}^{ii'}(\mathbf{q}, \kappa\kappa')=\bar{B}_{\alpha\beta}{}^{ii'}(\mathbf{q}, \kappa\kappa')+$a nonregular part, where the first term includes not only the short-range contribution (which is always regular at $\mathbf{q}=0$), but also $\bar{B}_{\alpha\beta}{}^{c,ii'}(\mathbf{q}, \kappa\kappa')$. Using this representation, the eigenvalue equation becomes (for $i=t$)

$$\begin{aligned}\omega_j{}^2(\mathbf{q})e_\alpha{}^t(\kappa \mid \mathbf{q}j)m_\kappa=&\sum_{\kappa'}\sum_{\beta}\sum_{i'}\bar{B}_{\alpha\beta}{}^{ti'}(\mathbf{q}, \kappa\kappa')e_\beta{}^{i'}(\kappa' \mid \mathbf{q}j)+(4\pi/v)e^2\sum_{k\epsilon\kappa}(q_\alpha/q)Z(\kappa k)\sum_{\beta}\sum_{\kappa'}\sum_{k'\epsilon\kappa'}Z(\kappa'k')\\&\times\{e_\beta{}^t(\kappa' \mid \mathbf{q}j)(q_\beta/q)+\sum_{\sigma\rho}e_\beta{}^r(\kappa' \mid \mathbf{q}j)(q_\sigma/q)\epsilon_{\sigma\beta\rho}X_\rho(k')\}\\=&\sum_{\kappa'}\sum_{\beta}\sum_{i'}\bar{B}_{\alpha\beta}{}^{ti'}(\mathbf{q}, \kappa\kappa')e_\beta{}^{i'}(\kappa' \mid \mathbf{q}j)+(4\pi/v)e^2\sum_{k\epsilon\kappa}Z(\kappa k)(q_\alpha/q)\\&\times\sum_{\kappa'}\sum_{k'\epsilon\kappa'}Z(\kappa'k')\{[\mathbf{e}^t(\kappa' \mid \mathbf{q}j)\cdot\mathbf{q}/q]+q^{-1}\mathbf{q}\cdot[\mathbf{e}^r(\kappa' \mid \mathbf{q}j)\times\mathbf{X}(k')]\}.\end{aligned} \tag{IV.C.2}$$

If we associate a dipole moment

$$\mathbf{p}(\kappa')=e\sum_{k'\epsilon\kappa'}Z(\kappa'k')\{\mathbf{e}^t(\kappa' \mid \mathbf{q}j)+\mathbf{e}^r(\kappa' \mid \mathbf{q}j)\times\mathbf{X}(k')\}, \tag{IV.C.3}$$

with the κ'th unit consequent to the displacements, then, following Born and Huang, we may write

$$\omega_j{}^2(\mathbf{q})e_\alpha{}^t(\kappa \mid \mathbf{q}j)m_\kappa=\sum_{\kappa'}\sum_{\beta}\sum_{i'}\bar{B}_{\alpha\beta}{}^{ii'}(\mathbf{q}, \kappa\kappa')e_\beta{}^{i'}(\kappa' \mid \mathbf{q}j)-e\sum_{k\epsilon\kappa}Z(\kappa k)E_\alpha, \tag{IV.C.4}$$

where E_α is the αth component of the amplitude $\mathbf{E}$ of the macroscopic field due to a lattice of dipoles $\mathbf{p}(l\kappa)$, and is explicitly given by

$$E_\alpha=-(4\pi/v)(q_\alpha/q)\{(\mathbf{q}/q)\cdot\sum_{\kappa'}\mathbf{p}(\kappa')\}. \tag{IV.C.5}$$

Similarly, we have (for $i=r$)

$$\begin{aligned}\omega_j{}^2(\mathbf{q})\sum_{\gamma}\mathcal{I}_{\alpha\gamma}(\kappa)e_\gamma{}^r(\kappa \mid \mathbf{q}j)=&\sum_{\kappa'}\sum_{\beta}\sum_{i'}\bar{B}_{\alpha\beta}{}^{ri'}(\mathbf{q}, \kappa\kappa')e_\beta{}^{i'}(\kappa' \mid \mathbf{q}j)-e\sum_{k\epsilon\kappa}Z(\kappa k)\sum_{\mu\nu}E_\mu\epsilon_{\mu\alpha\nu}X_\nu(k)\\=&\sum_{\kappa'}\sum_{\beta}\sum_{i'}\bar{B}_{\alpha\beta}{}^{ri'}(\mathbf{q}, \kappa\kappa')e_\beta{}^{i'}(\kappa' \mid \mathbf{q}j)-([\sum_{k\epsilon\kappa}ez(\kappa k)\mathbf{X}(k)]\times\mathbf{E})_\alpha.\end{aligned} \tag{IV.C.6}$$

The above equations display explicitly the influence of the macroscopic field on the dynamics. If the field is not properly built into the calculations, i.e., if the Coulombic effects are not treated properly, then of course the effects of the field will not be properly reproduced.

Equations (IV.C.4)–(IV.C.6) have some interesting consequences which are best illustrated with a specific example. Consider the long-wavelength modes in $CaWO_4$, which is a uniaxial crystal. From group-theoretical analysis it is known that there is a doubly degenerate mode involving the librations of the WO_4^{--} ions which has the same transformation properties as the dipole-moment operator $\mathbf{M}$, and that therefore it is infrared active. In other words, we expect these modes to exhibit a behavior similar to that sketched for the modes ② and ③ in Fig. 22.

Let us suppose that the modes are *purely librational*, i.e., $\mathbf{e}^t(\kappa \mid \mathbf{q}j)\equiv 0$ for all κ. From (IV.C.3) we see that the associated dipole moment is given by

$$\mathbf{p}(WO_4)=\mathbf{e}^r(WO_4)\times[e\sum_{k\epsilon WO_4}Z(WO_4k)\mathbf{X}(k)].$$

If we assume the WO_4^{--} ion to be a rigid regular tetrahedron,[12] the quantity in the bracket vanishes identically, and one therefore does not expect the mode to appear in infrared absorption. Further, on the basis of Eq. (IV.C.6), one does not expect any anisotropic

[12] Experimental evidence (Kay *et al.*, 1964) suggests that the WO_4^{--} ion in $CaWO_4$ is not a regular tetrahedron but is slightly distorted. This does not, however, affect our argument.

behavior since the nonregular part (which is responsible for the effect) does not make any contribution. In actual fact, however, Barker (1964) (see also Porto and Scott, 1967, especially their Table I) sees the mode in question in his infrared experiments, as also the anisotropic effects, which proves that it is not purely librational in character. There is probably some admixture from the translational modes resulting in a net dipole moment for the mode in question, or there is an admixture from the internal vibrations. The latter is quite a likely possibility in $CaWO_4$ since the frequencies of the internal vibrations are not very much higher than those of the external modes. More specifically, the lowest internal vibration frequency has a value 237 cm^{-1} (Barker, 1964; Porto and Scott, 1967), while the infrared-active librations have a frequency of 202 cm^{-1}.

In general, modes that are purely librational and which involve ions that carry no net dipole moment, i.e., for which

$$[\sum_{k\epsilon\kappa} eZ(\kappa k)\mathbf{X}(k)]$$

vanishes, are not expected, within the framework of the external-mode approximation, to exhibit any infrared activity or anisotropic effects as discussed earlier, even though group theoretically they may have the same transformation properties as the dipole-moment operator **M**.[13] Experimental contradiction of this expectation is indicative of admixture from other modes, most likely from the internal vibrations which effectively distort the ion and produce a nonvanishing dipole moment. This of course requires that the frequencies of the internal vibrations be not too different from that of the librational frequency. In passing, it is interesting to observe that the lack of infrared activity we have been discussing is reminiscent of the situation in molecular physics where molecules not possessing a net dipole moment do not exhibit a pure rotation spectrum in infrared absorption.

D. Survey of the Treatment of Coulomb Interactions in the Literature

So far, very few calculations for complex ionic crystals have been reported in the literature. One of the earliest is due to Asano and Tomishima (1957c), who were interested in the dynamics of $NaClO_4$. These authors do not give analytical expressions for the lattice sums of the Coulomb terms as we have done. Further, they restrict their attention to the $\mathbf{q}=0$ modes and make a multipole expansion of the potential due to the ClO_4^- radical retaining only the lower-order terms.

The only complex ionic crystals for which full-fledged dispersion relations calculations have been made are NH_4Cl (Parlinski, 1968, 1969) and $NaNO_2$ (Dolling, 1968). These calculations have already been referred to, and the treatment of the short-range forces has been discussed. Here we shall consider the Coulomb part alone.

D.1 NH_4Cl

The electrostatic effects in NH_4Cl are treated by Parlinski using a rigid-ion model. The Cl^- ion is treated as a point with charge $-e$, while the NH_4^+ ion is regarded as a tetrahedron with charges $(+e/4)$ located at the hydrogen sites, leading to a net charge $+e$. However, in evaluating the (tt) contributions, the detailed charge structure of NH_4^+ is ignored, and it is treated as a point charge $+e$ located at the nitrogen site. In other words, the various (tt) type Coulomb contributions are evaluated as in CsCl. Reference to our expressions (IV.B.6) and (IV.B.14) shows that this is an approximation when the NH_4^+ ion is involved. In fact, it is equivalent to replacing the tetrahedral charge distribution associated with the NH_4^+ ion by a monopole.

As far as the (tr), (rt), and (rr) contributions are concerned, Parlinski evaluates the Coulomb part of the force constants, viz., $\phi_{\alpha\beta}{}^{c,ii'}$ exactly, taking into account the tetrahedral charge structure. However, in calculating the contribution to the dynamical matrix, the summation over the lattice sites is restricted to third neighbors and not carried through over all neighbors as we have done in our formal expressions. Parlinski justifies his truncation by the argument that $\phi_{\alpha\beta}{}^{tr}$, $\phi_{\alpha\beta}{}^{rt}$, and $\phi_{\alpha\beta}{}^{rr}$ decrease rapidly with increasing distance between the pair of units concerned. It seems to us that in general the truncation is not a desirable procedure as the delicate effects of macroscopic fields may not be properly reproduced.

In the case of NH_4Cl, however, the truncation process does not affect the long-wavelength behavior of the torsional modes since they are not infrared active.

D.2 $NaNO_2$

$NaNO_2$ contains two ions, Na^+ and NO_2^-. The latter is a nonlinear molecular group like the water molecule and has a permanent dipole moment whose value is taken as the effective charge on nitrogen multiplied by the distance of that atom from the midpoint between the oxygen pair. As usual, the electrostatic effects are treated in the rigid-ion (i.e., nonpolarizable ion) approximation (Dolling, 1968; Sakurai *et al.*, 1970). Two approaches were considered; in the first it was assumed that the NO_2^- ion could be represented as a point ion, thereby ignoring its dipole moment. Such an assumption is actually more appropriate to the high-temperature paraelectric phase rather than to the room temperature ferroelectric

[13] In this context, it is useful to remember that the group-theoretical method of predicting infrared activity involves essentially a converse argument. In other words, we pick out modes which have the same transformation properties as X, Y, and Z, and then identify them as infrared active since they transform the same way the components of **M** do. The fact that a mode transforms as X, Y, Z does not guarantee that it has a nonvanishing dipole moment **M**. The case discussed above illustrates this point. A more familiar example is that of the $\mathbf{q}=0$ acoustic modes. These involve lateral translations of the crystal and clearly do not involve any dipole moments.

phase since in the former, the NO_2^- dipole moments are directed equally and randomly along the $+$ and $-b$ directions. In other words, the NO_2^- ion was treated as a monopole in the first model. The Coulombic contributions therefore entered only the (tt) parts. In the second approach, the full charge structure of the NO_2^- ion was taken into account, and the various contributions were evaluated basically as in Sec. IV.B but with several simplifying assumptions. As is to be expected, the first model did not reproduce the observed anisotropic behavior of the librational modes at $\mathbf{q}=0$ while the second model did. This underscores the need for care in the use of the monopole approximation for ionic clusters (cf. also the last sentence in Sec. IV.D.1).

E. Polaritons

In Secs. IV.B and IV.C, we treated the interactions between the various charges in the crystal via Coulomb interactions alone. This corresponds to the so-called electrostatic approximation. Inclusion of retardation effects hitherto ignored drastically modifies the nature of the dispersion relations for infrared-active modes in the region $q \lesssim 10^5$ cm^{-1}, and leads to polaritons which are coupled phonon–photon excitations (Born and Huang, 1954; Loudon, 1964). Polaritons have been observed experimentally in GaP (Henry and Hopfield, 1965) and ZnO (Porto *et al.*, 1967). (For other references on this subject see Wright, 1969). One would expect by analogy that the combination of external modes with photons should lead to polaritons in complex crystals also.

Formally, it is possible to allow for photon–phonon admixture by supplementing the phonon equations previously discussed as follows: Let us first write (II.A.21) and (IV.C.4, 6) as

$$[\bar{\mathbf{B}}(\mathbf{q})-\omega^2(\mathbf{q})\,\mathbf{m}]\mathbf{U}+\mathbf{Z}^+\mathbf{E}=0. \qquad \text{(IV.E.1)}$$

Here $\mathbf{Z}^+$ is a $(3\mu+6\nu)\times 3$-dimensional rectangular "effective charge" matrix with elements

$$\begin{aligned}(\mathbf{Z}^+)_{\alpha\kappa i,\beta} &= -\Big[e\sum_{k\epsilon\kappa} Z(\kappa k)\Big]\delta_{\alpha\beta} && \text{for } i=t\\ &= -\Big[e\sum_{k\epsilon\kappa}\sum_{\nu} Z(\kappa k)\epsilon_{\beta\alpha\nu}X_\nu(k)\Big] && \text{for } i=r.\end{aligned} \qquad \text{(IV.E.2)}$$

Following Pick (1970) we now supplement (IV.E.1) with the equation

$$\mathbf{Z}\mathbf{U}+(1/4\pi)\,(n^2\mathbf{Q}-\boldsymbol{\varepsilon})\,\mathbf{E}=0. \qquad \text{(IV.E.3)}$$

Here $n^2=(c^2q^2/\omega^2)$ denotes the square of the refractive index, and $\mathbf{Q}$ is a 3×3 matrix with elements

$$Q_{\alpha\beta}=\delta_{\alpha\beta}-\hat{q}_\alpha\hat{q}_\beta, \qquad (\hat{q}_\alpha=q_\alpha/|\,\mathbf{q}\,|). \qquad \text{(IV.E.4)}$$

$\boldsymbol{\varepsilon}$ is the dielectric tensor. Without the first term, Eq. (IV.E.3) reduces to

$$(1/4\pi)\,(n^2\mathbf{Q}-\boldsymbol{\varepsilon})\,\mathbf{E}=0, \qquad \text{(IV.E.5)}$$

which has nontrivial solutions for $\mathbf{E}$ only when

$$|\,n^2\mathbf{Q}-\boldsymbol{\varepsilon}\,|=0. \qquad \text{(IV.E.6)}$$

The last equation is the well-known Fresnel's equation of optics. It is probably more familiar to the reader in the form

$$\frac{\hat{q}_x^2}{(1/n^2-1/\epsilon_x)}+\frac{\hat{q}_y^2}{(1/n^2-1/\epsilon_y)}+\frac{\hat{q}_z^2}{(1/n^2-1/\epsilon_z)}=0. \qquad \text{(IV.E.7)}$$

This form of Fresnel's equation is easily derived from (IV.E.5) by writing it first as

$$(1/4\pi)\,n^2\mathbf{Q}\mathbf{E}=\boldsymbol{\varepsilon}\mathbf{E}=\mathbf{D},$$

and then making use of the fact that

$$\mathbf{q}\cdot\mathbf{D}=0,$$

since $\mathbf{q}$, the wave vector of the electromagnetic wave, is normal to the dielectric displacement $\mathbf{D}$. Equations (IV.E.6) and (IV.E.7) describe the propagation of photons in the crystal.

Due to the presence of the first term in (IV.E.3), however, the photon is coupled to the lattice, which leads to coupled photon–phonon modes. It must be pointed out that in the context of coupled modes, the electric field $\mathbf{E}$ in Eq. (IV.E.1) has a different significance compared to what it has if one were considering the electrostatic approximation. In the latter case, $\mathbf{E}$ would be a purely longitudinal field, i.e., parallel to $\mathbf{q}$ [see Eq. (IV.C.5)], whereas the electric field in the present case includes transverse components also. Correspondingly, there are additional contributions to $\bar{\mathbf{B}}(\mathbf{q})$ as compared to the electrostatic case.

The dispersion relations for these coupled photon–phonon modes are obtained from the determinental equation (Pick, 1970)

$$\begin{vmatrix}\bar{\mathbf{B}}(\mathbf{q})-\omega^2(\mathbf{q})\,\mathbf{m} & \mathbf{Z}^+\\ \mathbf{Z} & (1/4\pi)\,(n^2\mathbf{Q}-\boldsymbol{\varepsilon})\end{vmatrix}=0, \qquad \text{(IV.E.8)}$$

which follows readily from Eqs. (IV.E.1) and (IV.E.3). One can recover from the above equation the solution corresponding to the electrostatic approximation by considering appropriate limits, viz., $\omega\approx$external-mode frequencies and also $\ll c\,|\,\mathbf{q}\,|$ (Pick, 1970).

The preceding discussion is entirely formal. Apart from some preliminary investigations by Asano and Tomishima (1957b), very little theoretical or experimental work has been reported concerning coupled photon–(external)phonon modes; hopefully this area will be explored in the future.

V. GROUP THEORY OF EXTERNAL MODES

A. Extension of the Work of Maradudin and Vosko

In Sec. I, we made a case for the external-mode approach on the grounds that it leads to simplifications in the dynamical problem. Notwithstanding this, it turns out that practical calculations often require the diagonalization of fairly large matrices. Considerable help in accomplishing this can be had, however, using

group theory. Besides simplifying the diagonalization of the dynamical matrix $\mathbf{B}(\mathbf{q})$, group theory is also of value in classifying and labeling the various modes. The present section is devoted to a discussion of these topics.

The role of group theory in classifying the $\mathbf{q}=0$ external modes is well established in the spectroscopic literature (Bhagavantam and Venkatarayudu, 1948; Halford, 1946; Winston and Halford, 1949; Davydov, 1962). The first attempt to extend the analysis to other regions of the Brillouin zone was made by Chen and Dvorak (1968). However, this work does not clarify some points that are of practical importance, and for this reason we review the subject afresh. Our treatment here closely follows the work of Maradudin and Vosko (1968) (hereinafter referred to as MV), who have given a comprehensive discussion of the role of group theory in relation to standard Born–von Kármán formalism. It will be presumed that the reader is acquainted at least with the essential points of MV's article. Our notation also will generally follow that of MV.

The basic principle underlying the application of group theory to the eigenvalue problem

$$\mathbf{AX}=\lambda\mathbf{X},$$

where λ and $\mathbf{X}$ are eigenvalues and eigenfunctions, respectively, of $\mathbf{A}$, is to discover a group of unitary transformations which commute with $\mathbf{A}$. This not only enables us to classify the eigenvalues and the eigenvectors using group-theoretic labels, but also aids in simplifying the eigenvalue problem. The Born–von Kármán dynamical equation

$$\mathbf{D}(\mathbf{q})\,\mathbf{e}(\mathbf{q}j)=\omega_j^2(\mathbf{q})\,\mathbf{e}(\mathbf{q}j)$$

is an example of the above type of eigenvalue problem.

In our case, we have a slightly more generalized problem of the form

$$\mathbf{AX}=\lambda\mathbf{BX}.$$

What is necessary in this instance is to discover a group of transformations which commute simultaneously with $\mathbf{A}$ and $\mathbf{B}$. If this is possible, then one can proceed as before and classify both the eigenvalues and eigenvectors, as well as simplify the determination of the eigenvalues.

Now, in solid state applications, be it lattice dynamics or band structure calculations, the eigenvalue problem usually pertains to a particular vector $\mathbf{q}$ in the Brillouin zone, and it is customary to follow Bouckaert *et al.* (1936) and consider the group of transformations which describe in the space of Bloch functions associated with that $\mathbf{q}$, the effect of the group of operations

$$G(\mathbf{q})=\{\mathcal{R}_m\},\qquad \mathcal{R}_m=\{\mathbf{R}\mid\mathbf{V}(R)+\mathbf{X}(m)\}.$$

As before, $\mathbf{R}$ denotes the rotational part, $\mathbf{V}(R)$ the associated fractional translation if any, and $\mathbf{X}(m)$ a lattice translation. This group $G(\mathbf{q})$ is called the group of the wave vector, and is a subgroup of the full space group G. Its special characteristic is that it is comprised of space group elements $\mathcal{R}_m$ whose rotational parts $\mathbf{R}$ have the property

$$\mathbf{Rq}=\mathbf{q}\quad\text{or}\quad\mathbf{q}+\mathbf{G},$$

where $\mathbf{G}$ is a vector of the reciprocal lattice.

In our work, however, we shall follow MV's approach and consider instead just the group $G_0(\mathbf{q})$ comprised of the set $\{\mathbf{R}\}$ of the rotational parts alone. This group is called the point group of the wave vector.

MV show that it is possible to construct unitary operators $\mathbf{T}(\mathbf{q};\mathbf{R})$ in the space of the eigenvectors of the dynamical matrix $\mathbf{D}(\mathbf{q})$ such that

(i) $\mathbf{T}(\mathbf{q};\mathbf{R})$ commutes with $\mathbf{D}(\mathbf{q})$ for all $\mathbf{R}\in G_0(\mathbf{q})$;
(ii) the set of matrices $T(\mathbf{q})=\{\mathbf{T}(\mathbf{q};\mathbf{R})\}$ $[\mathbf{R}\in G_0(\mathbf{q})]$ furnish a reducible multiplier representation of $G_0(\mathbf{q})$.

MV also show that as a result, the eigenvectors of $\mathbf{D}(\mathbf{q})$ transform according to the irreducible multiplier representations (IMR) of $G_0(\mathbf{q})$, and this fact permits simplifications in the diagonalization process. MV also discuss the advantages of using $G_0(\mathbf{q})$ and the multiplier representation approach as compared to the traditional one of using $G(\mathbf{q})$ and its irreducible representations.

In our case, too, it is possible to construct unitary matrices with similar properties and consequences. The only additional point to be ensured is that the matrices commute with $\mathbf{m}$ or $\mathbf{m}^p$ as the case may be.

To begin, we shall consider the dynamics in the fixed frame. Using basically the same kind of arguments as in Secs. 2 and 3 of MV, we first construct a $(3\mu+6\nu)$-dimensional unitary matrix $\mathbf{\Gamma}(\mathbf{q};\mathcal{S}_m)$ $[\mathcal{S}_m=\{\mathbf{S}\mid\mathbf{V}(S)+\mathbf{X}(m)\}]$ with elements as below:

$$\Gamma_{\alpha\beta}{}^{ij}(\kappa\kappa'\mid\mathbf{q};\mathcal{S}_m)=S_{\alpha\beta}\delta(\kappa,F_0(\kappa';S))C^i(S)\delta_{ij}\times\exp\{i\mathbf{q}\cdot[\mathcal{S}_m^{-1}\mathbf{X}(\kappa)-\mathbf{X}(\kappa')]\}.\quad\text{(V.A.1)}$$

Here $\mathcal{S}_m$ is a general element of the space group G and does not necessarily belong to $G(\mathbf{q})$. The quantity $\delta(\kappa,F_0(\kappa';S))$ describes interchanges in the sublattices, if any. It is a Kronecker delta, and vanishes unless κ corresponds to the sublattice $F_0(\kappa';S)$ arrived at from the sublattice κ' via $\mathcal{S}_m$, in which case it (the Kronecker delta) is equal to unity. Equation (V.A.1) is to be compared with MV's Eq. (2.37). The only points of difference are that we have two more labels, viz., i and j for the matrix elements, and that there is an additional term $C^i(S)\delta_{ij}$ on the right-hand side. We remind the reader that the indices i and j comprehensively represent t and r, which signify translation and rotation, respectively, and that

$$C^i(S)=1\text{ for all }\mathbf{S}\text{ if }i=t$$

$$=\left.\begin{matrix}1\\-1\end{matrix}\right\}\text{for }\mathbf{S}\begin{cases}\text{proper rotation}\\\text{improper rotation}\end{cases}\text{if }i=r.$$

The proof that $\mathbf{\Gamma}(\mathbf{q};\mathcal{S}_m)$ is unitary is essentially the same as given by MV in their Eq. (3.1).

Next we introduce a matrix $\mathbf{T}(\mathbf{q};\mathbf{R})$ in terms of $\mathbf{\Gamma}(\mathbf{q};\mathcal{R}_m)$ just as MV do in (3.17), i.e.,

$$\mathbf{T}(\mathbf{q};\mathbf{R})=\exp\{i\mathbf{q}\cdot[\mathbf{V}(R)+\mathbf{X}(m)]\}\,\mathbf{\Gamma}(\mathbf{q};\mathcal{R}_m). \quad \text{(V.A.2a)}$$

In component form we have

$$T_{\alpha\beta}{}^{ij}(\kappa\kappa'\mid\mathbf{q};\mathbf{R})=R_{\alpha\beta}\delta(\kappa,F_0(\kappa';R))C^i(R)\delta_{ij}\times\exp\{i\mathbf{q}\cdot[\mathbf{X}(\kappa)-\mathbf{R}\mathbf{X}(\kappa')]\}. \quad \text{(V.A.2b)}$$

Since $\mathbf{\Gamma}(\mathbf{q};\mathcal{R}_m)$ is unitary, it immediately follows that $\mathbf{T}(\mathbf{q};\mathbf{R})$ is also.

We shall now establish that

(i) $\mathbf{T}(\mathbf{q};\mathbf{R})$ as defined above commutes both with $\mathbf{B}(\mathbf{q})$ as well as with $\mathbf{m}$;

(ii) the set $T(\mathbf{q})=\{\mathbf{T}(\mathbf{q};\mathbf{R})\}$ $[\mathbf{R}\in G_0(\mathbf{q})]$ furnishes a $(3\mu+6\nu)$-dimensional multiplier representation of $G_0(\mathbf{q})$.

Consider the ${}_{\mu\nu}{}^{ij}(KK')$th element of the product

$$\mathbf{T}(\mathbf{q};\mathbf{R})\mathbf{B}(\mathbf{q})\mathbf{T}^+(\mathbf{q};\mathbf{R}).$$

We have

$$[\mathbf{T}(\mathbf{q};\mathbf{R})\mathbf{B}(\mathbf{q})\mathbf{T}^+(\mathbf{q};\mathbf{R})]_{\mu\nu}{}^{ij}(KK')=\sum_{\kappa\kappa'}\sum_{\alpha\beta}\sum_{mn}T_{\mu\alpha}{}^{im}(K\kappa\mid\mathbf{q};\mathbf{R})B_{\alpha\beta}{}^{mn}(\mathbf{q},\kappa\kappa')T_{\nu\beta}{}^{jn*}(K'\kappa'\mid\mathbf{q};\mathbf{R})$$

$$=\sum_{\kappa\kappa'}\sum_{\alpha\beta}\sum_{mn}R_{\mu\alpha}\delta(K,F_0(\kappa;R))C^i(R)\delta_{im}\exp\{i\mathbf{q}\cdot[\mathbf{X}(K)-\mathbf{R}\mathbf{X}(\kappa)]\}$$

$$\times\sum_{l'}\phi_{\alpha\beta}{}^{mn}(l\kappa;l'\kappa')\exp\{i\mathbf{q}\cdot[\mathbf{X}(l')-\mathbf{X}(l)]\}R_{\nu\beta}\delta(K',F_0(\kappa';R))C^j(R)\delta_{jn}\exp\{-i\mathbf{q}\cdot[\mathbf{X}(K')-\mathbf{R}\mathbf{X}(\kappa')]\}$$

$$=\sum_{\alpha\beta}\sum_{l'}R_{\mu\alpha}\phi_{\alpha\beta}{}^{ij}(lF_0^{-1}(K;R);l'F_0^{-1}(K';R))R_{\nu\beta}C^i(R)C^j(R)\exp\{i\mathbf{q}\cdot[\mathbf{X}(l')-\mathbf{X}(l)]\}$$

$$\times\exp\{i\mathbf{q}\cdot[\mathbf{X}(K)-\mathbf{X}(K')-\mathbf{R}\mathbf{X}(F_0^{-1}(K;R))+\mathbf{R}\mathbf{X}(F_0^{-1}(K';R))]\}. \quad \text{(V.A.3)}$$

In this expression, $F_0^{-1}(K;R)$ and $F_0^{-1}(K';R)$ denote the sublattices from which one must start in order to arrive at K and K', respectively, via the space-group operation $\{\mathbf{R}\mid\mathbf{V}(R)\}$.

Let us write

$$\{\mathbf{R}\mid\mathbf{V}(R)\}\mathbf{X}(lF_0^{-1}(K;R))=\mathbf{X}(LK).$$

Simplifying the left-hand side and rearranging, we obtain

$$-\mathbf{X}(K)+\mathbf{R}\mathbf{X}(F_0^{-1}(K;R))=\mathbf{X}(L)-\mathbf{R}\mathbf{X}(l)-\mathbf{V}(R). \quad \text{(V.A.4a)}$$

Similarly, we obtain

$$-\mathbf{X}(K')+\mathbf{R}\mathbf{X}(F_0^{-1}(K';R))=\mathbf{X}(L')-\mathbf{R}\mathbf{X}(l')-\mathbf{V}(R), \quad \text{(V.A.4b)}$$

where $(L'K')$ is the unit arrived at from $(l'F_0^{-1}(K';R))$ by $\{\mathbf{R}\mid\mathbf{V}(R)\}$. If we use these results and further remember that

$$\sum_{\alpha\beta}R_{\mu\alpha}\phi_{\alpha\beta}{}^{ij}(lF_0^{-1}(K;R);l'F_0^{-1}(K';R))R_{\nu\beta}C^i(R)C^j(R)=\phi_{\mu\nu}{}^{ij}(LK;L'K') \quad \text{(V.A.5)}$$

[see Eq. (II.A.13)], Eq. (V.A.3) becomes

$$[\mathbf{T}(\mathbf{q};\mathbf{R})\mathbf{B}(\mathbf{q})\mathbf{T}^+(\mathbf{q};\mathbf{R})]_{\mu\nu}{}^{ij}(KK')=\sum_{L'}\phi_{\mu\nu}{}^{ij}(LK;L'K')\exp\{i\mathbf{q}\cdot[\mathbf{X}(L')-\mathbf{X}(L)]\}$$

$$=B_{\mu\nu}{}^{ij}(\mathbf{q},KK'). \quad \text{(V.A.6)}$$

In the last-but-one step, we have replaced the summation over l' by one over L' since the two are equivalent. Equation (V.A.6) shows that $\mathbf{T}(\mathbf{q};\mathbf{R})$ commutes with $\mathbf{B}(\mathbf{q})$.

Next consider

$$[\mathbf{T}(\mathbf{q};\mathbf{R})\mathbf{m}\mathbf{T}^+(\mathbf{q};\mathbf{R})]_{\mu\nu}{}^{ij}(KK').$$

Remembering from Sec. II that $\mathbf{m}$ is diagonal in the sublattice index and that characterizing translations and rotations, we obtain on writing the matrix product explicitly

$$\sum_{\alpha\beta}\sum_{\kappa\kappa'}\sum_{mn}R_{\mu\alpha}\delta(K,F_0(\kappa;R))C^i(R)\delta_{im}\exp\{i\mathbf{q}\cdot[\mathbf{X}(K)-\mathbf{R}\mathbf{X}(\kappa)]\}m_{\alpha\beta}{}^{mm}(\kappa\kappa)\delta_{mn}\delta(\kappa,\kappa')\times R_{\nu\beta}\delta(K',F_0(\kappa';R))C^j(R)\delta_{nj}\exp\{-i\mathbf{q}\cdot[\mathbf{X}(K')-\mathbf{R}\mathbf{X}(\kappa')]\}.$$

When we perform the summations over the indices, m, n, and κ', this becomes

$$\sum_{\alpha\beta}\sum_{\kappa}R_{\mu\alpha}\delta(K,F_0(\kappa;R))C^i(R)\delta_{ij}C^j(R)m_{\alpha\beta}{}^{ii}(\kappa\kappa)R_{\nu\beta}\delta(K',F_0(\kappa;R))\exp\{i\mathbf{q}\cdot[\mathbf{X}(K)-\mathbf{X}(K')]\}.$$

Next we sum over κ, and use the property that

$$\delta(K',F_0[F_0^{-1}(K;R);R])=\delta(K',K).$$

This reduces the above expression to

$$\sum_{\alpha\beta}[R_{\mu\alpha}m_{\alpha\beta}{}^{ii}(F_0^{-1}(K;R)F_0^{-1}(K;R))R_{\nu\beta}]\delta_{ij}\delta(K,K')C^i(R)C^j(R)\exp\{i\mathbf{q}\cdot[\mathbf{X}(K)-\mathbf{X}(K')]\}.$$

From Sec. II we know that the quantity in the bold bracket above can be written as $m_{\mu\nu}{}^{ii}(KK)$ [cf. Eq. (II.A.14)]. We can thus write the above expression as

$$\{m_{\mu\nu}{}^{ii}(KK)\delta_{ij}\delta(K,K')\}C^i(R)C^j(R)\exp\{i\mathbf{q}\cdot[\mathbf{X}(K)-\mathbf{X}(K')]\}$$
$$=m_{\mu\nu}{}^{ij}(KK')C^i(R)C^j(R)\exp\{i\mathbf{q}\cdot[\mathbf{X}(K)-\mathbf{X}(K')]\}.$$

Recalling the fact that m is diagonal both in i and K, we see that we may safely drop the exponential as well as the product $C^i(R)C^j(R)$ in above result. We thus obtain

$$[\mathsf{T}(\mathbf{q};\mathbf{R})\,\mathsf{m}\mathsf{T}^+(\mathbf{q};\mathbf{R})]_{\mu\nu}{}^{ij}(KK')=m_{\mu\nu}{}^{ij}(KK'), \quad \text{(V.A.7)}$$

which means that $\mathsf{T}(\mathbf{q};\mathbf{R})$ also commutes with m.

We must next demonstrate that $T(\mathbf{q})=\{\mathsf{T}(\mathbf{q};\mathbf{R})\}$ furnishes a multiplier representation of $G_0(\mathbf{q})$, i.e., we must prove, as MV do, that

$$\mathsf{T}(\mathbf{q};\mathbf{R}_i)\mathsf{T}(\mathbf{q};\mathbf{R}_j)=\phi(\mathbf{q};\mathbf{R}_i,\mathbf{R}_j)\mathsf{T}(\mathbf{q};\mathbf{R}_i\mathbf{R}_j), \quad \text{(V.A.8a)}$$

where the multiplier $\phi(\mathbf{q};\mathbf{R}_i,\mathbf{R}_j)$ is given by

$$\phi(\mathbf{q};\mathbf{R}_i,\mathbf{R}_j)=\exp\{i[\mathbf{q}-\mathbf{R}_i^{-1}\mathbf{q}]\cdot\mathbf{V}(R_j)\}. \quad \text{(V.A.8b)}$$

The proof follows almost exactly that given by MV in (3.18) and need not be repeated here. The only additional fact we must remember is that

$$C^l(R_i)C^l(R_j)=C^l(R_iR_j). \quad \text{(V.A.9)}$$

Result (V.A.9) follows since two proper or two improper rotations always combine to give a proper rotation, while a proper and an improper rotation combine to give an improper rotation.

Given the two important facts just discussed, namely, that there exists a set of unitary matrices $T(\mathbf{q})=\{\mathsf{T}(\mathbf{q};\mathbf{R})\}$ $[\mathbf{R}\in G_0(\mathbf{q})]$ which commute with $\mathsf{B}(\mathbf{q})$ as well as with m, and which furnish a $(3\mu+6\nu)$-dimensional (reducible) multiplier representation of $G_0(\mathbf{q})$, we can assert, as MV do, that barring accidental degeneracies (a rare occurrence), the set of eigenvectors $\mathbf{e}(\mathbf{q}\sigma 1)$, $\mathbf{e}(\mathbf{q}\sigma 2)$, $\cdots$, $\mathbf{e}(\mathbf{q}\sigma f_\sigma)$ belonging to the f_σ-fold degenerate eigenvalue $\omega_\sigma{}^2(\mathbf{q})$ will transform according to an IMR of $G_0(\mathbf{q})$. The practical utility of this observation is twofold. Firstly, it enables the eigenvalues and eigenvectors to be classified using group-theoretic labels. Secondly, as in standard lattice dynamics, it suggests that the problem of determining the eigenvalues and eigenvectors can be simplified if one starts with a basis set of $(3\mu+6\nu)$ vectors in the space of $\{\mathbf{e}(\mathbf{q}j)\}$, which have the same transformation properties as do the eigenvectors.

We shall now elaborate on these points. To classify the eigenvalues and eigenvectors, one resorts to the familiar reduction formula

$$c_s=h^{-1}\sum_{\mathbf{R}\in G_0(\mathbf{q})}\chi^{(s)}(\mathbf{q};\mathbf{R})^*\chi(\mathbf{q};\mathbf{R}), \quad \text{(V.A.10)}$$

where

$$\chi^{(s)}(\mathbf{q};\mathbf{R})=\mathrm{Tr}\,[\boldsymbol{\tau}^{(s)}(\mathbf{q};\mathbf{R})],$$
$$\chi(\mathbf{q};\mathbf{R})=\mathrm{Tr}\,[\mathsf{T}(\mathbf{q};\mathbf{R})], \quad \text{(V.A.11)}$$

and h is the order of $G_0(\mathbf{q})$. The quantity c_s in (V.A.10) is the number of times the IMR $\tau^{(s)}(\mathbf{q})$ of dimensionality f_s occurs in the $(3\mu+6\nu)$-dimensional reducible multiplier representation $T(\mathbf{q})$. Correspondingly, there will be c_s eigenvalues $\omega_{s,1}{}^2(\mathbf{q})$, $\omega_{s,2}{}^2(\mathbf{q})$, $\cdots$, $\omega_{s,c_s}{}^2(\mathbf{q})$, each of which will be f_s-fold degenerate. The associated eigenvectors will be labeled

$$\{\mathbf{e}(\mathbf{q}s11),\mathbf{e}(\mathbf{q}s12),\cdots,\mathbf{e}(\mathbf{q}s1f_s)\},$$
$$\{\mathbf{e}(\mathbf{q}s21),\mathbf{e}(\mathbf{q}s22),\cdots,\mathbf{e}(\mathbf{q}s2f_s)\}\cdots,$$
$$\{\mathbf{e}(\mathbf{q}sc_s1),\mathbf{e}(\mathbf{q}sc_s2),\cdots,\mathbf{e}(\mathbf{q}sc_sf_s)\}.$$

In this way, even without solving the problem numerically, we can determine the number of distinct eigenvalues, their degeneracies, and the symmetry properties of the associated eigenvectors.

Next comes the task of simplifying the eigenvalue problem. For this purpose one constructs the projection operator $P_{\lambda\lambda}{}^{(s)}(\mathbf{q})$ defined by

$$P_{\lambda\lambda}{}^{(s)}(\mathbf{q})=(f_s/h)\sum_{\mathbf{R}\in G_0(\mathbf{q})}\tau_{\lambda\lambda}{}^{(s)}(\mathbf{q};\mathbf{R})^*\mathsf{T}(\mathbf{q};\mathbf{R}), \quad \text{(V.A.12)}$$

where $\tau_{\lambda\lambda}{}^{(s)}(\mathbf{q};\mathbf{R})$ is the $\lambda\lambda$th element of the matrix corresponding to the element $\mathbf{R}$ in the IMR $\tau^{(s)}(\mathbf{q})$.[14] By applying this operator systematically on $(3\mu+6\nu)$ orthogonal vectors in the space of $\{\mathbf{e}(\mathbf{q}j)\}$, we can project out c_s orthogonal vectors. These after normalization may be labeled $\xi(\mathbf{q}s1\lambda)$, $\xi(\mathbf{q}s2\lambda)$, $\cdots$, $\xi(\mathbf{q}sc_s\lambda)$. Each of these c_s vectors will transform according to the λth row of the IMR $\tau^{(s)}(\mathbf{q})$. The partners of these vectors may be generated by applying to them the operator

$$P_{\mu\lambda}{}^{(s)}(\mathbf{q})$$
$$=(f_s/h)\sum_{\mathbf{R}\in G_0(\mathbf{q})}\tau_{\mu\lambda}{}^{(s)}(\mathbf{q};\mathbf{R})^*\mathsf{T}(\mathbf{q};\mathbf{R}) \quad (\mu\neq\lambda). \quad \text{(V.A.13)}$$

In this way, we can obtain c_s orthonormal sets

$$\{\xi(\mathbf{q}s11),\cdots,\xi(\mathbf{q}s1f_s)\},$$
$$\{\xi(\mathbf{q}s21),\cdots,\xi(\mathbf{q}s2f_s)\},\cdots,$$
$$\{\xi(\mathbf{q}sc_s1),\cdots,\xi(\mathbf{q}sc_sf_s)\},$$

[14] A systematic method of constructing IMR's has been given by Sahni and Venkataraman (1970). Fairly exhaustive tables of IMR's are available in a book by Kovalev (1964). See also Zak (1969).

corresponding to the c_s occurrences of $\tau^{(s)}(\mathbf{q})$ in $T(\mathbf{q})$. The process can be repeated for all IMR's with nonzero occurrences, and a total of $(3\mu+6\nu)$ vectors $\{\xi(\mathbf{q}sa\lambda)\}$ may be constructed. [s runs over all inequivalent IMR's of $G_0(\mathbf{q})$ which have nonzero occurrence; a is the repetition index and can take values 1, 2, $\cdots$, c_s; λ is the row index and runs over 1, 2, $\cdots$, f_s.] The symmetry-adapted vectors $\{\xi(\mathbf{q}sa\lambda)\}$ have the virtue that in terms of these

$$\left.\begin{aligned}\xi^+(\mathbf{q}s'a'\lambda')\,\mathsf{B}(\mathbf{q})\,\xi(\mathbf{q}sa\lambda)=0\\ \xi^+(\mathbf{q}s'a'\lambda')\,\mathsf{m}\xi(\mathbf{q}sa\lambda)=0\end{aligned}\right\}\text{unless } s=s' \text{ and } \lambda=\lambda'. \tag{V.A.14}$$

This is the statement of the usual matrix element theorem. Equation (V.A.14) shows that if we were to construct a $(3\mu+6\nu)$-dimensional matrix $\boldsymbol{\xi}(\mathbf{q})$ similar to $\mathsf{e}(\mathbf{q})$, then $\boldsymbol{\xi}^+(\mathbf{q})\mathsf{B}(\mathbf{q})\boldsymbol{\xi}(\mathbf{q})$ will be block diagonal if in assembling $\boldsymbol{\xi}(\mathbf{q})$, we group all symmetry vectors belonging to the same s and same λ together. If the IMR $\tau^{(s)}(\mathbf{q})$ of dimensionality f_s occurs c_s times in $T(\mathbf{q})$, then there will be f_s diagonal blocks each of dimensionality c_s. m also will be transformed by $\boldsymbol{\xi}(\mathbf{q})$ into a similar structure.

The problem of finding the eigenvalues is thus simplified and it is possible to deal with those belonging to different IMR's separately. Thus, to find $\omega_{s,1}^2(\mathbf{q})$, $\cdots$, $\omega_{s,c_s}^2(\mathbf{q})$, we have only to consider one of the c_s dimensional blocks mentioned above. The explicit equations to be solved are obtained as follows:

Let us write

$$\mathsf{e}(\mathbf{q}sa\lambda)=\sum_{b=1}^{c_s}M(sa\lambda,\,sb\lambda)\,\xi(\mathbf{q}sb\lambda), \tag{V.A.15}$$

where $M(sa\lambda,\,sb\lambda)$ are complex coefficients. [Group theory forbids the inclusion on the right-hand side, of symmetry vectors which do not transform according to the λth row of $\tau^{(s)}(\mathbf{q})$.] Substitute (V.A.15) in the equation

$$\mathsf{B}(\mathbf{q})\,\mathsf{e}(\mathbf{q}sa\lambda)=\omega^2(\mathbf{q})\,\mathsf{me}(\mathbf{q}sa\lambda). \tag{V.A.16}$$

We get

$$\sum_{b=1}^{c_s}\mathsf{B}(\mathbf{q})\,\xi(\mathbf{q}sb\lambda)M(sa\lambda,\,sb\lambda)$$

$$=\omega^2(\mathbf{q})\sum_{b'=1}^{c_s}\mathsf{m}\xi(\mathbf{q}sb'\lambda)M(sa\lambda,\,sb'\lambda).$$

Multiplying both sides from the left by $\xi^+(\mathbf{q}sb''\lambda)$, where b'' is one of the set 1, 2, $\cdots$, c_s, and subsequently rearranging, we obtain

$$\sum_{b=1}^{c_s}\{\xi^+(\mathbf{q}sb'\lambda)\,(\mathsf{B}(\mathbf{q})-\omega^2(\mathbf{q})\,\mathsf{m})\xi(\mathbf{q}sb\lambda)\}$$

$$\times M(sa\lambda,\,sb\lambda)=0\quad(b'=1,\,2,\,\cdots,\,c_s). \tag{V.A.17}$$

The condition for which this system of c_s equations has nontrivial solutions for the coefficients $M(sa\lambda,\,sb\lambda)$ is that

$$|\,\xi^+(\mathbf{q}sb'\lambda)\,\mathsf{B}(\mathbf{q})\,\xi(\mathbf{q}sb\lambda)$$

$$-\omega^2(\mathbf{q})\,\xi^+(\mathbf{q}sb'\lambda)\,\mathsf{m}\xi(\mathbf{q}sb\lambda)\,|=0. \tag{V.A.18}$$

This determinantal equation must be solved by brute force, no further simplification due to symmetry being possible. However, it is a much simpler equation than the full determinantal equation (II.A.29). Solving the above equation gives the c_s distinct eigenvalues $\omega_{s,1}^2(\mathbf{q}),\cdots,\omega_{s,c_s}^2(\mathbf{q})$ corresponding to the IMR $\tau^{(s)}(\mathbf{q})$. The complex coefficients $M(sa\lambda,\,sb\lambda)$ are then solved for by introducing these frequencies successively in (V.A.17). Actually, since the equations are homogeneous, one can solve only for (c_s-1) complex quantities [or equivalently $(2c_s-2)$ real quantities]. The remaining one is fixed (to within an arbitrary phase factor) by the normalization constraint

$$\mathsf{e}^+(\mathbf{q}sa\lambda)\,\mathsf{me}(\mathbf{q}sa\lambda)=M,$$

where M is the mass of the primitive unit cell. [Recall (II.A.33).] This completes the problem as far as eigenvalues and eigenvectors pertaining to the IMR $\tau^{(s)}(\mathbf{q})$ are concerned.

We see in this way that the dynamical problem can be broken down into a number of smaller problems using the methods of group theory. Note in particular that if $c_s=1$, then (V.A.17) simplifies to

$$\xi^+(\mathbf{q}s\lambda)\,\mathsf{B}(\mathbf{q})\,\xi(\mathbf{q}s\lambda)=\omega_s^2(\mathbf{q})\,\xi^+(\mathbf{q}s\lambda)\,\mathsf{m}\xi(\mathbf{q}s\lambda)$$

or

$$\omega_s^2(\mathbf{q})=[\xi^+(\mathbf{q}s\lambda)\,\mathsf{B}(\mathbf{q})\,\xi(\mathbf{q}s\lambda)][\xi^+(\mathbf{q}s\lambda)\,\mathsf{m}\xi(\mathbf{q}s\lambda)]^{-1}.$$

In other words, the frequency corresponding to an IMR which occurs only once, is obtainable purely from group-theoretic considerations, no further diagonalization as in (V.A.18) being necessary. Additionally, if $\xi(\mathbf{q}s\lambda)$ is so scaled that

$$\xi^+(\mathbf{q}s\lambda)\,\mathsf{m}\xi(\mathbf{q}s\lambda)=M,$$

then $\xi(\mathbf{q}s\lambda)$ is the eigenvector for that mode.

Besides space-group symmetry (with which we have so far been concerned), consideration must also be given to the effects of time-reversal symmetry. MV have given a thorough discussion of this topic, and their arguments follow through completely in the present case, too. The only minor modification required to their work concerns the definition of the anti-unitary operator $\mathsf{T}(\mathbf{q};\,\mathsf{S}_-\mathsf{R})$. This is defined by

$$\mathsf{T}(\mathbf{q};\,\mathsf{S}_-\mathsf{R})=K_0\exp\{-i\mathbf{q}\cdot[\mathbf{V}(S_-R)+\mathbf{X}(m)]\}$$

$$\times\boldsymbol{\Gamma}(\mathbf{q};\,\{\mathsf{S}_-\mathsf{R}\,|\,\mathbf{V}(S_-R)+\mathbf{X}(m)\}), \tag{V.A.19}$$

where K_0 is the complex conjugation operator and $\{\mathsf{S}_-\mathsf{R}\,|\,\mathbf{V}(S_-R)+\mathbf{X}(m)\}$ is a space-group operation whose rotational part $\mathsf{S}_-\mathsf{R}$ is such that

$$(\mathsf{S}_-\mathsf{R})\,\mathbf{q}=-\mathbf{q}\quad\text{or}\quad(\mathsf{G}-\mathbf{q}).$$

Structurally, (V.A.19) is identical with MV's (3.40a). However, the matrix $\mathbf{\Gamma}$ in the present case must be constructed as in (V.A.1). By using the same kind of arguments as used by MV, it can be shown that the matrix defined in (V.A.19) commutes with $\mathbf{B}(\mathbf{q})$ and also $\mathbf{m}$. This fact is of value in discussing the additional degeneracies (if any) produced by time-reversal symmetry, and in determining the structure of the dynamical matrix, as has been pointed out by MV.

The foregoing considerations pertain to the dynamics in the fixed frame. Essentially the same considerations apply to the principal-axes case also. In detail, however, small differences of practical importance need to be noted, particularly, in regard to the construction of symmetry-adapted vectors. One could use the projection operator technique as described earlier and construct $\xi(\mathbf{q}sa\lambda)$ from which $\xi^P(\mathbf{q}sa\lambda)$ may be arrived at via the transformation

$$\xi^{i,P}(\kappa \mid \mathbf{q}sa\lambda) = \mathbf{A}(\kappa)\xi^i(\kappa \mid \mathbf{q}sa\lambda). \qquad \text{(V.A.20)}$$

Alternately, one could redefine $\mathbf{T}(\mathbf{q};\mathbf{R})$ and build into it the transformation of axes. Thus one could work with $\mathbf{T}^P(\mathbf{q};\mathbf{R})$ with elements

$$T_{\alpha\beta}^{ij,P}(\kappa\kappa' \mid \mathbf{q};\mathbf{R}) = \mathfrak{R}_{\alpha\beta}(\kappa'\kappa)C^i(R)\delta_{ij}\delta(\kappa, F_0(\kappa';R)) \times \exp\{i\mathbf{q}\cdot[\mathbf{X}(\kappa)-\mathbf{R}\mathbf{X}(\kappa')]\}, \qquad \text{(V.A.21a)}$$

where

$$\mathfrak{R}_{\alpha\beta}(\kappa'\kappa) = [\mathbf{A}(\kappa)\mathbf{R}\mathbf{A}^{\mathrm{tr}}(\kappa')]_{\alpha\beta}. \qquad \text{(V.A.21b)}$$

[Recall (II.B.7).] Note that

$$= \mathrm{Tr}\,\mathfrak{R}(\kappa\kappa) = \mathrm{Tr}\,\mathbf{R}$$

from which it readily follows that

$$\mathrm{Tr}\,[\mathbf{T}(\mathbf{q};\mathbf{R})] = \mathrm{Tr}\,[\mathbf{T}^P(\mathbf{q};\mathbf{R})],$$

a result which is to be expected. This means that if one is *just* interested in determining the number of occurrences c_s, then the reduction formulas (V.A.10) and (V.A.11) may be employed rather than the one involving the more cumbersome $\mathbf{T}^P(\mathbf{q};\mathbf{R})$, even though the dynamics as such might be considered in the principal-axes frame.

We might mention here that if, in addition to employing the principal-axes frame, one also uses weighted displacements, then the eigenvalue problem assumes a simpler form as in standard lattice dynamics [see (II.A.27) and (II.B.24)]. In this case, the formal theory of MV can be borrowed almost intact with slight redefinitions as indicated above.

In Sec. II, we remarked (without giving details) that the dynamical matrix, eigenfrequencies, and eigenvectors exhibit symmetries related to the rotational symmetry of the crystal. These can be established using group-theoretical arguments. Firstly, it can be shown that

$$\mathbf{\Gamma}(\mathbf{q};\mathcal{S}_m)\mathbf{B}(\mathbf{q})\mathbf{\Gamma}^+(\mathbf{q};\mathcal{S}_m) = \mathbf{B}(\mathbf{Sq}). \qquad \text{(V.A.22)}$$

[See also Eq. (3.5) in MV.] The matrices $\mathbf{B}(\mathbf{q})$ and $\mathbf{B}(\mathbf{Sq})$ are thus related to each other by a unitary transformation. Further, it is easy to prove as in (V.A.7) that

$$\mathbf{\Gamma}(\mathbf{q};\mathcal{S}_m)\mathbf{m}\mathbf{\Gamma}^+(\mathbf{q};\mathcal{S}_m) = \mathbf{m}. \qquad \text{(V.A.23)}$$

It follows immediately that the sets of eigenvalues $\{\omega_j^2(\mathbf{Sq})\}$ and $\{\omega^2(\mathbf{q})\}$ are identical. By a suitable labeling of the branch indices, we therefore have

$$\omega_j(\mathbf{q}) = \omega_j(\mathbf{Sq}). \qquad \text{(V.A.24)}$$

Finally, the eigenvector $\mathbf{e}(\mathbf{S}\mathbf{q}j)$ is related to $\mathbf{e}(\mathbf{q}j)$ by

$$\mathbf{e}(\mathbf{S}\mathbf{q}j) = \text{phase factor} \times \mathbf{\Gamma}(\mathbf{q};\mathcal{S}_m)\mathbf{e}(\mathbf{q}j).$$

Following MV, we choose the phase factor such that

$$\mathbf{e}(\mathbf{S}\mathbf{q}j) = \mathbf{\Gamma}(\mathbf{q};\{\mathbf{S} \mid \mathbf{V}(S)\})\mathbf{e}(\mathbf{q}j), \qquad \text{(V.A.25)}$$

which exhibits the relationship of the eigenvectors associated with different vectors in the star of $\mathbf{q}$.

It is appropriate at this juncture to comment on the work of Chen and Dvorak (1968). As already mentioned, this represents the first attempt to apply group-theoretical considerations to external modes with $\mathbf{q}\neq 0$. Chen and Dvorak work with $G(\mathbf{q})$ and matrices which are closely related to our $\mathbf{\Gamma}(\mathbf{q},\mathcal{R}_m)$. The small differences in the phase factors as compared to the elements of our matrices arise from the fact that they define $u_\alpha^i(l\kappa)$ as

$$u_\alpha^i(l\kappa) = U_\alpha^i(\kappa \mid \mathbf{q})\exp\{i[\mathbf{q}\cdot(\mathbf{X}(l)+\mathbf{X}(\kappa))-\omega(\mathbf{q})t]\}$$

instead of as in (II.A.20). Further, judging from the absence of off-diagonal inertia components in their equations of motion, it would appear that they are considering the dynamics in the principal-axis frame although no explicit statement to that effect is made. The appropriate reinterpretation required for $\mathbf{R}$ [see Eq. (V.A.21b)] in this connection has, however, not been pointed out by them. It turns out that the distinction between $\mathbf{R}$ and $\mathfrak{R}$ is not important in all the crystals considered by them as examples, viz., hexamine, adamantane, and NH_4Cl, which is perhaps why they omitted to offer the necessary clarification.

B. An Example

We shall consider a detailed example by way of illustrating the application of group theory to the study of external modes. The crystal we shall discuss will be $CaWO_4$, which has been investigated by infrared experiments (Barker, 1964), Raman scattering (Russel and Loudon, 1965; Porto and Scott, 1967), and slow-neutron scattering (King and Steinman, 1969).

$CaWO_4$ belongs to the space group C_{4h}^6. The tetragonal unit cell has four molecules and is shown in Fig. 26. The primitive cell, however, contains only two molecules, the Cartesian coordinates of the various ions

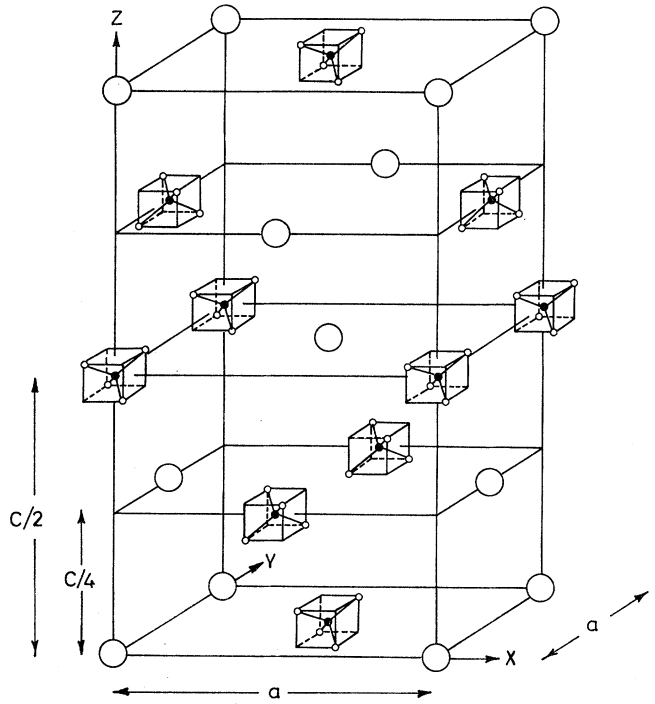

FIG. 26. Tetragonal unit cell of $CaWO_4$.

being

Ca 1 ($\kappa=1$)	$(0, 0, 0)$
Ca 2 ($\kappa=2$)	$(0, \frac{1}{2}a, \frac{1}{4}c)$
WO_4 1 ($\kappa=3$)	$(\frac{1}{2}a, \frac{1}{2}a, 0)$
WO_4 2 ($\kappa=4$)	$(\frac{1}{2}a, 0, \frac{1}{4}c)$.

a and c are the unit cell parameters. The basis vectors of the direct lattice are chosen to be

$$\mathbf{a}_1=\tfrac{1}{2}a\mathbf{i}+\tfrac{1}{2}a\mathbf{j}-\tfrac{1}{2}c\mathbf{k},$$
$$\mathbf{a}_2=\tfrac{1}{2}a\mathbf{i}-\tfrac{1}{2}a\mathbf{j}+\tfrac{1}{2}c\mathbf{k},$$
$$\mathbf{a}_3=-\tfrac{1}{2}a\mathbf{i}+\tfrac{1}{2}a\mathbf{j}+\tfrac{1}{2}c\mathbf{k}. \qquad \text{(V.B.1)}$$

The basis vectors of the reciprocal lattice are therefore given by

$$\mathbf{b}_1=(2\pi/a)\mathbf{i}+(2\pi/a)\mathbf{j},$$
$$\mathbf{b}_2=(2\pi/a)\mathbf{i}+(2\pi/c)\mathbf{k},$$
$$\mathbf{b}_3=(2\pi/a)\mathbf{j}+(2\pi/c)\mathbf{k}. \qquad \text{(V.B.2)}$$

The shape of the Brillouin zone depends on the (c/a) ratio. If $(c/a)>\sqrt{2}$, a condition that is fulfilled in $CaWO_4$, then the Brillouin zone is as in Fig. 27.

Now the WO_4^{--} ion in $CaWO_4$ is very nearly a spherical top.[11] Approximating it as such, we may choose the principal axes at will; for convenience we shall choose them to be parallel to the crystal-fixed Cartesian axes illustrated in Fig. 26. Furthermore, we shall absorb the mass and moment-of-inertia factors into the dynamical matrix and write it as

$$\mathbf{D}(\mathbf{q})=\begin{bmatrix}
\mathbf{D}^{tt}(\mathbf{q},11) & \mathbf{D}^{tt}(\mathbf{q},12) & \mathbf{D}^{tt}(\mathbf{q},13) & \mathbf{D}^{tr}(\mathbf{q},13) & \mathbf{D}^{tt}(\mathbf{q},14) & \mathbf{D}^{tr}(\mathbf{q},14)\\
\mathbf{D}^{tt}(\mathbf{q},21) & \mathbf{D}^{tt}(\mathbf{q},22) & \mathbf{D}^{tt}(\mathbf{q},23) & \mathbf{D}^{tr}(\mathbf{q},23) & \mathbf{D}^{tt}(\mathbf{q},24) & \mathbf{D}^{tr}(\mathbf{q},24)\\
\mathbf{D}^{tt}(\mathbf{q},31) & \mathbf{D}^{tt}(\mathbf{q},32) & \mathbf{D}^{tt}(\mathbf{q},33) & \mathbf{D}^{tr}(\mathbf{q},33) & \mathbf{D}^{tt}(\mathbf{q},34) & \mathbf{D}^{tr}(\mathbf{q},34)\\
\mathbf{D}^{rt}(\mathbf{q},31) & \mathbf{D}^{rt}(\mathbf{q},32) & \mathbf{D}^{rt}(\mathbf{q},33) & \mathbf{D}^{rr}(\mathbf{q},33) & \mathbf{D}^{rt}(\mathbf{q},34) & \mathbf{D}^{rr}(\mathbf{q},34)\\
\mathbf{D}^{tt}(\mathbf{q},41) & \mathbf{D}^{tt}(\mathbf{q},42) & \mathbf{D}^{tt}(\mathbf{q},43) & \mathbf{D}^{tr}(\mathbf{q},43) & \mathbf{D}^{tt}(\mathbf{q},44) & \mathbf{D}^{tr}(\mathbf{q},44)\\
\mathbf{D}^{rt}(\mathbf{q},41) & \mathbf{D}^{rt}(\mathbf{q},42) & \mathbf{D}^{rt}(\mathbf{q},43) & \mathbf{D}^{rr}(\mathbf{q},43) & \mathbf{D}^{rt}(\mathbf{q},44) & \mathbf{D}^{rr}(\mathbf{q},44)
\end{bmatrix}. \qquad \text{(V.B.3)}$$

Here, we have

$$D_{\alpha\beta}{}^{ii'}(\mathbf{q},\kappa\kappa')=\{m_{\alpha\alpha}{}^{ii}(\kappa\kappa)m_{\beta\beta}{}^{i'i'}(\kappa'\kappa')\}^{-1/2}\times\sum_{l'}\phi_{\alpha\beta}{}^{ii'}(0\kappa;l'\kappa')\exp[i\mathbf{q}\cdot\mathbf{X}(l')], \qquad \text{(V.B.4)}$$

with

$$m_{\alpha\alpha}{}^{ii}(\kappa\kappa)=m_\kappa;\quad i=t,\quad \alpha=x,y,z,\quad \kappa=1,\cdots,4;$$
$$=I;\quad i=r,\quad \alpha=x,y,z,\quad \kappa=3,4.$$

I denotes the moment of inertia of the WO_4^{--} ion.

We consider the symmetry aspects for $\mathbf{q}$ along Λ. Specifically, we shall

(i) classify the external modes at Λ using group-theoretic labels;
(ii) construct symmetry-adapted vectors for Λ using projection operator techniques;
(iii) discuss the restrictions on the structure of the dynamical matrix for the point Λ imposed by crystal symmetry;
(iv) block diagonalize the dynamical matrix so constructed.

The elements of the space group of $CaWO_4$ are given by

$$\{\mathsf{E}\mid 0\},\quad \{\mathsf{C}_4[001]\mid \tau\},\quad \{\mathsf{C}_2[001]\mid 0\},$$
$$\{\mathsf{C}_4^{-1}[001]\mid \tau\},\quad \{\sigma(001)\mid \tau\},\quad \{\mathsf{S}_4[001]\mid 0\},$$
$$\{\mathsf{I}\mid \tau\},\quad \{\mathsf{S}_4^{-1}[001]\mid 0\},$$

and products of these with translational elements $\mathcal{E}_m=\{\mathsf{E}\mid m_1\mathbf{a}_1+m_2\mathbf{a}_2+m_3\mathbf{a}_3\}$, where m_1, m_2, m_3 are integers and $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are as in (V.B.1). τ is a fractional translation given by

$$\tau=\tfrac{1}{2}a\mathbf{i}+\tfrac{1}{4}c\mathbf{k}.$$

The other symbols have the following meanings:

$\mathsf{C}_n[uvw]$ anticlockwise rotation by $(2\pi/n)$ about the direction $[uvw]$;
$\mathsf{S}_n[uvw]$ $\mathsf{C}_n[uvw]$ followed by a reflection in a plane normal to $[uvw]$;
$\sigma(uvw)$ reflection in the plane (uvw);
I inversion.

The three-dimensional matrices corresponding to the various point group operations are shown in Table V.

The point group $G_0(\Lambda)$ corresponding to the point Λ is isomorphic to the molecular point group C_4. The IMR's are all one dimensional and are listed in Table VI.

Consider now the classification of the modes at Λ. This requires first the construction of the set of matrices

$$T(\Lambda)=\{\mathsf{T}(\Lambda;\mathsf{R})\}\quad [\mathsf{R}\in G_0(\Lambda)].$$

The exponential factors $\exp\{i\mathbf{q}\cdot[\mathbf{X}(\kappa)-\mathsf{R}\mathbf{X}(\kappa')]\}$ necessary for this purpose [see Eq. (V.A.2b)] are summarized in Table VII. Using this table, the T matrices are found to be

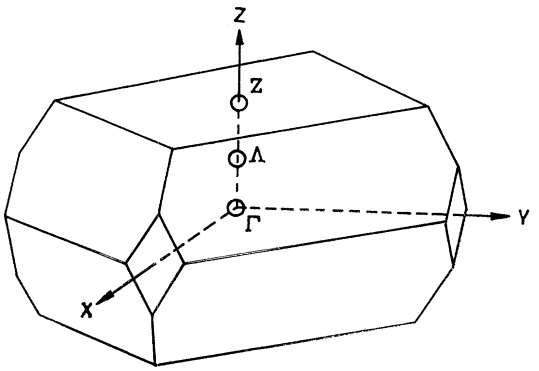

FIG. 27. Brillouin zone for $CaWO_4$.

$$\mathsf{T}(\Lambda;\mathsf{E})=\begin{bmatrix}\mathsf{A}_1 & \cdot & \cdot & \cdot\\ \cdot & \mathsf{A}_1 & \cdot & \cdot\\ \cdot & \cdot & \mathsf{B}_1 & \cdot\\ \cdot & \cdot & \cdot & \mathsf{B}_1\end{bmatrix};$$

$$\mathsf{A}_1=\mathsf{E},$$

$$\mathsf{B}_1=\begin{bmatrix}\mathsf{E} & \\ & \mathsf{E}\end{bmatrix},\qquad \text{(V.B.5a)}$$

$$\mathsf{T}(\Lambda;\mathsf{C}_4[001])=\begin{bmatrix}\cdot & \mathsf{A}_2 & \cdot & \cdot\\ \mathsf{A}_2^{*} & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \mathsf{B}_2\\ \cdot & \cdot & \mathsf{B}_2^{*} & \cdot\end{bmatrix};$$

$$\mathsf{A}_2=u\mathsf{C}_4[001],$$

$$\mathsf{B}_2=u\begin{bmatrix}\mathsf{C}_4[001] & \\ & \mathsf{C}_4[001]\end{bmatrix},\qquad \text{(V.B.5b)}$$

$$\mathsf{T}(\Lambda;C_2[001])=\begin{bmatrix}\mathsf{A}_3 & \cdot & \cdot & \cdot\\ \cdot & \mathsf{A}_3 & \cdot & \cdot\\ \cdot & \cdot & \mathsf{B}_3 & \cdot\\ \cdot & \cdot & \cdot & \mathsf{B}_3\end{bmatrix};$$

$$\mathsf{A}_3=\mathsf{C}_2[001],$$

$$\mathsf{B}_3=\begin{bmatrix}\mathsf{C}_2[001] & \\ & \mathsf{C}_2[001]\end{bmatrix},\qquad \text{(V.B.5c)}$$

$$\mathsf{T}(\Lambda;\mathsf{C}_4^{-1}[001])=\begin{bmatrix}\cdot & \mathsf{A}_4 & \cdot & \cdot\\ \mathsf{A}_4^{*} & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \mathsf{B}_4\\ \cdot & \cdot & \mathsf{B}_4^{*} & \cdot\end{bmatrix};$$

$$\mathsf{A}_4=u\mathsf{C}_4^{-1}[001],$$

$$\mathsf{B}_4=u\begin{bmatrix}\mathsf{C}_4^{-1}[001] & \\ & \mathsf{C}_4^{-1}[001]\end{bmatrix}.$$

(V.B.5d)

The traces of these matrices are easily determined to be

$$\chi(\Lambda;\mathbf{E})=18,$$
$$\chi(\Lambda;\mathbf{C}_4[001])=0,$$
$$\chi(\Lambda;\mathbf{C}_2[001])=-6,$$
$$\chi(\Lambda;\mathbf{C}_4^{-1}[001])=0. \qquad \text{(V.B.6)}$$

The decomposition of $T(\Lambda)$ is now immediately effected using (V.A.10), and the results are summarized in the last column of Table VI.

Next we take up the construction of the symmetry vectors. This is done through the use of the projection-operator technique outlined in the previous subsection. Actually, the situation is quite simple in the present case since we have only one-dimensional IMR's to deal with.

Consider $P(\Lambda_1)$ where

$$P(\Lambda_1)=\sum_{\mathbf{R}\in G_0(\Lambda)}\chi^*(\Lambda_1;\mathbf{R})T(\Lambda;\mathbf{R}). \qquad \text{(V.B.7)}$$

The quantity $\chi(\Lambda_1;\mathbf{R})$ is the character corresponding to element $\mathbf{R}$ in the IMR Λ_1. In writing (V.B.7) we have omitted the usual group-theoretic normalization factor (f_s/h) [see (V.A.12)] since we shall be normalizing the symmetry adapted vectors anyway. Using Table V and the matrices $\mathbf{T}(\Lambda;\mathbf{R})$ given in (V.B.5), it is easily seen that

$$P(\Lambda_1)=\begin{bmatrix} \mathbf{A} & \mathbf{A}u & 0 & 0 & 0 & 0 \\ \mathbf{A}u^* & \mathbf{A} & 0 & 0 & 0 & 0 \\ 0 & 0 & \mathbf{A} & 0 & \mathbf{A}u & 0 \\ 0 & 0 & 0 & \mathbf{A} & 0 & \mathbf{A}u \\ 0 & 0 & \mathbf{A}u^* & 0 & \mathbf{A} & 0 \\ 0 & 0 & 0 & \mathbf{A}u^* & 0 & \mathbf{A} \end{bmatrix},$$

with

$$\mathbf{A}=\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 2 \end{bmatrix}.$$

By applying this operator systematically on the 18 orthonormal basis vectors

$$\begin{bmatrix}1\\0\\0\\\vdots\\0\\0\end{bmatrix}\begin{bmatrix}0\\1\\0\\\vdots\\0\\0\end{bmatrix}\cdots\begin{bmatrix}0\\0\\0\\\vdots\\0\\1\end{bmatrix}\quad\begin{matrix}\uparrow\\ 18\text{ elements}\\ \downarrow\end{matrix}$$

spanning the 18-dimensional space of the present problem, we can project out six nonzero vectors of which only three are linearly independent. These, after normalization, have the following components:

$$\begin{bmatrix}0\\0\\1/\sqrt{2}\\0\\0\\u^*/\sqrt{2}\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\end{bmatrix}\begin{bmatrix}0\\0\\0\\0\\0\\0\\0\\1/\sqrt{2}\\0\\0\\0\\0\\0\\u^*/\sqrt{2}\\0\\0\end{bmatrix}\begin{bmatrix}0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\1/\sqrt{2}\\0\\0\\0\\0\\0\\u^*/\sqrt{2}\end{bmatrix}$$

$\uparrow$ Ca:1 trans. components $\downarrow$

$\uparrow$ Ca:2 trans. components $\downarrow$

$\uparrow$ WO_4:3 trans. components $\downarrow$

$\uparrow$ WO_4:3 rot. components $\downarrow$

$\uparrow$ WO_4:4 trans. components $\downarrow$

$\uparrow$ WO_4:4 rot. components. $\downarrow$

(V.B.8)

By following a similar procedure, we can construct three vectors transforming according to Λ_2, and two sets of six vectors each transforming according to Λ_3 and Λ_4. These are then assembled into the matrix $\boldsymbol{\xi}(\Lambda)$ as shown on page 459.

As already pointed out, the eigenvectors are linear combinations of symmetry-adapted vectors having the same transformation properties. Thus, in the present problem, the three eigenvectors $\mathbf{e}(\Lambda_1, a)$ $(a=1, 2, 3)$ will be linear combinations of the three symmetry vectors corresponding to Λ_1 given in (V.B.8).

It is clear that even without solving the full problem, we can make some comments about the eigenvectors. We can, for example, say that

(i) the Λ_1 modes involve only the translations of the Ca^{++} and WO_4^{--} ions along the z axis, and their

$$\xi(\Lambda)=\begin{bmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & 0 \\
1/\sqrt{2} & 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -iu^*/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & iu^*/\sqrt{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & iu^*/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & -iu^*/\sqrt{2} & 0 & 0 & 0 & 0 & 0 \\
u^*/\sqrt{2} & 0 & 0 & -u^*/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 1/\sqrt{2} & 0 & 0 \\
0 & 1/\sqrt{2} & 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 1/\sqrt{2} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 1/\sqrt{2} \\
0 & 0 & 1/\sqrt{2} & 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -iu^*/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & iu^*/\sqrt{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & iu^*/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & -iu^*/\sqrt{2} & 0 & 0 & 0 \\
0 & u^*/\sqrt{2} & 0 & 0 & -u^*/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -iu^*/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & iu^*/\sqrt{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & iu^*/\sqrt{2} & 0 & 0 & 0 & 0 & -iu^*/\sqrt{2} & 0 & \\
0 & 0 & u^*/\sqrt{2} & 0 & 0 & -u^*/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{bmatrix}.$$

Λ_1 Λ_2 Λ_3 Λ_4

(V.B.9)

TABLE V. Three-dimensional matrices for the point-group operations of C_{4h}^6.

$$E=\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix} \qquad \sigma(001)=\begin{bmatrix}1&0&0\\0&1&0\\0&0&-1\end{bmatrix}$$

$$C_4[001]=\begin{bmatrix}0&-1&0\\1&0&0\\0&0&1\end{bmatrix} \qquad S_4[001]=\begin{bmatrix}0&-1&0\\1&0&0\\0&0&-1\end{bmatrix}$$

$$C_2[001]=\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix} \qquad I=\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&-1\end{bmatrix}$$

$$C_4^{-1}[001]=\begin{bmatrix}0&1&0\\-1&0&0\\0&0&1\end{bmatrix} \qquad S_4^{-1}[001]=\begin{bmatrix}0&1&0\\-1&0&0\\0&0&-1\end{bmatrix}$$

librations about the z axis,

(ii) the librations and translations are coupled.

This should serve to illustrate the significance and importance of constructing the symmetry vectors. In addition, of course $\xi(\Lambda)$ serves to transform $D(\Lambda)$ into block-diagonal form. Before carrying out this transformation, we need first to discuss the restrictions imposed by symmetry on the structure of $D(\Lambda)$.

TABLE VI. IMR's for $G_0(\Lambda)$ and the decomposition of $T(\Lambda)$.

IMR	E	$C_4[001]$	$C_2[001]$	$C_4^{-1}[001]$	c_{Λ_i}
Λ_1	1	1	1	1	3
Λ_2	1	−1	1	−1	3
Λ_3	1	i	−1	$-i$	6
Λ_4	1	$-i$	−1	i	6
$\mathrm{Tr}T(\Lambda;R)$	18	0	−6	0	

TABLE VII. Exponential factors for $\Lambda[=(0, 0, 2\pi\eta/c)]$. Only the factors for those pairs of sublattices which are interchanged consequent to the symmetry operation, are listed. The factors for all other sublattice pairs are irrelevant. In this context observe that interchanges are possible only between sublattices occupied by chemically identical units.[a]

$\kappa\kappa'$	E	$C_4[001]$	$C_2[001]$	$C_4^{-1}[001]$
11	1		1	
12		u		u
21		u^*		u^*
22	1		1	
33	1		1	
34		u		u
43		u^*		u^*
44	1		1	

[a] $u=\exp(-i\pi\eta/2)$.

The over-all structure of $D(q)$ has been previously indicated in (V.B.3). Let us write it more compactly as

$$\begin{array}{c} \\ 3\\3\\6\\6 \end{array}\begin{array}{c} \begin{matrix}3&3&6&6\end{matrix}\\ \begin{bmatrix}D(q,11)&D(q,12)&D(q,13)&D(q,14)\\D(q,21)&D(q,22)&D(q,23)&D(q,24)\\D(q,31)&D(q,32)&D(q,33)&D(q,34)\\D(q,41)&D(q,42)&D(q,43)&D(q,44)\end{bmatrix} \end{array}. \tag{V.B.10}$$

The numbers along the borders signify the dimensions of the matrices along the edge concerned.

Now it is possible to discover interrelations among the elements of $D(\Lambda)$ using purely symmetry arguments. This is analogous to the simplification of the force constant matrices. (See for example, Sec. III.) The simplifications sought for arise basically from the commutation relation (V.A.6). To illustrate, let us take R to be $C_4^{-1}[001]$ and evaluate

$$T(\Lambda;C_4^{-1}[001])D(\Lambda)T^+(\Lambda;C_4^{-1}[001]).$$

Using (V.B.5d), we obtain

$$\begin{bmatrix}A_4D(\Lambda,22)A_4^+ & A_4D(\Lambda,21)A_4^{tr} & A_4D(\Lambda,24)B_4^+ & A_4D(\Lambda,23)B_4^{tr}\\ A_4{}^*D(\Lambda,12)A_4^+ & A_4{}^*D(\Lambda,11)A_4^{tr} & A_4{}^*D(\Lambda,14)B_4^+ & A_4{}^*D(\Lambda,13)B_4^{tr}\\ B_4D(\Lambda,42)A_4^+ & B_4D(\Lambda,41)A_4^{tr} & B_4D(\Lambda,44)B_4^+ & B_4D(\Lambda,43)B_4^{tr}\\ B_4{}^*D(\Lambda,32)A_4^+ & B_4{}^*D(\Lambda,31)A_4^{tr} & B_4{}^*D(\Lambda,34)B_4^+ & B_4{}^*D(\Lambda,33)B_4^{tr}\end{bmatrix}. \tag{V.B.11}$$

Comparing (V.B.10) and (V.B.11), we get

$$\mathbf{A}_4\mathbf{D}(\Lambda, 22)\mathbf{A}_4^{+}=\mathbf{D}(\Lambda, 11), \qquad \text{(V.B.12a)}$$

$$\mathbf{A}_4{}^{*}\mathbf{D}(\Lambda, 11)\mathbf{A}_4^{tr}=\mathbf{D}(\Lambda, 22), \qquad \text{(V.B.12b)}$$

$$\mathbf{A}_4{}^{*}\mathbf{D}(\Lambda, 12)\mathbf{A}_4^{+}=\mathbf{D}(\Lambda, 21), \quad \text{etc.} \qquad \text{(V.B.12c)}$$

Consider Eqs. (V.B.12a) and (V.B.12b). From these we get upon simplification the interrelations

$$\begin{aligned} &D_{yz}{}^{tt}(\Lambda, 11)=D_{zx}{}^{tt}(\Lambda, 11)\\ &=D_{xz}{}^{tt}(\Lambda, 22)=D_{zy}{}^{tt}(\Lambda, 22)=0;\\ &D_{xx}{}^{tt}(\Lambda, 11)=D_{yy}{}^{tt}(\Lambda, 22);\\ &D_{yx}{}^{tt}(\Lambda, 11)=-D_{xy}{}^{tt}(\Lambda, 22);\\ &D_{zz}{}^{tt}(\Lambda, 11)=D_{zz}{}^{tt}(\Lambda, 22);\\ &D_{yy}{}^{tt}(\Lambda, 11)=D_{xx}{}^{tt}(\Lambda, 22). \end{aligned}$$

We can therefore write $\mathbf{D}(\Lambda, 11)$ and $\mathbf{D}(\Lambda, 22)$ quite generally as

$$\mathbf{D}(\Lambda, 11)=\begin{bmatrix} \alpha(11) & \beta(11) & 0\\ \beta^{*}(11) & \gamma(11) & 0\\ 0 & 0 & \delta(11) \end{bmatrix},$$

$$\mathbf{D}(\Lambda, 22)=\begin{bmatrix} \gamma(11) & -\beta^{*}(11) & 0\\ -\beta(11) & \alpha(11) & 0\\ 0 & 0 & \delta(11) \end{bmatrix}. \qquad \text{(V.B.13)}$$

Here we have used Greek symbols to denote the distinct matrix elements. We observe that as a consequence of crystal symmetry, the elements of $\mathbf{D}(\Lambda, 22)$ can be specified in terms of those of $\mathbf{D}(\Lambda, 11)$.

Next, considering (V.B.12c) and remembering further that $\mathbf{D}(\Lambda, 21)=\mathbf{D}^{+}(\Lambda, 12)$, we can write $\mathbf{D}(\Lambda, 12)$ as

$$\mathbf{D}(\Lambda, 12)=\begin{bmatrix} \alpha(12) & \beta(12) & 0\\ \gamma(12) & v\alpha^{*}(12) & 0\\ 0 & 0 & \delta(12) \end{bmatrix}, \qquad \text{(V.B.14)}$$

where $v=u^2=\exp(-i\pi\eta)$. Furthermore, $u^{*}\beta(12)$ and $u^{*}\gamma(12)$ are imaginary, while $u^{*}\delta(12)$ is real.

The structure of the other submatrices in $\mathbf{D}(\Lambda)$ can be obtained in a similar fashion. The process can be repeated using the other unitary operators given in (V.B.5). It turns out, however, that these do not lead to any further simplifications.

In addition to unitary operators $\mathbf{T}(\mathbf{q}; \mathbf{R})$ belonging to $G_0(\mathbf{q})$, there may also be anti-unitary operators which commute with $\mathbf{B}(\mathbf{q})$ or $\mathbf{D}(\mathbf{q})$, as discussed in Sec. V.A. We must explore whether these lead to any further simplifications. In the present case, $\mathfrak{d}(001)$ sends $\mathbf{q}$ to $-\mathbf{q}$ for $\mathbf{q}$ along Λ. In other words, $\mathfrak{d}(001)$ plays the role of $\mathbf{S}_{-}$ [see (V.A.19) and the discussion following it]. We therefore have an additional commutation relation

$$\mathbf{T}(\Lambda; \mathfrak{d}(001))\mathbf{D}(\Lambda)\mathbf{T}^{-1}(\Lambda; \mathfrak{d}(001))=\mathbf{D}(\Lambda), \qquad \text{(V.B.15)}$$

where $\mathbf{T}(\Lambda; \mathfrak{d}(001))$ is given explicitly as

$$\mathbf{T}(\Lambda; \mathfrak{d}(001))=K_0\exp[-i\mathbf{q}\cdot\boldsymbol{\tau}]\boldsymbol{\Gamma}(\Lambda; \{\mathfrak{d}(001)\mid\boldsymbol{\tau}\}). \qquad \text{(V.B.16)}$$

From the definition of $\boldsymbol{\Gamma}$ given in (V.A.1) we have

$$\boldsymbol{\Gamma}(\Lambda; \{\mathfrak{d}(001)\mid\boldsymbol{\tau}\})=\begin{bmatrix} 0 & \mathbf{A} & 0 & 0\\ \mathbf{A} & 0 & 0 & 0\\ 0 & 0 & 0 & \mathbf{B}\\ 0 & 0 & \mathbf{B} & 0 \end{bmatrix},$$

$$\mathbf{A}=\mathfrak{d}(001),$$

$$\mathbf{B}=\begin{bmatrix} \mathfrak{d}(001) & \\ & -\mathfrak{d}(001) \end{bmatrix}. \qquad \text{(V.B.17)}$$

Observe the negative sign at the bottom right in the matrix for $\mathbf{B}$. This arises because $\mathfrak{d}$ is an improper rotation.

From (V.B.15) we obtain several new relations. For example, if we consider the top left-hand corner blocks on either side, then

$$\begin{bmatrix} \alpha(11) & \beta(11) & 0\\ \beta^{*}(11) & \gamma(11) & 0\\ 0 & 0 & \delta(11) \end{bmatrix}^{*} = \begin{bmatrix} \gamma(11) & -\beta^{*}(11) & 0\\ -\beta(11) & \alpha(11) & 0\\ 0 & 0 & \delta(11) \end{bmatrix}.$$

Remembering that $\alpha(11)$, $\gamma(11)$, and $\delta(11)$ are real, we have

$$\alpha(11)=\gamma(11), \qquad \beta(11)=-\beta(11)=0.$$

Taking note of the extra relations of the above type, we can write $\mathbf{D}(\Lambda)$ finally in the following form:

$$\mathbf{D}(\Lambda, 11)=\begin{bmatrix} \alpha(11) & 0 & 0\\ 0 & \alpha(11) & 0\\ 0 & 0 & \delta(11) \end{bmatrix},$$

$$\mathsf{D}(\Lambda, 12) = \begin{bmatrix} \alpha(12) & \beta(12) & 0 \\ \beta(12) & v\alpha^*(12) & 0 \\ 0 & 0 & \delta(12) \end{bmatrix},$$

$$\mathsf{D}(\Lambda, 13) = \begin{bmatrix} \alpha(13) & \beta(13) & 0 & \lambda(13) & \mu(13) & 0 \\ -\beta(13) & \alpha^*(13) & 0 & \mu^*(13) & -\lambda^*(13) & 0 \\ 0 & 0 & \epsilon(13) & 0 & 0 & \phi(13) \end{bmatrix},$$

$$\mathsf{D}(\Lambda, 14) = \begin{bmatrix} \alpha(14) & \beta(14) & 0 & \lambda(14) & \mu(14) & 0 \\ -v^*\beta^*(14) & v\alpha^*(14) & 0 & v\mu^*(14) & -v\lambda^*(14) & 0 \\ 0 & 0 & \epsilon(14) & 0 & 0 & \phi(14) \end{bmatrix},$$

$$\mathsf{D}(\Lambda, 22) = \mathsf{D}(\Lambda, 11),$$

$$\mathsf{D}(\Lambda, 23) = \begin{bmatrix} \alpha^*(14) & \beta^*(14) & 0 & -\lambda^*(14) & -\mu^*(14) & 0 \\ -v^*\beta(14) & v^*\alpha(14) & 0 & -v^*\mu(14) & v^*\lambda(14) & 0 \\ 0 & 0 & v^*\epsilon(14) & 0 & 0 & v^*\phi(14) \end{bmatrix},$$

$$\mathsf{D}(\Lambda, 24) = \begin{bmatrix} \alpha^*(13) & \beta^*(13) & 0 & -\lambda^*(13) & -\mu^*(13) & 0 \\ -\beta(13) & \alpha(13) & 0 & -\mu(13) & \lambda(13) & 0 \\ 0 & 0 & \epsilon(13) & 0 & 0 & \phi(13) \end{bmatrix},$$

$$\mathsf{D}(\Lambda, 33) = \begin{bmatrix} \alpha(33) & 0 & 0 & \lambda(33) & \mu(33) & 0 \\ 0 & \alpha(33) & 0 & \mu^*(33) & -\lambda^*(33) & 0 \\ 0 & 0 & \delta(33) & 0 & 0 & \phi(33) \\ \lambda^*(33) & \mu(33) & 0 & \xi(33) & 0 & 0 \\ \mu^*(33) & -\lambda(33) & 0 & 0 & \xi(33) & 0 \\ 0 & 0 & -\phi(33) & 0 & 0 & \psi(33) \end{bmatrix},$$

$$\mathsf{D}(\Lambda, 34) = \begin{bmatrix} \alpha(34) & \beta(34) & 0 & \lambda(34) & \mu(34) & 0 \\ \beta(34) & v\alpha^*(34) & 0 & v\mu^*(34) & -v\lambda^*(34) & 0 \\ 0 & 0 & \delta(34) & 0 & 0 & \phi(34) \\ -\lambda(34) & -v\mu^*(34) & 0 & \xi(34) & \eta(34) & 0 \\ -\mu(34) & -v\lambda^*(34) & 0 & \eta(34) & v\xi^*(34) & 0 \\ 0 & 0 & v\phi^*(34) & 0 & 0 & \psi(34) \end{bmatrix},$$

$$\mathsf{D}(\Lambda,44)=\begin{bmatrix} \alpha(33) & 0 & 0 & -\lambda^*(33) & -\mu^*(33) & 0 \\ 0 & \alpha(33) & 0 & -\mu(33) & \lambda(33) & 0 \\ 0 & 0 & \delta(33) & 0 & 0 & \phi(33) \\ -\lambda(33) & -\mu^*(33) & 0 & \xi(33) & 0 & 0 \\ -\mu(33) & \lambda^*(33) & 0 & 0 & \xi(33) & 0 \\ 0 & 0 & -\phi(33) & 0 & 0 & \psi(33) \end{bmatrix}. \tag{V.B.18}$$

The restrictions on the various elements to be noted are that: $u^*\beta(12)$, $u^*\beta(34)$, $u^*\eta(34)$, $\phi(13)$, $u^*\phi(14)$, $\phi(33)$, $u^*\phi(34)$ are all imaginary; in addition, $u^*\delta(12)$, $u^*\delta(34)$, $u^*\psi(34)$, $\epsilon(13)$, $u^*\epsilon(14)$ are all real. The remaining elements of $\mathsf{D}(\Lambda)$ can be written from the results of (V.B.18) by using the Hermitian property of $\mathsf{D}(\Lambda)$.

The form deduced above for $\mathsf{D}(\Lambda)$ is the most general one consistent with crystal symmetry. We observe that whereas by considering the Hermitian property alone there will be 171 independent elements in $\mathsf{D}(\Lambda)$, systematic use of group-theoretic arguments shows that there are only 33 independent elements. Furthermore, we know that 156 elements of $\mathsf{D}(\Lambda)$ are identically equal to zero. *These results are independent of the force fields between atoms.* Results of this kind are of great value when undertaking practical calculations, for one can avoid evaluating redundant and zero elements. In the present case, for example, only 33 out of a maximum of 171 need be evaluated. It is of course entirely possible that special assumptions about the nature of the forces can introduce further simplifications.

What remains now is to bring $\mathsf{D}(\Lambda)$ into the block-diagonal form $\mathfrak{D}(\Lambda)$. This is done by performing the transformation

$$\mathfrak{D}(\Lambda)=\boldsymbol{\xi}^+(\Lambda)\mathsf{D}(\Lambda)\boldsymbol{\xi}(\Lambda). \tag{V.B.19}$$

Since $\mathsf{D}(\Lambda)$ and $\boldsymbol{\xi}(\Lambda)$ are known, evaluation of (V.B.19) is a straightforward (though slightly tedious!) matter. The resulting $\mathfrak{D}(\Lambda)$ has the form

$$\mathfrak{D}(\Lambda)=\begin{bmatrix} \mathfrak{D}(\Lambda_1) & & & \\ & \mathfrak{D}(\Lambda_2) & & \\ & & \mathfrak{D}(\Lambda_3) & \\ & & & \mathfrak{D}(\Lambda_4) \end{bmatrix}. \tag{V.B.20}$$

Explicitly, therefore, we have

$$\mathfrak{D}(\Lambda_1)=\begin{bmatrix} \delta(11)+u^*\delta(12), & \epsilon(13)+u^*\epsilon(14), & \phi(13)+u^*\phi(14) \\ \epsilon(13)+u^*\epsilon(14), & \delta(33)+u^*\delta(34), & \phi(33)+u^*\phi(34) \\ -\phi(13)-u^*\phi(14), & -\phi(33)-u^*\phi(34), & \psi(33)+u^*\psi(34) \end{bmatrix}. \tag{V.B.21}$$

Similar expressions may be written for the other submatrices $\mathfrak{D}(\Lambda_2)$, $\mathfrak{D}(\Lambda_3)$, and $\mathfrak{D}(\Lambda_4)$. We shall not give them here but merely note that they are of dimensions 3, 6, and 6 respectively, which are also the values of c_{Λ_2}, c_{Λ_3}, and c_{Λ_4}. [See remarks following Eq. (V.A.14).]

The problem of finding the eigenvalues $\omega_j^2(\mathbf{q}=\Lambda)$ is thus reduced to diagonalizing the relatively small matrices $\mathfrak{D}(\Lambda_i)$ which clearly represents a great saving of computational labor, reinforcing further the usefulness of group theory in practical calculations. In fact in the present case, the IMR's Λ_3 and Λ_4 are equivalent, owing to time-reversal symmetry. This means that $\mathfrak{D}(\Lambda_3)$ will yield eigenvalues identical to those of $\mathfrak{D}(\Lambda_4)$ which simplifies the calculations even further.

C. Site-Group and Factor-Group Methods

Our discussion of the group-theoretical applications will not be complete without reference to the methods employed in the spectroscopic literature (Bhagavantham and Venkatarayudu, 1948; Halford, 1946; Winston and Halford, 1949; Davydov, 1962).

Spectroscopists confine their attention to the $\mathbf{q}=0$ modes since these are the ones relevant to most of their experiments. Usually, group theory is employed purely for classification purposes, and two techniques

called site-group method and factor-group method are used.

In the site-group method, each molecule is treated individually and in relation to the symmetry of the site, i.e., the symmetry of the immediate environment. Formally, this is done by first constructing the site group. This is defined as the group of elements common to both the space group of the crystal and to the point group of the molecule (Craig and Walmsley, 1968). The operations of the site group when performed about the molecule leave not only the molecule in question invariant, but also the entire crystal. Necessarily, the elements of the site group must have no fractional translations associated with them, i.e., they must have the form $\{\mathbf{S} \mid 0\}$. For example, the site group of the WO_4^{--} ion in $CaWO_4$ is described by the molecular point group S_4, consisting of the elements $\mathbf{E}$, $\mathbf{C}_2[001]$, $\mathbf{S}_4[001]$, and $\mathbf{S}_4^{-1}[001]$.

Having found the site group, the various modes of motion of the molecule are then classified in terms of the irreducible representations of this point group. Usually the method is applied to classify the internal vibrations of the molecule concerned, and that, too, in the spirit of a crystal field splitting. In other words, one examines how the symmetry of the vibrational mode classified as per the point group of the molecule is altered when reclassified in terms of the site symmetry. The alteration, if any, is then viewed as due to the perturbation produced by the local environment of the molecule. It is clear that this is a restricted approach and is of practically no utility as far as the external modes are concerned. To illustrate, the translational modes in $CaWO_4$ involve the motion of all ions, and it makes little sense to consider just one ion and discuss its translational motions alone.

In the factor-group method, the classification of the $\mathbf{q}=0$ modes is done using the factor group $(G/\mathfrak{T})$, where G is the space group, and $\mathfrak{T}$ the translational subgroup. The factor group $(G/\mathfrak{T})$ is isomorphic to the point group G_0 of the crystal. When we remember that $G_0 \equiv G_0(\mathbf{q}=0)$, it becomes clear that classification in terms of the irreducible representations of $(G/\mathfrak{T})$ is effectively the same as using the IMR's of $G_0(\mathbf{q}=0)$. In other words, the factor-group approach, though using a different jargon, is essentially the same as MV's approach for $\mathbf{q}=0$.

VI. SUMMARY

In this article, we have reviewed the study of external modes in complex crystals with emphasis on the theoretical aspects. In the process, we have clarified some points which have not been discussed adequately in the existing literature. In addition, we have also called attention to areas which need further work, both theoretical and experimental.

After a preliminary introduction, we discussed in Sec. II the extension of the Born–von Kármán formalism to external modes. Two convenient frames of reference were considered in developing the theory, and their relative merits as well as their interrelation were pointed out.

In Sec. III we reviewed the presently available results—experimental and theoretical—concerning dispersion relations for external modes in complex crystals.

The role of macroscopic electric fields was explored in Sec. IV. Here we considered a rigid-ion model of a complex (ionic) crystal and offered a generalization of Kellerman's work, pointing out also its limitations. The paucity of work concerning polaritons was also indicated.

The group-theoretical aspects were studied in Sec. V. Our treatment closely follows the earlier work of Maradudin and Vosko, who discussed group theory in relation to standard Born–von Kármán formalism. In extending their work to external modes, the essential points to be borne in mind are that (i) in the present problem one has to deal with displacements some of which transform like axial vectors, and (ii) the eigenvalue problem is of a more generalized nature unless one considers the principal-axis frame and weighted displacements. In the latter case, care is required in discussing the effect of space-group operations. We have also briefly discussed the techniques used by spectroscopists in classifying the $\mathbf{q}=0$ modes and their relationship to the more generalized treatment.

In conclusion, it should be clear from a perusal of this article that a systematic study of external modes is just beginning, and the present article is intended not only to give a state-of-the-art report but also (hopefully!) to stimulate further activity. In this context, it is relevant to mention that we have omitted completely a discussion of the elastic properties (Deprez and Fouret, 1966; Ludwig, 1967; Walmsley, 1968; Parlinski, 1968) for the reason that the subject has not yet been treated comprehensively in the literature.

Also, we have not considered extending the rigid-ion model to allow for polarization effects, say, via the shell model which has proved to successful in the case of simple ionic crystals (Woods *et al.*, 1960). The main reason for our not doing so is that introduction of the shell model leads to a proliferation of parameters. Since even with the rigid-ion model one has several parameters to contend with, inclusion of polarization effects with an attendant increase in parameters did not seem worthwhile at present. The situation could conceivably change in the future as more experimental data becomes available.

VII. GLOSSARY

Lattice Dynamical Symbols

μ	Number of single atoms in the unit cell
ν	Number of molecular groups in the unit cell

n	Number of atoms in the unit cell
N	Number of cells in the (periodic) crystal
v	Volume of the unit cell
l	Cell index
κ	Sublattice index
k	Atom index
m_κ	Mass of the κth unit
M	Mass of the unit cell
$\mathcal{I}_{\alpha\beta}(\kappa)$, $\mathcal{I}_{\alpha\beta}{}^{P}(\kappa)$	$\alpha\beta$th element of the moment-of-inertia tensor of the κth molecular group
$\mathbf{a}_i$ $(i=1, 2, 3)$	Basis vectors of the direct lattice
$\mathbf{X}(l)$	Direct lattice vector
(l_1, l_2, l_3)	Components of $\mathbf{X}(l)$ along $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$
$\mathbf{X}(\kappa)$	Position of center of mass of the κth unit with respect to the cell in which it is located
$\mathbf{X}(k)$	Position of the kth atom with respect to the center of mass of the molecular group to which it belongs
$\mathbf{X}(l\kappa)$	$=\mathbf{X}(l)+\mathbf{X}(\kappa)$
$\mathbf{X}(l\kappa k)$	$=\mathbf{X}(l)+\mathbf{X}(\kappa)+\mathbf{X}(k)$
$\mathbf{G}$	Vector of the reciprocal lattice
superscript i, i', etc.	Index symbolizing t or r
superscript P	Quantity pertains to principal-axis frame
$u_\alpha{}^{i}(l\kappa)$, $u_\alpha{}^{i,P}(l\kappa)$	Displacement component of the ith type of the $(l\kappa)$th unit
T	Kinetic energy
Φ	Potential energy
Φ_2	Harmonic part of the potential energy
H	Hamiltonian
$\mathcal{S}_m=\{\mathbf{S} \mid \mathbf{V}(S)+\mathbf{X}(m)\}$	Typical space-group element with rotational part $\mathbf{S}$, lattice translation $\mathbf{X}(m)$, and fractional translation $\mathbf{V}(S)$
$C^i(S)$	$\begin{cases}=1 \text{ if } i=t \\ =\lvert \mathbf{S} \rvert \text{ if } i=r\end{cases}$
$\lvert \mathbf{A} \rvert$	Determinant of the matrix $\mathbf{A}$
$\mathbf{A}^{-1}$	Inverse of $\mathbf{A}$
$\mathbf{A}^{\mathrm{tr}}$	Transpose of $\mathbf{A}$
$\mathbf{A}^{+}$	Hermitian conjugate of $\mathbf{A}$
$\mathbf{A}^{*}$	Complex conjugate of $\mathbf{A}$
$\mathbf{0}_n$	Null matrix of order n
$\mathbf{1}_n$	Unit matrix of order n
$\in$	Mathematical symbol for "contained in"
$\kappa \in \mathrm{II}$	κ restricted to type II vibrating units
$\epsilon_{\alpha\beta\gamma}$	Levi–Civita symbol
$\phi_{\alpha\beta}{}^{ii'}(l\kappa; l'\kappa')$, $\phi_{\alpha\beta}{}^{ii',P}(l\kappa; l'\kappa')$	$\alpha\beta$th element of the (ii')th type force constant tensor connecting $(l\kappa)$ and $(l'\kappa')$
(ξ, η, ζ)	Eulerian angles
$A_{\alpha\beta}(\kappa)$	$\alpha\beta$th element of the transformation $\mathbf{A}(\kappa)$ from an orthogonal frame at κ parallel to crystal-fixed axes to the principal axes of the unit concerned
$\mathcal{S}(\kappa; K)$	$=\mathbf{A}(K)\mathbf{S}\mathbf{A}^{\mathrm{tr}}(\kappa)$
$\mathbf{q}$	Wave vector of vibrational wave
$U_\alpha{}^{i}(\kappa \mid \mathbf{q})$, $U_\alpha{}^{i,P}(\kappa \mid \mathbf{q})$	Component of the wave amplitude $\mathbf{U}(\mathbf{q})$, $\mathbf{U}^P(\mathbf{q})$ of κth unit, associated with wavevector $\mathbf{q}$
$\omega_j(\mathbf{q})$	Frequency of phonon of wavevector $\mathbf{q}$ corresponding to the jth branch
$B_{\alpha\beta}{}^{ii'}(\mathbf{q}, \kappa\kappa')$, $B_{\alpha\beta}{}^{ii'P}(\mathbf{q}, \kappa\kappa')$	Element of the dynamical matrix $\mathbf{B}(\mathbf{q})$, $\mathbf{B}^P(\mathbf{q})$

$m_{\alpha\beta}{}^{ii'}(\kappa\kappa')$, $m_{\alpha\beta}{}^{ii',P}(\kappa\kappa')$	Element of the "mass-moment-of-inertia tensor" $\mathbf{m}$, $\mathbf{m}^P$ associated with the unit cell
$e_\alpha{}^i(\kappa \mid \mathbf{q}j)$, $e_\alpha{}^{i,P}(\kappa \mid \mathbf{q}j)$	Component of the eigenvector $\mathbf{e}(\mathbf{q}j)$, $\mathbf{e}^P(\mathbf{q}j)$
$\mathbf{e}(\mathbf{q})$, $\mathbf{e}^P(\mathbf{q})$	Eigenvector matrix
$\mathbf{\Omega}(\mathbf{q})$	Eigenvalue matrix
$D_{\alpha\beta}{}^{ii',P}(\mathbf{q}, \kappa\kappa')$	Element of the dynamical matrix $\mathbf{D}^P(\mathbf{q})$ with weighted force constants
$V_\alpha{}^{i,P}(\kappa \mid \mathbf{q})$	Component of the weighted wave amplitude $\mathbf{V}^P(\mathbf{q})$
$E_\alpha{}^{i,P}(\kappa \mid \mathbf{q}j)$	Component of the eigenvector $\mathbf{E}(\mathbf{q}j)$ of $\mathbf{D}^P(\mathbf{q})$
$\Delta(\mathbf{Q})$	Periodic delta function; $=0$ if $\mathbf{Q}\neq\mathbf{G}$, $=1$ if $\mathbf{Q}=\mathbf{G}$
$g(\omega)$	Frequency distribution function
$g^t(\omega)$	Translational part of the frequency distribution function
$g^r(\omega)$	Rotational part of the frequency distribution function
$a_{\mathbf{q}j}{}^+$, $a_{\mathbf{q}j}$	Creation and annihilation operators

Symbols Used in the Treatment of Electric Field Effects

e	$+4.8\times10^{-10}$ esu
$Z(\kappa k)e$	Charge on kth atom in κth molecular group
$k\in\kappa$	Atom k contained in the molecular group κ
$\phi_{\alpha\beta}{}^c(l\kappa k; l'\kappa'k')$	Coulombic part of the force constant connecting the atom pair $(l\kappa k-l'\kappa'k')$
$\phi_{\alpha\beta}{}^{e,ii'}(l\kappa; l'\kappa')$	Electrostatic contribution to the force constant connecting $(l\kappa)$ and $(l'\kappa')$
$B_{\alpha\beta}{}^{e,ii'}(\mathbf{q}, \kappa\kappa')$	Electrostatic contribution to the dynamical matrix
$\bar{B}_{\alpha\beta}{}^{e,ii'}(\mathbf{q}, \kappa\kappa')$	Regular part of the electrostatic contribution $B_{\alpha\beta}{}^{e,ii'}(\mathbf{q}, \kappa\kappa')$
$\mathfrak{B}_{\alpha\beta}(\mathbf{q}, \mathbf{r})$	Reciprocal space series associated with Coulombic lattice sums
$\mathfrak{C}_{\alpha\beta}(\mathbf{q}, \mathbf{r})$	Real space series associated with Coulombic lattice sums
η	Parameter in the expressions for the Coulombic lattice sums whose value is chosen such that both the real space and reciprocal space series are rapidly convergent
$\mathbf{p}(\kappa)$	Dipole moment produced by the vibrations of the κth unit
E_α	Component of the macroscopic electric field $\mathbf{E}$
n^2	Square of the refractive index
$\boldsymbol{\varepsilon}$	Dielectric tensor
$(\mathbf{Z}^+)_{\alpha\kappa i,\beta}$	Element of the "effective charge" tensor defined in Eq. (IV.E.2)

Group-Theoretical Symbols

G	Space group
G_0	Point group
$\mathfrak{I}$	Translational subgroup
$(G/\mathfrak{I})$	Factor group isomorphic to G_0
$G(\mathbf{q})$	Group of the wave vector
$G_0(\mathbf{q})$	Point group of the wave vector
$\{\ \}$	Set of like quantities
$\mathcal{S}_m=\{\mathbf{S} \mid \mathbf{V}(S)+\mathbf{X}(m)\}$	A general element of G
$\mathcal{R}_m=\{\mathbf{R} \mid \mathbf{V}(R)+\mathbf{X}(m)\}$	A general element of $G(\mathbf{q})$
K_0	Complex conjugation operator
$\mathbf{S}_-$	An element of G_0 which sends a given $\mathbf{q}$ to $-\mathbf{q}$
$\{\mathbf{S}_-\mathbf{R} \mid \mathbf{V}(S_-R)+\mathbf{X}(m)\}$	Representative space-group operation whose rotational part $\mathbf{S}_-\mathbf{R}$ sends $\mathbf{q}$ to $-\mathbf{q}$
$F_0(\kappa; S)$	Sublattice arrived at from κ via $\mathcal{S}_m$
$F_0{}^{-1}(\kappa; S)$	Sublattice from which one must start to arrive at κ via $\mathcal{S}_m$
$\delta(\kappa, F_0(\kappa'; S))$	Kronecker delta which is equal to zero when $\kappa\neq F_0(\kappa'; S)$, and is equal to 1 when $\kappa=F_0(\kappa'; S)$
$\phi(\mathbf{q}; \mathbf{R}_i, \mathbf{R}_j)$	Multiplier associated with a pair of elements $\mathbf{R}_i$ and $\mathbf{R}_j$ of $G_0(\mathbf{q})$
$\Gamma_{\alpha\beta}{}^{ii'}(\kappa\kappa' \mid \mathbf{q}; \mathcal{S}_m)$	Element of the unitary matrix $\mathbf{\Gamma}(\mathbf{q}; \mathcal{S}_m)$ which describes the transformation of eigenvectors under the space-group operation $\mathcal{S}_m$
$T_{\alpha\beta}{}^{ii'}(\kappa\kappa' \mid \mathbf{q}; \mathbf{R})$, $(T_{\alpha\beta}{}^{ii',P}(\kappa\kappa' \mid \mathbf{q}; \mathbf{R}))$	Element of the unitary operator $\mathbf{T}(\mathbf{q}; \mathbf{R})$, $(\mathbf{T}^P(\mathbf{q}; \mathbf{R}))$ which commutes with the dynamical matrix $\mathbf{B}(\mathbf{q})$ $(\mathbf{B}^P(\mathbf{q}))$ and $\mathbf{m}(\mathbf{m}^P)$

$\mathbf{T}(\mathbf{q}; \mathbf{S}_-\mathbf{R})$	Anti-unitary operator which also commutes with the dynamical matrix
$T(\mathbf{q})=\{\mathbf{T}(\mathbf{q}; \mathbf{R})\}$	Set of unitary operators which furnish a $(3\mu+6\nu)$-dimensional reducible multiplier representation of $G_0(\mathbf{q})$
IMR	Irreducible multiplier representation
$\tau^{(s)}(\mathbf{q})=\{\boldsymbol{\tau}^{(s)}(\mathbf{q}; \mathbf{R})\}$	IMR of $G_0(\mathbf{q})$
$\tau_{\lambda\lambda'}{}^{(s)}(\mathbf{q}; \mathbf{R})$	$\lambda\lambda'$th element of the matrix $\boldsymbol{\tau}^{(s)}(\mathbf{q}; \mathbf{R})$ corresponding to the group element $\mathbf{R}$, in the IMR $\tau^{(s)}(\mathbf{q})$
$\chi(\mathbf{q}; \mathbf{R})$	Trace of $\mathbf{T}(\mathbf{q}; \mathbf{R})$
$\chi^{(s)}(\mathbf{q}; \mathbf{R})$	Trace of $\boldsymbol{\tau}^{(s)}(\mathbf{q}; \mathbf{R})$
c_s	Number of occurrences of $\tau^{(s)}(\mathbf{q})$ in $T(\mathbf{q})$
f_s	Dimensionality of $\tau^{(s)}(\mathbf{q})$
h	Order of $G_0(\mathbf{q})$
(s, a, λ)	s, symbol for inequivalent IMR's of $G_0(\mathbf{q})$; a, repetition index $(a=1, 2, \cdots, c_s)$; λ, row index $(\lambda=1, 2, \cdots, f_s)$
$P_{\mu\lambda}{}^{(s)}(\mathbf{q})$, $P_{\lambda\lambda}{}^{(s)}(\mathbf{q})$	Projection operator
$\xi(\mathbf{q}, sa\lambda)$, $\xi^P(\mathbf{q}, sa\lambda)$	Symmetry-adapted vector

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APPENDIX I

In this Appendix, we wish to draw the attention of the reader to some aspects of the generalized eigenvalue problem (Bellman, 1960; Choquet-Bruhat, 1967; Korn and Korn, 1968) encountered in Sec. II.

Let $\mathbf{A}$ and $\mathbf{B}$ be two square matrices of dimension n. We call the numbers λ eigenvalues of $\mathbf{A}$ relative to $\mathbf{B}$ if there exist nonzero vectors $\mathbf{X}$ satisfying the relation

$$\mathbf{AX}=\lambda\mathbf{BX}. \tag{AI.1}$$

The corresponding vectors $\mathbf{X}$ are called the eigenvectors of $\mathbf{A}$ relative to $\mathbf{B}$. In what follows, we shall assume that $\mathbf{A}$ and $\mathbf{B}$ are Hermitian. A sufficient condition, for the eigenvalues to be real, is that one of the matrices $\mathbf{A}$ or $\mathbf{B}$ is definite (Choquet-Bruhat, 1967). Referring back to Sec. II, it will be noticed that the eigenvalue problem formulated there has the same form as (AI.1). Furthermore, both $\mathbf{B}(\mathbf{q})$ as well as $\mathbf{m}$ [or $\mathbf{B}^p(\mathbf{q})$ and $\mathbf{m}^p$ as the case may be] are Hermitian, and in addition $\mathbf{m}$ ($\mathbf{m}^p$) is positive definite. It follows therefore that the eigenvalues $\{\omega_j^2(\mathbf{q})\}$ are real.

Suppose now that $\mathbf{B}\equiv 1_n$. The eigenvalue problem (AI.1) then reduces to the standard form

$$\mathbf{AX}=\lambda\mathbf{X}. \tag{AI.2}$$

In this case, it is well known that since $\mathbf{A}$ is Hermitian, the eigenvectors $\mathbf{X}(i)$ can be chosen to satisfy the orthonormality relations

$$\sum_{k=1}^{n} X_k^*(i)X_k(j)=\delta_{ij}. \tag{AI.3}$$

When $\mathbf{B}\neq 1_n$, the eigenvectors $\mathbf{X}(i)$ cannot in general be chosen to satisfy (AI.3). To better appreciate the reason for this, let us rewrite (AI.1) as

$$(\mathbf{B}^{-1}\mathbf{A})\mathbf{X}=\lambda\mathbf{X}, \tag{AI.4}$$

which shows that if $\mathbf{X}(i)$ is an eigenvector of $\mathbf{A}$ relative to $\mathbf{B}$, then it is also an eigenvector of the matrix $(\mathbf{B}^{-1}\mathbf{A})$. Now in spite of the similarity of (AI.2) and (AI.4), the eigenvectors $\mathbf{X}(i)$ of $(\mathbf{B}^{-1}\mathbf{A})$ cannot in general be chosen to satisfy the orthonormality conditions (AI.3) unless $\mathbf{B}^{-1}\mathbf{A}$ is Hermitian. The latter is possible only if $\mathbf{B}^{-1}$ and $\mathbf{A}$ commute, and in general this need not be so.

It turns out, however, that even though $\mathbf{B}^{-1}\mathbf{A}$ is not Hermitian like $\mathbf{A}$ and $\mathbf{B}$, it is Hermitian in a slightly different sense.

Let $\mathbf{a}$ and $\mathbf{b}$ be two vectors in the space of the $\mathbf{X}(i)$'s. The fact that $\mathbf{A}$ and $\mathbf{B}$ are Hermitian implies

$$\begin{aligned}(\mathbf{a}, \mathbf{Ab})&=(\mathbf{Aa}, \mathbf{b}),\\ (\mathbf{a}, \mathbf{Bb})&=(\mathbf{Ba}, \mathbf{b}),\end{aligned} \tag{AI.5}$$

where we have employed the notation $(\mathbf{a}, \mathbf{b})$ to denote the scalar product between the two vectors $\mathbf{a}$ and $\mathbf{b}$. Introduce now a slightly more general scalar product by the definition

$$(\mathbf{a}, \mathbf{b})_B\equiv(\mathbf{a}, \mathbf{Bb}), \tag{AI.6}$$

where $\mathbf{B}$ is assumed to be positive definite. The matrix $(\mathbf{B}^{-1}\mathbf{A})$ will then be Hermitian in the above sense, i.e.,

$$(\mathbf{B}^{-1}\mathbf{Aa}, \mathbf{b})_B=(\mathbf{a}, \mathbf{B}^{-1}\mathbf{Ab})_B. \tag{AI.7}$$

This relation is easily proved. From the right-hand side,

$$(\mathbf{a}, \mathbf{B}^{-1}\mathbf{A}\mathbf{b})_B = (\mathbf{a}, \mathbf{B}\mathbf{B}^{-1}\mathbf{A}\mathbf{b}) = (\mathbf{A}\mathbf{a}, \mathbf{b}) \quad [\text{from (AI.5)}].$$

On the other hand,

$$(\mathbf{B}^{-1}\mathbf{A}\mathbf{a}, \mathbf{b})_B = (\mathbf{B}^{-1}\mathbf{A}\mathbf{a}, \mathbf{B}\mathbf{b}) = (\mathbf{B}\mathbf{B}^{-1}\mathbf{A}\mathbf{a}, \mathbf{b}) \quad (\text{since } \mathbf{B} \text{ is Hermitian}) = (\mathbf{A}\mathbf{a}, \mathbf{b}).$$

Hence (AI.7) holds, and $\mathbf{B}^{-1}\mathbf{A}$ is Hermitian, provided the scalar products are defined as in (AI.6). It is natural to expect therefore that the eigenvectors $\mathbf{X}(i)$ of $\mathbf{B}^{-1}\mathbf{A}$ (or equivalently, the eigenvectors $\mathbf{X}(i)$ of $\mathbf{A}$ relative to $\mathbf{B}$) satisfy modified orthogonality relations based on (AI.6). In other words, we expect the $\mathbf{X}(i)$'s can be chosen such that

$$(\mathbf{X}(i), \mathbf{X}(j))_B = (\mathbf{X}(i), \mathbf{B}\mathbf{X}(j)) = \delta_{ij}. \quad \text{(AI.8)}$$

This in fact can be proved, and it is based on this that we wrote Eq. (II.A.35).

APPENDIX II

In this Appendix, we shall summarize the results required in the evaluation of the Coulombic contributions to the dynamical matrix (see Sec. IV.B). All the electrostatic contributions involve essentially a periodic sum of the form

$$\sum_{l'} \phi_{\alpha\beta}{}^{c}(0A; l'B) \exp[i\mathbf{q}\cdot\mathbf{X}(l')], \quad \text{(AII.1)}$$

where $\phi_{\alpha\beta}{}^{c}(0A; l'B)$ is the electrostatic part of the force constant between atom A in cell 0, and atom B in cell l', and is given explicitly by

$$\phi_{\alpha\beta}{}^{c}(0A; l'B) = -(\partial^2/\partial r_\alpha \partial r_\beta)[Z_A Z_B e^2/|\mathbf{X}(l') - \mathbf{X}(A) + \mathbf{X}(B)|] = Z_A Z_B e^2 \{\delta_{\alpha\beta}/R^3 - 3R_\alpha R_\beta/R^5\}_{R=|\mathbf{X}(l')-\mathbf{X}(A)+\mathbf{X}(B)|}. \quad \text{(AII.2)}$$

Here $Z_A e$ and $Z_B e$ denote, respectively, the charges on the two atoms and $\mathbf{X}(A)$ and $\mathbf{X}(B)$ their positions in the unit cell.

It is well known (Kellermann, 1940; BH, Chap. V) that by an extension of a procedure originally due to Ewald (1917, 1921), the series

$$\sum_{l'} -(\partial^2/\partial X_\alpha \partial X_\beta)[1/|\mathbf{X}(l') - \mathbf{X}|] \exp[i\mathbf{q}\cdot\mathbf{X}(l')] \quad \text{(AII.3)}$$

underlying (AII.1) can be written in terms of two rapidly convergent series, one in real space and the other in reciprocal space. Explicitly, we have

$$-\sum_{l'} (\partial^2/\partial X_\alpha \partial X_\beta)[1/|\mathbf{X}(l') - \mathbf{X}|] \exp[i\mathbf{q}\cdot\mathbf{X}(l')] = 4\mathfrak{B}_{\alpha\beta}(\mathbf{q}, \mathbf{X}) - \mathfrak{C}_{\alpha\beta}(\mathbf{q}, \mathbf{X}), \quad \text{(AII.4)}$$

where

$$\mathfrak{B}_{\alpha\beta}(\mathbf{q}, \mathbf{X}) = \frac{\pi}{v} \sum_{\mathbf{G}} \frac{(\mathbf{G}+\mathbf{q})_\alpha (\mathbf{G}+\mathbf{q})_\beta}{(\mathbf{G}+\mathbf{q})^2} \exp\left(-\frac{(\mathbf{G}+\mathbf{q})^2}{4\eta^2}\right) \times \exp[i(\mathbf{G}+\mathbf{q})\cdot\mathbf{X}], \quad \text{(AII.5)}$$

and

$$\mathfrak{C}_{\alpha\beta}(\mathbf{q}, \mathbf{X}) = \sum_{l'} \exp[i\mathbf{q}\cdot\mathbf{X}(l')] \left\{ \frac{(\mathbf{X}(l')-\mathbf{X})_\alpha (\mathbf{X}(l')-\mathbf{X})_\beta}{|\mathbf{X}(l')-\mathbf{X}|^5} \times \left[3\,\mathrm{erfc}\,(y) + \frac{e^{-y^2}}{\pi^{1/2}}(4y^3+6y)\right] - \frac{\delta_{\alpha\beta}}{|\mathbf{X}(l')-\mathbf{X}|^3} \times \left[\mathrm{erfc}\,(y) + \frac{2y}{\pi^{1/2}} e^{-y^2}\right] \right\}. \quad \text{(AII.6)}$$

In the above expressions, we have

$$y = \eta |\mathbf{X}(l') - \mathbf{X}|$$

and

$$\mathrm{erfc}\,(y) = 1 - \frac{2}{\pi^{1/2}} \int_0^y e^{-x^2} dx.$$

$\mathbf{G}$ is a vector of the reciprocal lattice and is defined such that

$$\mathbf{G}\cdot\mathbf{X}(l) = 2\pi \times \text{integer}.$$

The quantity η is a parameter to be chosen such that both the series (AII.5) and (AII.6) converge rapidly.

From Eqs. (AII.5) and (AII.6) the following properties of $\mathfrak{B}_{\alpha\beta}$ and $\mathfrak{C}_{\alpha\beta}$ can be noted:

$$\mathfrak{B}_{\alpha\beta}(\mathbf{q}, \mathbf{X}) = \mathfrak{B}_{\beta\alpha}(\mathbf{q}, \mathbf{X}),$$
$$\mathfrak{B}_{\alpha\beta}{}^{*}(\mathbf{q}, \mathbf{X}) = \mathfrak{B}_{\alpha\beta}(\mathbf{q}, -\mathbf{X}),$$
$$\mathfrak{C}_{\alpha\beta}(\mathbf{q}, \mathbf{X}) = \mathfrak{C}_{\beta\alpha}(\mathbf{q}, \mathbf{X}),$$
$$\mathfrak{C}_{\alpha\beta}{}^{*}(\mathbf{q}, \mathbf{X}) = \mathfrak{C}_{\alpha\beta}(\mathbf{q}, -\mathbf{X}). \quad \text{(AII.7)}$$

Extensive use is made of formulas (AII.4)–(AII.7) in the derivations of Sec. IV.B. In some instances, it is necessary to consider sums of the form

$$-\sum_{l'} (\partial^2/\partial X_\alpha \partial X_\beta)[1/|\mathbf{X}(l') - \mathbf{X}|] \quad \text{(AII.8)}$$

or

$$\{-\sum_{l'} (\partial^2/\partial X_\alpha \partial X_\beta)[1/|\mathbf{X}(l') - \mathbf{X}|]\}_{\mathbf{X}=0}. \quad \text{(AII.9)}$$

From (AII.4) we have

$$-\sum_{l'} (\partial^2/\partial X_\alpha \partial X_\beta)[1/|\mathbf{X}(l') - \mathbf{X}|] = 4\mathfrak{B}_{\alpha\beta}(\mathbf{q}\equiv 0, \mathbf{X}) - \mathfrak{C}_{\alpha\beta}(\mathbf{q}\equiv 0, \mathbf{X}), \quad \text{(AII.10)}$$

$$\{-\sum_{l'}(\partial^2/\partial X_\alpha \partial X_\beta[1/|\mathbf{X}(l')-\mathbf{X}|]\}_{\mathbf{X}=0}$$
$$=4\mathfrak{B}_{\alpha\beta}(\mathbf{q}\equiv 0,0)-\mathfrak{C}_{\alpha\beta}(\mathbf{q}\equiv 0,0). \quad \text{(AII.11)}$$

The above expressions, however, contain some ill-defined terms in contrast to (AII.4). Specifically, these are the leading terms in $\mathfrak{B}_{\alpha\beta}(\mathbf{q}\equiv 0,\mathbf{X})$ and in $\mathfrak{C}_{\alpha\beta}(\mathbf{q}\equiv 0,0)$. The former is of the form

$$(\pi/v)[G_\alpha G_\beta/G^2]_{\mathbf{G}\equiv 0},$$

and is clearly ill-defined. The same applies to the expression

$$\left\{\frac{X_\alpha(l')X_\beta(l')}{|\mathbf{X}(l')|^5}\left[3+\frac{4\eta^3|\mathbf{X}(l')|^3+6\eta|\mathbf{X}(l')|}{\pi^{1/2}}\right]-\frac{\delta_{\alpha\beta}}{|\mathbf{X}(l')|^3}\left[1+\frac{2\eta|\mathbf{X}(l')|}{\pi^{1/2}}\right]\right\}_{l'=0},$$

which is the leading term in $\mathfrak{C}_{\alpha\beta}(\mathbf{q}\equiv 0,0)$. It turns out, however, that these ill-defined terms do not cause any difficulty in practical work as there is always a cancellation.

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