A NEW MODEL FOR THE LATTICE DYNAMICS OF ALKALI HALIDES

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Abstract

Qualitative properties of the electronic band structure of a KCl crystal are used to derive a simple two-parameter model for the correlation function $c(q, q')$ which arises in the theory of lattice dynamics. This function relates the adiabatic deformation of the electronic band structure to the vibration of the ion cores. Expressions for the dynamical matrices are derived. The model is ready for a direct computer evaluation of the phonon frequencies to test its validity.

I. INTRODUCTION

The general theory of lattice dynamics was originally developed by Born and his collaborators (see e.g. Born and Huang 1954). This theory pictures a crystal as composed of atoms or ions which vibrate about their lattice sites and which interact strongly with one another, so that the atomic vibrations are not independent but are correlated in the form of travelling waves (phonons). The basic problem then becomes the calculation of the potential of interaction among the ions. Once this is done the dynamical matrices may be calculated and diagonalized to give the phonon frequencies and eigenvectors.

The simplest model for the alkali halide crystals is the point ion model, which pictures the NaCl crystal, for example, as being composed of rigid ions of Na^+ and Cl^- interacting through their Coulomb potentials and through a short-range overlap repulsion. This approximate description gives a good account of the static lattice properties of the alkali halides such as the cohesive energy and the compressibility, but the phonon frequencies calculated from the point ion model do not agree with the frequencies measured by inelastic neutron scattering (Hardy 1962; Woods *et al.* 1963). The reason for this situation is as follows. Except for the very small zero-point vibrational energy, the static lattice energy is just the total potential (energy) of the Na^+ and Cl^- lattice with all ions at rest and located at their equilibrium lattice sites. Although the ions are not really rigid, they remain unpolarized (in low order moments) because every lattice site is a centre of crystalline symmetry and hence the Coulomb potential of each ion, as seen by the other ions, is essentially that of a point charge. When the ions vibrate, however, they move into regions where the field gradients are strong and so become polarized. The strong multipole interactions among the ions then make an important contribution to the vibrational energy and the phonon frequencies.

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Shell models have been devised to account for the polarization effects in vibrational properties of ionic crystals (see e.g. Cowley *et al.* 1963). These many-parameter models can indeed be made to fit the measured phonon frequencies quite well but the connection of the shell model parameters with other physical properties is generally obscure. In this paper a new model is proposed for the lattice dynamics of ionic crystals, a model based on a few parameters which are related to the dielectric properties of the crystal in question.

The present author (Wallace 1972) has recently used the band structure theory of crystals to give a formal description of the total potential of a crystal of ions moving within the adiabatic approximation. Here the picture is slightly different from Born's original picture: the crystal is composed of ion cores and one or more electronic bands which contain the outer atomic electrons. The number of electrons that may be taken from each atom and assigned to the electronic bands is, in principle, arbitrary and so may be chosen to produce a physically realistic model. The total potential of interaction between ion cores consists now of two contributions: the direct ion–ion interaction and the indirect ion–electron–ion interaction, the latter being an effective interaction among ions which proceeds through the band electrons. The value of this description lies in the fact that the ion cores can be taken to be small and rigid so that they do not overlap with one another during their vibrations, and hence their direct interactions are indeed just the Coulomb interactions among point charges. This Coulomb part of the potential is not at all like that of the original point ion model, however, since in the band structure theory *all* ions are positively charged. The band structure contribution to the interionic potential is formulated in terms of a generalized dielectric function, which describes the variation of the electronic band structure energy that results from a variation of the positions of the ion cores. In this way the complicated problem of the purely ionic model, namely, the problem of the polarization of large ions when they vibrate, is restated in more appropriate language as the problem of the deformation of the electronic band structure during the vibration of small and rigid ion cores.

From the band structure theory of the crystal potential it is possible to derive a simple formula for the dynamical matrices, in which the band structure contribution appears through a correlation function $c(q, q')$ which is related to the inverse of the dielectric function. Physically, $c(q, q')$ relates the q Fourier component of the electron–electron potential to the q' Fourier component of an arbitrary displacement of the ion cores from their equilibrium lattice sites. For the nearly-free-electron metals, the band structure theory of lattice dynamics contains the local pseudopotential theory, which has been shown to give a good description of both the static and vibrational properties of these metals in terms of a diagonal Hartree dielectric function and a small effective ion core potential (a pseudopotential) which couples the ions to the conduction electrons. It is therefore likely that the band structure theory will prove useful for ionic crystals as well.

It is proposed to apply the theory through a simple parameterized model for the correlation function. In Section II the qualitative properties of the band electron wavefunctions are used to develop a model for $c(q, q')$, with particular reference to NaCl and KCl. For the alkali halides the dielectric function, and hence also $c(q, q')$,

is *essentially* nondiagonal for, if it were otherwise, the longitudinal and transverse optic modes would be degenerate at $k = 0$. In Section III, the dynamical matrices are written down and the optic mode frequencies at $k = 0$ are obtained.

II. CORRELATION FUNCTION MODEL

The lattice vectors for the NaCl lattice are $R(N) + R(\mu)$, where N indicates the unit cell and μ indicates the ion in the unit cell. The vectors $R(N)$ form an f.c.c. primitive lattice

$$R(N) = (a/\sqrt{2})(N_1 x + N_2 y + N_3 z), \tag{1}$$

where a is the lattice parameter (the distance between nearest Cl ion sites), x, y, and z are unit vectors along the cartesian axes, and N_1, N_2, and N_3 are integers with the condition $N_1 + N_2 + N_3 = $ even. We take $\mu = 0$ for the Cl sites, $\mu = 1$ for the Na sites, and write

$$R(\mu=0) = 0 \quad \text{and} \quad R(\mu=1) = (a/\sqrt{2})z. \tag{2}$$

The inverse lattice vectors are given by

$$Q(P) = (\sqrt{2}\pi/a)(P_1 x + P_2 y + P_3 z), \tag{3}$$

where P_1, P_2, and P_3 are integers and are either all even or all odd (b.c.c. inverse lattice). Some useful results of the cubic symmetry of the inverse lattice are:

$$\sum_Q f(|Q|)Q_i Q_j \cos\{Q.R(\mu)\} = \tfrac{1}{3}\delta_{ij} \sum_Q f(|Q|)Q^2 \cos\{Q.R(\mu)\}, \tag{4}$$

$$\sum_Q f(|Q|)k.Q k_i Q_j \cos\{Q.R(\mu)\} = \tfrac{1}{3}k_i k_j \sum_Q f(|Q|)Q^2 \cos\{Q.R(\mu)\}. \tag{5}$$

Here the summation is taken over all vectors Q, $f(|Q|)$ is any function of $|Q|$ such that the sums converge, i and j are used throughout for cartesian indices, and k in equation (5) is an arbitrary vector.

Turning now to the electronic band structure, we consider three calculations for KCl which are in agreement qualitatively, if not in detail. Howland (1958) calculated the valence bands in the LCAO approximation, Oyama and Miyakawa (1966) did an OPW calculation of the conduction band, and De Cicco (1967) calculated valence and conduction bands by the APW method. These calculations show that the highest (filled) valence band is nearly Cl 3p in character and about 1 eV wide; about 10 eV below this is a narrow K 3p band; and lower still are the Cl 3s and K 3s bands. The (empty) conduction band is complicated, having Cl s, p, and d character, with the d states lying lowest, and the bandgap between valence and conduction bands is about 6 eV. The band calculations also show that the valence electrons have negligible density at the K^+ lattice sites. As a first model we therefore propose to consider only the Cl 3p valence band, and take the remaining electrons to be tightly bound into rigid ion cores; the ion cores are therefore K^{1+} and Cl^{5+}, and the valence band contains six electrons per ion pair.

The band structure results can be used to estimate the q dependence of the matrix element $\langle \psi_\lambda | \exp(iq \cdot r) | \psi_{\lambda'} \rangle$, where r is the position variable (the variable of integration), ψ_λ a valence electron wavefunction, and $\psi_{\lambda'}$ a valence or conduction electron wavefunction. The question here is: how does this matrix element converge at large q? Since ψ_λ is a Cl 3p function which does not overlap the K^+ lattice site, the slowest convergence arises from the part of $\psi_{\lambda'}$ in the conduction band which has Cl s character. By using hydrogen-like radial functions we find (qualitatively) that

$$\langle \psi_\lambda | \exp(iq \cdot r) | \psi_{\lambda'} \rangle \propto q^{-4} \qquad \text{at large } q. \tag{6}$$

The general definition and properties of $c(q, q')$ have been given by Wallace (1972, especially Section 21). The significant properties which will help to model the correlation function for KCl may be summarized as:

(1) $c(q, q')$ should have a simple zero as $q \to 0$ and as $q' \to 0$.

(2) $c(q, q')$ should be odd in q and odd in q'. Thus from (1) it appears that $c(q, q')$ should go as $q \cdot q'$ for small q or small q'.

(3) For short wavelength components, i.e. for q and q' both of the order of the first inverse lattice vector Q, the transverse correlations containing terms like $q_x q_y'$ should be important.

(4) At large q or q', it follows from the estimate of equation (6) that $c(q, q')$ should converge at least as fast as q^{-4} or q'^{-4}. We note that $c(q, q')$ will converge faster than this estimate if the s part of the conduction electrons is of negligible importance.

(5) $c(q, q')$ vanishes unless $q' = q + Q$, where Q is any inverse lattice vector, including zero.

From these remarks we can construct the model correlation function:

$$
\begin{aligned}
c(q, q') = \delta_{q', q+Q} \Big(&\alpha q \cdot q' \, (1 + q^2/\kappa^2)^{-5/2} \, (1 + q'^2/\kappa^2)^{-5/2} \\
&+ \beta q^2 q'^2 \sum_{i \neq j} q_i q_j' (1 + q^2/\kappa^2)^{-7/2} (1 + q'^2/\kappa^2)^{-7/2} \Big),
\end{aligned}
\tag{7}
$$

where α, β, and κ are adjustable parameters. From the derivation of equation (6) by means of hydrogen-like radial functions, we expect κ to be of order Z_0/a_0, where Z_0 is the Cl ion charge ($5+$) and a_0 is the Bohr radius. From dimensional arguments and simple sum rules, we expect α to be of order $-\hbar^2/2mE^2$, where E is the gap between valence and conduction bands. The parameter β is related to the splitting of longitudinal and transverse optic modes at $k = 0$ through equations (15) and (16) of Section III. The term containing $q \cdot q'$ in equation (7) is the longitudinal part of the correlation function, which is important at small q or q', and the term in the cartesian components of q and q' is the transverse part, which becomes important at larger q and q'.

To complete the formulation of the dynamical matrices, it is necessary to specify the bare ion potentials $v_\mu(r)$ which are seen by the valence electrons. The question here is: for a lattice of K^{1+} and Cl^{5+} ions, what local potential should be associated with

each ion so that a self-consistent valence band calculation would yield a reasonable Cl 3p valence band? We are asking, in other words, for a rigid K^{1+} potential and a rigid Cl^{5+} potential, and it is reasonable to expect that a local pseudopotential for each ion would be appropriate. The K^{1+} potential, for example, should be the same as the metallic K^{1+} pseudopotential, while the Cl^{5+} potential may be approximated by means of pseudopotential theory or might be taken as a parameterized local potential. In any case, in the region outside the ion core, each potential is clearly that due to a point charge:

$$v_\mu(r) = -Z_\mu e^2/r \qquad r > r_c, \tag{8}$$

where Z_μ is the ion core charge and r_c is the core radius. The Fourier coefficients $v_\mu(q)$ then have the property

$$v_\mu(q) \to -4\pi e^2 Z_\mu/q^2 V_C \qquad \text{as} \qquad q \to 0, \tag{9}$$

where V_C is the unit cell volume of the crystal.

The proposed model correlation function has three parameters which, however, are not all independent since there is a translational invariance condition coupling them. This is the long wavelength condition (Wallace 1972, equation (23.84)) which for the present model simplifies to

$$\alpha = Z_0 Z_1 \{h_0 Z_1 + h_1 Z_0 - (4\pi e^2/V_C)Z_0 Z_1\}^{-1}, \tag{10}$$

where the functions h_0 and h_1 are defined by

$$h_\mu = \tfrac{1}{3} \sum_Q' Q^2 (1 + Q^2/\kappa^2)^{-5/2} v_\mu(Q) \cos\{Q \cdot R(\mu)\} \tag{11}$$

and the summation, as denoted by the prime, is taken over all vectors Q except $Q = 0$. Hence α can be eliminated with equation (10), leaving a two-parameter model for the lattice dynamics of KCl. The same model should be applicable to NaCl.

III. DYNAMICAL MATRICES

For a given phonon wave vector k, the elements of the dynamical matrix are $D_{ij}(\mu v, k)$, where μ, v represent lattice sites within a unit cell. For the NaCl lattice the dynamical matrix is 6×6. In the band structure theory there are two contributions to $D_{ij}(\mu v, k)$: that arising from the electronic band energy, i.e. the ion–electron–ion interaction, and denoted by $D_{ij}(\mu v, k)_E$ and that arising from the direct ion–ion Coulomb interaction and denoted by $D_{ij}(\mu v, k)_I$. The latter contribution is further divided by the Ewald method into two terms: the Fourier sum part $D_{ij}(\mu v, k)_{IF}$ and the lattice sum part $D_{ij}(\mu v, k)_{IL}$. Expressions for these three matrix element contributions are given by equations (23.75)–(23.77) of Wallace (1972).

For computational purposes it is convenient to simplify the formula for the dynamical matrix elements by cancelling out certain $Q = 0$ terms between $D_{ij}(\mu v, k)_E$

and $D_{ij}(\mu v, \boldsymbol{k})_{\mathrm{IF}}$ by introducing the short-wavelength translational invariance condition (equation (23.83) of Wallace 1972) into $D_{ij}(\mu v, \boldsymbol{k})_{\mathrm{E}}$ and by then combining parts of $D_{ij}(\mu v, \boldsymbol{k})_{\mathrm{IF}}$ and $D_{ij}(\mu v, \boldsymbol{k})_{\mathrm{IL}}$ through the theta function transformation. The manipulation is straightforward, and use of the lattice and inverse lattice symmetries enables the indirect and direct contributions to the dynamical matrix for the NaCl lattice to be written in the real symmetric forms:

$$D_{ij}(\mu v, \boldsymbol{k})_{\mathrm{E}} = (M_\mu M_v)^{-\frac{1}{2}}$$

$$\times \sum_{\boldsymbol{Q}\boldsymbol{Q}'} c(\boldsymbol{Q}+\boldsymbol{k}, \boldsymbol{Q}'+\boldsymbol{k})(\boldsymbol{Q}+\boldsymbol{k})_i (\boldsymbol{Q}'+\boldsymbol{k})_j v_\mu(\boldsymbol{Q}+\boldsymbol{k}) v_v(\boldsymbol{Q}'+\boldsymbol{k}) \cos\{\boldsymbol{Q}.\boldsymbol{R}(\mu)\}\cos\{\boldsymbol{Q}'.\boldsymbol{R}(v)\}$$

$$-\delta_{\mu v} M_\mu^{-1} \sum_{\boldsymbol{Q}}{}' \sum_{\boldsymbol{Q}'}{}' c(\boldsymbol{Q}, \boldsymbol{Q}') Q_i Q'_j \sum_\pi v_\mu(\boldsymbol{Q}) v_\pi(\boldsymbol{Q}') \cos\{\boldsymbol{Q}.\boldsymbol{R}(\mu)\}\cos\{\boldsymbol{Q}'.\boldsymbol{R}(\pi)\}, \qquad (12)$$

$$D_{ij}(\mu v, \boldsymbol{k})_{\mathrm{I}} = (M_\mu M_v)^{-\frac{1}{2}}(4\pi e^2/V_{\mathrm{C}})Z_\mu Z_v$$

$$\times \sum_{\boldsymbol{Q}} \exp(-|\boldsymbol{Q}+\boldsymbol{k}|^2/4\eta^2)\,|\boldsymbol{Q}+\boldsymbol{k}|^{-2}(\boldsymbol{Q}+\boldsymbol{k})_i(\boldsymbol{Q}+\boldsymbol{k})_j \cos[\boldsymbol{Q}.\{\boldsymbol{R}(\mu)-\boldsymbol{R}(v)\}]$$

$$+(M_\mu M_v)^{-\frac{1}{2}} \sum_N{}'' \Phi_{ij}(0\mu, Nv)_{\mathrm{IL}} \cos[\boldsymbol{k}.\{\boldsymbol{R}(N)+\boldsymbol{R}(v)-\boldsymbol{R}(\mu)\}]$$

$$+\delta_{\mu v}\delta_{ij} M_\mu^{-1}(4\pi e^2/3V_{\mathrm{C}})Z_\mu \left(\sum_\pi Z_\pi - (\eta/\pi^{\frac{1}{2}})^3 V_{\mathrm{C}} Z_\mu\right). \qquad (13)$$

Here M_μ is the mass of ion μ; η is the Ewald convergence factor, to be chosen so that the lattice and inverse lattice sums converge rapidly; the doubly primed summation is to be taken over all N when $\mu \neq v$ and over all N except $N = 0$ when $\mu = v$; and the potential energy coefficient $\Phi_{ij}(0\mu, Nv)_{\mathrm{IL}}$ is defined by equation (23.64) of Wallace (1972).

The eigenvalues of the dynamical matrix for wave vector $\boldsymbol{k}$ are $\{\omega(\boldsymbol{k}s)\}^2$, where $s = 1, 2, \ldots, 6$ labels the six phonon modes for each $\boldsymbol{k}$ and $\omega(\boldsymbol{k}s)$ are the phonon frequencies. The matrix elements $D_{ij}(\mu v, \boldsymbol{k})$ are continuous as $\boldsymbol{k} \to 0$ and, for the present model, it is possible to diagonalize the matrix at $\boldsymbol{k} = 0$ to obtain explicit expressions for the corresponding phonon frequencies. The results are:

for the three acoustic modes at $\boldsymbol{k} = 0$

$$\omega^2 = 0; \qquad (14)$$

for the longitudinal optic mode at $\boldsymbol{k} = 0$

$$\omega^2 = \bar{M}^{-1}\{(4\pi e^2/3V_{\mathrm{C}})Z_0 Z_1 - \alpha(h_0 h_1 + h) - 2\beta(g_0 g_1 + g)\}; \qquad (15)$$

and for the transverse optic modes at $\boldsymbol{k} = 0$

$$\omega^2 = \bar{M}^{-1}\{(4\pi e^2/3V_{\mathrm{C}})Z_0 Z_1 - \alpha(h_0 h_1 + h) + \beta(g_0 g_1 + g)\}. \qquad (16)$$

The functions used are defined by

$$\bar{M} = M_0 M_1/(M_0 + M_1); \qquad (17)$$

$$h = \tfrac{2}{9} \sum_{\boldsymbol{Q}}{}' Q^4(1 + Q^2/\kappa^2)^{-5} v_0(\boldsymbol{Q}) v_1(\boldsymbol{Q}) \cos\{\boldsymbol{Q}.\boldsymbol{R}(1)\}; \qquad (18)$$

$$g_\mu = \tfrac{1}{3} \sum_{Q}{}' Q^4 (1 + Q^2/\kappa^2)^{-7/2} v_\mu(Q) \cos\{Q \cdot R(\mu)\} \; ; \tag{19}$$

$$g = \sum_{Q}{}' Q^4 (1 + Q^2/\kappa^2)^{-7} (\tfrac{2}{9}Q^4 - Q_x^4) v_0(Q) v_1(Q) \cos\{Q \cdot R(1)\} . \tag{20}$$

In equations (18) and (20), $R(1)$ means $R(\mu = 1)$ as defined by equation (2).

In conclusion, our philosophy is to consider the correlation function of equation (7) as a model for the lattice dynamics of NaCl or KCl. This model may be tested by computer evaluation of the expressions (12) and (13) for the dynamical matrix elements to see if the theoretical phonon frequencies can be made to agree with the measured phonon frequencies. The correlation function and its corresponding dielectric function can then be judged as meaningful to the extent that theory agrees with experiment, although further insight into the nature of these two functions may be obtained to the extent that the model may fail.

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