PHYSICAL REVIEW B VOLUME 9, NUMBER 6 15 MARCH 1974

Determination of interatomic interactions in complex ionic crystals from structural and lattice-dynamical data*

L. L. Boyer†

Solid State and Materials Laboratory, Princeton University, Princeton, New Jersey 08540

(Received 18 October 1973)

Structural and lattice-dynamical data contain a large amount of information about the interactions in ionic or partially ionic crystals with complex structures. As the complexity of the structure increases, i.e., as the number of ions per unit cell, n, becomes large, these become even richer sources of information. These data already exist for a large number of materials, but only recently has it been systematically used to determine interactions in very complex ($n > 20$) crystals. Very good agreement with experiment was obtained using the rigid-ion approximation with adjustable charges. The object of this paper is to provide the reader with an essentially self-contained treatment of the statics and dynamics of rigid-ion crystals and show how the experimental data may be effectively used to determine the interactions. For very complex crystals the model is primarily determined from the structural data alone using static-equilibrium conditions. This is fortunate since the static-equilibrium conditions are relatively easy to solve compared to the dynamical problem. Methods for making the most of the structural data are discussed. Lattice dynamics in the rigid-ion approximation and the transformation to symmetry coordinates are reviewed. Rotational invariance is shown to be a consequence of the static-equilibrium conditions. Practical considerations which arise in solving the dynamical problem are discussed.

I. INTRODUCTION

The purpose of this paper and the following paper[1] is to describe a method for determining interatomic interactions in ionic or partially ionic solids. The method is especially powerful for crystals with very complex structures, i.e., those with a large number of ions per unit cell, and it is on this aspect of the problem that we focus our attention. Specifically, we assume that the ions are point charges and that the short-range interactions are central and pairwise (rigid-ion model). Noninteger charges are permitted to allow for partially ionic bonds and compensate for the fact that the ions are themselves polarizable.

In principle the problem is very simple. One assumes the measured structure is in static equilibrium under the combined influence of the Coulomb and short-range forces. The resultant static-equilibrium conditions[2] (SEC) impose constraints on the first derivations of the short-range potentials (with respect to bond length) while the dynamical problem depends also on the second derivatives. Both the static and dynamic problems depend on the ionic charges. The object is to determine the correct charge distribution and short-range potentials from structural and dynamical measurements. This basic approach is, of course, nothing new and, in fact, originated in the classic work of Kellermann on the lattice dynamics of NaCl.[3] He determined the first derivative of the short-range energy between Na^+ and Cl^- from the lattice constant by invoking static equilibrium and the second derivative from the compressibility.

One finds that as the crystal structure becomes increasingly more complex more and more about the interatomic potentials can be learned from the SEC. Raman and infrared spectra also become richer sources of information, but for very complex structures the primary input is obtained from the structure through the SEC. In fact, recent lattice-dynamical calculations on $Gd_4(MoO_4)_6$ show surprisingly good agreement with x-ray, Raman, and neutron scattering data using a rigid-ion model with only three adjustable parameters.[4] The first derivatives of eight short-range bonds were determined from the SEC while the three additional parameters, two second derivatives and one relating the distribution of charge in the MoO_4^{-2} group, were determined from Raman scattering data. However, in this work we did not make the greatest possible use of either the structural or the lattice-dynamical data. The SEC were only approximately satisfied, and since we did not perform a symmetry analysis of the modes the comparison with Raman measurements was only semiquantitative. Although this was sufficient for our purpose of predicting the essential features of the transition in this material, it was clear that more could be learned about the interatomic potentials by improvements within the rigid-ion model. More recently this method has been applied to another material, fluorapatite $[Ca_{10}(PO_4)_6F_2]$, with the goal of squeezing the maximum amount of information from the SEC and Raman spectra given the rigid-ion approximation. Results of this investigation, which are reported in the following paper,[1] show very good agreement between experiment and theory and further demonstrate the power of this method when applied to very complex structures. Striefler and Barsh,[5] and Cran and Sangster[6] have also employed SEC in determining models for moderately complex crystals.

For the most part the major difficulties which arise in applying this method to very complex crystals result from the sheer size of the dynamical matrix. Clearly these difficulties have to be overcome by effectively using the computer. In other words, the dynamical problem must be programmed in the most general way possible, thus reducing the human effort. For the rigid-ion model it is a relatively simple matter to program the general expressions for the dynamical matrix, and a package of subroutines has been written for this purpose. Thus, given only the crystal structure, the mass and charge of the ions, the first and second derivatives of the short-range potentials, and the wave vector, the dynamical matrix is determined. This is surely possible for more sophisticated models as well although we have not yet attempted it. Programming the transformation to symmetry coordinates in its complete generality is not so straightforward, but certainly possible. In fact, we have written a subroutine to do this job which is considerably shorter than that required to construct the dynamical matrix, and it computes the transformation matrix in only a fraction of the time needed to compute the dynamical matrix. This subroutine, consisting of 132 FORTRAN statements, is listed and described in detail elsewhere.[7]

The main purpose of this paper is to review the lattice-dynamical problem emphasizing those aspects which are important in dealing with very complex crystals. The static equilibrium conditions are also discussed, but to a lesser extent.

In Sec. II we present the basic theory for the lattice dynamics of rigid-ion crystals in the harmonic approximation. Numerous other sources, notably Born and Huang[8] offer equivalent treatments but here the discussion is more concise since we limit ourselves to this model and treat it classically. Also, the introduction of periodic boundary conditions and associated jargon is from a somewhat different point of view. In addition we show that static equilibrium with respect to macroscopic strains is necessary and sufficient for rotational invariance.

In Sec. III the symmetry properties of the dynamical matrix are reviewed and the construction of symmetry coordinates is discussed using group-representation theory. Again, more general and detailed discussions may be found elsewhere; e.g., see the review of Maradudin and Vosko.[9]

In Sec. IV we discuss practical considerations relating to the application of the SEC and the dynamical theory to very complex crystals.

II. LATTICE DYNAMICS AND THE RIGID-ION MODEL

Consider a perfect crystal of point ions with n ions per primitive (Bravias) unit cell. Let $x_\alpha(l,k) = x_\alpha(l) + x_\alpha(k)$ be the αth component of the position of the (l, k) ion in the static lattice with respect to a Cartesian coordinate system. In general we use the index l to denote a set of three integers (l_1, l_2, l_3). Here they are the components of $\vec{x}(l)$ with respect to the primitive lattice vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$; i.e., $\vec{x}(l) = l_1\vec{a}_1 + l_2\vec{a}_2 + l_3\vec{a}_3$. In the following discussion we use $l = 0$ and $l - l'$ to mean (0, 0, 0) and $(l_1 - l_1', l_2 - l_2', l_3 - l_3')$. The index k labels the ions within a single cell, and $\vec{x}(k)$ is the position of the αth ion in the $l = 0$ cell.

Now suppose the ions are displaced slightly to new positions $\vec{r}(l, k) = \vec{x}(l, k) + \vec{u}(l, k)$. We define $\vec{r}(ll', kk') \equiv \vec{r}(l, k) - \vec{r}(l', k')$ with $\vec{x}(ll', kk')$ and $\vec{u}(ll', kk')$ similarly defined. Since the sites $\vec{x}(l, k)$ are those of the undistorted lattice we may write $\vec{x}(ll', kk') = \vec{x}(l - l', kk') = \vec{x}(l - l') + \vec{x}(k) - \vec{x}(k')$.

Considering only central pairwise interactions the potential energy of the crystal may be written

$$\Phi = \frac{1}{2}\sum_{ll'}\sum_{kk'} \phi(r(ll', kk')) , \tag{1}$$

where ϕ denotes the *total* interaction between the ion pairs and $r(ll', kk') = |\vec{r}(ll', kk')|$. In the summation, k and k' take on values from 1 to n while l and l' are summed over all possible triplets of integers. We account for the fact that a given ion does not interact with itself by imposing the condition $\phi(r(ll, kk)) = 0$ for all l and k.

Expanding $\phi(r)$ to second order in $\vec{u}$ about $\vec{x}$ for each ion pair,

$$\Phi = \frac{1}{2}\sum_{ll'}\sum_{kk'} \Big\{\phi(x(l - l', kk')) + \sum_{\alpha} [l - l', kk']_\alpha u_\alpha(ll', kk') + \frac{1}{2}\sum_{\alpha\beta} [l - l', kk']_{\alpha\beta}\, u_\alpha(ll', kk') u_\beta(ll', kk')\Big\} , \tag{2}$$

where

$$[l - l', kk']_\alpha = \phi'(x)\, \frac{x_\alpha}{x}\bigg|_{\vec{x} = \vec{x}(l - l', kk')} , \tag{3}$$

$$[l - l', kk']_{\alpha\beta} = \left[\left(\phi''(x) - \frac{\phi'(x)}{x}\right)\frac{x_\alpha x_\beta}{x^2} + \frac{\phi'(x)}{x}\,\delta_{\alpha\beta}\right]\bigg|_{\vec{x} = \vec{x}(l - l', kk')} , \tag{4}$$

and the primes denote derivatives with respect to bond length.

The zero-order terms do not enter into the dynamical problem and can be scaled to zero. Since the positions $\vec{x}(l, k)$ are assumed to be the equilibrium positions of the static lattice, the first-order contribution also vanishes. The resultant static-equilibrium conditions (SEC) are discussed in Born and Huang,[8] and recently, Boyer and Hardy[2] have pointed out their importance in dealing with complex crystal structures. In the later work, the Coulomb and short-range contributions are written separately with the Coulomb portion given in terms of Ewald sums.

Having imposed the SEC the potential energy becomes

$$\Phi=\frac{1}{4}\sum_{ll'}\sum_{kk'}\sum_{\alpha\beta}[l-l',kk']_{\alpha\beta}u_\alpha(ll',kk')u_\beta(ll',kk') . \tag{5}$$

Now suppose the crystal is displaced by an arbitrary infinitesimal rotation given by

$$\begin{aligned} u_1(ll',kk') &= \theta_3 x_2(l-l',kk') - \theta_2 x_3(l-l',kk') ,\\ u_2(ll',kk') &= \theta_1 x_3(l-l',kk') - \theta_3 x_1(l-l',kk') ,\\ u_3(ll',kk') &= \theta_2 x_1(l-l',kk') - \theta_1 x_2(l-l',kk') , \end{aligned} \tag{6}$$

where θ_α is the magnitude of the rotation about the α axis. Substituting Eq. (6) into Eq. (5) Φ reduces to

$$\Phi_\theta=\frac{1}{4}\sum_{ll'}\sum_{kk'}\sum_{\alpha\beta}\theta_\alpha\theta_\beta\,\frac{\phi'(x(l-l',kk'))}{x(l-l',kk')}\,x_\alpha(l-l',kk') \times x_\beta(l-l',kk') . \tag{7}$$

The terms in the sum over l and l' depend only on $l-l'$, and Φ_θ must vanish for all possible infinitesimal rotations; hence,

$$\sum_l\sum_{kk'}\frac{\phi'(x(l,kk'))}{x(l,kk')}\,x_\alpha(l,kk')x_\beta(l,kk')=0 \tag{8}$$

for all α and β. These are precisely the conditions required for static equilibrium with respect to macroscopic strains. Thus, in the harmonic approximation, satisfying the SEC automatically ensures the rotational invariance of the potential energy.

The potential energy takes the form

$$\Phi=\frac{1}{2}\sum_{ll'}\sum_{kk'}\sum_{\alpha\beta}\Phi_{\alpha\beta}(l-l',kk')u_\alpha(l,k)u_\beta(l',k') \tag{9}$$

when we define

$$\Phi_{\alpha\beta}(l,kk')=\begin{cases}\sum_{lk''}[l,kk'']_{\alpha\beta} & \text{for } (l,kk')=(0,kk)\\ -[l,kk']_{\alpha\beta} & \text{otherwise .}\end{cases} \tag{10}$$

Notice that

$$\Phi_{\alpha\beta}(0,kk)=-\sum_{lk'}\Phi_{\alpha\beta}(l,kk') . \tag{11}$$

A more common approach is to begin with the potential energy in the form given in Eq. (9) (which has the appearance of depending on the absolute displacements) and *invoke* translational invariance to obtain Eq. (11). Here, we have chosen to begin by writing the potential energy in terms of relative displacements and, as a result, we obtain Eq. (11).

The kinetic energy is given by

$$T=\frac{1}{2}\sum_{lk\alpha}\dot{w}_\alpha^2(l,k) , \tag{12}$$

where

$$w_\alpha(l,k)\equiv(m_k)^{1/2}u_\alpha(l,k) \tag{13}$$

and m_k is the mass of the kth ion. In these coordinates the potential energy is

$$\Phi=\frac{1}{2}\sum_{ll'}\sum_{kk'}\sum_{\alpha\beta}D_{\alpha\beta}(l-l',kk')w_\alpha(l,k)w_\beta(l',k') , \tag{14}$$

where

$$D_{\alpha\beta}(l,kk')\equiv\Phi_{\alpha\beta}(l,kk')(m_k m_{k'})^{-1/2} . \tag{15}$$

Now we assume that the dynamical state of the system is periodic in a superlattice with primitive lattice vectors $L\vec{a}_1$, $L\vec{a}_2$, and $L\vec{a}_3$, where L is some positive integer. Specifically, we require $\vec{u}(l,k) = \vec{u}((l_1+L,l_2,l_3),k) = \vec{u}((l_1,l_2+L,l_3),k) = \vec{u}((l_1,l_2,l_3+L),k)$ and similarly for $\dot{\vec{u}}$. Having imposed these periodic boundary conditions, we need only consider the energy of one supercell (primitive unit cell of the superlattice). In other words, the sum over l in Eq. (12) is such that l_1, l_2, and l_3 take on any L consecutive integers, while in Eq. (14) we restrict either l or l' to one supercell and sum the other index over the entire lattice. The $3nL^3$ independent coordinates are coupled through Eq. (14). This, of course, renders the dynamical problem intractable in these coordinates for any reasonably large value L, since the solution would require the diagonalization of a matrix of rank $3nL^3$.

In general, if $f(p)$ is a periodic function of the discrete variable p, where p is any integer, and $f(p)=f(p+L)$, then $f(p)$ may be written

$$f(p)=\sum_{p'}g(p')\,e^{i(2\pi/L)pp'} , \tag{16}$$

where

$$g(p)=\frac{1}{L}\sum_{p'}f(p')\,e^{-i(2\pi/L)pp'} \tag{17}$$

and the sum over p' includes any L consecutive integers. Clearly, $g(p)$ is also periodic with a period of L. The validity of these expanded forms results from the fact that

$$\sum_{p'}e^{i(2\pi/L)pp'}=\begin{cases}L & \text{if } p \text{ is a multiple of } L\\ 0 & \text{otherwise,}\end{cases} \tag{18}$$

as is easily demonstrated by substituting Eq. (17) into Eq. (16) or vice versa.

The assumption of periodic boundary conditions therefore allows us to write

$$w_\alpha(l,k)=\sum_{l'}W_\alpha(k,l')\,e^{i(2\pi/L)l'\cdot l} , \tag{19}$$

where

$$l'\cdot l \equiv l'_1 l_1 + l'_2 l_2 + l'_3 l_3 \tag{20}$$

and the sum over l' is such that l'_1, l'_2, and l'_3 take on L consecutive integers.

The displacements must be real and hence

$$W_\alpha(k,l) = W^*_\alpha(k,-l)\ . \tag{21}$$

We define

$$D_{\alpha\beta}(kk',l) \equiv \sum_{l'} D_{\alpha\beta}(l',kk')\, e^{-(2\pi/L)l\cdot l'}\ , \tag{22}$$

where l' is summed over all integer triplets, and $D_{\alpha\beta}(l,kk')$ is given by Eq. (15). $D_{\alpha\beta}(kk',l)$ is an element of a Hermitian matrix of rank $3n$. We denote its jth eigenvalue by $\omega^2(j,l)$ and the (α,k) component of the corresponding eigenvector by $e_\alpha(kj,l)$; $j=1,2,\ldots,3n$. Thus,

$$\sum_{k'\beta} D_{\alpha\beta}(kk',l)\, e_\beta(k'j,l) = \omega^2(j,l)\, e_\alpha(kj,l)\ . \tag{23}$$

From Eq. (22)

$$D_{\alpha\beta}(kk',l) = D^*_{\alpha\beta}(kk',-l)\ , \tag{24}$$

and hence,

$$\omega^2(j,l) = \omega^2(j,-l) \tag{25}$$

and

$$e_\alpha(kj,l) = e^*_\alpha(kj,-l)\ . \tag{26}$$

The eigenvectors satisfy the closure condition

$$\sum_j e^*_\alpha(kj,l) e_\beta(k'j,l) = \delta_{\alpha\beta}\delta_{kk'} \tag{27}$$

and the orthonormality condition

$$\sum_{\alpha k} e^*_\alpha(kj,l) e_\alpha(kj',l) = \delta_{jj'}\ . \tag{28}$$

Thus we may expand $W_\alpha(k,l)$ in a linear combination of either $e^*_\alpha(kj,l)$ or $e_\alpha(kj,l)$:

$$W_\alpha(k,l) = \sum_j Q(j,l) e_\alpha(kj,l)\ , \tag{29}$$

where

$$Q(j,l) = \sum_{\alpha k} W_\alpha(k,l) e^*_\alpha(kj,l)\ . \tag{30}$$

From Eqs. (21), (26), and (30) we have

$$Q(j,l) = Q^*(j,-l)\ . \tag{31}$$

When Eq. (29) is substituted into Eq. (19) and the resultant expression substituted into the potential energy [Eq. (14)], with similar substitutions for the time derivatives into the kinetic energy [Eq. (12)], the Hamiltonian is completely decoupled into a sum of $3nL^3$ independent oscillators with frequencies $\omega^2(j,l)$:

$$H = \frac{L}{2}\sum_{lj}\left[\dot{Q}(j,l)\dot{Q}^*(j,l) + \omega^2(j,l)Q(j,l)Q^*(j,l)\right]\ . \tag{32}$$

The derivation is straightforward and makes use of the facts and definitions expressed in Eqs. (18), (22), (23), and (30). From Eqs. (13), (19), and (29) the displacements become

$$u_\alpha(l,k) = (m_k)^{-1/2}\sum_{jl'} Q(j,l')e_\alpha(kj,l')\, e^{i(2\pi/L)l'\cdot l}\ . \tag{33}$$

The reality of the displacements is assured because of the conditions expressed in Eqs. (26) and (31).

There are two modifications of the above theory that commonly appear in the literature. First of all, we are free to replace $(l'\cdot l)$ by

$$l'\cdot l = (L/2\pi)\vec{q}(l')\cdot\vec{x}(l)\ , \tag{34}$$

where $\vec{x}(l)$ is given by

$$x_\alpha(l) = \sum_\beta A_{\alpha\beta} l_\beta\ , \tag{35}$$

$A_{\alpha\beta}$ is the βth component of the primitive lattice vector $\vec{a}_\alpha$, and $\vec{q}(l)$ is defined by

$$q_\alpha(l) \equiv \frac{2\pi}{L}\sum_\beta A^{-1}_{\alpha\beta} l_\beta\ . \tag{36}$$

$\vec{q}(l)$ has dimensions of inverse length and is said to be a "wave vector" of "reciprocal space." Those wave vectors for which l_1, l_2, and l_3 are each a multiple of L are "reciprocal-lattice vectors"

$$Q_\alpha(l) = 2\pi\sum_\beta A^{-1}_{\alpha\beta} l_\beta\ . \tag{37}$$

Two wave vectors are, of course, equivalent if they differ by a reciprocal-lattice vector. Since any value of wave vector can be attained by suitably choosing l and L we often drop the artificial l dependence of $\vec{q}(l)$ in future discussion.

The above theory can be modified further by including the phase factor $e^{\pm\vec{q}\cdot\vec{x}(k)}$ in the expansion of the displacements [Eq. (19)]. This necessitates the factor $e^{\pm\vec{q}\cdot[\vec{x}(k)-\vec{x}(k')]}$ in the definition of the dynamical matrix [Eq. (22)]. Whereas the choice of the signs in these exponentials was completely arbitrary in the foregoing analysis, one must now be careful. The choice of expanding $W_\alpha(k,\vec{q})$ in terms of $e_\alpha(kj,\vec{q})$ or $e^*_\alpha(kj,\vec{q})$ [see Eq. (29)] is no longer available. If the signs in the two exponentials are chosen to be the same then only the $e^*_\alpha(kj,\vec{q})$ expansion will decouple the potential energy, but if the signs are opposite, then $e_\alpha(kj,\vec{q})$ is the correct choice. We chose to write the displacements as

$$u_\alpha(l,k) = (m_k)^{-1/2}\sum_{l'j} Q(j,l')e_\alpha(kj,l')\, e^{i\vec{q}(l')\cdot\vec{x}(l,k)}\ , \tag{38}$$

which necessarily leads to the definition

$$D_{\alpha\beta}(kk',\vec{q}) \equiv \sum_l D_{\alpha\beta}(l,kk')\, e^{-i\vec{q}\cdot\vec{x}(l,kk')} \tag{39}$$

for the dynamical matrix.

In the previous discussion the pairwise potentials ϕ were assumed to include both Coulomb and short-range interactions. Owing to the long-range nature of the Coulomb interaction the form given above for the dynamical matrix is not absolutely convergent. However, the Coulomb part, $C_{\alpha\beta}(kk',\vec{q})$, can be written in a rapidly convergent form using Ewald's method. The result is

$$C_{\alpha\beta}(kk',\vec{q})=\frac{z_k z_{k'}}{(m_k m_{k'})^{1/2}}[G_{\alpha\beta}(kk',\vec{q})+H_{\alpha\beta}(kk',\vec{q})] - \frac{z_k}{m_k}\delta_{kk'}\sum_{k''} z_{k''}[\overline{G}_{\alpha\beta}(kk'')+H_{\alpha\beta}(kk'',0)], \tag{40}$$

where

$$G_{\alpha\beta}(kk',\vec{q})=\frac{4\pi}{v}\sum_{l}\left\{\frac{(Q_\alpha(l)+q_\alpha)Q_\beta(l)+q_\beta)}{|\vec{Q}(l)+\vec{q}|^2}\times\exp\left[-\frac{|\vec{Q}(l)+\vec{q}|^2}{4\epsilon^2}+i\vec{Q}(l)\cdot\vec{x}(kk')\right]\right\} - \delta_{kk'}\delta_{\alpha\beta}\frac{4\epsilon^3}{3\pi^{1/2}}, \tag{41}$$

$$\overline{G}_{\alpha\beta}(kk')=G_{\alpha\beta}(kk',0)-\frac{4\pi}{v}\frac{q_\alpha q_\beta}{q^2}, \tag{42}$$

$$H_{\alpha\beta}(kk',\vec{q})=-\sum_{l} h_{\alpha\beta}(\vec{x}(l,kk'))\,e^{-i\vec{q}\cdot\vec{x}(l,kk')}-\delta_{kk'}h_{\alpha\beta}(0), \tag{43}$$

and

$$h_{\alpha\beta}(\mathrm{x})=\left[\mathrm{erfc}(x\epsilon)+\frac{2\epsilon x}{\pi^{1/2}}e^{-x^2\epsilon^2}\right]\left[\frac{3x_\alpha x_\beta}{x^5}-\frac{\delta_{\alpha\beta}}{x^3}\right] + \frac{4\epsilon^3}{\pi^{1/2}}\frac{x_\alpha x_\beta}{x^2}e^{-x^2\epsilon^2}. \tag{44}$$

In the above expressions erfc is the complementary error function, v is the volume per unit cell (triple scalar product of the lattice vectors) z_k is the charge of the kth ion, and ϵ is an arbitrary parameter which is chosen to ensure rapid convergence.

Notice that $C_{\alpha\beta}(kk',\vec{q})$ is not regular at $\vec{q}=0$ and depends on the direction of $\vec{q}$ as $\vec{q}\to 0$. The nonregular part is related to the macroscopic electric field oscillations that accompany the long-wavelength vibrations.[8] However, it is still meaningful to treat the $\vec{q}=0$ dynamical matrix, where $\vec{q}=0$ implies the nonregular part is omitted, since including it only affects the infrared active modes.

III. CONSTRUCTION OF SYMMETRY COORDINATES

In Sec. II we saw how the translational symmetry of the lattice reduced the dynamical problem from that of diagonalizing a matrix of rank $3nL^3$ to diagonalizing L^3 matrices, each of rank $3n$. Now we shall see how additional symmetry operations can further simplify the dynamical problem.

Let the ions be permanently labeled by the indices (l,k), and allow the Cartesian coordinate system to undergo an arbitrary transformation consisting of a rotation and (or) reflection plus a translation of its origin. The αth component of the position of the (l,k) ion with respect to this new system is given by

$$x_\alpha^\rho(l,k)=\sum_{\rho}\theta_{\alpha\beta}^\rho x_\beta(l,k)+t_\alpha^\rho, \tag{45}$$

where $\overleftrightarrow{\theta}^\rho$ is the rotation and (or) reflection matrix and $\vec{t}^\rho$ is the translation vector with its tail at the origin of the transformed frame and its components taken with respect to the transformed frame.

Since $\vec{x}(l,kk')$ denotes the position of the (l,k) ion relative to the $(0,k)$ ion,

$$x_\alpha^\rho(l,kk')=\sum_{\beta}\theta_{\alpha\beta}^\rho x_\beta(l,kk') \tag{46}$$

does not depend on $\vec{t}^\rho$. Substituting Eq. (46) into Eq. (4)

$$[l,kk']_{\alpha\beta}^\rho=\sum_{\gamma\delta}[l,kk']_{\gamma\delta}\theta_{\alpha\gamma}^\rho\theta_{\beta\delta}^\rho, \tag{47}$$

and thus, from Eqs. (10) and (15),

$$D_{\alpha\beta}^\rho(l,kk')=\sum_{\gamma\delta}D_{\gamma\delta}(l,kk')\theta_{\alpha\gamma}^\rho\theta_{\beta\delta}^\rho. \tag{48}$$

Clearly, $D_{\alpha\beta}^\rho(kk',\vec{q})$ is defined by

$$D_{\alpha\beta}^\rho(kk',\vec{q})\equiv\sum_{l}D_{\alpha\beta}^\rho(l,kk')\,e^{-i\vec{q}\cdot\vec{x}^\rho(l,kk')}, \tag{49}$$

and its eigenvalues $\omega_\rho^2(j,\vec{q})$ and eigenvectors $e_\alpha^\rho(kj,\vec{q})$ satisfy

$$\sum_{k'\beta}D_{\alpha\beta}^\rho(kk',\vec{q})e_\beta^\rho(k'j,\vec{q})=\omega_\rho^2(j,\vec{q})\,e_\alpha^\rho(kj,\vec{q}). \tag{50}$$

Substituting Eqs. (48) and (46) into Eq. (49) we have

$$D_{\alpha\beta}^\rho(kk',\vec{q})=\sum_{l}\sum_{\gamma\delta}D_{\gamma\delta}(l,kk')\theta_{\alpha\gamma}^\rho\theta_{\beta\delta}^\rho\times\exp\left[-i\sum_{\sigma\mu}q_\sigma\theta_{\sigma\mu}^\rho x_\mu(l,kk')\right]. \tag{51}$$

Making the definition

$$q_\alpha^\rho\equiv\sum_{\beta}\theta_{\beta\alpha}^\rho q_\beta \tag{52}$$

Eq. (51) becomes

$$D_{\alpha\beta}^\rho(kk',\vec{q})=\sum_{\gamma\delta}D_{\gamma\delta}(kk',\vec{q}^\rho)\theta_{\alpha\gamma}^\rho\theta_{\beta\delta}^\rho. \tag{53}$$

Substituting Eq. (53) into Eq. (50),

$$\sum_{k'\beta}\sum_{\gamma\delta}D_{\gamma\delta}(kk',\vec{q}^\rho)\theta_{\alpha\gamma}^\rho\theta_{\beta\delta}^\rho e_\beta^\rho(k'j,\vec{q})=\omega_\rho^2(j,\vec{q})e_\alpha^\rho(kj,\vec{q}). \tag{54}$$

Since $\overleftrightarrow{\theta}^\rho$ is an orthogonal transformation,

$$\sum_{\gamma}\theta_{\alpha\gamma}^\rho\theta_{\beta\gamma}^\rho=\sum_{\gamma}\theta_{\gamma\alpha}^\rho\theta_{\gamma\beta}^\rho=\delta_{\alpha\beta}. \tag{55}$$

Multiplying both sides of Eq. (54) by $\theta_{\alpha\sigma}^\rho$ and summing over α, using Eq. (55), the resultant equation is

$$\sum_{k'\beta}\sum_{\delta}D_{\sigma\delta}(kk',\vec{q}^\rho)\theta_{\beta\delta}^\rho e_\beta^\rho(k'j,\vec{q})=\omega_\rho^2(j,\vec{q})\sum_{\alpha}\theta_{\alpha\sigma}^\rho e_\alpha^\rho(kj,\vec{q}), \tag{56}$$

which implies that $\omega_\rho^2(j,\vec{q})=\omega^2(j,\vec{q}^\rho)$ and

$$e_\alpha(kj, \vec{q}^\rho) = \sum_\beta \theta^\rho_{\beta\alpha} e^\rho_\beta(kj, \vec{q}) \; . \qquad (57)$$

We now assume that the transformation ρ [Eq. (45)] is a symmetry operation. Thus, for every ion (l,k) there is an ion (l_ρ, k_ρ) such that

$$\vec{x}^\rho(l,k) = \vec{x}(l_\rho, k_\rho) \; . \qquad (58)$$

k and k_ρ refer to symmetrically equivalent ions and, therefore, have the same mass. Clearly,

$$\vec{x}^\rho(l-l', kk') = \vec{x}(l_\rho - l'_\rho, k_\rho k'_\rho) , \qquad (59)$$

and from Eqs. (4), (10), and (15)

$$D^\rho_{\alpha\beta}(l-l', kk') = D_{\alpha\beta}(l_\rho - l'_\rho, k_\rho k'_\rho) \; . \qquad (60)$$

Substituting Eqs. (59) and (60) into Eq. (49)

$$D^\rho_{\alpha\beta}(kk', \vec{q}) = \sum_{l''} D_{\alpha\beta}(l_\rho - l'_\rho, k_\rho k'_\rho)\, e^{-i\vec{q}\cdot\vec{x}(l''_\rho,\, k_\rho k'_\rho)} , \qquad (61)$$

where $l'' = l - l'$ and $l''_\rho = l_\rho - l'_\rho$. Summing over l'' is the same as summing over l''_ρ. Hence,

$$D^\rho_{\alpha\beta}(kk', \vec{q}) = D_{\alpha\beta}(k_\rho k'_\rho, \vec{q}) \; . \qquad (62)$$

Substituting Eq. (62) into Eq. (50) requires $\omega^2_\rho(j, \vec{q}) = \omega^2(j, \vec{q})$ and

$$e^\rho_\alpha(kj, \vec{q}) = e_\alpha(k_\rho j, \vec{q}) \; . \qquad (63)$$

Substituting Eq. (63) into Eq. (57) yields the following important result:

$$e_\alpha(kj, \vec{q}^\rho) = \sum_\beta e_\beta(k_\rho j, \vec{q})\theta^\rho_{\beta\alpha} \; . \qquad (64)$$

The set of all symmetry operations is a group known as the space group and the set of all lattice translations is an invariant subgroup of the space group.[10] Nothing in Eq. (64) is affected by lattice translations and thus one needs to consider only the factor group F of the space group with respect to the subgroup of lattice translations. Furthermore, we only need to consider those elements of F for which $\vec{q}^\rho$ and $\vec{q}$ are equivalent, i.e., differ only by a reciprocal-lattice vector. These elements form a subgroup of F, called the group of the wave vector $\vec{q}$, which we denote by $F_{\vec{q}}$. Equation (64) defines a $3n \times 3n$ representation of $F_{\vec{q}}$ that may be used to further simplify the dynamical problem in the manner prescribed by group-representation theory.

It is convenient to define the indices i and j from the pairs (αk) and $(\beta k')$ by $i = (\alpha - 1)n + k$ and $j = (\beta - 1)n + k'$ so that the elements of the dynamical matrix and representation matrices are written $D_{ij}(\vec{q})$ and $R_{ij}(\rho)$. One constructs the unitary matrix $U_{ij}(\vec{q})$, which block diagonalizes the dynamical matrix, from symmetry coordinates obtained from the projection operator

$$P^\nu_{ij}(\vec{q}) \propto \sum_\rho x^*_\nu(\rho, \vec{q}) R_{ij}(\rho) , \qquad (65)$$

where $x_\nu(\rho, \vec{q})$ is the character of the ρth operation in the νth irreducible representation of $F_{\vec{q}}$ and the summation is over those ρ in $F_{\vec{q}}$. The characters are those of the point group $\overleftrightarrow{\theta}^\rho$ with ρ in $F_{\vec{q}}$. The number of linearly independent coordinates, obtained by applying $\overleftrightarrow{\mathrm{P}}^\nu(\vec{q})$ to arbitrary $3n$-dimensional column vectors, is the dimension of the νth irreducible representation, $d_\nu(\vec{q})$, times its multiplicity,

$$m_\nu(\vec{q}) = \frac{1}{g_{\vec{q}}} \sum_\rho x^*_\nu(\rho, \vec{q}) x(\rho) , \qquad (66)$$

where $x(\rho)$ is the character of $\overleftrightarrow{\mathrm{R}}(\rho)$ and $g_{\vec{q}}$ is the number of elements in $F_{\vec{q}}$. When orthonormalized and arranged in groups with the same ν these coordinates form the matrix $\overleftrightarrow{\mathrm{U}}(\vec{q})$. The block-diagonalized dynamical matrix

$$\overleftrightarrow{\mathrm{B}}(\vec{q}) = \overleftrightarrow{\mathrm{U}}^\dagger(\vec{q}) \overleftrightarrow{\mathrm{D}}(\vec{q}) \overleftrightarrow{\mathrm{U}}(\vec{q}) \qquad (67)$$

consists of $p(\vec{q})$ matrices of rank $d_\nu(\vec{q}) m_\nu(\vec{q})$, where $p(\vec{q})$ is the number of irreducible representations of $F_{\vec{q}}$.

IV. PRACTICAL CONSIDERATIONS

The static-equilibrium conditions (SEC) are a set of linear equations in the unknown first derivatives of the short-range potentials. Specifically,

$$\sum_{lk} \phi'(x(l,kk')) \frac{x_\alpha(l,kk')}{x(l,kk')} + F_\alpha(k') = 0 \qquad (68)$$

and

$$\frac{1}{2} \sum_{lkk'} \phi'(x(l,kk')) \frac{x_\alpha(l,kk') x_\beta(l,kk')}{x(l,kk')} + f_{\alpha\beta} = 0 , \qquad (69)$$

where ϕ denotes the short-range potentials, and $F_\alpha(k)$ and $f_{\alpha\beta}$ are the Coulomb contributions to the SEC and are given explicitly in Ref. 2. Equation (68) results from minimizing the potential energy with respect to internal strains and requires that the net force on the k' ion is zero. Equation (69) comes from minimizing with respect to external strains and says that the Coulomb stress tending to collapse the crystal must be balanced by the short-range stress trying to explode the crystal.

The number of independent SEC is the number of parameters required to define the crystal structure. The crystal structure is given by the three lattice vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ and the n basis vectors $\vec{x}(k)$. For the most general case, there are $6 + 3(n-1)$ independent SEC. The six external-strain conditions correspond to the six parameters needed to specify the lattice. For more symmetric crystal lattices this number is reduced to correspond to the number of lattice parameters. The $3n$ internal-strain conditions correspond to the three components of the n basis vectors, but one of the $\vec{x}(k)$ is arbitrary because we can put the origin anywhere, so $3(n-1)$ of these are independent. When symmetry other than lattice translations exists many of the ions may be identical to other ions in a single unit cell. Identical ions occupy symmetrically equivalent positions, and these are tabulated in the *International Tables for X-Ray Crystallography*[11] for all of the 230 space groups. Each set of equivalent positions is given a label (Wyckoff symbol) denoting its site symmetry. The number of parameters in a set of equivalent positions is the number of linearly independent internal-strain conditions due to a set of identical ions with that site symmetry. These symmetry effects which are inherent in the SEC are easily seen by inspecting the values computed for the Coulomb coefficients. This makes it easy to select a complete set of independent SEC from those given by Eqs. (68) and (69).

In the rigid-ion approximation, two pairs of ions are identical (have the same potential) if the ions in one pair are identical to the ions in the other and they have equal bond lengths. If the electron clouds of the ions in a given pair are in direct contact its short-range potential should be included in the model and its first derivative is an unknown in the SEC. It is convenient to label the short-range potentials $\phi(1)$, $\phi(2)$, etc., according to their bond lengths $x(1)$, $x(2)$, etc. In rare cases, two nonidentical bonds included in the model may have the same bond length, but, in general, for complex crystals, the short-range interactions are uniquely labeled by their bond lengths. This makes it easy for the computer to recognize and identify identical short-range forces in the computation of the coefficients of the various $\phi'(i)$ in Eqs. (68) and (69). The summation over l in these equations must include those terms for which $|l_\alpha| \leq 1$.

These coefficients form an $s \times p$ matrix, where s is the number of independent SEC and p is the number of short-range potentials included in the model. Clearly we must have $p \geq s$ to completely satisfy the SEC. For $p > s$, $p - s$ of the unknowns must be determined by other means, such as, from lattice-dynamical data. The question of which of these unknowns would best be determined from the SEC may be answered by comparing the values for the determinants of the matrices obtained by eliminating $p - s$ of the columns from the larger $s \times p$ matrix. The most effective use of the structural data is obtained from the matrix with the greatest determinant. On the other hand, if the determinant is small, the matrix is nearly singular and the solution may be thought of as depending on the difference between two nearly equal structure parameters. A very nearly singular condition may result when all the ϕ' parameters belonging to a tightly bound molecular group are included as unknowns in the SEC. This is illustrated in the following paper for the PO_4^{-3} group in fluorapatite.

For very complex crystals the SEC may provide information about the charge of the ions and the second derivatives of the short-range potentials as well as the first derivatives. Let two bonds be designated as "similar" if the ions in one pair have the same charge and mass as the ions in the other pair. Similar bonds may be assumed to have the same potential function. If a few similar bonds have nearly the same bond length, say x_0, then the ϕ' values for these bonds should be approximately the same if the charge distribution is correct. Thus we may write $\phi'(x) = \phi'(x_0) + \phi''(x_0)(x - x_0)$. The SEC then determine $\phi'(x_0)$ and $\phi''(x_0)$, and consequently $\phi'(x)$ is determined for each of these bonds and $\phi''(x)$ is given approximately by $\phi''(x_0)$. Alternatively, a particular form for the potential of similar bonds may be chosen with the parameters of the potential determined by the SEC. However, the solution is more difficult to obtain since the resultant SEC are no longer linear and an iterative procedure must be used. This is illustrated in the following paper, where a Born-Mayer form is chosen for the potential between calcium and oxygen ions. Clearly, the advantage of this approach is that it reduces the number of unknown parameters in the model and thus, more information is obtained from the SEC. On the other hand, it relies on assumptions regarding the similarity of bonds and the form of their potential. The merit of these assumptions may ultimately be judged by comparing computed phonon frequencies to lattice-dynamical data.

The difficulties involved in performing lattice-dynamical calculations for very complex crystals primarily results from the huge size of the dynamical matrix. Effective use of the computer is imperative. Our philosophy has been to program the lattice-dynamical problem in the most general way possible. It is a relatively simple matter to program the general expressions in Sec. II for the dynamical matrix. The transformation to symmetry coordinates (Sec. III) is a little trickier. Worlton and Warren[12] have published a program for this purpose, but it is rather large, consisting of ~1600 cards, and is limited to crystals with $n \leq 20$. We have written a 135-card subroutine which will compute $\overleftrightarrow{U}(\vec{q})$ [Eq. (67)] for very complex crystal structures.[7]

The expressions for the dynamical matrix of a general rigid-ion crystal are given in Sec. II. The Coulomb part is given explicitly in terms of the charge of the ions, the mass of the ions, the basis vectors, the lattice vectors, and the wave vector by the expressions in Eqs. (35), (37), (40)–(44). The convergence parameter should be chosen such that $1/\epsilon$ is on the order of the length of the lattice vectors. The optimum value for ϵ may be determined by computing a few of the elements for several values of ϵ. When ϵ is carefully chosen sufficient accuracy may be obtained by summing over just those l for which $|l_\alpha| \leq 2$. This also applies to the computation of the Coulomb contributions to the SEC.

The short-range part of the dynamical matrix is given by Eqs. (4), (10), (15), (35), and (39), in which ϕ refers to the short-range part of the potentials. For simple structures the summation over l in Eq. (39) is usually done by hand for each element, but for complex crystals this is a prohibitive amount of human labor. The sum is easily done by computer when the bonds are labeled according to their lengths as discussed above in the computation of the coefficient matrix for the SEC. The input to the short-range part is the crystal structure, the wave vector, the mass of the ions, and the first and second derivatives of the short-range potentials.

For the most part the crucial input to the dynamical problem, namely, the charge of the ions and the values of $\phi'(i)$ and $\phi''(i)$, is obtained from the SEC. Most of the $\phi'(i)$ values are given directly by the SEC while the charge distribution and the values for $\phi''(i)$, or rough estimates thereof, result from assumptions regarding the similarity of bonds. Supporting information may be taken from the molecular dynamics of tightly bound composite ions, as is illustrated in the following paper, where we consider the vibration of the free phosphate ion.

Refinements of this approximate model are made from the lattice-dynamical data. Raman scattering measurements are especially convenient if the crystal has inversion symmetry. In this case, the Raman and infrared active modes are completely decoupled and thus the Raman active modes do not depend on the direction of the wave vector. That is, the nonregular part of $C_{\alpha\beta}(kk',\vec{q})$ as $\vec{q} \to 0$ [see Eq. (40)] can be omitted without affecting the Raman active vibrations. In any case, the long-wavelength phonons are certainly the most expedient sources of information. The computations are easier because the long-wavelength dynamical matrix is real, and a vast amount of Raman and infrared data already exist for complex ionic crystals. Of course any completely reliable model must be accurate for all wave vectors.

For simple structures it is often possible to derive an analytic expression for the frequencies of various long-wavelength modes. For complex crystals the dependence of the frequencies on the adjustable parameters must be determined numerically. Also, the measured spectrum is a much richer source of information, which makes it difficult to establish a generally applicable fitting procedure. As a general rule, of course, one should try to fit those features in the spectrum which are most sensitive to the adjustable parameters (see, for example, the method used in the following paper). In any case it is clear that the frequencies must be computed repeatedly, each time systematically adjusting the parameters in order to obtain the best values.

As these computations can be quite lengthy, it is important to take measures to make them as efficient as possible. Obviously, the matrix $\overleftrightarrow{U}$ [Eq. (67)] need only be computed once. It takes considerably more time to compute the Coulomb part of the dynamical matrix than the short-range part. Thus one should determine the best short-range parameters for a given charge distribution, rather than vice versa, since the Coulomb part is computed and block diagonalized just once in the process. The short range part may be written

$$\overleftrightarrow{D} = \sum_i \phi''(i)\overleftrightarrow{D}_2(i) + \sum_i \phi'(i)\overleftrightarrow{D}_1(i), \tag{70}$$

where the coefficient matrices $\overleftrightarrow{D}_1(i)$ and $\overleftrightarrow{D}_2(i)$ are computed and block diagonalized just once. This reduces the computations considerably since otherwise $\overleftrightarrow{D}$ would have to be computed and the matrix multiplications $\overleftrightarrow{U}^\dagger \overleftrightarrow{D}\, \overleftrightarrow{U}$ performed for each model refinement.

ACKNOWLEDGMENT

This work evolved from earlier work at the University of Nebraska in collaboration with Professor J. R. Hardy.

---

*Work supported by Grant No. DE02492 of the National Institute of Health.

†Present address: Code 6440, Naval Research Laboratory, Washington, D. C. 20375.

[1] L. L. Boyer and P. A. Fleury, following paper, Phys. Rev. B 9, 2693 (1974).

[2] L. L. Boyer and J. R. Hardy, Phys. Rev. B 7, 2886 (1973).

[3] E. W. Kellerman, Philos. Trans. R. Soc. Lond. 238, 513 (1940).

[4] L. L. Boyer and J. R. Hardy, Phys. Rev. B 8, 2205 (1973).

[5] M. E. Striefler and G. R. Barsch, J. Phys. Chem. Solids 33, 2229 (1972).

[6] G. C. Cran and M. J. L. Sangster, J. Phys. C 5, 1008 (1972).

[7] L. L. Boyer (unpublished).

[8] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., London, 1954).

[9] A. A. Maradudin and S. H. Vosko, Rev. Mod. Phys. 40,

1 (1968).

[10] For a clear and concise presentation of group-representation theory see J. W. Leech and D. J. Newman, *How to Use Groups* (Methuen, London, 1969).

[11] *International Tables for X-ray Crystallography*, edited by N. F. M. Henry and K. Lorsdale (Kynoch, Birmingham, England).

[12] T. G. Worlton and J. L. Warren, Comput. Phys. Commun. 3, 88 (1972).