DIELECTRIC SATURATION IN IONIC CRYSTALS

II.* DEFORMABLE IONS

By J. Oitmaa†

[*Manuscript received January* 26, 1968]

Summary

The lowest order field-dependent term in the static dielectric constant is calculated for an ionic crystal with deformable ions, and is evaluated numerically for NaI using a simple shell model. Some terms of higher order are also calculated.

I. Introduction

In general the static dielectric constant of a crystal would be expected to be a function of the external electric field E, since the change in dipole moment caused by a given change in the field strength would be less at high fields, when the crystal already has a large dipole moment, than at low fields. For a centro-symmetrical crystal the field-dependent static dielectric constant ϵ_s can be written as a Taylor expansion in powers of the field strength as

$$\epsilon_s = \epsilon_0 + \epsilon_2 E^2 + \epsilon_4 E^4 + \ldots . \tag{1.1}$$

In most situations the field-independent term ϵ_0 dominates.

In a previous paper (Oitmaa 1967*a*; hereafter referred to as Part I), in which references to earlier experimental and theoretical work are given, the lowest order contribution to the coefficient ϵ_2 was calculated for the alkali halides using a rigid ion model. It was found that the field dependence of the dielectric constant is directly attributable to the anharmonic terms in the crystal potential energy. The lowest order contribution evaluated in Part I was due to a particular quartic anharmonic term.

We consider a thin rod of dielectric (e.g. Szigeti 1959; this was also implicit in Part I) for which the macroscopic and external fields are identical. The static dielectric constant is then given by

$$\epsilon_s - \epsilon_\infty = -\frac{4\pi}{EV}\left(\frac{\partial F}{\partial E}\right)_{V,T}, \tag{1.2}$$

where F is the Helmholtz free energy of the crystal of volume V. To obtain the dielectric constant it is thus necessary to calculate the free energy of an anharmonic crystal in the presence of an external electric field.

In Part I the free energy was calculated by a straightforward application of perturbation theory. In the present paper we use a slightly different formulation of perturbation theory, in which the various terms are represented by diagrams (e.g.

* Part I, *Aust. J. Phys.*, 1967, **20**, 11–27.

† School of Physics, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033; present address: Department of Physics, University of California, Irvine, California 92664, U.S.A.

Cowley 1963; Parry and Turner 1964; Wilcox 1965). Some of the advantages of using diagrams are

(1) they often lead to greater clarity and insight into the structure of the perturbation series,

(2) they provide a systematic way of obtaining all of the terms of a given order, and

(3) it is sometimes possible to sum certain classes of terms to all orders, and in this way to obtain physical approximations that cannot be readily obtained from a conventional perturbation theory.

In Section II the Hamiltonian of the model is obtained. This Hamiltonian contains higher order dipole moments that do not occur in a rigid ion model but do occur when the ions are deformable. In Section III the formalism of the diagrammatic perturbation theory to be used is summarized. In Section IV the free energy and dielectric constant are obtained, and in Section V the result is evaluated numerically for NaI using a simple shell model. Finally, in Section VI some higher order correction terms are calculated.

II. Hamiltonian

In the theory of an anharmonic crystal, and in many-body problems in general, it is usually most convenient to express the Hamiltonian and other operators in terms of creation and annihilation operators for the elementary excitations. In terms of these operators the Hamiltonian of an anharmonic crystal, in the absence of an external field, can be written (e.g. Born and Huang 1954; Cowley 1963)

$$H = H_0 + \gamma H_3 + \gamma^2 H_4 + \ldots , \tag{2.1}$$

where

$$H_0 = \sum_{\lambda} \hbar\omega_\lambda (a^*_\lambda a_\lambda + \tfrac{1}{2}) , \tag{2.2}$$

$$H_3 = \sum_{\lambda_1\lambda_2\lambda_3} V(\lambda_1\lambda_2\lambda_3) A_{\lambda_1} A_{\lambda_2} A_{\lambda_3} , \tag{2.3}$$

$$H_4 = \sum_{\lambda_1\lambda_2\lambda_3\lambda_4} V(\lambda_1\lambda_2\lambda_3\lambda_4) A_{\lambda_1} A_{\lambda_2} A_{\lambda_3} A_{\lambda_4} . \tag{2.4}$$

In these expressions H_0 is the harmonic Hamiltonian and H_3 and H_4 are respectively the cubic and quartic anharmonic terms. The parameter γ is the usual order parameter that indicates the number of factors of $\bar{u}/r_0$ by which a particular term is smaller than the harmonic term, $\bar{u}$ being some sort of mean displacement and r_0 the nearest neighbour distance. For convenience the double suffix $\boldsymbol{q}j$ for each phonon mode has been replaced by a single suffix λ. The operators a^*_λ and a_λ are respectively the creation and annihilation operators for the phonons of mode λ, and have the usual properties. The operator A_λ is defined by

$$A(\boldsymbol{q}j) = a(\boldsymbol{q}j) + a(-\boldsymbol{q}j)^* \tag{2.5}$$

and is related to the normal coordinate $Q(\boldsymbol{q}j)$ of Part I by

$$A(\boldsymbol{q}j) = (2\omega(\boldsymbol{q}j)/\hbar)^{\frac{1}{2}} Q(\boldsymbol{q}j) . \tag{2.6}$$

The anharmonic coefficients $V(\lambda_1\lambda_2\lambda_3)$ and $V(\lambda_1\lambda_2\lambda_3\lambda_4)$ are related to those of Part I by

$$V(\boldsymbol{q}_1 j_1; \boldsymbol{q}_2 j_2; \boldsymbol{q}_3 j_3) = \frac{1}{6N^{\frac{1}{2}}} \Delta(\boldsymbol{q}_1+\boldsymbol{q}_2+\boldsymbol{q}_3)\left(\frac{\hbar^3}{8\omega(\boldsymbol{q}_1 j_1)\,\omega(\boldsymbol{q}_2 j_2)\,\omega(\boldsymbol{q}_3 j_3)}\right)^{\frac{1}{2}} \times \Phi(\boldsymbol{q}_1 j_1; \boldsymbol{q}_2 j_2; \boldsymbol{q}_3 j_3) \tag{2.7}$$

and

$$V(\boldsymbol{q}_1 j_1; \boldsymbol{q}_2 j_2; \boldsymbol{q}_3 j_3; \boldsymbol{q}_4 j_4) = \frac{1}{24N} \Delta(\boldsymbol{q}_1+\boldsymbol{q}_2+\boldsymbol{q}_3+\boldsymbol{q}_4) \times \left(\frac{\hbar^4}{16\omega(\boldsymbol{q}_1 j_1)\,\omega(\boldsymbol{q}_2 j_2)\,\omega(\boldsymbol{q}_3 j_3)\,\omega(\boldsymbol{q}_4 j_4)}\right)^{\frac{1}{2}} \times \Phi(\boldsymbol{q}_1 j_1; \boldsymbol{q}_2 j_2; \boldsymbol{q}_3 j_3; \boldsymbol{q}_4 j_4)\,. \tag{2.8}$$

In the presence of an external electric field E, in the x direction, the Hamiltonian of the crystal becomes

$$H(E) = H - EM\,, \tag{2.9}$$

where M is the x component of the dipole moment of the crystal. M can be expanded as a series in the phonon coordinates A_λ (Born and Huang 1954) to give

$$M = \mathscr{M}_0 A_0 + \gamma \sum_{\lambda_1\lambda_2} \mathscr{M}(\lambda_1\lambda_2) A_{\lambda_1} A_{\lambda_2} + \gamma^2 \sum_{\lambda_1\lambda_2\lambda_3} \mathscr{M}(\lambda_1\lambda_2\lambda_3) A_{\lambda_1} A_{\lambda_2} A_{\lambda_3} + \ldots . \tag{2.10}$$

The suffix 0 refers to that $\boldsymbol{q} = 0$ optic mode which has displacements in the x direction, i.e. the mode (04). The first term in (2.10) contains both the effect of the displacements of the ions as a whole and the first-order effect of the electronic deformations, while the second and third terms are due entirely to electronic deformation.

III. Perturbation Formalism

We consider a general system having a Hamiltonian

$$H = H_0 + V\,, \tag{3.1}$$

where H_0 is the unperturbed Hamiltonian, which will hereafter be taken to be the harmonic Hamiltonian (2.2), and V is the sum of all perturbation terms.

The free energy can then be obtained from the partition function Z according to

$$F = -\beta^{-1} \ln Z\,, \tag{3.2}$$

where

$$Z = \mathrm{Tr}\{\exp(-\beta H)\} \tag{3.3}$$

and $\beta = 1/kT$.

The exponential operator in (3.3) can be expanded in powers of the perturbation V (e.g. Parry and Turner 1964) as

$$\exp(-\beta H) = \exp(-\beta H_0) \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_0^\beta \mathrm{d}u_1 \ldots \int_0^\beta \mathrm{d}u_n\, \mathrm{T}\{\tilde{V}(u_1) \ldots \tilde{V}(u_n)\}\,. \tag{3.4}$$

In this expansion the $\tilde{V}(u)$ operators are defined by

$$\tilde{V}(u) = \exp(uH_0)\, V \exp(-uH_0)\,, \tag{3.5}$$

which is a type of interaction representation, and T is the Dyson ordering operator, which orders the $\tilde{V}(u_i)$ operators so that the u_i's are in descending order with the largest on the left, and so on. For example

$$\mathrm{T}\,\tilde{V}(u_1)\,\tilde{V}(u_2) = \left.\begin{array}{ll} \tilde{V}(u_1)\,\tilde{V}(u_2)\,, & u_1 > u_2\,; \\ \tilde{V}(u_2)\,\tilde{V}(u_1)\,, & u_1 < u_2\,. \end{array}\right\} \tag{3.6}$$

Using the expansion (3.4) the partition function (3.3) becomes

$$Z = Z_0\left(1 + \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \int_0^\beta \mathrm{d}u_1 \ldots \int_0^\beta \mathrm{d}u_n \,\langle \mathrm{T}\,\tilde{V}(u_1) \ldots \tilde{V}(u_n)\rangle_0\right), \tag{3.7}$$

where Z_0 is the partition function of the unperturbed system and $\langle\ \rangle_0$ denotes the unperturbed canonical ensemble average, i.e.

$$\langle 0\rangle_0 = Z_0^{-1}\,\mathrm{Tr}\{\exp(-\beta H_0)\,0\}\,. \tag{3.8}$$

In evaluating the thermodynamic average in (3.5) the $\tilde{V}(u)$ operators are first written explicitly in terms of the phonon coordinates A_λ. It is then necessary to find the unperturbed average of an ordered product of A_λ operators. This can be done by using Wick's theorem (e.g. Gaudin 1960), which states that the average of an ordered product is equal to the sum of the products of all possible "contractions". A contraction is the unperturbed expectation value of the ordered product of two operators. In the present case the only nonvanishing contractions are of the form

$$\begin{aligned} g(\lambda, u) &= \langle \mathrm{T}\,\tilde{A}_\lambda(u)^*\,\tilde{A}_\lambda(0)\rangle_0 \\ &= \bar{n}_\lambda \exp(+\,|\,u\,|\,\hbar\omega_\lambda) + (\bar{n}_\lambda + 1)\exp(-\,|\,u\,|\,\hbar\omega_\lambda)\,, \end{aligned} \tag{3.9}$$

where $\bar{n}_\lambda$ is the mean occupation number of the mode λ, given by

$$\bar{n}_\lambda = \{\exp(\beta\hbar\omega_\lambda - 1)\}^{-1}\,. \tag{3.10}$$

In addition to being an even function of u, $g(\lambda, u)$ also satisfies the periodicity condition

$$g(\lambda, u+\beta) = g(\lambda, u)\,, \qquad -\beta < u < 0\,, \tag{3.11}$$

and so can be expanded in a Fourier series

$$g(\lambda, u) = \sum_{l=-\infty}^{\infty} g_l(\lambda) \exp(2\pi i l u/\beta)\,. \tag{3.12}$$

The Fourier coefficients are given by

$$\begin{aligned} g_l(\lambda) &= \frac{1}{2\beta} \int_{-\beta}^{\beta} g(\lambda, u) \exp(-2\pi i l u/\beta)\, \mathrm{d}u \\ &= \frac{2\omega_\lambda}{\beta\hbar} \frac{1}{\omega_l^2 + \omega_\lambda^2}\,, \end{aligned} \tag{3.13}$$

where

$$\omega_l = 2\pi l/\beta\hbar . \tag{3.14}$$

The Fourier coefficient $g_l(\lambda)$ is called the "free phonon propagator".

Returning to the partition function (3.7), the procedure then is to substitute for $\tilde{V}(u)$ in terms of the A_λ's from (2.3), (2.4), (2.9), and (2.10) and then to take all possible contractions of the A_λ's. If the Fourier expansion (3.12) is then substituted for each contraction, the u-integrations in (3.7) can be carried out directly, using the result

$$\int_0^\beta du \exp\{2\pi i(l_1-l_2)u/\beta\} = \beta\,\delta_{l_1 l_2} . \tag{3.15}$$

The above procedure can be most conveniently carried out in terms of diagrams. We consider the nth term in (3.7). Since each of the $\tilde{V}$ factors contains a number of separate perturbation terms, there are many combinations that all contribute to the nth term. For each perturbation term we draw a vertex with a number of lines, representing the A_λ operators, joined to it. The process of contraction is then represented by joining up the lines, pairwise, in all possible ways.

The nth-order contribution to Z is then obtainable from the following rules.

(1) Draw all topologically distinct diagrams with n vertices.

(2) With each phonon line labelled λ associate a factor

$$g_l(\lambda) = \frac{2\omega_\lambda}{\beta\hbar}\frac{1}{\omega_l^2+\omega_\lambda^2} .$$

(3) At each vertex conserve $\boldsymbol{q}$ vectors, since each of the perturbation terms contains a delta function in the $\boldsymbol{q}$'s.

(4) At each vertex insert the appropriate coefficient.

(5) At each vertex conserve the ω_l's because of the u-integrations (3.15).

(6) Insert a factor $\{(-1)^n/n!\}\beta^n$, where β^n comes from the n u-integrations.

(7) Multiply by a combinational factor, representing the number of equivalent ways of pairing the operators, and also the number of permutations in (3.7) if there are several perturbation terms.

(8) Sum over the independent λ's and l's.

This type of perturbation formalism was first developed by Matsubara (1955) and has been further developed by Bloch and de Dominicis (1958), Luttinger and Ward (1960), and others. Specific application of this formalism to a system of interacting phonons has been made by Maradudin and Fein (1962) and Cowley (1963).

In the present work it is convenient to distinguish between those perturbation vertices that arise from the anharmonic terms (2.3) and (2.4), and those that are due to the perturbation of the external field, given by $-EM$, with M given by (2.10). Following Wilcox (1965) we will call the former "internal vertices", represented by ●, and the latter "external vertices", represented by o.

The possible first-order diagrams, i.e. those with one perturbation vertex, are shown in Figure 1.

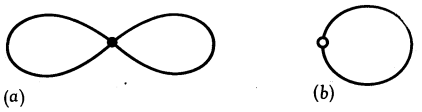

Fig. 1.—First-order contributions to Z.

The diagram in Figure 1(a) gives the contribution

$$-\gamma^2 3\beta \sum_{\lambda_1\lambda_2 l_1 l_2} V(\lambda_1-\lambda_1\,\lambda_2-\lambda_2)\, g_{l_1}(\lambda_1)\, g_{l_2}(\lambda_2)$$

$$= -\gamma^2 3\beta \sum_{\lambda_1\lambda_2} V(\lambda_1-\lambda_1\,\lambda_2-\lambda_2)\,(2\bar{n}_{\lambda_1}+1)(2\bar{n}_{\lambda_2}+1)\,. \qquad (3.16)$$

The diagram in Figure 1(b) has the value

$$-\gamma E \sum_{\lambda l} \mathscr{M}(\lambda-\lambda)\, g_l(\lambda) = -\gamma E \sum_{\lambda} \mathscr{M}(\lambda-\lambda)\,(2\bar{n}_\lambda+1)\,,$$

which vanishes for a centro-symmetrical crystal.

Some of the second-order diagrams that contribute to the partition function are shown in Figure 2.

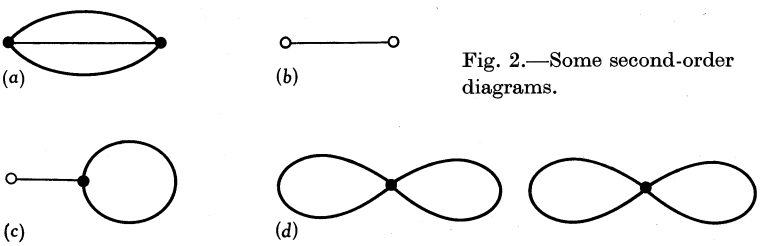

Fig. 2.—Some second-order diagrams.

It is important to distinguish between "connected" and "disconnected" diagrams. A disconnected diagram is one, such as Figure 2(d), which consists of several parts that are not connected by a phonon line.

If we denote the contribution of the connected diagrams to the partition function by L, then the contribution from all disconnected diagrams with n components is $L^n/n!$. Hence

$$Z = Z_0\left(1+\sum_{n=1}^{\infty} L^n/n!\right) = Z_0\, \mathrm{e}^{L}\,. \qquad (3.17)$$

The free energy is from (3.2) and (3.17) given by

$$F = F_0-\beta^{-1}L\,. \qquad (3.18)$$

Thus only the connected diagrams contribute to the free energy. This is a well-known result (Cowley 1963) and results in the automatic elimination from F of those diagrams with the wrong volume dependence (Goldstone 1957; Hugenholtz 1957).

IV. Free Energy and Dielectric Constant

As mentioned in Section III, to obtain the free energy it is necessary to consider only the connected diagrams. Furthermore, since we have included in the Hamiltonian (2.1) terms up to order γ^2 we can consistently only consider those diagrams that give contributions to F up to order γ^2.

From (2.4) and (2.10) it follows that each external vertex gives a factor of $-E$ to a diagram. This shows one advantage of the diagrammatic formulation, namely, that the field dependence of the contribution of any diagram to the free energy is given immediately by the number of external vertices in the diagram in question.

The diagrams that give contributions to the free energy of a centro-symmetrical crystal, up to order γ^2, are shown in Figure 3. The γ and E dependence is shown for each diagram.

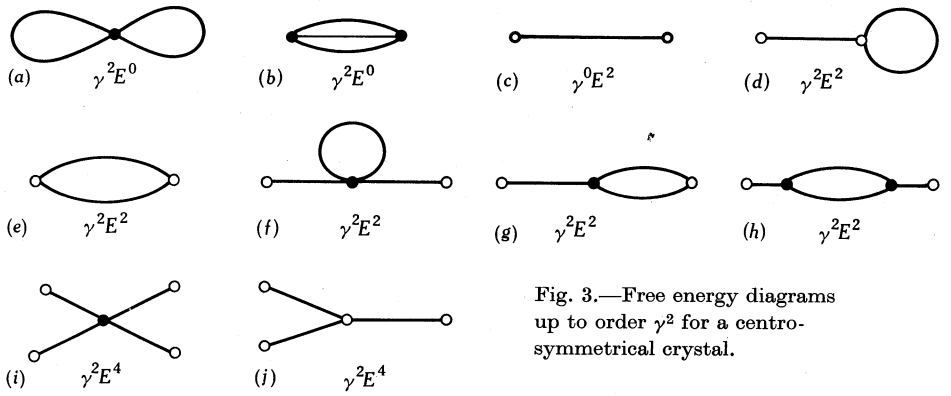

Fig. 3.—Free energy diagrams up to order γ^2 for a centro-symmetrical crystal.

There are nine additional diagrams that give contributions to F up to this order, but these vanish for a centro-symmetrical crystal because of the selection rules

$$V(0\lambda{-}\lambda) = 0\,, \qquad \mathscr{M}(\lambda{-}\lambda) = 0\,. \tag{4.1}$$

For a centro-symmetrical crystal the free energy can then be written, using (3.18) and the diagrams in Figure 3, as

$$F = F_0 - \gamma^2\beta^{-1}[(a)+(b)] - E^2\beta^{-1}(c) - \gamma^2E^2\beta^{-1}[(d)+(e)+(f)+(g)+(h)] - \gamma^2E^4\beta^{-1}[(i)+(j)] + O(>\gamma^2)\,. \tag{4.2}$$

The first term F_0 is the free energy of a harmonic crystal in the absence of an external field. The second term (diagrams (a) and (b)) is the usual correction due to the anharmonic terms, but still in the absence of the electric field. The third term (diagram (c)) is the correction to the free energy of a harmonic crystal due to the external field, and gives rise to the field-independent dielectric constant of the harmonic crystal. The fourth term (diagrams (d), (e), (f), (g), and (h)) depends both on the anharmonicity and the field, and gives anharmonic contributions to the

field-independent dielectric constant. This term has been evaluated by Szigeti (1959) for the quantum mechanical case and by Wilcox (1965) for the classical case, and gives rise to the observed temperature dependence of the field-independent dielectric constant. The last term (diagrams (i) and (j)) gives a contribution to the dielectric constant that is proportional to E^2, i.e. the lowest order contribution to the field-dependent part of the dielectric constant.

From (1.2) and (4.2) the static dielectric constant is given by

$$\epsilon_s = \epsilon_\infty + (8\pi/\beta V)(c) + \gamma^2(8\pi/\beta V)[(d)+(e)+(f)+(g)+(h)] + \gamma^2(16\pi/\beta V)[(i)+(j)]E^2 + \ldots . \tag{4.3}$$

Comparing this with the phenomenological expansion (1.1), the lowest order contribution to the coefficient ϵ_2 is given by

$$\epsilon_2 = \gamma^2(16\pi/\beta V)[(i)+(j)]. \tag{4.4}$$

Evaluating the contributions of the diagrams (i) and (j) by means of the rules given in Section III, we obtain

$$\epsilon_2 = -\gamma^2(128\pi \mathscr{M}_0^3/V\hbar^4\omega_0^4)\{2\mathscr{M}_0 V(0000) - \hbar\omega_0 \mathscr{M}(000)\}. \tag{4.5}$$

Allowing for differences in notation, the first term in this result is equivalent to the result obtained in Part I for the rigid ion model. The second term arises solely from the deformability of the ions.

V. Evaluation for the Alkali Halides

The general result (4.5) will now be evaluated for the alkali halides. The model to be used is the simple anharmonic shell model with only the negative ion polarizable and with short range repulsive forces between shells of nearest neighbours. This model has been discussed in a previous paper (Oitmaa 1967*b*).

The coefficients in (4.5) can be expressed in terms of the coefficients used in Oitmaa (1967*b*) as

$$\left.\begin{aligned} V(0000) &= \tfrac{1}{24}N^{-1}(\hbar/2\omega_0)^2 \Psi(04;04;04;04), \\ \mathscr{M}_0 &= N^{\frac{1}{2}}(\hbar/2\omega_0)^{\frac{1}{2}} M(04), \\ \mathscr{M}(000) &= \tfrac{1}{6}N^{-\frac{1}{2}}(\hbar/2\omega_0)^{3/2} M(04;04;04). \end{aligned}\right\} \tag{5.1}$$

Using these results (4.5) can be written as

$$\epsilon_2 = -\gamma^2(2\pi M(04)^4/3v\omega_0^8)\{\Psi(04;04;04;04) - (4\omega_0^2/M(04))M(04;04;04)\}. \tag{5.2}$$

From Appendix I it follows that

$$\Psi(04;04;04;04) = \Phi(04;04;04;04) + \eta\Phi^R(04;04;04;04), \tag{5.3}$$

where $\Phi(04;04;04;04)$ and $\Phi^R(04;04;04;04)$ are respectively the total and repulsive anharmonic coefficients for rigid ions. The parameter η is given by

$$\eta = -4(R - YC)/(R + k + Y^2C), \tag{5.4}$$

where R is defined in terms of the derivatives of the short range repulsive potential $\phi_R(r)$ by

$$R = 2\phi_R''(r_0) + (4/r_0)\phi_R'(r_0) \tag{5.5}$$

and where

$$C = -4\pi e^2/3v. \tag{5.6}$$

In this work we consider both the repulsive and Coulomb contributions to the coefficient $\Phi(04;04;04;04)$. The Coulomb contribution is considerably less than the repulsive part, and to simplify the calculation we consider the Coulomb contribution only for nearest neighbours. The coefficient $\Phi(04;04;04;04)$ is then given by

$$\Phi(04;04;04;04) = \frac{1}{\bar{m}^2}\left(2\phi^{(4)}(r_0) + \frac{12}{r_0^2}\phi''(r_0) - \frac{12}{r_0^3}\phi'(r_0)\right), \tag{5.7}$$

where $\phi(r)$ is the total nearest neighbour potential given by

$$\phi(r) = \phi_R(r) - e^2/r \tag{5.8}$$

and $\bar{m}$ is the reduced mass given by

$$\bar{m}^{-1} = m_1^{-1} + m_2^{-1}. \tag{5.9}$$

From Appendix II it follows that the dipole moment coefficients are given by

$$M(04) = (e/\bar{m}^{\frac{1}{2}})(1+\chi), \tag{5.10}$$

where

$$\chi = Y(R - YC)/(R + k + Y^2C) \tag{5.11}$$

and

$$M(04;04;04) = \{eY\bar{m}^{\frac{1}{2}}/(R + k + Y^2C)\}\Phi^R(04;04;04;04). \tag{5.12}$$

For a thin rod of dielectric the frequency ω_0 of the $q = 0$ optic mode, with displacements parallel to the long direction, can be obtained from the theory in Oitmaa (1967*b*) as

$$\bar{m}\omega_0^2 = R + C - (R - YC)^2/(R + k + Y^2C). \tag{5.13}$$

This result is equivalent to the expression obtained by Woods, Cochran, and Brockhouse (1960) for the infrared absorption frequency of this model.

The adjustable parameters Y and k can be obtained by using the results (Havinga 1960)

$$\frac{Y^2e^2}{R+k} = \alpha_\infty, \qquad \frac{(1+Y)^2e^2}{k} + \frac{e^2}{R} = \alpha_0, \tag{5.14}$$

where the polarizabilities α_∞ and α_0 are given by

$$\frac{4\pi}{3v}\alpha_0 = \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \qquad \text{and} \qquad \frac{4\pi}{3v}\alpha_\infty = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}. \tag{5.15}$$

The result (5.2) can then be evaluated numerically. We do this for NaI, using the following room-temperature data (Born and Huang 1954): $r_0 = 3{\cdot}231 \times 10^{-8}$ cm, $\epsilon_0 = 6{\cdot}60$, $\epsilon_\infty = 2{\cdot}91$, $e = 4{\cdot}803 \times 10^{-10}$ e.s.u., $m_1 = 3{\cdot}809 \times 10^{-23}$ g, $m_2 = 21{\cdot}027 \times 10^{-23}$ g.

For the short range repulsive potential we use a Born–Mayer potential of the form

$$\phi_{\mathrm{R}}(r) = D\exp(-r/\rho)\,, \tag{5.16}$$

with

$$\rho = 0{\cdot}363\times10^{-8}\ \mathrm{cm}, \qquad D\exp(-r_0/\rho) = 2{\cdot}33\times10^{-13}\ \mathrm{erg}.$$

These data then give the results:

$$R = 2{\cdot}742\times10^{4}\ \mathrm{erg\ cm^{-2}},\quad v = 6{\cdot}746\times10^{-23}\ \mathrm{cm^3},\quad C = -1{\cdot}432\times10^{4}\ \mathrm{erg\ cm^{-2}},$$

$$Y = -2{\cdot}106,\quad k = 13{\cdot}58\times10^{4}\ \mathrm{erg\ cm^{-2}},\quad \bar{m} = 3{\cdot}225\times10^{-23}\ \mathrm{g},$$

$$\omega_0 = 2{\cdot}01\times10^{13}\ \mathrm{sec^{-1}},\quad \eta = 0{\cdot}110,\quad \chi = 0{\cdot}058,$$

$$\Phi(04;04;04;04) = 2{\cdot}269\times10^{66},\qquad \Phi^{\mathrm{R}}(04;04;04;04) = 2{\cdot}798\times10^{66}.$$

From these results it follows that

$$\Psi(04;04;04;04) = 2{\cdot}576\times10^{66},\quad M(04) = 89{\cdot}46,\quad M(04;04;04) = -1{\cdot}611\times10^{41}.$$

Substituting these results in (5.2) gives for NaI

$$\epsilon_2 = -4{\cdot}11\times10^{-10}\quad (\mathrm{CGS}).$$

This compares with $-1{\cdot}32\times10^{-10}$ that was obtained in Part I for NaI on the basis of a rigid ion model. Thus for the shell model the predicted value of the coefficient ϵ_2 is increased by a factor of approximately three over the rigid ion result. Some of this increase is due to the fact that the linear dipole moment coefficient and the quartic anharmonic coefficient are increased in the shell model, but most of the increase in ϵ_2 is due to the contribution of an additional term (depending on the third-order dipole moment coefficient) which does not appear for the rigid ion model. This term arises solely from the deformability of the ions.

VI. Some Higher Order Terms

In Section IV the lowest order contributions to the field-dependent terms in the dielectric constant expansion (1.1) were obtained. These contributions arose from terms in the free energy proportional to γ^2E^4. These terms did not depend explicitly on the temperature but only implicitly through the weak temperature dependence of r_0 and hence of ω_0 and of the anharmonic coefficients.

Further contributions to the field-dependent terms in (1.1) can be obtained by expanding the free energy to higher order than γ^2. For consistency, higher order terms must then also be included in the Hamiltonian (2.1). By evaluating such higher order contributions to the dielectric constant we obtain a check on the convergence of the perturbation expansion.

In this section we include terms up to order γ^4 in the Hamiltonian, i.e. terms up to sixth order in the particle displacements in the potential energy expansion. The free energy is then also expanded up to order γ^4. Since we are only interested in terms that give contributions to the dielectric constant proportional to E^2, or higher powers of E, it is only necessary to consider the free energy diagrams that are proportional to E^4 or higher powers of E.

For a centro-symmetrical crystal there are 5 free energy diagrams proportional to $\gamma^4 E^6$, shown in Figure 4. For a crystal without a centre of symmetry there are 28 additional diagrams of this type. These diagrams give the lowest order contribution to the E^4 term in the expansion (1.1). This contribution is again independent of the temperature.

Several of these terms were evaluated for NaI. For a large field of 1000 e.s.u. cm^{-1} (3×10^5 V cm^{-1}) the change in dielectric constant due to these terms was smaller by a factor of at least 10^4 than the change calculated in Section V. Thus these terms are completely negligible. From this we can conclude that any decrease that might occur in the dielectric constant of such simple ionic crystals at large fields would be proportional to the square of the field strength.

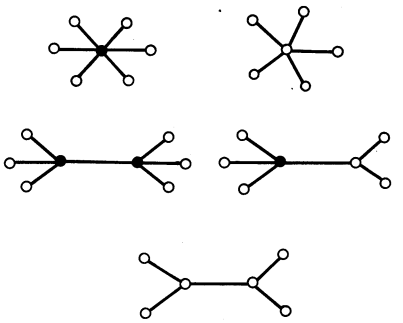

Fig. 4.—Free energy diagrams proportional to $\gamma^4 E^6$ for a centro-symmetrical crystal.

There also occur a total of 89 free energy diagrams proportional to $\gamma^4 E^4$, of which 29 are nonvanishing for a centro-symmetrical crystal. The 29 diagrams are shown in Figure 5.

These 29 diagrams give additional contributions to the E^2 term in the expansion (1.1). These contributions all involve a single or multiple summation over the normal modes of the crystal and are explicitly dependent on the temperature, in contrast to the lowest order contributions evaluated in Section IV. The summations were evaluated numerically by taking a sample of $\boldsymbol{q}$ vectors evenly distributed throughout the first Brillouin zone. The sample used was the same as that used by Hardy (1962), which is a slight modification of that used originally by Kellermann (1940). This sample consists of 48 distinct $\boldsymbol{q}$'s, which by symmetry corresponds to exactly 1000 points in the zone. In this work it was necessary to distinguish between $\boldsymbol{q}$'s that merely involved an interchange of x and y, or x and z, components, since the anharmonic coefficients involved were not symmetric in x, y, z. This made it necessary to consider 106 distinct $\boldsymbol{q}$'s corresponding to the 1000 points. The 29 terms were then evaluated numerically for various temperatures between 0°K and 500°K using the IBM 360/50 computer of the University of New South Wales Computing Centre. One approximation that was made in evaluating these higher order terms was to replace the modified shell model anharmonic coefficients Ψ by the rigid ion ones Φ. This should not introduce an error of more than about 10% and greatly decreases the amount of work involved in calculating the various anharmonic coefficients.

The variation with temperature of the total contribution of these diagrams to the coefficient ϵ_2 in (1.1) is shown in Figure 6. At high temperatures the variation

with temperature is almost linear. Using this result and the result of Section V, the high temperature dielectric constant of NaI can be expressed in the form

$$\epsilon_s = \epsilon_0 - (4 \cdot 0 - 1 \cdot 6 \times 10^{-3} T) E^2 . \tag{6.1}$$

At low temperatures the variation with T is more complicated.

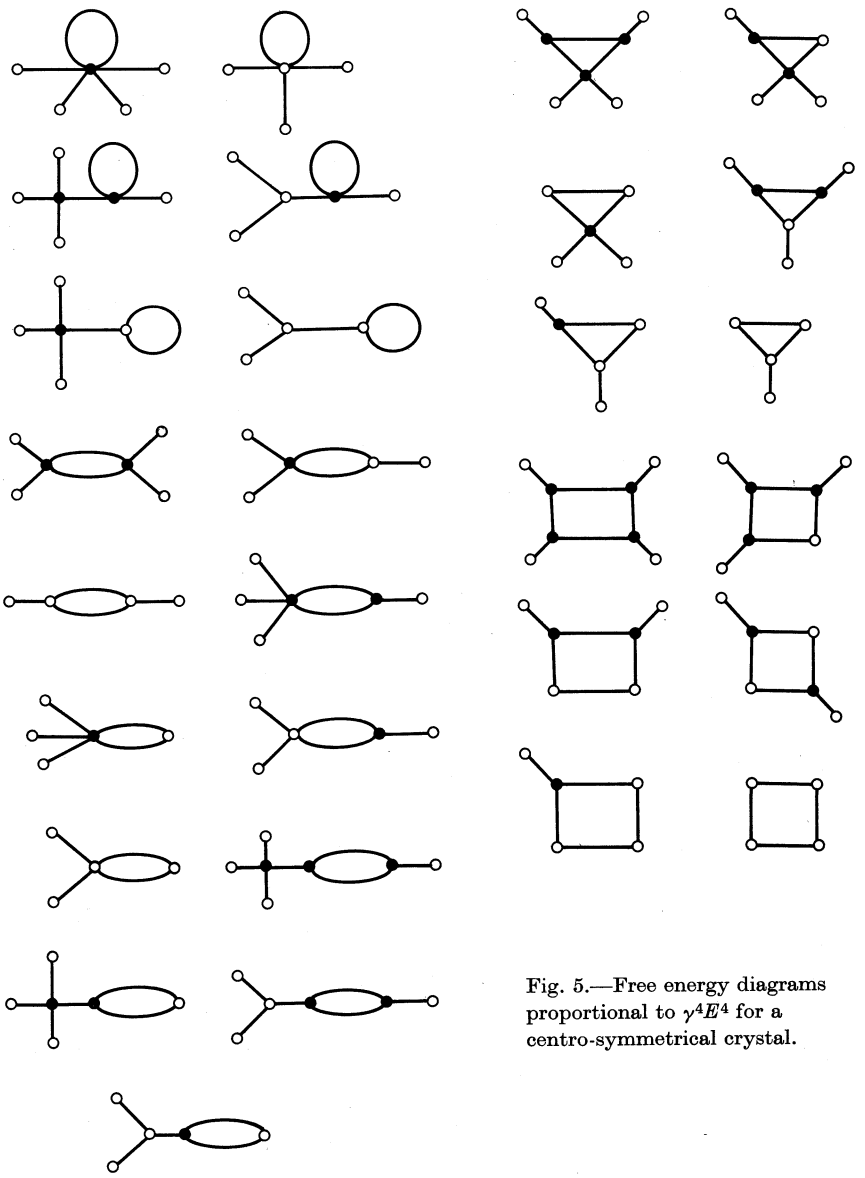

Fig. 5.—Free energy diagrams proportional to $\gamma^4 E^4$ for a centro-symmetrical crystal.

At all temperatures the contribution of these terms to the coefficient ϵ_2 is of the order of 10–20% of the lowest order term, and so the perturbation expansion appears to be quite good.

VII. Discussion

The lowest order contribution to the coefficient of the E^2 term in the phenomenological expansion (1.1) of the static dielectric constant of a crystalline solid with deformable ions has been calculated. This contribution is independent of the temperature, and the same result can in fact be obtained for a classical static lattice model. For NaI this results in a small decrease in the static dielectric constant of 4×10^{-4} in a field of 1000 e.s.u. cm^{-1}.

The next order terms give a temperature-dependent contribution to this coefficient which is of the order of 10% of the lowest order contribution. This situation is completely analogous to that which occurs with the ordinary field-independent static dielectric constant ϵ_0. To a first approximation ϵ_0 is independent of the temperature and can be obtained for a static lattice model. Higher order terms, which at low temperatures must be calculated quantum mechanically, give a small temperature-dependent correction to ϵ_0.

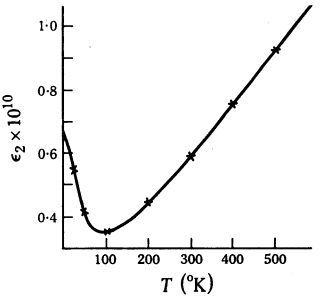

Fig. 6.—Contribution to ϵ_2 of the diagrams of order γ^4.

The lowest order contribution to the coefficient of the E^4 term in the expansion (1.1) is also independent of the temperature. The change in dielectric constant due to this term is negligible compared with the change due to the E^2 term. Thus any decrease that might be observed in the static dielectric constant of simple ionic crystals, such as the alkali halides, would be proportional to the square of the field strength.

VIII. Acknowledgments

The author wishes to thank Professor J. J. O'Dwyer for suggesting this problem to him and for many helpful discussions. He also wishes to thank Mr. P. L. Sanger for supplying the data used in Section VI, and for assistance with the computing. The data were obtained from a programme written originally by Dr. A. W. Pryor.

IX. References

Bloch, C., and de Dominicis, C. (1958).—*Nucl. Phys.* **7**, 449.

Born, M., and Huang, K. (1954).—"Dynamical Theory of Crystal Lattices." (Clarendon Press: Oxford.)

Cowley, R. A. (1963).—*Adv. Phys.* **12**, 421.

Gaudin, N. (1960).—*Nucl. Phys.* **15**, 89.

Goldstone, J. (1957).—*Proc. R. Soc.* A **239**, 267.

HARDY, J. R. (1962).—*Phil. Mag.* (8) **7**, 315.
HAVINGA, E. E. (1960).—*Phys. Rev.* **119**, 1193.
HUGENHOLTZ, N. M. (1957).—*Physica* **23**, 481.
KELLERMANN, E. W. (1940).—*Phil. Trans. R. Soc.* **238**, 513.
LUTTINGER, J. M., and WARD, J. C. (1960).—*Phys. Rev.* **118**, 1417.
MARADUDIN, A. A., and FEIN, A. E. (1962).—*Phys. Rev.* **128**, 2589.
MATSUBARA, T. (1955).—*Prog. theor. Phys., Kyoto* **14**, 351.
OITMAA, J. (1967*a*).—*Aust. J. Phys.* **20**, 11.
OITMAA, J. (1967*b*).—*Aust. J. Phys.* **20**, 495.
PARRY, W. E., and TURNER, R. E. (1964).—*Rep. Prog. Phys.* **27**, 23.
SZIGETI, B. (1959).—*Proc. R. Soc.* A **252**, 217.
WILCOX, R. M. (1965).—*Phys. Rev.* **139**, A1281.
WOODS, A. D. B., COCHRAN, W., and BROCKHOUSE, B. N. (1960).—*Phys. Rev.* **119**, 980.

APPENDIX I

Shell Model Anharmonic Coefficient

The shell model anharmonic coefficient $\Psi(04;04;04;04)$ is given from Oitmaa (1967*b*) by

$$\Psi(04;04;04;04) = \sum_{\substack{l'l''l''' \\ \kappa\kappa'\kappa''\kappa'''}} \frac{e_x(\kappa \mid 04)\, e_x(\kappa' \mid 04)\, e_x(\kappa'' \mid 04)\, e_x(\kappa''' \mid 04)}{(m_\kappa m_{\kappa'} m_{\kappa''} m_{\kappa'''})^{\frac{1}{2}}} \times \psi_{xxxx}(0\kappa, l'\kappa', l''\kappa'', l'''\kappa''') . \tag{A1}$$

This expression can be simplified considerably by using the invariance relations

$$\psi_{xxxx}(l\kappa, l'\kappa', l''\kappa'', l'''\kappa''') = \psi_{xxxx}(0\kappa, (l'-l)\kappa', (l''-l)\kappa'', (l'''-l)\kappa''')$$

and

$$\sum_{l\kappa} \psi_{xxxx}(l\kappa, l'\kappa', l''\kappa'', l'''\kappa''') = 0 ,$$

the latter of which implies that

$$\sum_{l} \psi_{xxxx}(l1, l'\kappa', l''\kappa'', l'''\kappa''') = -\sum_{l} \psi_{xxxx}(l2, l'\kappa', l''\kappa'', l'''\kappa''') .$$

Using these invariance relations and the result

$$\frac{e_x(1 \mid 04)}{m_1^{\frac{1}{2}}} - \frac{e_x(2 \mid 04)}{m_2^{\frac{1}{2}}} = \left(\frac{1}{m_1} + \frac{1}{m_2}\right)^{\frac{1}{2}} ,$$

the expression (A1) simplifies to

$$\Psi(04;04;04;04) = \left(\frac{1}{m_1} + \frac{1}{m_2}\right)^2 \sum_{l'l''l'''} \psi_{xxxx}(01, l'1, l''1, l'''1) . \tag{A2}$$

The anharmonic force constant $\psi_{xxxx}(01, l'1, l''1, l'''1)$ is given by the result (3.15) of Oitmaa (1967*b*). Using this result, the expression (A2) can be simplified to give

$$\Psi(04;04;04;04) = \frac{1}{m^2}\left(\Phi_{xxxx}(01,01,01,01) - 4\sum_{l\kappa}(BD)_{xx}(1\kappa,0)\,\Phi^{\mathrm{R}}_{xxxx}(0\kappa,l1,l1,l1)\right), \tag{A3}$$

where $\Phi_{xxxx}(01,01,01,01)$ and $\Phi^{\mathrm{R}}_{xxxx}(0\kappa,l1,l1,l1)$ are rigid ion force constants and **B** and **D** are $3n\times 3n$ matrices, defined in Oitmaa (1967*b*).

Using the result of Part I for the rigid ion coefficients $\Phi(04;04;04;04)$ and $\Phi^{\mathrm{R}}(04;04;04;04)$, and using the explicit forms, for the NaCl structure, of the 6×6 matrices **B** and **D** for $\boldsymbol{q} = 0$, gives for (A3)

$$\Psi(04;04;04;04) = \Phi(04;04;04;04) + \eta\Phi^{\mathrm{R}}(04;04;04;04), \tag{A4}$$

where

$$\begin{aligned}\eta &= -4(BD)_{xx}(11,0) + 4(BD)_{xx}(12,0)\\ &= -4\frac{k_1(R - Y_2C) + k_2(R + Y_1C) + RC(Y_1 + Y_2)^2}{k_1k_2 + k_1(R + Y_2^2C) + k_2(R + Y_1^2C) + RC(Y_1 + Y_2)^2},\end{aligned} \tag{A5}$$

where k_1, k_2, and Y_1, Y_2 are respectively the core–shell force constants and the shell charges for the positive and negative ions.

For the simpler case, if only the negative ion is polarizable, putting $k_1 \to \infty$, $k_2 = k$, $Y_1 = 0$, and $Y_2 = Y$ we obtain

$$\eta = -4(R - YC)/(R + k + Y^2C). \tag{A6}$$

For $k \to \infty$, $\eta \to 0$ so that (A4) reduces to the rigid ion result.

Appendix II

Dipole Moment Coefficients

From the result (4.4) of Oitmaa (1967*b*) the first-order dipole moment coefficient $M(04)$ is given by

$$M(04) = e\sum_{\kappa} m_\kappa^{-\frac{1}{2}} Z_\kappa e_x(\kappa \mid 04) - e\sum_{\kappa\kappa'} m_{\kappa'}^{-\frac{1}{2}} Y_\kappa e_x(\kappa' \mid 04)(BD)_{xx}(\kappa'\kappa, 0). \tag{A7}$$

Writing out the summations and using the results of Appendix I for the case when only the negative ion is polarizable gives

$$M(04) = e\bar{m}^{-\frac{1}{2}}(1 + \chi), \tag{A8}$$

where

$$\chi = Y(R - YC)/(R + k + Y^2C). \tag{A9}$$

For $k \to \infty$, $\chi \to 0$ so that (A8) reduces to the rigid ion result.

From the result (4.6) of Oitmaa (1967*b*) the third-order dipole moment coefficient $M(04;04;04)$ is given by

$$M(04;04;04) = -e \sum_{\substack{l_3 l_4 l_5 \\ \kappa_1 \kappa_2 \kappa_3 \kappa_4 \kappa_5}} \frac{Y_{\kappa_1} e_x(\kappa_3 \mid 04)\, e_x(\kappa_4 \mid 04)\, e_x(\kappa_5 \mid 04)}{(m_{\kappa_3} m_{\kappa_4} m_{\kappa_5})^{\frac{1}{2}}} \times D_{xx}(\kappa_1 \kappa_2, 0)\, \Phi^{\mathrm{R}}_{xxxx}(0\kappa_2, l_3 \kappa_3, l_4 \kappa_4, l_5 \kappa_5). \quad \text{(A10)}$$

For two-body forces only, the force constants in this expression are nonzero only if they refer to at most two distinct ions. For this case (A10) can be simplified to give

$$M(04;04;04) = e(m_1^{-1}+m_2^{-1})^{3/2} \sum_{\kappa} Y_\kappa \{D_{xx}(\kappa 1, 0) - D_{xx}(\kappa 2, 0)\} \sum_{l} \Phi^{\mathrm{R}}_{xxxx}(01, 01, 01, l2)$$

$$= \zeta \Phi^{\mathrm{R}}(04;04;04;04), \quad \text{(A11)}$$

where

$$\zeta = e\bar{m}^{\frac{1}{2}} \frac{Y_1 k_2 - Y_2 k_1}{k_1 k_2 + k_1(R + Y_2^2 C) + k_2(R + Y_1^2 C) + RC(Y_1 + Y_2)^2}. \quad \text{(A12)}$$

For the case when only the negative ion is polarizable (A12) simplifies to

$$\zeta = eY\bar{m}^{\frac{1}{2}}/(R + k + Y^2 C). \quad \text{(A13)}$$

For $k \to \infty$ this gives $\zeta \to 0$, so that (A11) reduces to the rigid ion result, namely, that the higher order dipole moments vanish.