

Temperature Dependence of the Dielectric Constant of Paraelectric Materials*

B. D. SILVERMAN AND R. I. JOSEPH

Research Division, Raytheon Company, Waltham, Massachusetts

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An expression is obtained for the dielectric constant of a displacive ferroelectric in its unpolarized phase. This has been derived with the use of a Hamiltonian treated by Szigeti in connection with the temperature-dependent dielectric constant of the alkali halides. In the present work, however, it is assumed that the "soft ferroelectric mode" is unstable in the harmonic approximation, i.e., has an imaginary frequency associated with it. The linear response can be obtained exactly for this Hamiltonian. It is shown that the lowest order anharmonic interaction that can stabilize this mode is of fourth order. In the classical limit, the potential energy terms and the term linear in the electronic moment lead to a Curie-Weiss behavior of the dielectric constant. The most significant effect arising from the presence of terms of higher order than linear in the electric moment is to make the Curie constant temperature dependent. It is suggested that an observed temperature-independent contribution to the dielectric constant cannot be unambiguously attributed to the electronic polarization or temperature-independent infrared active modes of the system.

INTRODUCTION

ABOVE the ferroelectric transition, the dielectric constant of BaTiO_3 and related isomorphs is large and exhibits a Curie-Weiss type temperature dependence. It has been suggested that this behavior results from a near cancellation of the short-range restoring forces and the long-range driving forces on the ions.¹ Anharmonic terms in the lattice potential energy are held responsible for the temperature dependence of the dielectric constant. Since the Curie temperature is positive, the anharmonic interactions stabilize the system above its transition temperature. Cochran² has suggested that the Curie-Weiss behavior of the dielectric constant results from the temperature dependence of a long-wavelength transverse optical mode of the lattice. The suggested temperature dependence of this mode has been observed in SrTiO_3 by Barker and Tinkham³ from infrared reflectivity measurements and more recently by Cowley⁴ from the inelastic scattering of slow neutrons. At the transition temperature the frequency of this mode should go to zero and the lattice displacements associated with this mode become unstable. A transition is made to the ferroelectric state. If anharmonic interactions do stabilize the system above the transition temperature, the harmonic part of the frequency associated with this mode is an imaginary quantity. One cannot systematically consider the effects of anharmonic interactions on the equilibrium properties of a paraelectric material by expanding the free energy in powers of the anharmonic coupling coefficients about the harmonic state. Such an expansion would lead to divergences. To avoid this difficulty, all quantities should be expanded about their thermal averages.⁵ In this manner, one can

systematically derive the thermal equilibrium properties of a ferroelectric material in its unpolarized phase.

To illustrate this procedure, we will derive an expression for the temperature-dependent dielectric constant of a paraelectric material.⁶ A Hamiltonian such as Szigeti⁷ treated in discussing the temperature dependence of the dielectric constant of the alkali halides will be considered. Therefore, not only will third- and fourth-order anharmonic terms in the potential energy expansion be taken into account, but also electron cloud deformation through the presence of a second- and third-order electronic moment. The long-wavelength transverse optical modes which become unstable causing a transition to the ferroelectric state are, however, assigned imaginary frequencies. All such modes will be collectively labelled with zero wave vector and treated as a single mode in the following analysis. Thus, $k=0$ will mean that we consider a mode with wavelength large compared with the lattice parameter but small compared with the sample size. This procedure is possible since the total number of such wavelengths is small compared with the total number of wavelengths of the optical branch.⁸ Also, since the phase transition of BaTiO_3 is relatively free of fluctuation effects, it appears that at the transition very few of the lattice modes become unstable.⁹ Indeed, as Anderson has pointed out, the very basis of Devonshire's success in using the same free energy function for both paraelectric and ferroelectric phases of BaTiO_3 is due to the small number of unstable modes at the transition.

The Hamiltonian that is treated in the following section includes all lowest order effects of anharmonic interactions and electron deformations on the dielectric constant. It will be shown that the exact linear response

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¹ A. F. Devonshire, *Phil. Mag.* **40**, 1040 (1949); J. C. Slater, *Phys. Rev.* **78**, 748 (1950).

² W. Cochran, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1960), Vol. 9, p. 387.

³ A. S. Barker, Jr., and M. Tinkham, *Phys. Rev.* **125**, 1527 (1962).

⁴ R. A. Cowley, *Phys. Rev. Letters* **9**, 159 (1962).

⁵ D. J. Hooton, *Phil. Mag.* **46**, 422 (1955).

⁶ A preliminary version of the paper was presented at the American Physical Society meeting in Seattle on Aug. 27, 1962. R. I. Joseph and B. D. Silverman, *Bull. Am. Phys. Soc.* **7**, 438 (1962).

⁷ B. Szigeti, *Proc. Roy. Soc. (London)* **A252**, 217 (1959).

⁸ T. H. K. Barron, *Phys. Rev.* **123**, 1995 (1961).

⁹ P. W. Anderson, in *Fizika dielektrikov*, edited by G. I. Skanavi (Akad. Nauk SSSR, Fizicheskii Inst. im P. N. Lebedeva, Moscow, 1960), in Russian.

can be obtained for this Hamiltonian. The fourth-order anharmonic interaction with a positive coupling coefficient stabilizes the system at temperatures above the transition temperature. Third-order anharmonic interactions of either sign raise the instability temperature. The largest effect due to the presence of the electronic deformation terms is the contribution to an additive constant term F , appearing in the dielectric constant at temperatures high compared with the Curie temperature.

$$\epsilon - 1 = C/(T - T_c) + F.$$

This indicates that one cannot unambiguously assign the origin of such a term to the electronic polarization or to the other "hard" optical modes of the lattice.

TEMPERATURE-DEPENDENT DIELECTRIC CONSTANT

The Hamiltonian of the system is

$$\begin{aligned} H = & \sum_k \hbar \omega_k^a (a_k^{a*} a_k^a + \frac{1}{2}) + \sum_k \hbar \omega_k^o (a_k^{o*} a_k^o + \frac{1}{2}) + \frac{1}{2} [(\dot{p}_0^o)^2 - (\omega_0^o q_0^o)^2] - \alpha E N^{1/2} q_0^o \\ & + \sum_k \left[\frac{q_0^o}{\sqrt{N}} F(k) + EA(k) \right] \frac{\hbar}{(\omega_k^o \omega_k^a)^{1/2}} (a_k^a + a_{-k}^{a*}) (a_{-k}^o + a_k^{o*}) + \sum_k \left[\frac{(q_0^o)^2}{N} G^o(k) + E \frac{q_0^o}{\sqrt{N}} B^o(k) \right] \\ & \times \frac{\hbar}{\omega_k^o} (a_k^o + a_{-k}^{o*}) (a_{-k}^o + a_k^{o*}) + \sum_k \left[\frac{(q_0^o)^2}{N} G^a(k) + E \frac{q_0^o}{\sqrt{N}} B^a(k) \right] \frac{\hbar}{\omega_k^a} (a_k^a + a_{-k}^{a*}) (a_{-k}^a + a_k^{a*}) \\ = & H_1 + H_2 + \frac{1}{2} [(\dot{p}_0^o)^2 - (\omega_0^o q_0^o)^2] - \alpha E N^{1/2} q_0^o + H_3 + H_4 + H_5. \quad (1) \end{aligned}$$

The first two terms, H_1 and H_2 , in Eq. (1) are the harmonic contributions to the energy from all modes other than those that become unstable in the harmonic approximation. The ω_k^a and ω_k^o are the frequencies of the acoustical and optical modes having wave vector k , respectively. The a_k^* and a_k are just the usual creation—destruction operators for a mode of wave vector k which satisfy the following commutation relations:

$$[a_k, a_{k'}] = [a_k^*, a_{k'}^*] = 0; \quad [a_k, a_{k'}^*] = \delta_{kk'}.$$

The third term is the contribution to the energy from the mode that becomes unstable at the transition. q_0^o

and \dot{p}_0^o are the normal mode coordinate and conjugate momentum, respectively, of this long-wavelength transverse mode. The negative of $(\omega_0^o)^2$ is the square of the imaginary harmonic frequency of this mode. The only difference between the Hamiltonian of Eq. (1) and the one treated by Szigeti⁷ is due to the presence of this term. This term will allow a lattice instability to develop at a positive temperature. The fourth term in Eq. (1) is due to the presence of a linear electric moment. α , $A(k)$, and $B(k)$ describe the linear, second-order, and third-order moment, respectively. The total electric moment M , is written

$$\begin{aligned} M = & \alpha N^{1/2} q_0^o - \sum_k A(k) \frac{\hbar}{(\omega_k^o \omega_k^a)^{1/2}} (a_k^a + a_{-k}^{a*}) (a_{-k}^o + a_k^{o*}) \\ & - \sum_k \frac{q_0^o}{\sqrt{N}} B^o(k) \frac{\hbar}{\omega_k^o} (a_k^o + a_{-k}^{o*}) (a_{-k}^o + a_k^{o*}) - \sum_k \frac{q_0^o}{\sqrt{N}} B^a(k) \frac{\hbar}{\omega_k^a} (a_k^a + a_{-k}^{a*}) (a_{-k}^a + a_k^{a*}). \end{aligned}$$

This term then contributes $-EM$ to the energy. E is the macroscopic field and N is the number of ion pairs. The calculation is performed for two atoms per unit cell and the transverse optical mode of this model is chosen as the soft temperature-dependent ferroelectric mode. This enables us to calculate the temperature dependence of the dielectric constant from the soft mode. Contributions to the dielectric constant arising from other optical vibrations appear just as additive constants in the final result. The fifth term in the Hamiltonian H_3 , arises from the presence of a second-order moment and third-order potential. $F(k)$ describes the third-order anharmonic coupling. Since the creation-destruction operators appear in the same way for the moment and potential terms, they have been grouped together accordingly. The last two terms in the Hamiltonian H_4 and H_5 , are contributions from a third-order moment and fourth-order potential. $G^o(k)$ and $G^a(k)$ describe the fourth-

order anharmonic couplings for optical modes and acoustic modes, respectively. Moment and potential terms have again been grouped for convenience. This Hamiltonian has been derived by the assumption of a cubic structure with a center of symmetry for the material under consideration. The ideal perovskite structure fulfills these requirements.

The Hamiltonian [Eq. (1)] is transformed by a unitary transformation

$$e^{-iS} H e^{iS} = H + i[H, S] - \frac{1}{2} [[H, S], S] + \dots, \quad (2)$$

with transformation operator S given by

$$\begin{aligned} S = & i \frac{q_0^o}{\sqrt{N}} \sum_k \omega_k^o g(k) (a_k^a + a_{-k}^{a*}) (a_{-k}^o - a_k^{o*}) \\ & - i \frac{q_0^o}{\sqrt{N}} \sum_k \omega_k^a g(k) (a_k^a - a_{-k}^{a*}) (a_{-k}^o + a_k^{o*}). \quad (3) \end{aligned}$$

This form has been chosen for S so that H_3 can be eliminated from the transformed Hamiltonian by suitably choosing the $g(k)$.

$$i[(H_1+H_2), S]+H_3=0. \tag{4}$$

Therefore,

$$g(k)=\frac{\sqrt{N}}{q_0^\circ}\left[\frac{q_0^\circ}{\sqrt{N}}F(k)+EA(k)\right]\frac{1}{(\omega_k^\circ\omega_k^{\circ*})^{1/2}\Delta_k}, \tag{5}$$

since

$$[(H_1+H_2), S] = \frac{iq_0^\circ\hbar}{\sqrt{N}}\sum_k g(k)\Delta_k(a_k^a+a_{-k}^{a*})(a_{-k}^\circ+a_k^{\circ*}), \tag{6}$$

and where

$$\Delta_k=[(\omega_k^a)^2-(\omega_k^\circ)^2].$$

Other commutation relations of use are:

$$[H_3,S]=2i\sum_k\left|\frac{q_0^\circ}{\sqrt{N}}F(k)+EA(k)\right|^2\frac{\hbar}{\omega_k^\circ\Delta_k}(a_k^\circ+a_{-k}^{\circ*})(a_{-k}^\circ+a_k^{\circ*}) - 2i\sum_k\left|\frac{q_0^\circ}{\sqrt{N}}F(k)+EA(k)\right|^2\frac{\hbar}{\omega_k^a\Delta_k}(a_k^a+a_{-k}^{a*})(a_{-k}^a+a_k^{a*}), \tag{7}$$

$$[H_4,S]=-4i\sum_k\left[\frac{(q_0^\circ)^2}{N}G^\circ(k)+E\frac{q_0^\circ}{\sqrt{N}}B^\circ(k)\right]\frac{q_0^\circ}{\sqrt{N}}\hbar g(k)(a_{-k}^\circ+a_k^{\circ*})(a_k^a+a_{-k}^{a*}), \tag{8}$$

$$[H_5,S]=4i\sum_k\left[\frac{(q_0^\circ)^2}{N}G^a(k)+E\frac{q_0^\circ}{\sqrt{N}}B^a(k)\right]\frac{q_0^\circ}{\sqrt{N}}\hbar g(k)(a_k^a+a_{-k}^{a*})(a_{-k}^\circ+a_k^{\circ*}), \tag{9}$$

$$[[H_1+H_2), S], S]=-2\sum_k\left|\frac{q_0^\circ}{\sqrt{N}}F(k)+EA(k)\right|^2\frac{\hbar}{\omega_k^\circ\Delta_k}(a_k^\circ+a_{-k}^{\circ*})(a_{-k}^\circ+a_k^{\circ*}) + 2\sum_k\left|\frac{q_0^\circ}{\sqrt{N}}F(k)+EA(k)\right|^2\frac{\hbar}{\omega_k^a\Delta_k}(a_k^a+a_{-k}^{a*})(a_{-k}^a+a_k^{a*}). \tag{10}$$

The following relations have been used to write the preceding results in the form shown:

$$G^\circ(-k)=G^\circ(k), \quad B^\circ(-k)=B^\circ(k), \\ G^a(-k)=G^a(k), \quad B^a(-k)=B^a(k).$$

With the use of these commutation relations, the transformed Hamiltonian H_T can be written

$$H_T=\sum_k\hbar\omega_k^a(a_k^{a*}a_k^a+\frac{1}{2})+\sum_k\hbar\omega_k^\circ(a_k^{\circ*}a_k^\circ+\frac{1}{2})+\frac{1}{2}[(p_0^\circ)^2-(\omega_0^\circ q_0^\circ)^2]-\alpha EN^{1/2}q_0^\circ+\sum_k\left[\frac{(q_0^\circ)^2}{N}G^\circ(k)+E\frac{q_0^\circ}{\sqrt{N}}B^\circ(k)\right] \\ \times\frac{\hbar}{\omega_k^\circ}(a_k^\circ+a_{-k}^{\circ*})(a_{-k}^\circ+a_k^{\circ*})+\sum_k\left[\frac{(q_0^\circ)^2}{N}G^a(k)+E\frac{q_0^\circ}{\sqrt{N}}B^a(k)\right]\frac{\hbar}{\omega_k^a}(a_k^a+a_{-k}^{a*})(a_{-k}^a+a_k^{a*}) \\ -\sum_k\left|\frac{q_0^\circ}{\sqrt{N}}F(k)+EA(k)\right|^2\frac{\hbar}{\omega_k^\circ\Delta_k}(a_k^\circ+a_{-k}^{\circ*})(a_{-k}^\circ+a_k^{\circ*})+\sum_k\left|\frac{q_0^\circ}{\sqrt{N}}F(k)+EA(k)\right|^2 \\ \times\frac{\hbar}{\omega_k^a\Delta_k}(a_k^a+a_{-k}^{a*})(a_{-k}^a+a_k^{a*})+4\sum_k\left[\frac{(q_0^\circ)^2}{N}G^\circ(k)+E\frac{q_0^\circ}{\sqrt{N}}B^\circ(k)\right]\left[\frac{q_0^\circ}{\sqrt{N}}F(k)+EA(k)\right] \\ \times\frac{\hbar}{(\omega_k^\circ\omega_k^a)^{1/2}\Delta_k}(a_{-k}^\circ+a_k^{\circ*})(a_k^a+a_{-k}^{a*})-4\sum_k\left[\frac{(q_0^\circ)^2}{N}G^a(k)+E\frac{q_0^\circ}{\sqrt{N}}B^a(k)\right]\left[\frac{q_0^\circ}{\sqrt{N}}F(k)+EA(k)\right] \\ \times\frac{\hbar}{(\omega_k^\circ\omega_k^a)^{1/2}\Delta_k}(a_{-k}^\circ+a_k^{\circ*})(a_k^a+a_{-k}^{a*})-\frac{1}{2}[[H'',S],S]+\dots, \tag{11}$$

where H'' is $H-(H_1+H_2)$. Terms linear in the third-order anharmonic coupling coefficient $F(k)$ and second-order moment coefficient $A(k)$ have been eliminated from the Hamiltonian. Terms bilinear in both coefficients do, how-

ever, appear. The preceding transformation has been performed since only the terms diagonal in the creation-destruction operator that we have exhibited explicitly in the Hamiltonian [Eq. (11)] will contribute to the linear response of the system. This will be shown in what follows. Let us group the diagonal terms and label them H_D . Since the state of thermal equilibrium will be considered, one can also set

$$a_k^* a_k = a_{-k}^* a_{-k}. \quad (12)$$

Therefore,

$$\begin{aligned} H_D = & \sum_k \hbar \omega_k^a (a_k^{a*} a_k^a + \frac{1}{2}) + \sum_k \hbar \omega_k^o (a_k^{o*} a_k^o + \frac{1}{2}) + \frac{1}{2} \left\{ (p_0^o)^2 + \left[\frac{4}{N} \sum_k \frac{\hbar}{\omega_k^o} G^o(k) (a_k^{o*} a_k^o + \frac{1}{2}) + \frac{4}{N} \sum_k \frac{\hbar}{\omega_k^a} G^a(k) \right. \right. \\ & \times (a_k^{a*} a_k^a + \frac{1}{2}) - \frac{4}{N} \sum_k |F(k)|^2 \frac{\hbar}{\omega_k^o \Delta_k} (a_k^{o*} a_k^o + \frac{1}{2}) + \frac{4}{N} \sum_k |F(k)|^2 \frac{\hbar}{\omega_k^a \Delta_k} (a_k^{a*} a_k^a + \frac{1}{2}) - (\omega_0^o)^2 \left. \right\} (q_0^o)^2 \\ & - \alpha E N^{1/2} q_0^o + \frac{2Fq_0^o}{\sqrt{N}} \sum_k B^o(k) \frac{\hbar}{\omega_k^o} (a_k^{o*} a_k^o + \frac{1}{2}) + \frac{2Eq_0^o}{\sqrt{N}} \sum_k B^a(k) \frac{\hbar}{\omega_k^a} (a_k^{a*} a_k^a + \frac{1}{2}) \\ & - \frac{4Eq_0^o}{\sqrt{N}} \sum_k F(k) A(-k) \frac{\hbar}{\omega_k^o \Delta_k} (a_k^{o*} a_k^o + \frac{1}{2}) + \frac{4Eq_0^o}{\sqrt{N}} \sum_k F(k) A(-k) \frac{\hbar}{\omega_k^a \Delta_k} (a_k^{a*} a_k^a + \frac{1}{2}) \\ & - 2F^2 \sum_k |A(k)|^2 \frac{\hbar}{\omega_k^o \Delta_k} (a_k^{o*} a_k^o + \frac{1}{2}) + 2E^2 \sum_k |A(k)|^2 \frac{\hbar}{\omega_k^a \Delta_k} (a_k^{a*} a_k^a + \frac{1}{2}). \quad (13) \end{aligned}$$

The partition function of the system is

$$Z = \sum_n \langle n | e^{-\beta H} | n \rangle = \sum_n \langle n | e^{-\beta H_D - \beta H'} | n \rangle; \quad \beta = 1/k_B T. \quad (14)$$

H' contains all terms nondiagonal in the creation-destruction operator and diagonal terms originating from $[[H'', S], S]$ and higher order commutators.

Expand the partition sum in powers of H'

$$\begin{aligned} Z = & \sum_n \langle n | e^{-\beta H_D} | n \rangle + \sum_n \sum_{n'=1}^{\infty} (-1)^{n'} \int_0^{\beta} d\lambda_1 \int_0^{\lambda_1} d\lambda_2 \int_0^{\lambda_2} d\lambda_3 \\ & \dots \int_0^{\lambda_{n'-1}} d\lambda_n \langle n | e^{(\lambda_1 - \beta) H_D} H' e^{(\lambda_2 - \lambda_1) H_D} H' \dots e^{-\lambda_n H_D} | n \rangle = Z^0 + Z'. \quad (15) \end{aligned}$$

It will be shown that in the limit of infinite normalization volume, i.e., $N \rightarrow \infty$, Z' will not contribute to the linear response. The free energy F can be written

$$F = - (1/\beta) \ln Z, \quad (16)$$

and, hence, the polarization is given by

$$P = - \partial F / \partial E = (1/\beta Z) (\partial Z / \partial E). \quad (17)$$

To obtain the linear response it is therefore only necessary to examine, at most, terms quadratic in the electric field.

Let us consider

$$Z^0 = \sum_n \langle n | e^{-\beta H_D} | n \rangle. \quad (18)$$

The trace is evaluated in a representation for which the $a_k^* a_k$ are diagonal. One can then write

$$Z^0 = \sum_{n_0, n_k} \langle n_0 | e^{-\beta H_D(n_k, q_0^o)} | n_0 \rangle, \quad (19)$$

with $H_D(n_k, q_0^o)$ given by Eq. (13), however with $a_k^{a*} a_k^a$ and $a_k^{o*} a_k^o$ replaced by n_k^a and n_k^o , respectively.

n_k^a and n_k^o are just the phonon occupation numbers for the k th acoustic and optical mode, respectively. Note that one can consider the coefficient in front of $(q_0^o)^2$ as the square of an effective frequency Ω which is dependent upon the occupation of all nonzero wave vector phonon states.

$$\begin{aligned} \Omega^2(n_k) = & \frac{4}{N} \sum_k \frac{\hbar}{\omega_k^o} G^o(k) (n_k^o + \frac{1}{2}) + \frac{4}{N} \sum_k \frac{\hbar}{\omega_k^a} G^a(k) \\ & \times (n_k^a + \frac{1}{2}) - \frac{4}{N} \sum_k |F(k)|^2 \frac{\hbar}{\omega_k^o \Delta_k} (n_k^o + \frac{1}{2}) \\ & + \frac{4}{N} \sum_k |F(k)|^2 \frac{\hbar}{\omega_k^a \Delta_k} (n_k^a + \frac{1}{2}) - (\omega_0^o)^2. \quad (20) \end{aligned}$$

It will be shown that n_k^a and n_k^o can be rigorously replaced by average values $\langle n_k^a \rangle$ and $\langle n_k^o \rangle$ to be defined. If $\Omega^2(\langle n_k \rangle)$ is positive at all temperatures, the material will not make a transition to a ferroelectric state at any temperature. If this quantity changes sign at a temper-

ature for which the phonon occupation numbers can be replaced by their classical values, then

$$\Omega^2 \sim (T - T_c), \quad (21)$$

and above the transition the dielectric constant should follow a Curie-Weiss law. This is observed for such materials as BaTiO₃, PbTiO₃, and KNbO₃. If the square of this frequency changes sign at a temperature for which the phonon occupation numbers deviate signifi-

cantly from the classical values, then deviations from a Curie-Weiss behavior of the dielectric constant will be observed before the material goes through a phase transformation.¹⁰ This is apparently observed in KTaO₃.¹¹

Since we are interested in the linear response, the partition function is expanded to terms in E^2 . Terms linear in E are dropped since they will vanish when the average over the q_0^o coordinate is performed.

$$\begin{aligned} Z^0 = \sum_{n_0, n_k} \left\langle n_0 \left| \exp \left\{ -\beta \sum_k \hbar \omega_k^a (n_k^a + \frac{1}{2}) - \beta \sum_k \hbar \omega_k^o (n_k^o + \frac{1}{2}) - \frac{1}{2} \beta [p_0^{o2} + \Omega^2 (n_k) q_0^{o2}] \right\} \right. \right. \\ \times \left\{ 1 + \frac{1}{2} \beta^2 E^2 q_0^{o2} \left[-\alpha N^{1/2} + \frac{2}{\sqrt{N}} \sum_k B^o(k) \frac{\hbar}{\omega_k^o} (n_k^o + \frac{1}{2}) + \frac{2}{\sqrt{N}} \sum_k B^a(k) \frac{\hbar}{\omega_k^a} (n_k^a + \frac{1}{2}) \right. \right. \\ \left. \left. - \frac{4}{\sqrt{N}} \sum_k F(k) A(-k) \frac{\hbar}{\omega_k^o \Delta_k} (n_k^o + \frac{1}{2}) + \frac{4}{\sqrt{N}} \sum_k F(k) A(-k) \frac{\hbar}{\omega_k^a \Delta_k} (n_k^a + \frac{1}{2}) \right] \right. \\ \left. \left. + 2\beta E^2 \sum_k |A(k)|^2 \frac{\hbar}{\omega_k^o \Delta_k} (n_k^o + \frac{1}{2}) - 2\beta E^2 \sum_k |A(k)|^2 \frac{\hbar}{\omega_k^a \Delta_k} (n_k^a + \frac{1}{2}) \right\} \right| n_0 \rangle. \quad (22) \end{aligned}$$

In the limit of infinite normalization volume, i.e., $N \rightarrow \infty$, the result of performing the sums over the n_k is to just replace the n_k by their thermal average $\langle n_k \rangle$ in all terms except the first two appearing in the exponential. $\langle n_k \rangle$ is given by

$$\langle n_k \rangle = \frac{\sum_{n_k} n_k e^{-\beta \hbar \omega_k (n_k + \frac{1}{2})}}{\sum_{n_k} e^{-\beta \hbar \omega_k (n_k + \frac{1}{2})}}. \quad (23)$$

This statement can be proved as follows. Expand all terms in the partition sum about the thermal average $\langle n_k \rangle$, except the first two appearing in the exponential. The first term in the expansion is just Eq. (22), with all the n_k replaced by $\langle n_k \rangle$ except the first n_k^a and n_k^o in the exponential, i.e.,

$$\langle Z^0 \rangle = \sum_{n_0, n_k} \langle n_0 | \exp[-\beta \sum_k \hbar \omega_k^a (n_k^a + \frac{1}{2}) - \beta \sum_k \hbar \omega_k^o (n_k^o + \frac{1}{2})] R(\langle n_k^a \rangle, \langle n_k^o \rangle, q_0^o) | n^o \rangle. \quad (24)$$

R is easily defined by comparing Eq. (24) with (22). It can be seen that all terms quadratic in the applied field are proportional to the number of ion pairs in the normalization volume. In view of Eq. (17) the polarization is, therefore, proportional to the normalization volume as expected.¹²

The next term in the expansion is

$$\sum_{n_0, n_k} \left\langle n_0 \left| \exp[-\beta \sum_k \hbar \omega_k^a (n_k^a + \frac{1}{2}) - \beta \sum_k \hbar \omega_k^o (n_k^o + \frac{1}{2})] \sum_{k'} \frac{\partial R(n_{k'}^a, n_{k'}^o, q_0^o)}{\partial n_{k'}} \right|_{(n_{k'})} (n_{k'} - \langle n_{k'} \rangle) \right| n_0 \rangle. \quad (25)$$

All such terms vanish identically with the use of Eq. (23). The only nonvanishing term in next order is

$$\sum_{n_0, n_k} \left\langle n_0 \left| \exp[-\beta \sum_k \hbar \omega_k^a (n_k^a + \frac{1}{2}) - \beta \sum_k \hbar \omega_k^o (n_k^o + \frac{1}{2})] \sum_{k'} \frac{1}{2!} \frac{\partial^2 R(n_{k'}^a, n_{k'}^o, q_0^o)}{\partial n_{k'}^2} \right|_{(n_{k'})} (n_{k'} - \langle n_{k'} \rangle)^2 \right| n_0 \rangle. \quad (26)$$

Contributions from this term that are quadratic in the applied field vary as N^0 and are therefore neglected. Contributions to the terms independent of the applied field vanish as N^{-1} when $N \rightarrow \infty$. In a similar fashion, it can be seen that all higher order terms in such an expansion also vanish in the limit of infinite normalization volume. Therefore, fluctuations about the thermal values $\langle n_k \rangle$ do not contribute to the linear response.

Similarly, one can show that contributions to the linear response from H' [Eq. (14)] also vanish in the limit of infinite normalization volume. For that part of H' which is nondiagonal in the creation-destruction operators, there are no linear terms of the form

¹⁰ J. H. Barrett, Phys. Rev. **86**, 118 (1952).

¹¹ J. K. Hulm, B. T. Matthias, and E. A. Long, Phys. Rev. **79**, 885 (1950).

¹² "Polarization" as defined here is the dipole moment per normalization volume.

$$-\sum_n \int_0^\beta d\lambda_1 \langle n | e^{(\lambda_1 - \beta)H_D} H' e^{-\lambda_1 H_D} | n \rangle. \quad (27)$$

The first nonvanishing contribution will come from a term of second order in H' , namely,

$$\sum_n \int_0^\beta d\lambda_1 \int_0^{\lambda_1} d\lambda_2 \langle n | e^{(\lambda_1 - \beta)H_D} H' e^{(\lambda_2 - \lambda_1)H_D} H' e^{-\lambda_2 H_D} | n \rangle. \quad (28)$$

Contributions from this term that are quadratic in the applied field vary as N^0 and are, therefore, neglected. Contributions to terms independent of the applied vanish as N^{-1} as $N \rightarrow \infty$. In a similar fashion, it can be seen that all higher order terms in such an expansion do not contribute to the linear response. An examination of the terms of H' that are diagonal in the creation-destruction operators will also show that they cannot contribute to the linear response of the system, so we can write [using Eqs. (17) and (24)]

$$P = \frac{1}{\beta \langle Z^0 \rangle} \frac{\partial \langle Z^0 \rangle}{\partial E}. \quad (29)$$

Equation (29) is an exact expression for the linear response of the system described by the Hamiltonian given by Eq. (1) in the limit of infinite normalization volume.

To evaluate $\langle Z^0 \rangle$, matrix elements between the zero wave vector states must be taken and then the sums performed over all phonon occupation numbers. Since the final result is independent of the number of $k=0$ phonons, this procedure can be simplified by treating p_0^o and q_0^o as classical variables. One can, therefore, write

$$\langle Z^0 \rangle = \int_{-\infty}^{\infty} dp_0^o \int_{-\infty}^{\infty} dq_0^o R(\langle n_k^a \rangle, \langle n_k^o \rangle, q_0^o) \sum_{n_k} \exp[-\beta \sum_k \hbar \omega_k^a (n_k^a + \frac{1}{2}) - \beta \sum_k \hbar \omega_k^o (n_k^o + \frac{1}{2})], \quad (30)$$

which gives

$$\begin{aligned} \langle Z^0 \rangle = \sum_{n_k} \exp[-\beta \sum_k \hbar \omega_k^a (n_k^a + \frac{1}{2}) - \beta \sum_k \hbar \omega_k^o (n_k^o + \frac{1}{2})] & \frac{2\pi}{\beta \Omega} \left\{ 1 + 2\beta E^2 \sum_k |A(k)|^2 \frac{\hbar}{\omega_k^o \Delta_k} (\langle n_k^o \rangle + \frac{1}{2}) \right. \\ & - 2\beta E^2 \sum_k |A(k)|^2 \frac{\hbar}{\omega_k^a \Delta_k} (\langle n_k^a \rangle + \frac{1}{2}) + \frac{\beta E^2}{2\Omega^2} \left[-\alpha N^{1/2} + \frac{2}{\sqrt{N}} \sum_k B^o(k) \frac{\hbar}{\omega_k^o} (\langle n_k^o \rangle + \frac{1}{2}) + \frac{2}{\sqrt{N}} \sum_k B^a(k) \right. \\ & \left. \left. \times \frac{\hbar}{\omega_k^a} (\langle n_k^a \rangle + \frac{1}{2}) - \frac{4}{\sqrt{N}} \sum_k F(k) A(-k) \frac{\hbar}{\omega_k^o \Delta_k} (\langle n_k^o \rangle + \frac{1}{2}) + \frac{4}{\sqrt{N}} \sum_k F(k) A(-k) \frac{\hbar}{\omega_k^a \Delta_k} (\langle n_k^a \rangle + \frac{1}{2}) \right]^2 \right\}. \quad (31) \end{aligned}$$

Using Eqs. (29), (31), the definition of the dielectric constant ϵ ,

$$(\epsilon - 1) = \frac{4\pi}{Nv} \frac{P}{E} \quad (v \text{ is the volume of the unit cell}), \quad (32)$$

and the average phonon occupation number [Eq. (23)],

$$\langle n_k \rangle = \frac{1}{e^{\hbar \omega_k / kT} - 1}, \quad (33)$$

one can write

$$\begin{aligned} \epsilon - 1 = \frac{8\pi}{Nv} \sum_k |A(k)|^2 \frac{\hbar}{\omega_k^o \Delta_k} \coth \frac{\hbar \omega_k^o}{2kT} - \frac{8\pi}{Nv} \sum_k |A(k)|^2 \frac{\hbar}{\omega_k^a \Delta_k} \coth \frac{\hbar \omega_k^a}{2kT} \\ + \frac{4\pi}{Nv} \frac{1}{\Omega^2} \left[-\alpha N^{1/2} + \frac{1}{\sqrt{N}} \sum_k B^o(k) \frac{\hbar}{\omega_k^o} \coth \frac{\hbar \omega_k^o}{2kT} + \frac{1}{\sqrt{N}} \sum_k B^a(k) \frac{\hbar}{\omega_k^a} \coth \frac{\hbar \omega_k^a}{2kT} \right. \\ \left. - \frac{2}{\sqrt{N}} \sum_k F(k) A(-k) \frac{\hbar}{\omega_k^o \Delta_k} \coth \frac{\hbar \omega_k^o}{2kT} + \frac{2}{\sqrt{N}} \sum_k F(k) A(-k) \frac{\hbar}{\omega_k^a \Delta_k} \coth \frac{\hbar \omega_k^a}{2kT} \right]^2, \quad (34) \end{aligned}$$

with

$$\Omega^2 = \frac{2}{N} \sum_k \frac{\hbar}{\omega_k^o} G^o(k) \coth \frac{\hbar \omega_k^o}{2kT} + \frac{2}{N} \sum_k \frac{\hbar}{\omega_k^a} G^a(k) \coth \frac{\hbar \omega_k^a}{2kT} - \frac{2}{N} \sum_k |F(k)|^2 \frac{\hbar}{\omega_k^o \Delta_k} \coth \frac{\hbar \omega_k^o}{2kT} + \frac{2}{N} \sum_k |F(k)|^2 \frac{\hbar}{\omega_k^a \Delta_k} \coth \frac{\hbar \omega_k^a}{2kT} - (\omega_0^o)^2. \quad (35)$$

If the deformation terms are absent, we obtain

$$\epsilon - 1 = 4\pi(\alpha^2/v)/\Omega^2. \quad (36)$$

In the classical limit of high temperature

$$\Omega^2 \sim (T - T_c), \quad (37)$$

and the dielectric constant follows a Curie-Weiss law.

$$\epsilon - 1 = C/(T - T_c). \quad (38)$$

If the system does not spontaneously polarize at any positive temperature, it is then stabilized at $T=0$ by zero-point quantum-mechanical fluctuations. The dielectric constant [Eq. (36)] is independent of temperature in the vicinity of absolute zero. Note, however, that at intermediate temperatures the temperature dependence of the dielectric constant is, in general, different from the temperature dependence of Barrett's expression.¹⁰ This difference arises since Barrett's calculation is based upon an Einstein model of the lattice and neglects the variation of lattice frequencies with wave vector.

In the classical limit, the dielectric constant with inclusion of the deformation terms [Eq. (34)] can be written as

$$\epsilon - 1 = AT + [C/(T - T_c)][1 + BT + DT^2]. \quad (39)$$

A, B, C, D are temperature-independent constants. The term linear in temperature appears since the presence of a second-order electronic moment makes it possible for the field to drive modes other than the soft mode. This term should contribute a very small amount to the total dielectric constant. The presence of the higher order electronic moments also produces a temperature-dependent Curie constant. The third-order moment and the product of second-order moment with the third-order potential contribute to the linear temperature dependence of the Curie constant. The quadratic temperature-dependent term involves the squares of the coupling coefficients appearing in the linear term. One

can, therefore, conclude that the largest effect on the dielectric constant arising from the treatment of the deformation terms is to make the Curie constant vary linearly with temperature. At temperatures high compared with the Curie temperature, the dielectric constant [Eq. (39)] can be written

$$\epsilon - 1 = [C/(T - T_c)] + F. \quad (40)$$

Therefore, if one fits the temperature dependence of the dielectric constant with an expression of the form of Eq. (40) over a wide range of temperature above the Curie temperature, one cannot attribute the value obtained for F solely to the presence of temperature-independent infrared active modes. Electronic deformations may contribute to this term.¹³

In the preceding discussion we have treated the crystal as if it were clamped, i.e., we have neglected any effect due to thermal expansion. If one knows the pressure dependence of the dielectric constant, compressibility, and volume coefficient of thermal expansion, the temperature dependence of the dielectric constant of the material at fixed volume can be separated from the temperature dependence due to thermal expansion.¹⁴ To obtain an accurate separation of the intrinsic temperature effect from this volume effect, these three quantities must be known over the range of temperatures for which the dielectric constant is measured. Such data are not available at present and, therefore, preclude the possibility of making an accurate comparison of our results with experiment.

¹³ There can, however, be one additional contribution to this constant term. This arises from terms which are of the sixth order in the potential energy and do not appear in the Szigeti Hamiltonian. This number can be of the same order of magnitude as the contribution to this constant arising from the electronic deformations.

¹⁴ E. E. Havinga, J. Phys. Chem. Solids **18**, 1 (1961); R. Fuchs, Technical Report 167, Laboratory for Insulation Research, Massachusetts Institute of Technology (unpublished).