

Nonlinear Dielectric Constant of a Paraelectric Material*

R. I. JOSEPH AND B. D. SILVERMAN

Raytheon Company, Research Division, Waltham, Massachusetts

(Received 17 June 1963)

An expression is obtained for the nonlinear dielectric constant of a paraelectric material. This is given in terms of the coupling parameters of the Born-von Kármán lattice dynamical theory. Deviations from the Devonshire phenomenological theory are discussed.

1. INTRODUCTION

THE connection between lattice dynamics and the dielectric properties of the hard ferroelectrics (e.g., BaTiO₃ and its isomorphs) has been made both theoretically¹ and experimentally.² It is now generally agreed that the interesting temperature-dependent properties of ferroelectric materials arise from a long-wavelength transverse optical mode which becomes unstable at the ferroelectric phase transition. Above the transition temperature the frequency of this long-wavelength mode is not determined solely by harmonic interactions between the constituent ions. In fact, it appears that harmonic interactions are not sufficient to stabilize this mode and provide a real frequency. The stabilization of this mode can be brought about by a consideration of anharmonic interactions. Since anharmonic interactions perform such a fundamental role with regard to the stability of the system, they cannot be treated in the usual fashion. That is to say, one cannot simply expand the partition function in powers of the anharmonic coupling coefficients and retain only the first few terms in such an expansion. It has been shown, however, that statistical theory can be done for a paraelectric material by a simple modification of the usual procedure.³ In Ref. 3, it was shown how one could obtain the linear dielectric constant of a paraelectric material in the language of Born-von Kármán lattice dynamics. In the present paper this calculation is extended to a consideration of the nonlinear response.

In Sec. 2 the Hamiltonian is discussed. This Hamiltonian is a modified version of the one treated by Szigeti⁴ in connection with the temperature dependence of the dielectric constant of the alkali halides. The major difference, however, is that all long-wavelength transverse

optical modes which are unstable in the harmonic approximation are collectively labelled with zero wave vector and assigned an imaginary frequency. Terms quartic in this mode coordinate are also included in the Hamiltonian. An expression for the nonlinear dielectric constant above the transition is then obtained in Sec. 3. It is shown in Sec. 4 that the temperature dependence of the nonlinear response is almost the same as results from the Devonshire theory.⁵ Devonshire expanded the free energy in powers of the polarization:

$$F(P, T) = F(0, T) + A(T - T_c)P^2 + BP^4 + CP^6, \quad (1)$$

with A , B , and C as temperature-independent constants. Measurements of the nonlinear dielectric response of BaTiO₃ have shown the coefficient B to be temperature dependent.^{6,7} The contributions to the linear temperature dependence of B are discussed in Sec. 4. In particular, it is shown that electron cloud deformation contributes to the linear temperature variation of this coefficient. There have been previous calculations of the nonlinear response of a paraelectric material; however, these have been based essentially upon an independent ion model of the lattice⁸ and do not exhibit the full complexity of the temperature variation of B .

2. HAMILTONIAN

Consider the following Hamiltonian⁹:

$$\mathcal{H} = \mathcal{H}_1 - e^* E N^{1/2} q_0^o + \mathcal{H}_2, \quad (2)$$

where

$$\begin{aligned} \mathcal{H}_1 = & -\frac{1}{2}(\omega_0^o q_0^o)^2 + \frac{1}{2} \sum_k (\omega_k^o q_k^o)^2 + \frac{1}{2} \sum_k (\omega_k^a q_k^a)^2 \\ & + N^{-1/2} q_0^o \sum_k A_k q_{-k}^o q_k^a \\ & + N^{-1} F(q_0^o)^4 + N^{-1} (q_0^o)^2 \sum_k F_k (q_k^o)^2 \\ & + N^{-1} (q_0^o)^2 \sum_k G_k (q_k^a)^2, \quad (3) \end{aligned}$$

* Work supported in part by the Electronics Research Directorate of the U. S. Air Force Cambridge Research Center, Air Research and Development Command.

¹ P. W. Anderson, in *Fizika Dielektrikov*, edited by G. I. Skanavi (Akademičâ Nauk SSSR Fisicheskii Inst. im P. N. Lebedeva, Moscow, 1960) in Russian; W. Cochran, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis Ltd., London, 1960), Vol. 9, p. 387; V. L. Ginzberg, *Usp. Fiz. Nauk* **77**, 621 (1962) [translation: Soviet Phys.—Usp. **5**, 649 (1963)]; R. Landauer, H. Juretschke, and P. Sorokin, (unpublished).

² A. S. Barker, Jr. and M. Tinkham, *Phys. Rev.* **125**, 1527 (1962); R. A. Cowley, *Phys. Rev. Letters* **9**, 159 (1962); I. Lefkowitz, *Proc. Phys. Soc. (London)* **80**, 516 (1962); W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, *Phys. Rev.* **126**, 1710 (1962).

³ B. D. Silverman and R. I. Joseph, *Phys. Rev.* **129**, 2062 (1963).

⁴ B. Szigeti, *Proc. Roy. Soc. (London)* **A252**, 217 (1959).

⁵ A. F. Devonshire, *Phil. Mag.* **40**, 1040 (1949); **42**, 1065 (1951).

⁶ M. E. Drougard, R. Landauer, and D. R. Young, *Phys. Rev.* **98**, 1010 (1955).

⁷ E. Stern and A. Lurio, *Phys. Rev.* **123**, 117 (1961).

⁸ S. Triebwasser, *J. Phys. Chem. Solids* **3**, 53 (1957); V. Kh. Kozlovskii, *Fiz. Tverd. Tela* **2**, 1733 (1960) [translation: Soviet Phys.—Solid State **2**, 1566 (1961)].

⁹ Kinetic energy terms have not been included in the Hamiltonian, since they do not contribute to the dielectric response of the medium.

and

$$\begin{aligned} \mathcal{H}_2 = & E \sum_k X_k q_{-k}^o q_k^a \\ & + EN^{-1/2} q_0^o \sum_k Y_k (q_k^o)^2 + EN^{-1/2} q_0^o \sum_k Z_k (q_k^a)^2. \end{aligned} \quad (4)$$

The terms in the first line of Eq. (3) represent the harmonic part of the potential energy due to lattice displacements. (q_k^o and q_k^a are the normal coordinates of wave number k for the optical and acoustic mode, respectively.) q_0^o is the normal coordinate of that optical mode designated by zero wave number and has a purely imaginary frequency associated with it in the harmonic approximation (we denote this frequency by $i\omega_0^o$). $k=0$ designates a mode with wavelength long compared with the lattice parameter but small compared with the sample size. There are a large number of such modes; however, they are a small fraction of the total number of modes and are, therefore, treated as a single mode.^{10,11} The second, and third and fourth lines of Eq. (3) represent the third- and fourth-order anharmonic contributions to the potential energy, respectively. The constant F is assumed to be positive since this will lead to a positive B coefficient [see Eq. (1)]. Since the calculation is performed for a clamped crystal, this choice is in agreement with the results of Stern and Lurio⁷ for BaTiO₃. N is the number of ion pairs. The calculation is performed for two atoms per unit cell and the optical mode of this model is chosen as the soft temperature-dependent ferroelectric mode. The second term on the right of Eq. (2) represents the first-order effect of the electronic distortions plus the effect of the displacement of the ions as a whole. E is the macroscopic electric field. The first and second lines of Eq. (4) are the second- and third-order effects of electronic deformations, respectively. The remaining undefined quantities are constants. The summations over k exclude the value $k=0$. All multiplicative constants that do not affect the final result are also neglected. As discussed by Szigeti,⁴ the Hamiltonian has been simplified by the assumption of a cubic structure and a center of symmetry for the material under consideration. These assumptions concerning the structure are consistent with the perovskite structure in the unpolarized phase.

3. DIELECTRIC CONSTANT

Contributions to the dielectric constant quadratic in the electric field are obtained in this section. The largest contribution to this nonlinear response [the constant B of Eq. (1)] arises from the fourth-order term in the polarization mode coordinate. Anharmonic interactions and electron deformations will be shown to contribute to the linear temperature variation of B .

¹⁰ T. H. K. Barron, Phys. Rev. **123**, 1995 (1961).

¹¹ A more detailed analysis could, however, be performed if desired. That is, one could introduce a number of unstable modes into the Hamiltonian and if need be, consider the interactions between these.

The partition function of the system is given by

$$Z = \int_{-\infty}^{\infty} dq_0^o \int_{-\infty}^{\infty} \prod_k dq_k^o \int_{-\infty}^{\infty} \prod_k dq_k^a \exp\{-\beta\mathcal{H}\}, \quad (5)$$

where $\beta=1/k_B T$. The integrals over dq_k^o and dq_k^a may be readily performed. In doing this, use is made of the following symmetry properties for the coupling parameters:

$$\begin{aligned} A_k &= -A_{-k}, & X_k &= -X_{-k}, \\ F_k &= F_{-k}, & G_k &= G_{-k}, \\ Y_k &= Y_{-k}, & Z_k &= Z_{-k}. \end{aligned}$$

Equation (5) then becomes

$$\begin{aligned} Z = & \int_{-\infty}^{\infty} dq_0^o \prod_k [T_k(q_0^o)]^{-1/2} \\ & \times \exp\{-\beta[-\frac{1}{2}(\omega_0^o q_0^o)^2 - e^* EN^{1/2} q_0^o + N^{-1} F (q_0^o)^4]\}, \end{aligned} \quad (6)$$

where

$$T_k(q_0^o) = \alpha_k + \beta_k E + \gamma_k E^2,$$

with

$$\begin{aligned} \alpha_k &= (1 + N^{-1}(q_0^o)^2 \mu_k)(1 + N^{-1}(q_0^o)^2 \lambda_k) - N^{-1}(q_0^o)^2 \nu_k, \\ \beta_k &= N^{-1/2} q_0^o [\rho_k (1 + N^{-1}(q_0^o)^2 \lambda_k) \\ & \quad + \sigma_k (1 + N^{-1}(q_0^o)^2 \mu_k) - 2\tau_k \nu_k^{1/2}], \\ \gamma_k &= N^{-1}(q_0^o)^2 \rho_k \sigma_k - \tau_k^2, \end{aligned}$$

and

$$\begin{aligned} \mu_k &= 2F_k / (\omega_k^o)^2, & \rho_k &= 2Y_k / (\omega_k^o)^2, \\ \lambda_k &= 2G_k / (\omega_k^a)^2, & \sigma_k &= 2Z_k / (\omega_k^a)^2, \\ \nu_k^{1/2} &= A_k / \omega_k^o \omega_k^a, & \tau_k &= X_k / \omega_k^o \omega_k^a. \end{aligned} \quad (7)$$

If the function $T_k(q_0^o)$ was independent of q_0^o , the system would be in unstable equilibrium at $q_0^o=0$ and would make a transition to the polarized or ferroelectric state. The fourth-order terms that couple the uniform mode with the other modes stabilize the system above the transition temperature. This can be made evident if one rewrites Eq. (6) as

$$\begin{aligned} Z = & \int_{-\infty}^{\infty} dq_0^o \prod_k [(T_k(q_0^o))^{-1/2} \\ & \times \exp\{\frac{1}{2} N^{-1}(q_0^o)^2 (\lambda_k + \mu_k - \nu_k)\}] \\ & \times \exp\{-\beta[\frac{1}{2}(\tilde{\omega}_0^o q_0^o)^2 - e^* EN^{1/2} q_0^o + N^{-1} F (q_0^o)^4]\}, \end{aligned} \quad (8)$$

with use of $\prod_k \exp\{-\Lambda_k\} \cdot \exp\{\sum_k \Lambda_k\} \equiv 1$. The frequency "renormalization" or stabilization is independent of the electric field, so E can be considered set equal to zero for the present argument. The product expression of Eq. (8) is expanded in powers of $(q_0^o)^2$. It can be shown that the terms proportional to $(q_0^o)^2$ cancel, whereas the higher order terms vanish in the limit of infinite periodicity volume. Thus, this way of rewriting Eq. (6) regroups in the exponent, all nonvanishing

terms which would arise from an expansion of the partition function in powers of the anharmonic coupling parameters. The temperature dependent frequency $\bar{\omega}_0^\circ$ is given by

$$\bar{\omega}_0^\circ = \left[-(\omega_0^\circ)^2 + (N\beta)^{-1} \sum_k (\lambda_k + \mu_k - \nu_k) \right]^{1/2} \sim (T - T_c)^{1/2}. \quad (9)$$

T_c is the Curie temperature.

Since we wish to obtain an expression for the polarization as a power series in the electric field, the exponent and the product of the functions T_k [Eq. (8)] must be expanded in powers of the field. The expansion of the former is straightforward. The latter is obtained by first expanding the individual $T_k^{-1/2}$ functions and then picking out all relevant terms arising from the product of these functions. The partition function is then written as a power series in the electric field:

$$Z = 1 + aE^2 + bE^4 + \dots \quad (10)$$

Odd powers of the field do not appear since the Hamiltonian [Eq. (2)] describes a centrosymmetric crystal. The coefficients a and b are obtained by performing integrations over the polarization mode coordinate q_0° , the results of which will be discussed presently.

The dielectric constant is given by¹²

$$\begin{aligned} \epsilon - 1 &= (\partial P / \partial E) = 1/\beta (\partial^2 \ln Z / \partial E^2) \\ &= 2\beta^{-1}a + 12\beta^{-1}(b - \frac{1}{2}a^2)E^2 + \dots \\ &= \Gamma_0 + \Gamma_1 E^2 + \dots \end{aligned} \quad (11)$$

The linear dielectric constant corresponds to the classical limit of a previous result,³

$$\Gamma_0 = AT + [C/(T - T_c)](1 + BT + DT^2). \quad (12)$$

The origin of the constants A , B , C , and D and their experimental significance has been discussed in detail in Ref. 3. The coefficient Γ_1 of the quadratic dielectric response can be written

$$\begin{aligned} \Gamma_1 &= [(E_0 + E_1 T) / (T - T_c)^4] \\ &\quad \times (F_0 + F_1 T + F_2 T^2 + F_3 T^3 + F_4 T^4) \\ &\quad + [T / (T - T_c)^3] (D_0 + D_1 T + D_2 T^2 + D_3 T^3) \\ &\quad + [T / (T - T_c)^2] (C_0 + C_1 T + C_2 T^2) \\ &\quad + [T / (T - T_c)] (B_0 + B_1 T) + A_1 T. \end{aligned} \quad (13)$$

At temperatures high compared with T_c , this is just the first few terms of a Laurent series in temperature, with $E_0 F_0 T^{-4}$ the leading term. We emphasize that Eq. (13) gives the exact temperature dependence of the quadratic nonlinear response for the Hamiltonian of Eq. (2). Higher order anharmonic and moment terms, which have been neglected, will generate the rest of the series. The terms that vary as T^{-4} and T^{-3} in Eq. (13) are, however, of lowest order in the anharmonic and moment coupling parameter, and are there-

fore the most important if the series converges rapidly in powers of these coupling parameters.

To terms quadratic in the electric field, the largest contributions to the nonlinear dielectric constant from Eq. (13), are included in the following expression:

$$\epsilon - 1 = \Gamma_0 + [(M + HT) / (T - T_c)^4] E^2, \quad (14)$$

with¹³

$$\begin{aligned} M &= E_0 F_0, \\ H &= E_0 F_1 + E_1 F_0, \end{aligned} \quad (15)$$

and

$$\begin{aligned} E_0 &= -\frac{3}{2}F, \\ E_1 &= \frac{3}{8}k_B \left\{ (1/N) \sum_k (\lambda_k^2 + \mu_k^2 + \nu_k^2 - 2\lambda_k \nu_k - 2\mu_k \nu_k) \right\}, \\ F_0 &= 8(e^* T_c)^4 / (\omega_0^0)^8, \\ F_1 &= -[16(e^*)^3 k_B T_c^4 / (\omega_0^0)^8] \\ &\quad \times \left\{ (1/N) \sum_k (\rho_k + \sigma_k - 2\tau_k \nu_k^{1/2}) \right\}. \end{aligned} \quad (16)$$

4. COMPARISON WITH DEVONSHIRE THEORY

In the previous section, an expression was developed for the dielectric constant (or polarization) as a series in powers of the electric field. Let us now perform an inversion to express the electric field in powers of the polarization.^{14,15} The results can then be directly compared with the results of Devonshire's⁵ phenomenological theory.

Combining the results of Eqs. (11), (12), and (14), the polarization may be written

$$\begin{aligned} P &= E \{ \epsilon_1 + [C / (T - T_c)] \} \\ &\quad + \frac{1}{3} E^3 \{ (M + HT) / (T - T_c)^4 \} + \dots \end{aligned} \quad (17)$$

The first term on the right of this equation has been simplified by neglecting the small term linear in the temperature arising from the presence of a second-order moment and assuming $T \gg T_c$ so that $[T / (T - T_c)] = 1$. ϵ_1 can be assumed to consist of four contributions: a contribution from the other hard modes, from certain sixth-order potential energy terms (both of which until now have been neglected), from the electronic polarizability, and a contribution BC arising from the effect of electronic deformations. The result of inverting Eq. (17) is

$$\begin{aligned} E &= P \{ \epsilon_1 + [C / (T - T_c)] \}^{-1} - \frac{1}{3} P^3 \{ \epsilon_1 + [C / (T - T_c)] \}^{-4} \\ &\quad \times \{ (M + HT) / (T - T_c)^4 \} + \dots, \end{aligned} \quad (18)$$

¹³ Expressions relating all of the coefficients appearing in Eq. (13) to the coupling parameters are given in Raytheon Technical Memorandum T-458.

¹⁴ H. Jeffreys and B. S. Jeffreys, *Mathematical Physics*, (Cambridge University Press, Cambridge, England, 1956), 3rd ed., p. 379.

¹⁵ This inversion is equivalent to transforming from the Helmholtz to the Gibbs form of the free energy function.

¹² In units of $1/4\pi$ for cgs and ϵ_0 for mks.

which can be cast into the following form (again assuming $T \gg T_c$):

$$E = P \{ C^{-1}(-T_e + T + \sigma T^2) - \frac{1}{3} P^3 \{ C^{-4}(M + H'T) \} + \dots, \quad (19)$$

with

$$\begin{aligned} \sigma &= -(1/C) \epsilon_1 \\ H' &= H - 4M(\epsilon_1/C). \end{aligned} \quad (20)$$

Equation (19) is to be compared with Eq. (1), which results from Devonshire's assumed form of the free energy function. The largest temperature variation in this expression is associated with the Curie-Weiss behavior of the dielectric constant. This results since close cancellation of harmonic forces in the lattice enhances the temperature-dependent susceptibility arising from third- and fourth-order anharmonic contributions. The linear response will deviate from the Curie-Weiss behavior due to the presence of electronic polarizability, other optical modes, electronic deformations, and potential terms of higher order than the third and fourth. Lowest order contributions to such deviations are described by σ .

The largest contribution to the nonlinear response arises from the constant term M . From Eqs. (15) and (16), it is seen that the fourth-order potential term arising solely from the long-wavelength optical motion is responsible for this contribution. This contribution is included in Devonshire's free energy function. The coefficient of the P^3 term is also temperature dependent. The linear temperature variation of this term is described by the constant H' . From Eqs. (15), (16), and (20), it is seen that the presence of electronic polarizability, other optical modes, electronic deformations of second- and third-order, and third- and fourth-order anharmonic contributions contribute to the linear temperature variation of this coefficient. A complete treatment of all lowest order potential and moment contributions to H' would yield a much more complicated expression than found here. Indeed, fifth- and sixth-order

potential energy terms and fourth- and fifth-order moments will also contribute to H' . Contributions from these terms to H' can be obtained by a straightforward extension of the preceding calculation. In a previous calculation³ it was emphasized that deviations from the Curie-Weiss behavior of the linear dielectric constant cannot, in general, be simply interpreted in terms of the presence of electronic polarizability and other hard optical modes. Potential and moment terms also contribute. In this paper we wish to make the point that the linear temperature variation of the B coefficient involves contributions from a number of moment and potential terms. Hence, actual numerical calculations of contributions to the constant H' will, in general, not be particularly simple.

5. CONCLUSION

It has been shown how one can obtain an expression for the nonlinear dielectric constant of a paraelectric material in terms of the coupling parameters of the Born-von Kármán lattice dynamical theory. Up to the present time, all other calculations have been essentially single particle calculations and have neglected certain potential energy contributions made manifest by the lattice dynamical treatment. The role of electron cloud deformation has also been investigated and shown to contribute to the temperature dependence of the nonlinear response. Only order-of-magnitude estimates are possible at present to justify the origin of the observed effects. The detailed calculation that has been presented is of interest, however, since the quantities involved also have implications for the observed optical behavior of paraelectric materials. Indeed, as Szigeti has pointed out,¹⁶ widths of absorption bands, the presence of sidebands, etc., are determined by essentially the same coupling parameters that are involved in the temperature dependence of the dielectric response.

¹⁶ B. Szigeti, Proc. Roy. Soc. (London) A258, 377 (1960).