DIELECTRIC SATURATION IN IONIC CRYSTALS

I. RIGID ION MODEL

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Summary

The higher-order term in the static dielectric constant of an ionic crystal, which is proportional to the square of the applied field, is calculated using a rigid ion model. An explicit expression is obtained for this term, involving anharmonic coefficients, and is evaluated for NaCl.

I. Introduction

It has been observed experimentally by Herweg (1920) and Malsch (1928) that the static dielectric constant of many polar substances decreases as the strength of the applied field increases. This phenomenon is known as dielectric saturation. We can in general expand the dielectric constant as a power series in the applied field E, thus,

$$\epsilon_s = \epsilon_0 + \epsilon_1 E + \epsilon_2 E^2 + \ldots, \tag{1.1}$$

where ϵ_0 is the usual, field-independent, static dielectric constant and ϵ_1, ϵ_2 are small coefficients which depend on the structure of the substance involved.

For crystals with a centre of symmetry (e.g. ionic crystals of the NaCl structure) the term in (1.1) that is linear in E vanishes, because the dielectric constant must be invariant towards reversal of the direction of E.

The problem of the field dependence of the static dielectric constant has been treated classically by O'Dwyer (1951), who obtained a general expression involving the mean square and mean fourth dipole moment of a macroscopic sphere in the absence of a field.

Another classical calculation has been made by Ninio (1962), who obtained an expression in terms of constants directly related to the anharmonicity. Ninio used a one-dimensional model with nearest-neighbour interactions only, and so his result would not be expected to be quantitatively accurate for a real three-dimensional ionic crystal in which long-range Coulomb interactions are present.

In the present paper a quantum-mechanical calculation of the field-dependent dielectric constant is carried out using the theory of lattice dynamics developed by Born and von Kármán (cf. Born and Huang 1954; Cochran 1963). A three-dimensional model is used, and the long-range Coulomb interactions are taken into account. The only significant simplification is the representation of the ions by point charges. A better approximation would be obtained by taking account of the deformability of the ions by using a shell model (cf. Woods, Cochran, and Brockhouse 1960). It is hoped to present such a calculation in the future.

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If a harmonic crystal is subjected to an electric field the polarization produced is proportional to the field, giving a field-independent dielectric constant. Thus a harmonic crystal exhibits no saturation effect. The phenomenon of dielectric saturation in a crystal is, therefore, due to the presence of anharmonic terms in the potential energy.

II. The Hamiltonian of the Model

The Hamiltonian of the vibrating lattice, in the absence of an external electric field, can be written

$$H = H_0 + H_3 + H_4 + \ldots, \tag{2.1}$$

where H_0 is the harmonic Hamiltonian, given by

$$H_0 = \tfrac{1}{2} \sum_{l\kappa\alpha} (1/m_\kappa)\{p_\alpha(l\kappa)\}^2 + \Phi_0 + \tfrac{1}{2} \sum_{\substack{l\kappa\alpha \\ l'\kappa'\beta}} \Phi_{\alpha\beta}(l\kappa, l'\kappa')\, u_\alpha(l\kappa)\, u_\beta(l'\kappa'), \tag{2.2}$$

and H_3 and H_4 are respectively the cubic and quartic anharmonic terms, given by

$$H_3 = \frac{1}{3!} \sum_{\substack{l\kappa\alpha \\ l'\kappa'\beta \\ l''\kappa''\gamma}} \Phi_{\alpha\beta\gamma}(l\kappa, l'\kappa', l''\kappa'')\, u_\alpha(l\kappa)\, u_\beta(l'\kappa')\, u_\gamma(l''\kappa''), \tag{2.3}$$

$$H_4 = \frac{1}{4!} \sum_{\substack{l\kappa\alpha \\ l'\kappa'\beta \\ l''\kappa''\gamma \\ l'''\kappa'''\delta}} \Phi_{\alpha\beta\gamma\delta}(l\kappa, l'\kappa', l''\kappa'', l'''\kappa''')\, u_\alpha(l\kappa)\, u_\beta(l'\kappa')\, u_\gamma(l''\kappa'')\, u_\delta(l'''\kappa'''). \tag{2.4}$$

In the expressions (2.2), (2.3), and (2.4), $u_\alpha(l\kappa)$ is the α component of the displacement from equilibrium of the κth atom in the lth unit cell, and $p_\alpha(l\kappa)$ is the corresponding component of momentum. These are operators obeying the usual commutation rules

$$\left.\begin{aligned}
[u_\alpha(l\kappa), u_\beta(l'\kappa')]_- &= 0, \\
[p_\alpha(l\kappa), p_\beta(l'\kappa')]_- &= 0, \\
[u_\alpha(l\kappa), p_\beta(l'\kappa')]_- &= i\hbar\, \delta_{\alpha\beta}\, \delta_{ll'}\, \delta_{\kappa\kappa'}.
\end{aligned}\right\} \tag{2.5}$$

We have, in general, N unit cells in the crystal and n atoms per cell, so that

$$l = 1, 2, \ldots, N \qquad \kappa = 1, 2, \ldots, n\ ;$$

m_κ is the mass of an atom of type κ, Φ_0 is the potential energy of the static lattice, and the Φ coefficients are derivatives of the potential energy evaluated at the equilibrium positions of the atoms (at absolute zero and in the absence of zero-point energy).

It is known (e.g. Leibfried and Ludwig 1961) that it is insufficient to take account of the cubic anharmonic term alone in (2.1), because the quartic term gives contributions to the free energy of the same order of magnitude. However, higher-order terms can be consistently neglected.

In general, the successive force constants $\Phi_{\alpha\beta}$, $\Phi_{\alpha\beta\gamma}$, etc. are related to each other, as regards order of magnitude, by

$$\Phi_{\alpha\beta} \sim r_0\, \Phi_{\alpha\beta\gamma} \sim r_0^2\, \Phi_{\alpha\beta\gamma\delta},$$

where r_0 is the lattice parameter.   Thus, we can write the Hamiltonian (2.1) symbolically as

$$H = H_0 + \lambda H_3 + \lambda^2 H_4, \tag{2.6}$$

where λ is an order parameter which indicates the number of factors of r_0^{-1} contained in H_3 and H_4 relative to H_0. It can be set equal to unity at the end of the calculation.

In the presence of an external static field E in the x direction the Hamiltonian is

$$H(E) = H - EM, \tag{2.7}$$

where M is the x component of the dipole moment of the crystal, given by

$$M = e \sum_{l\kappa} Z_\kappa u_x(l\kappa), \tag{2.8}$$

eZ_κ being the charge on an ion of type κ.

It is convenient to introduce normal coordinates according to the definitions

$$\left. \begin{array}{l} u_\alpha(l\kappa) = (Nm_\kappa)^{-\frac{1}{2}} \sum_{\mathbf{q}j} e_\alpha(\kappa|\mathbf{q}j) \, Q(\mathbf{q}j) \exp\{2\pi i\, \mathbf{q}\cdot\mathbf{r}(l\kappa)\}, \\ p_\alpha(l\kappa) = (m_\kappa/N)^{\frac{1}{2}} \sum_{\mathbf{q}j} e_\alpha^*(\kappa|\mathbf{q}j) \, P(\mathbf{q}j) \exp\{-2\pi i\, \mathbf{q}\cdot\mathbf{r}(l\kappa)\}, \end{array} \right\} \tag{2.9}$$

where $e_\alpha(\kappa|\mathbf{q}j)$ is the $(\alpha\kappa)$ component of an eigenvector of the dynamical matrix, j labels the branches of the frequency spectrum, and the N allowed $\mathbf{q}$ values are uniformly distributed throughout the first Brillouin zone; $\mathbf{r}(l\kappa)$ is the equilibrium position of atom $(l\kappa)$.

Because $u_\alpha(l\kappa)$ and $p_\alpha(l\kappa)$ are Hermitian we impose the restrictions

$$e_\alpha(\kappa|-\mathbf{q}j) = e_\alpha^*(\kappa|\mathbf{q}j), \qquad Q(-\mathbf{q}j) = Q^*(\mathbf{q}j), \qquad P(-\mathbf{q}j) = P^*(\mathbf{q}j), \tag{2.10}$$

where * represents the Hermitian conjugate.

The operators obey the usual commutation rule

$$[Q(\mathbf{q}j), P(\mathbf{q}'j')]_- = i\hbar \, \Delta(\mathbf{q}-\mathbf{q}') \, \delta_{jj'}, \tag{2.11}$$

where

$$\Delta(\mathbf{q}) = \begin{cases} 1 & \text{if } \mathbf{q} \text{ is a reciprocal lattice vector (including 0)}, \\ 0 & \text{otherwise.} \end{cases}$$

Carrying out the transformation gives for the terms in (2.1)

$$H_0 = \tfrac{1}{2} \sum_{\mathbf{q}j} \{P^*(\mathbf{q}j) \, P(\mathbf{q}j) + \omega^2(\mathbf{q}j) \, Q^*(\mathbf{q}j) \, Q(\mathbf{q}j)\}, \tag{2.12}$$

$$H_3 = \tfrac{1}{6} N^{-\frac{1}{2}} \sum_{\substack{\mathbf{q}_1 \mathbf{q}_2 \mathbf{q}_3 \\ j_1 j_2 j_3}} \Delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3) \, \Phi(\mathbf{q}_1 j_1; \mathbf{q}_2 j_2; \mathbf{q}_3 j_3) \, Q(\mathbf{q}_1 j_1) \, Q(\mathbf{q}_2 j_2) \, Q(\mathbf{q}_3 j_3), \tag{2.13}$$

$$H_4 = \tfrac{1}{24} N^{-1} \sum_{\substack{\mathbf{q}_1 \mathbf{q}_2 \mathbf{q}_3 \mathbf{q}_4 \\ j_1 j_2 j_3 j_4}} \Delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3+\mathbf{q}_4) \, \Phi(\mathbf{q}_1 j_1; \mathbf{q}_2 j_2; \mathbf{q}_3 j_3; \mathbf{q}_4 j_4)$$

$$\times Q(\mathbf{q}_1 j_1) \, Q(\mathbf{q}_2 j_2) \, Q(\mathbf{q}_3 j_3) \, Q(\mathbf{q}_4 j_4), \tag{2.14}$$

where the Φ coefficients are given by

$$\Phi(\mathbf{q}_1 j_1; \mathbf{q}_2 j_2; \ldots; \mathbf{q}_s j_s) = \sum_{\substack{\kappa\alpha \\ l'\kappa'\beta \\ \cdots\cdots \\ l^{(s)}\kappa^{(s)}\gamma}} \frac{\Phi_{\alpha\beta\ldots\gamma}\{0\kappa, l'\kappa', \ldots, l^{(s)}\kappa^{(s)}\}}{\{m_\kappa m_{\kappa'} \ldots m_{\kappa^{(s)}}\}^{\frac{1}{2}}} e_\alpha(\kappa|\mathbf{q}_1 j_1) \ldots e_\gamma(\kappa^{(s)}|\mathbf{q}_s j_s)$$

$$\times \exp 2\pi i[\mathbf{q}_1 \cdot \mathbf{r}(0\kappa) + \ldots + \mathbf{q}_s \cdot \mathbf{r}\{l^{(s)}\kappa^{(s)}\}]. \quad (2.15)$$

The perturbation due to the external field becomes

$$H_E = -eE \sum_{l\kappa} Z_\kappa u_x(l\kappa)$$

$$= -E\alpha\, Q(04), \quad (2.16)$$

where $Q(04)$ is the normal coordinate of that particular optical mode with zero wave vector which has polarization in the x direction, and

$$\alpha = eN^{\frac{1}{2}} \sum_\kappa \frac{Z_\kappa e_x(\kappa|04)}{m_\kappa^{\frac{1}{2}}}. \quad (2.17)$$

Note that for $\mathbf{q} = 0$ there can be no distinction between longitudinal and transverse optic modes, which all vibrate with the characteristic infrared dispersion frequency ω_0. However, for small $\mathbf{q}$, such that the wavelength is large compared with the lattice distance but smaller than the dimensions of the crystal, there is a characteristic longitudinal branch with frequencies different from the two transverse branches. Much discussion has taken place recently on this point (Barron 1961; Rosenstock 1961; Fuchs and Kliewer 1965).

Thus, we have for the total Hamiltonian of the crystal in the presence of the perturbing field

$$H = H_0 + \lambda H_3 + \lambda^2 H_4 + H_E, \quad (2.18)$$

where the various terms are given by (2.12), (2.13), (2.14), and (2.16).

III. The Anharmonic Free Energy

The static dielectric constant is given by

$$\epsilon_s - 1 = \frac{4\pi \bar{M}_E}{EV}, \quad (3.1)$$

where V is the volume of the crystal and $\bar{M}_E$ is the mean dipole moment of the crystal while the field E is acting, given by

$$\bar{M}_E = -\left(\frac{\partial F}{\partial E}\right)_{V,T}. \quad (3.2)$$

The free energy F is given by

$$F = -(1/\beta) \ln Z, \quad (3.3)$$

where $\beta = 1/kT$, and the partition function Z is given by

$$Z = \text{Tr}\{e^{-\beta H}\}. \quad (3.4)$$

Therefore, to calculate ϵ_s up to the term proportional to E^2, we must expand Z and F up to order E^4. Thus we require to express Z as a power series in E. This can be done by perturbation theory.

The most obvious procedure would be to take H_0 as the unperturbed Hamiltonian and the remaining terms as a small perturbation. However, it is more convenient, following Szigeti (1959), to take $H_0 + H_E$ as the unperturbed Hamiltonian and the anharmonic terms as a small perturbation.

In the Hamiltonian $H_0 - E\alpha Q(04)$ the only effect of E is to shift the equilibrium position of $Q(04)$ to $\alpha E/\omega_0^2$ and to change each of its energy levels by $-\alpha^2 E^2/2\omega_0^2$ while the frequency ω_0 remains unaltered. None of the other Q's is affected by E.

Hence, we transform to new operators, defined by

$$\left.\begin{aligned}
\widetilde{P}(\mathbf{q}j) &= P(\mathbf{q}j), \\
\widetilde{Q}(\mathbf{q}j) &= Q(\mathbf{q}j) \qquad (\mathbf{q}j) \neq (04), \\
\widetilde{Q}(04) &= Q(04) - E\alpha/\omega_0^2.
\end{aligned}\right\} \tag{3.5}$$

Note that these operators are still canonically conjugate. We then obtain for the unperturbed Hamiltonian

$$H^{(0)} = H_0 + H_E$$
$$= \tfrac{1}{2} \sum_{\mathbf{q}j} \{\widetilde{P}^*(\mathbf{q}j)\widetilde{P}(\mathbf{q}j) + \omega^2(\mathbf{q}j)\widetilde{Q}^*(\mathbf{q}j)\widetilde{Q}(\mathbf{q}j)\} - \tfrac{1}{2}E^2\alpha^2/\omega_0^2. \tag{3.6}$$

This Hamiltonian has eigen-energies

$$E_n^{(0)} = \sum_{\mathbf{q}j} \hbar\,\omega(\mathbf{q}j)\{n(\mathbf{q}j) + \tfrac{1}{2}\} - \tfrac{1}{2}E^2\alpha^2/\omega_0^2, \tag{3.7}$$

where the $n(\mathbf{q}j)$ are integers greater than or equal to zero. Thus, we have for the total Hamiltonian

$$H = H^{(0)} + \lambda H_3 + \lambda^2 H_4, \tag{3.8}$$

and we have to transform H_3 and H_4 into the new coordinates. The result obtained for H_3 is

$$H_3 = H_3^{(0)} + E H_3^{(1)} + E^2 H_3^{(2)} + E^3 H_3^{(3)}, \tag{3.9}$$

where

$$H_3^{(0)} = \tfrac{1}{6} N^{-\frac{1}{2}} \sum_{\substack{\mathbf{q}_1\mathbf{q}_2\mathbf{q}_3 \\ j_1 j_2 j_3}} \Delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3)\, \Phi(\mathbf{q}_1 j_1; \mathbf{q}_2 j_2; \mathbf{q}_3 j_3)\, \widetilde{Q}(\mathbf{q}_1 j_1)\, \widetilde{Q}(\mathbf{q}_2 j_2)\, \widetilde{Q}(\mathbf{q}_3 j_3), \tag{3.10}$$

$$H_3^{(1)} = +\tfrac{1}{2} N^{-\frac{1}{2}}(\alpha/\omega_0^2) \sum_{\mathbf{q}j_1 j_2} \Phi(\mathbf{q}j_1; -\mathbf{q}j_2; 04)\, \widetilde{Q}(\mathbf{q}j_1)\, \widetilde{Q}(-\mathbf{q}j_2), \tag{3.11}$$

$$H_3^{(2)} = \tfrac{1}{2} N^{-\frac{1}{2}}(\alpha^2/\omega_0^4) \sum_j \Phi(0j; 04; 04)\, \widetilde{Q}(0j), \tag{3.12}$$

$$H_3^{(3)} = +\tfrac{1}{6} N^{-\frac{1}{2}}(\alpha^3/\omega_0^6)\, \Phi(04; 04; 04), \tag{3.13}$$

and the summations over modes include the mode $(0, 4)$.

The quartic anharmonic term can be transformed similarly, giving

$$H_4 = H_4^{(0)} + E H_4^{(1)} + E^2 H_4^{(2)} + E^3 H_4^{(3)} + E^4 H_4^{(4)}, \tag{3.14}$$

where

$$H_4^{(0)} = \tfrac{1}{24} N^{-1} \sum_{\substack{\mathbf{q}_1 \mathbf{q}_2 \mathbf{q}_3 \mathbf{q}_4 \\ j_1 j_2 j_3 j_4}} \Delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 + \mathbf{q}_4)\, \Phi(\mathbf{q}_1 j_1; \mathbf{q}_2 j_2; \mathbf{q}_3 j_3; \mathbf{q}_4 j_4)$$
$$\times \widetilde{Q}(\mathbf{q}_1 j_1)\, \widetilde{Q}(\mathbf{q}_2 j_2)\, \widetilde{Q}(\mathbf{q}_3 j_3)\, \widetilde{Q}(\mathbf{q}_4 j_4), \tag{3.15}$$

$$H_4^{(1)} = + \tfrac{1}{6} N^{-1} (\alpha/\omega_0^2) \sum_{\substack{\mathbf{q}_1 \mathbf{q}_2 \mathbf{q}_3 \\ j_1 j_2 j_3}} \Delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3)\, \Phi(\mathbf{q}_1 j_1; \mathbf{q}_2 j_2; \mathbf{q}_3 j_3; 04)$$
$$\times \widetilde{Q}(\mathbf{q}_1 j_1)\, \widetilde{Q}(\mathbf{q}_2 j_2)\, \widetilde{Q}(\mathbf{q}_3 j_3), \tag{3.16}$$

$$H_4^{(2)} = \tfrac{1}{4} N^{-1} (\alpha^2/\omega_0^4) \sum_{\mathbf{q} j_1 j_2} \Phi(\mathbf{q} j_1; -\mathbf{q} j_2; 04; 04)\, \widetilde{Q}(\mathbf{q} j_1)\, \widetilde{Q}(-\mathbf{q} j_2), \tag{3.17}$$

$$H_4^{(3)} = + \tfrac{1}{6} N^{-1} (\alpha^3/\omega_0^6) \sum \Phi(0j; 04; 04)\, \widetilde{Q}(0j), \tag{3.18}$$

$$H_4^{(4)} = \tfrac{1}{24} N^{-1} (\alpha^4/\omega_0^8) \Phi(04; 04; 04; 04). \tag{3.19}$$

Thus, we have to evaluate the partition function (3.4) for the Hamiltonian (3.8). The exponential operator in (3.4) can be expanded in the usual way by forming an integral equation and solving by iteration to yield

$$\exp(-\beta H) = \exp[-\beta \{ H^{(0)} + \lambda H_3 + \lambda^2 H_4 \}]$$

$$= \exp\{-\beta H^{(0)}\} \Big[1 - \beta \int_0^1 ds_1 \exp\{s_1 \beta H^{(0)}\} (\lambda H_3 + \lambda^2 H_4) \exp\{-s_1 \beta H^{(0)}\}$$

$$+ \beta^2 \int_0^1 ds_1 \int_0^{s_1} ds_2 \exp\{s_1 \beta H^{(0)}\}$$

$$\times (\lambda H_3 + \lambda^2 H_4) \exp\{-(s_1 - s_2)\beta H^{(0)}\}$$

$$\times (\lambda H_3 + \lambda^2 H_4) \exp\{-s_2 \beta H^{(0)}\}$$

$$+ \cdots \Big]. \tag{3.20}$$

Using (3.20) the partition function (3.4) becomes

$$Z = Z_0 + \lambda Z_1 + \lambda^2 Z_2 + \dots, \tag{3.21}$$

where

$$Z_0 = \mathrm{Tr}[\exp\{-\beta H^{(0)}\}], \tag{3.22}$$

$$Z_1 = -\beta\, \mathrm{Tr}\Big[\exp\{-\beta H^{(0)}\} \int_0^1 ds_1 \exp\{s_1 \beta H^{(0)}\} H_3 \exp\{-s_1 \beta H^{(0)}\} \Big], \tag{3.23}$$

$$Z_2 = -\beta\, \mathrm{Tr}\Big[\exp\{-\beta H^{(0)}\} \int_0^1 ds_1 \exp\{s_1 \beta H^{(0)}\} H_4 \exp\{-s_1 \beta H^{(0)}\} \Big]$$

$$+ \beta^2\, \mathrm{Tr}\Big[\exp\{-\beta H^{(0)}\} \int_0^1 ds_1 \int_0^{s_1} ds_2 \exp\{s_1 \beta H^{(0)}\} H_3 \exp\{-(s_1 - s_2)\beta H^{(0)}\}$$

$$\times H_3 \exp\{-s_2 \beta H^{(0)}\} \Big]. \tag{3.24}$$

Note that, since the Hamiltonian (3.8) was taken only as far as λ^2, Z can be expanded only to the same order.

The above expressions can be simplified using the cyclic theorem for traces and changing the order of integration in Z_2 (cf. Maradudin, Flinn, and Coldwell-Horsfall 1961), to yield

$$Z_0 = \sum_n \exp\{-\beta E_n^{(0)}\}, \tag{3.25}$$

$$Z_1 = -\beta \sum_n \exp\{-\beta E_n^{(0)}\} \langle n|H_3|n\rangle, \tag{3.26}$$

$$Z_2 = -\beta \sum_n \exp\{-\beta E_n^{(0)}\} \langle n|H_4|n\rangle + \beta \sum_{n,m}' \exp\{-\beta E_n^{(0)}\} \frac{\langle n|H_3|m\rangle\langle m|H_3|n\rangle}{E_m^{(0)} - E_n^{(0)}}$$
$$+ \tfrac{1}{2}\beta^2 \sum_n \exp\{-\beta E_n^{(0)}\} \langle n|H_3|n\rangle\langle n|H_3|n\rangle, \tag{3.27}$$

where the $E_n^{(0)}$ are given by (3.7) and the $|n\rangle$ are the eigenstates of the unperturbed Hamiltonian $H^{(0)}$. Substituting from (3.9) and (3.14) into (3.26) and (3.27) and using the fact that $H_3^{(0)}$, $H_3^{(2)}$, $H_4^{(1)}$, and $H_4^{(3)}$ have no diagonal matrix elements gives

$$Z_1 = EZ_1^{(1)} + E^3 Z_1^{(3)} \tag{3.28}$$

and

$$Z_2 = Z_2^{(0)} + E^2 Z_2^{(2)} + E^4 Z_2^{(4)} + E^6 Z_2^{(6)}, \tag{3.29}$$

where

$$Z_1^{(1)} = -\beta \sum_n \exp\{-\beta E_n^{(0)}\} \langle n|H_3^{(1)}|n\rangle, \tag{3.30}$$

$$Z_1^{(3)} = -\beta \sum_n \exp\{-\beta E_n^{(0)}\} \langle n|H_3^{(3)}|n\rangle, \tag{3.31}$$

$$Z_2^{(0)} = -\beta \sum_n \exp\{-\beta E_n^{(0)}\} \langle n|H_4^{(0)}|n\rangle + \beta \sum_{n,m}' \exp\{-\beta E_n^{(0)}\} \frac{\langle n|H_3^{(0)}|m\rangle\langle m|H_3^{(0)}|n\rangle}{E_m^{(0)} - E_n^{(0)}}, \tag{3.32}$$

$$Z_2^{(2)} = -\beta \sum_n \exp\{-\beta E_n^{(0)}\} \langle n|H_4^{(2)}|n\rangle$$

$$+ \beta \sum_{n,m}' \exp\{-\beta E_n^{(0)}\} \frac{\langle n|H_3^{(1)}|m\rangle\langle m|H_3^{(1)}|n\rangle}{E_m^{(0)} - E_n^{(0)}}$$

$$+ \tfrac{1}{2}\beta^2 \sum_n \exp\{-\beta E_n^{(0)}\} \langle n|H_3^{(1)}|n\rangle\langle n|H_3^{(1)}|n\rangle$$

$$+ \beta \sum_{n,m}' \exp\{-\beta E_n^{(0)}\} \frac{\langle n|H_3^{(0)}|m\rangle\langle m|H_3^{(2)}|n\rangle}{E_m^{(0)} - E_n^{(0)}}$$

$$+ \beta \sum_{n,m}' \exp\{-\beta E_n^{(0)}\} \frac{\langle n|H_3^{(2)}|m\rangle\langle m|H_3^{(2)}|n\rangle}{E_m^{(0)} - E_n^{(0)}}, \tag{3.33}$$

$$Z_2^{(4)} = -\beta \sum_n \exp\{-\beta E_n^{(0)}\} \langle n|H_4^{(4)}|n\rangle$$

$$+ \beta \sum_{n,m}{}' \exp\{-\beta E_n^{(0)}\} \frac{\langle n|H_3^{(2)}|m\rangle \langle m|H_3^{(2)}|n\rangle}{E_m^{(0)}-E_n^{(0)}}.$$

$$+ \beta^2 \sum_n \exp\{-\beta E_n^{(0)}\} \langle n|H_3^{(1)}|n\rangle \langle n|H_3^{(3)}|n\rangle, \tag{3.34}$$

$$Z_2^{(6)} = \tfrac{1}{2}\beta^2 \sum_n \exp\{-\beta E_n^{(0)}\} \langle n|H_3^{(3)}|n\rangle \langle n|H_3^{(3)}|n\rangle. \tag{3.35}$$

Using (3.21), (3.28), and (3.29) it is then possible to express the free energy (3.3) up to $O(\lambda^2)$ as a power series in E. However, for centro-symmetrical crystals several simplifications are possible. It can be shown that for such a crystal the coefficients $\Phi(0j; 04; 04)$ and $\Phi(04; 04; 04)$ vanish (see Appendix C). Thus $H_3^{(2)}$ and $H_3^{(3)}$ are identically zero. From energy considerations (the free energy must be an even function of E) it can be seen that the diagonal elements of $H_3^{(1)}$ must vanish. Thus from (3.28), (3.30), and (3.31) we have that $Z_1 = 0$, and the partition function can be written as

$$Z = Z_0 + \lambda^2 Z_2, \tag{3.36}$$

where

$$Z_2 = Z_2^{(0)} + E^2 Z_2^{(2)} + E^4 Z_2^{(4)} \tag{3.37}$$

and where

$$Z_2^{(0)} = -\beta \sum_n \exp\{-\beta E_n^{(0)}\} \langle n|H_4^{(0)}|n\rangle + \beta \sum_{n,m}{}' \exp\{-\beta E_n^{(0)}\} \frac{\langle n|H_3^{(0)}|m\rangle \langle m|H_3^{(0)}|n\rangle}{E_m^{(0)}-E_n^{(0)}}, \tag{3.38}$$

$$Z_2^{(2)} = -\beta \sum_n \exp\{-\beta E_n^{(0)}\} \langle n|H_4^{(2)}|n\rangle + \beta \sum_{n,m}{}' \exp\{-\beta E_n^{(0)}\} \frac{\langle n|H_3^{(1)}|m\rangle \langle m|H_3^{(1)}|n\rangle}{E_m^{(0)}-E_n^{(0)}}, \tag{3.39}$$

$$Z_2^{(4)} = -\beta \sum_n \exp\{-\beta E_n^{(0)}\} \langle n|H_4^{(4)}|n\rangle. \tag{3.40}$$

From (3.3) and (3.36) the free energy is given by

$$F = -\frac{1}{\beta}\ln(Z_0 + \lambda^2 Z_2)$$

$$= -\frac{1}{\beta}\ln Z_0 - \frac{\lambda^2}{\beta}\frac{Z_2}{Z_0}$$

$$= -\frac{1}{\beta}\ln Z_0 - \frac{\lambda^2}{\beta Z_0}\{Z_2^{(0)} + E^2 Z_2^{(2)} + E^4 Z_2^{(4)}\}. \tag{3.41}$$

Using the results (3.25) and (3.7) gives

$$Z_0 = \exp(\tfrac{1}{2}\beta E^2\alpha^2/\omega_0^2) \sum_n \exp\left[-\beta \sum_{\mathbf{q}j} \hbar\,\omega(\mathbf{q}j)\{n(\mathbf{q}j)+\tfrac{1}{2}\}\right],$$

so that

$$-\frac{1}{\beta}\ln Z_0 = -\frac{E^2\alpha^2}{2\omega_0^2} - \frac{1}{\beta}\ln\left(\sum_n \exp\left[-\beta \sum_{qj}\hbar\,\omega(\mathbf{q}j)\{n(\mathbf{q}j)+\tfrac{1}{2}\}\right]\right)$$

$$= -\frac{E^2\alpha^2}{2\omega_0^2} + F_0,$$

where F_0 is the free energy of a harmonic crystal in the absence of an external field. Thus, the free energy is given by

$$F = F_0 - \frac{E^2\alpha^2}{2\omega_0^2} - \frac{\lambda^2}{\beta Z_0}\{Z_2^{(0)}+E^2 Z_2^{(2)}+E^4 Z_2^{(4)}\}. \tag{3.42}$$

This is the result for the free energy of an anharmonic crystal in the presence of an external electric field. It is an even function of E, as expected for a centro-symmetrical crystal. The first term represents the free energy of a harmonic crystal in the absence of an external field, and the second term is the change in this due to the field. The remaining terms represent contributions to the free energy from the anharmonic terms in the potential energy. The term $-\lambda^2 Z_2^{(0)}/\beta Z_0$ is the usual correction to the free energy in the absence of a field, arising from cubic and quartic anharmonic terms (cf. Maradudin, Flinn, and Coldwell-Horsfall 1961), while the remaining two anharmonic terms appear only as a result of the external field.

IV. THE DIELECTRIC CONSTANT

The mean dipole moment of the crystal is given by (3.2) and (3.42) as

$$\bar{M}_E = \frac{\alpha^2}{\omega_0^2}E + \frac{\lambda^2}{\beta Z_0}\{2E Z_2^{(2)}+4E^3 Z_2^{(4)}\}, \tag{4.1}$$

and from (3.1) the static dielectric constant is given by

$$\epsilon_s-1 = \frac{4\pi}{V}\left\{\frac{\alpha^2}{\omega_0^2} + \frac{2\lambda^2 Z_2^{(2)}}{\beta Z_0} + \frac{4\lambda^2 Z_2^{(4)}}{\beta Z_0}E^2\right\},$$

so that

$$\epsilon_s = 1 + \frac{4\pi\alpha^2}{\omega_0^2 V} + \lambda^2\frac{8\pi Z_2^{(2)}}{\beta Z_0 V} + \lambda^2\frac{16\pi Z_2^{(4)}}{\beta Z_0 V}E^2. \tag{4.2}$$

Hence, we see that for a harmonic crystal the dielectric constant is (putting $\lambda=0$)

$$\epsilon_s^h = 1 + \frac{4\pi\alpha^2}{\omega_0^2 V}, \tag{4.3}$$

which is independent of the field. Thus, a harmonic crystal shows no dielectric saturation effects.

The third term in (4.2) represents the contribution from the anharmonic terms to the field-independent dielectric constant. This term has been calculated by Szigeti (1959) using a slightly different approach, and it can explain the observed temperature dependence of the ordinary field-independent dielectric constant.

The last term in (4.2) represents the saturation term. Comparing (4.2) with the phenomenological expansion (1.1) gives for the coefficient ϵ_2

$$\epsilon_2 = \frac{16\pi}{\beta V} \frac{Z_2^{(4)}}{Z_0}. \tag{4.4}$$

Use of (3.40) and (3.19) gives

$$Z_2^{(4)} = -\beta \sum_n \exp\{-\beta E_n^{(0)}\} \frac{1}{24N} \frac{\alpha^4}{\omega_0^8} \Phi(04; 04; 04; 04)$$

$$= -\frac{\beta}{24N} \frac{\alpha^4}{\omega_0^8} \Phi(04; 04; 04; 04) Z_0,$$

so that, from (4.4),

$$\epsilon_2 = -\frac{2\pi}{3NV} \frac{\alpha^4}{\omega_0^8} \Phi(04; 04; 04; 04). \tag{4.5}$$

This expression is independent of the temperature and in this regard agrees with the result obtained by Ninio (1962). Ninio's result contains also a contribution proportional to the square of the cubic anharmonic coefficient. In the present more realistic model this contribution vanishes.

V. Evaluation for NaCl Structure

The general expression (4.5) can be simplified for crystals of the NaCl structure. For this case (2.16) gives

$$\alpha = eN^{\frac{1}{2}} \left\{ \frac{e_x(1|04)}{m_1^{\frac{1}{2}}} - \frac{e_x(2|04)}{m_2^{\frac{1}{2}}} \right\},$$

and use of the results for $e_x(1|04)$ and $e_x(2|04)$ from Appendix A gives finally

$$\alpha = eN^{\frac{1}{2}} \left(\frac{1}{m_1} + \frac{1}{m_2} \right)^{\frac{1}{2}}. \tag{5.1}$$

Using this and the result for $\Phi(04; 04; 04; 04)$ from Appendix C gives

$$\epsilon_2 = -\frac{2\pi}{3N^2v} \frac{e^4 N^2\{(1/m_1)+(1/m_2)\}^2}{\omega_0^8} 2\left(M+2N\right)\left(\frac{1}{m_1} + \frac{1}{m_2}\right)^2$$

$$= -\frac{4\pi e^4(M+2N)\{(1/m_1)+(1/m_2)\}^4}{3v\omega_0^8}, \tag{5.2}$$

where v is the volume of a unit cell.

The infrared dispersion frequency ω_0 for this model is given by (Kellermann 1940)

$$\omega_0^2 = \frac{e^2}{v}\left(A+2B-\frac{4\pi}{3}\right)\left(\frac{1}{m_1} + \frac{1}{m_2}\right). \tag{5.3}$$

A and B are defined in terms of the derivatives of the short-range repulsive potential as follows:

$$\left[\frac{d^2\phi(r)}{dr^2}\right]_{r=r_0} = \frac{e^2A}{2v}; \qquad \frac{1}{r_0}\left[\frac{d\phi(r)}{dr}\right]_{r=r_0} = \frac{e^2B}{2v}.$$

For a Born–Mayer potential $\phi(r) = D\,e^{-r/\rho}$, this becomes

$$\left.\begin{aligned}\frac{D}{\rho^2}\exp(-r_0/\rho) &= \frac{e^2A}{2v},\\[2mm]-\frac{D}{r_0\rho}\exp(-r_0/\rho) &= \frac{e^2B}{2v}.\end{aligned}\right\} \tag{5.4}$$

The expression (5.2) can then be evaluated numerically for NaCl using the following data (Born and Huang 1954):

$$r_0 = 2\cdot814\times10^{-8}\ \text{cm};$$

$$\rho = 0\cdot328\times10^{-8}\ \text{cm};$$

$$D\exp(-r_0/\rho) = 2\cdot78\times10^{-13}\ \text{erg}.$$

This gives

$$v = 2r_0^3 = 4\cdot456\times10^{-23}\ \text{cm}^3; \qquad e = 4\cdot803\times10^{-10}\ \text{e.s.u.}; \qquad e^2/v = 5\cdot170\times10^3;$$

$$A = 10\cdot04; \qquad B = -1\cdot172; \qquad A+2B-4\pi/3 = 3\cdot505;$$

$$1/m_1+1/m_2 = 4\cdot31\times10^{22}\ \text{g}^{-1}.$$

These values give for ω_0, from (5.3),

$$\omega_0 = 2\cdot792\times10^{13}\ \text{sec}^{-1}.$$

Kellermann (1940) obtained a value of $2\cdot86\times10^{13}\ \text{sec}^{-1}$ by using an inverse power potential.

Also, from the definitions (C9) and (C10) we obtain

$$M = 24\cdot17\times10^{20}\ \text{erg cm}^{-4};$$

$$N = 1\cdot094\times10^{20}\ \text{erg cm}^{-4};$$

$$M+2N = 26\cdot36\times10^{20}\ \text{erg cm}^{-4}.$$

Substitution of these values into (5.2) gives

$$\epsilon_2 = -1\cdot23\times10^{-10}\ \text{(CGS)}. \tag{5.5}$$

The coefficient of E^2 in the expansion of the dielectric constant (1.1) has the value $-1\cdot23\times10^{-10}$ (CGS). Thus, an applied field of say 1000 e.s.u./cm (3×10^5 V/cm) causes a decrease in the static dielectric constant of $1\cdot2\times10^{-4}$, so that

$$\frac{\Delta\epsilon_s}{\epsilon_s} \sim 2\times10^{-5}.$$

This compares with Ninio's result of 19×10^{-5}.

VI. Acknowledgment

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Appendix A

Eigenvectors of the Dynamical Matrix for Alkali Halides

For alkali halides the elements of the 6×6 dynamical matrix are given by

$$D_{\alpha\beta}(\kappa\kappa', \mathbf{q}) = \frac{1}{(m_\kappa m_{\kappa'})^{\frac{1}{2}}} \sum_l \Phi_{\alpha\beta}(0\kappa, l\kappa') \exp[2\pi i \mathbf{q} \cdot \{\mathbf{r}(l\kappa') - \mathbf{r}(0\kappa)\}], \tag{A1}$$

with $\alpha, \beta = x, y, z$; $\kappa = 1, 2$. The components of the eigenvectors are given by the set of equations

$$\omega^2(\mathbf{q}j) e_\alpha(\kappa|\mathbf{q}j) = \sum_{\kappa'\beta} D_{\alpha\beta}(\kappa\kappa', \mathbf{q}) e_\beta(\kappa'|\mathbf{q}j), \tag{A2}$$

with $j = 1, 2, \ldots, 6$ labelling the various branches.

The eigenvectors satisfy the following orthogonality and completeness relations:

$$\sum_{\alpha\kappa} e_\alpha(\kappa|\mathbf{q}j) e_\alpha(\kappa|\mathbf{q}j') = \delta_{jj'}, \tag{A3}$$

$$\sum_j e_\alpha(\kappa|\mathbf{q}j) e_\beta(\kappa'|\mathbf{q}j) = \delta_{\alpha\beta} \delta_{\kappa\kappa'}. \tag{A4}$$

Consider the case when $\mathbf{q}$ is in a symmetry direction, in particular along $\langle 100 \rangle$. Then, for a longitudinal mode,

$$e_y(\kappa|\mathbf{q}j) = e_z(\kappa|\mathbf{q}j) = 0,$$

and (A2) reduces to

$$\left.\begin{aligned} D_{xx}(11, \mathbf{q}) e_x(1|\mathbf{q}j) + D_{xx}(12, \mathbf{q}) e_x(2|\mathbf{q}j) &= \omega^2(\mathbf{q}j) e_x(1|\mathbf{q}j), \\ D_{xx}(12, \mathbf{q}) e_x(1|\mathbf{q}j) + D_{xx}(22, \mathbf{q}) e_x(2|\mathbf{q}j) &= \omega^2(\mathbf{q}j) e_x(2|\mathbf{q}j). \end{aligned}\right\} \tag{A5}$$

These results hold for

$$j = \begin{cases} 1 & \text{longitudinal acoustic mode,} \\ 4 & \text{longitudinal optic mode.} \end{cases}$$

This gives the result

$$e_x(1|\mathbf{q}j) = \frac{\omega^2(\mathbf{q}j) - D_{xx}(22, \mathbf{q})}{D_{xx}(12, \mathbf{q})} \, e_x(2|\mathbf{q}j). \tag{A6}$$

The relations (A3) and (A4) give

$$\left. \begin{aligned} e_x(1|\mathbf{q}1)^2 + e_x(2|\mathbf{q}1)^2 &= 1; \\ e_x(1|\mathbf{q}4)^2 + e_x(2|\mathbf{q}4)^2 &= 1; \\ e_x(1|\mathbf{q}1)\, e_x(1|\mathbf{q}4) + e_x(2|\mathbf{q}1)\, e_x(2|\mathbf{q}4) &= 0; \\ e_x(1|\mathbf{q}1)^2 + e_x(1|\mathbf{q}4)^2 &= 1; \\ e_x(1|\mathbf{q}1)\, e_x(2|\mathbf{q}1) + e_x(1|\mathbf{q}4)\, e_x(2|\mathbf{q}4) &= 0. \end{aligned} \right\} \tag{A7}$$

From (A7) we can write

$$\left. \begin{aligned} e_y(1|\mathbf{q}1) &= \sin \alpha_q, \\ e_y(1|\mathbf{q}4) &= \cos \alpha_q, \\ e_y(2|\mathbf{q}1) &= \cos \alpha_q, \\ e_y(2|\mathbf{q}4) &= -\sin \alpha_q, \end{aligned} \right\} \tag{A8}$$

where

$$\tan \alpha_q = \frac{e_x(1|\mathbf{q}1)}{e_x(2|\mathbf{q}1)}$$

$$= \frac{D_{xx}(12, \mathbf{q})}{\omega^2(\mathbf{q}1) - D_{xx}(11, \mathbf{q})}. \tag{A9}$$

Similarly, for a transverse mode with polarization in the y direction, labelled by

$$j = \begin{cases} 2 & \text{transverse acoustic mode,} \\ 5 & \text{transverse optic mode,} \end{cases}$$

we can write

$$\left. \begin{aligned} e_y(1|\mathbf{q}2) &= \sin \beta_q, \\ e_y(1|\mathbf{q}5) &= \cos \beta_q, \\ e_y(2|\mathbf{q}2) &= \cos \beta_q, \\ e_y(2|\mathbf{q}5) &= -\sin \beta_q, \end{aligned} \right\} \tag{A10}$$

where

$$\tan \beta_q = \frac{D_{yy}(12, \mathbf{q})}{\omega^2(\mathbf{q}2) - D_{yy}(11, \mathbf{q})}. \tag{A11}$$

For $\mathbf{q} = 0$ we have, from (A9) and (A1),

$$\tan \alpha_0 = \frac{(m_1 m_2)^{-\frac{1}{2}} \sum_l \Phi_{xx}(01, l2)}{-m_1^{-1} \sum_l \Phi_{xx}(01, l1)},$$

since the frequency approaches zero as $\mathbf{q} \to 0$ for an acoustic mode.

From the fact that the potential energy must remain invariant for an infinitesimal translation it can be shown (Leibfried and Ludwig 1961) that

$$\sum_{l\kappa} \Phi_{xx}(01, l\kappa) = 0.$$

Using this fact gives

$$\tan \alpha_0 = (m_1/m_2)^{\frac{1}{2}}. \tag{A12}$$

Thus, we have the following result for the eigenvectors for $\mathbf{q} = 0$ (which are the same for longitudinal and transverse modes):

$$\left.\begin{array}{l} e_x(1|01) = - e_x(2|04) = \left(\dfrac{m_1}{m_1+m_2}\right)^{\frac{1}{2}}, \\[2mm] e_x(1|04) = e_x(2|01) \quad = \left(\dfrac{m_2}{m_1+m_2}\right)^{\frac{1}{2}}. \end{array}\right\} \tag{A13}$$

Appendix B

Anharmonic Force Constants in Alkali Halides

Several approximations will be made in calculating the third- and fourth-order force constants that appear in the expansion of the potential energy (2.1).

First, the anharmonicity of the Coulomb forces is neglected. Whereas the electrostatic forces behave like $1/r^3$, the short-range forces behave more like $1/r^{11}$ and will dominate the anharmonic effects.

Secondly, we assume two-body interactions only, so that the total potential energy is the sum of two-body potential energies. We can then assume a specific form for the nearest-neighbour repulsive potential. A Born–Mayer potential

$$\phi(r) = D e^{-r/\rho} \tag{B1}$$

is used. To evaluate the force constants it is necessary to label the nearest atoms. The labelling adopted is given in Figure 1. Because the potential energy is the sum of two-body interactions, coupling constants of the form $\Phi_{\alpha\beta\gamma}(l\kappa, l'\kappa', l''\kappa'')$ are zero for $(l\kappa) \neq (l'\kappa') \neq (l''\kappa'')$, and similarly for the fourth-order constants.

Using the definition and also the invariance relations

$$\left.\begin{array}{l} \sum_{l''\kappa''} \Phi_{\alpha\beta\gamma}(l\kappa, l'\kappa', l''\kappa'') = 0, \\[2mm] \sum_{l'''\kappa'''} \Phi_{\alpha\beta\gamma\delta}(l\kappa, l'\kappa', l''\kappa'', l'''\kappa''') = 0, \end{array}\right\} \tag{B2}$$

we obtain the results

$$\Phi_{xxx}(01, 12, 12) = \frac{D}{\rho^3} \exp(-r_0/\rho)$$

$$= - \Phi_{xxx}(01, 01, 12), \text{ etc.}, \tag{B3}$$

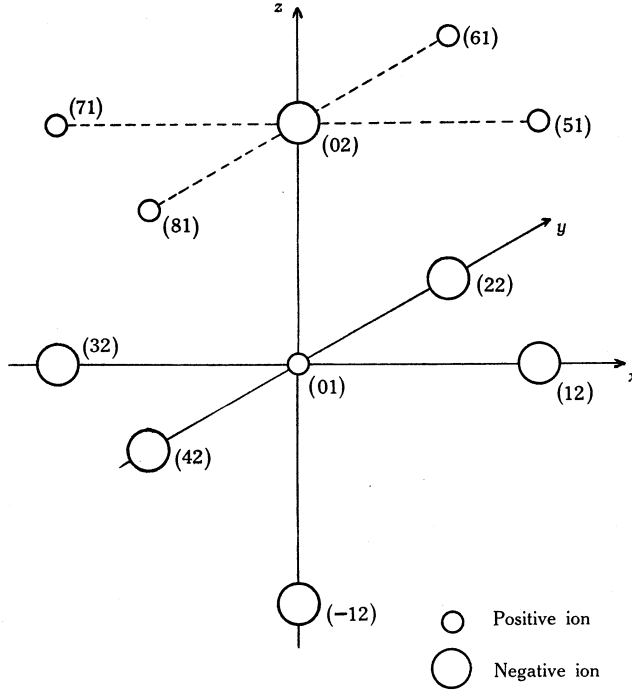$$\Phi_{xxz}(01, 01, 02) = \frac{D}{\rho^2 r_0^2}(r_0 + \rho) \exp(-r_0/\rho). \tag{B4}$$

Fig. 1.—Labelling of nearest-neighbour atoms for calculation of anharmonic force constants.

All third-order constants of other form vanish. Similarly, for the fourth-order constants we obtain

$$\Phi_{xxxx}(01;01;12;12) = \frac{D}{\rho^4}\exp(-r_0/\rho), \tag{B5}$$

$$\Phi_{xxxx}(01;01;02;02) = \frac{3D}{r_0^3\,\rho^2}(r_0+\rho)\exp(-r_0/\rho), \tag{B6}$$

$$\Phi_{xxxx}(01;01;01;01) = 2\Phi_{xxxx}(01;01;12;12)+4\Phi_{xxxx}(01;01;02;02), \tag{B7}$$

$$\Phi_{xxzz}(01;01;02;02) = -\frac{D}{r_0^3\,\rho^3}(r_0^2+r_0\rho+\rho^2)\exp(-r_0/\rho), \tag{B8}$$

$$\Phi_{xxyy}(01;01;02;02) = \frac{D}{r_0^3\,\rho^2}(r_0+\rho)\exp(-r_0/\rho), \tag{B9}$$

$$\Phi_{xxyy}(01;01;01;01) = 2\Phi_{xxyy}(01;01;02;02)+4\Phi_{xxyy}(01;01;12;12). \tag{B10}$$

All fourth-order constants of different form are zero.

Appendix C

Evaluation of the Coefficients $\Phi(04;04;04)$, $\Phi(05;04;04)$, *and* $\Phi(04;04;04;04)$

From the definition (2.14) we have

$$\Phi(\mathbf{q}_1 j_1; \mathbf{q}_2 j_2; \mathbf{q}_3 j_3) = \sum_{\substack{\kappa\alpha \\ l'\kappa'\beta \\ l''\kappa''\gamma}} \frac{\Phi_{\alpha\beta\gamma}(0\kappa, l'\kappa', l''\kappa'')}{(m_\kappa \, m_{\kappa'} \, m_{\kappa''})^{\frac{1}{2}}} \, e_\alpha(\kappa|\mathbf{q}_1 \, j_1) \, e_\beta(\kappa'|\mathbf{q}_2 \, j_2) \, e_\gamma(\kappa''|\mathbf{q}_3 \, j_3)$$

$$\times \exp[2\pi i\{\mathbf{q}_1 \cdot \mathbf{r}(0\kappa) + \mathbf{q}_2 \cdot \mathbf{r}(l'\kappa') + \mathbf{q}_3 \cdot \mathbf{r}(l''\kappa'')\}]. \quad (C1)$$

Thus, we have

$$\Phi(04;04;04) = \sum_{\substack{\kappa \\ l'\kappa' \\ l''\kappa''}} \frac{\Phi_{xxx}(0\kappa, l'\kappa', l''\kappa'')}{(m_\kappa \, m_{\kappa'} \, m_{\kappa''})^{\frac{1}{2}}} \, e_x(\kappa|04) \, e_x(\kappa'|04) \, e_x(\kappa''|04), \quad (C2)$$

since, for the mode (04),

$$e_y(\kappa|04) = e_z(\kappa|04) = 0.$$

From the results of Appendix B the only force constants contributing to (C2) are

$$\Phi_{xxx}(01, 01, 12), \quad \Phi_{xxx}(01, 12, 12), \quad \Phi_{xxx}(01, 12, 01);$$

$$\Phi_{xxx}(01, 01, 32), \quad \Phi_{xxx}(01, 32, 01), \quad \Phi_{xxx}(01, 32, 32);$$

$$\Phi_{xxx}(02, 02, 51), \quad \Phi_{xxx}(02, 51, 02), \quad \Phi_{xxx}(02, 51, 51);$$

$$\Phi_{xxx}(02, 02, 71), \quad \Phi_{xxx}(02, 71, 02), \quad \Phi_{xxx}(02, 71, 71).$$

By writing out the expression (C2) explicitly it can be seen that all the terms cancel, giving

$$\Phi(04;04;04) = 0. \quad (C3)$$

Similarly, from (C1) we have

$$\Phi(05;04;04) = \sum_{\substack{\kappa \\ l'\kappa' \\ l''\kappa''}} \frac{\Phi_{yxx}(0\kappa, l'\kappa', l''\kappa'')}{(m_\kappa \, m_{\kappa'} \, m_{\kappa''})^{\frac{1}{2}}} \, e_y(\kappa|05) \, e_x(\kappa'|04) \, e_x(\kappa''|04), \quad (C4)$$

where (05) refers to the $\mathbf{q} = 0$ optic mode with polarization in the y direction. It can be shown, by writing out explicitly the various terms, using (B4), that

$$\Phi(05;04;04) = 0. \quad (C5)$$

These two results (C3) and (C5) lead to the vanishing of the operators $H_3^{(2)}$ and $H_3^{(3)}$ in (3.9).

From the definition (2.14) we have for the general quartic coefficient

$$\Phi(\mathbf{q}_1 j_1 ; \mathbf{q}_2 j_2 ; \mathbf{q}_3 j_3 ; \mathbf{q}_4 j_4)$$

$$= \sum_{\substack{\kappa\alpha \\ l'\kappa'\beta \\ l''\kappa''\gamma \\ l'''\kappa'''\delta}} \frac{\Phi_{\alpha\beta\gamma\delta}(0\kappa, l'\kappa', l''\kappa'', l'''\kappa''')}{(m_\kappa\, m_{\kappa'}\, m_{\kappa''}\, m_{\kappa'''})^{\frac{1}{2}}}\, e_\alpha(\kappa|\mathbf{q}_1 j_1)\, e_\beta(\kappa'|\mathbf{q}_2 j_2)\, e_\gamma(\kappa''|\mathbf{q}_3 j_3)\, e_\delta(\kappa'''|\mathbf{q}_4 j_4)$$

$$\times \exp\big[2\pi\mathrm{i}\{\mathbf{q}_1\cdot\mathbf{r}(0\kappa) + \mathbf{q}_2\cdot\mathbf{r}(l'\kappa') + \mathbf{q}_3\cdot\mathbf{r}(l''\kappa'') + \mathbf{q}_4\cdot\mathbf{r}(l'''\kappa''')\}\big]. \quad (C6)$$

From this we obtain

$$\Phi(04;04;04) = \sum_{\substack{\kappa \\ l'\kappa' \\ l''\kappa'' \\ l'''\kappa'''}} \frac{\Phi_{xxxx}(0\kappa, l'\kappa', l''\kappa'', l'''\kappa''')}{(m_\kappa\, m_{\kappa'}\, m_{\kappa''}\, m_{\kappa'''})^{\frac{1}{2}}}$$

$$\times e_x(\kappa|04)\, e_x(\kappa'|04)\, e_x(\kappa''|04)\, e_x(\kappa'''|04). \quad (C7)$$

The nonvanishing terms in the summation can be written out explicitly, using the results (B5), (B6), and (B7), to give

$$\Phi(04;04;04) = 12\left(M+2N\right)\frac{\{e_x(1|04)\}^2\{e_x(2|04)\}^2}{m_1\, m_2}$$

$$+ 2\left(M+2N\right)\left[\frac{\{e_x(1|04)\}^4}{m_1^2} + \frac{\{e_x(2|04)\}^4}{m_2^2}\right]$$

$$- 8\left(M+2N\right)\frac{\{e_x(1|04)\}^3\, e_x(2|04)}{m_1(m_1\, m_2)^{\frac{1}{2}}}$$

$$- 8\left(M+2N\right)\frac{e_x(1|04)\,\{e_x(2|04)\}^3}{m_2(m_1\, m_2)^{\frac{1}{2}}}$$

$$= 2\left(M+2N\right)\left\{\frac{e_x(1|04)}{m_1^{\frac{1}{2}}} - \frac{e_x(2|04)}{m_2^{\frac{1}{2}}}\right\}^4, \quad (C8)$$

where

$$M = \frac{D}{\rho^4}\exp(-r_0/\rho), \quad (C9)$$

$$N = \frac{3D}{r_0^3\rho^2}\,(r_0+\rho)\exp(-r_0/\rho). \quad (C10)$$

Using the results from Appendix A for $e_x(1|04)$ and $e_x(2|04)$ gives

$$\Phi(04;04;04) = 2\left(M+2N\right)\left(\frac{1}{m_1} + \frac{1}{m_2}\right)^2. \quad (C11)$$