

Temperature Dependence of the Frequency Spectrum of a Paraelectric Material*

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The temperature-dependent frequency spectrum of a paraelectric material is discussed with use of an effective-harmonic-lattice equation of motion. For a given wave vector, the effective couplings between atoms are written as a sum of a temperature-independent part, arising from harmonic interactions, and a part linear in the temperature, arising from fourth- and third-order anharmonic interactions. The conditions required for the observed Curie-Weiss behavior of the dielectric constant and associated temperature dependence of certain long-wavelength transverse optical frequencies are examined. It is shown that the salient features of the temperature-dependent low-lying optical branch in SrTiO₃ can be understood by considering the effects of anharmonic interactions at constant volume.

I. INTRODUCTION

RECENTLY,^{1,2} expressions have been obtained for the temperature-dependent linear and nonlinear dielectric constant of a paraelectric material in terms of the Born-von Kármán lattice dynamical parameters. This involved the renormalization of a transverse optical frequency that is imaginary in the harmonic approximation. It was shown that at sufficiently high temperatures (temperatures above the Curie-Weiss temperature T_c), this frequency was real (positive), and temperature-dependent due to the presence of certain fourth- and third-order anharmonic potential energy terms. The temperature dependence of this frequency Ω was shown to vary as

$$\Omega^2 \sim T - T_c. \quad (1.1)$$

The intimate relation between such a temperature-dependent frequency and the Curie-Weiss behavior of the dielectric constant has been previously discussed.^{3,4}

The purpose of the present work is to extend the previous calculations to the case of temperature-dependent frequencies of arbitrary wave vector. This is of interest since the results of inelastic neutron scattering⁵ from strontium titanate have shown that the low-lying transverse optical frequency of long wavelength belongs to a branch which is significantly temperature-dependent for wave vectors along the [100] direction.

Bosman and Havinga⁶ have recently reported on the pressure and temperature dependence of the dielectric constant of various perovskite materials. Constant volume effects were quantitatively separated from

effects due to thermal expansion. In the nonpolar phase, it was found that the temperature dependence of the dielectric constant at constant volume is in the same direction as the net effect, the effect due to thermal expansion being smaller and in the opposite direction. Hence, effects at constant volume make the most significant contribution to the temperature-dependent dielectric constant or temperature-dependent transverse frequency. Since constant volume effects appear to provide the major contribution to the temperature-dependent long-wavelength optical modes, one might also expect that the more evident temperature-dependent character of the spectrum should also arise from effects at constant volume. Therefore, in what follows the theory is developed at constant volume as done previously. The effect of thermal expansion can be incorporated into the present work by a straightforward extension. Such an extension is closely related to the calculation of the pressure-dependent dielectric constant⁷ and will not affect any of the qualitative conclusions of the present work.

In Sec. II, expressions are given for the temperature-dependent frequencies of arbitrary wave vector in terms of the parameters of the rigid ion model. The conditions leading to the temperature dependence of the long-wavelength transverse optical modes [Eq. (1.1)] are examined. In Sec. III, two linear chain models are used to simply illustrate a number of the ideas presented. It will be shown that one of the chain models (diatomic chain) gives results which serve to illustrate the observed temperature-dependent optical branch in strontium titanate quite well.

II. LATTICE DYNAMICS

The calculation will be performed assuming the validity of the adiabatic approximation. Born⁸ has shown that the nuclear motion can be determined from a

* The results presented in this paper were reported at the March meeting of the American Physical Society, Philadelphia, Pennsylvania [Bull. Am. Phys. Soc. **9**, 214 (1964)].

¹ B. D. Silverman and R. I. Joseph, Phys. Rev. **129**, 2062 (1963).

² R. I. Joseph and B. D. Silverman, Phys. Rev. **133**, A207 (1964).

³ W. Cochran, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis Ltd., London, 1960), Vol. 9, p. 387; R. Landauer, H. Juretschke, and P. Sorokin (unpublished manuscript, 1958); V. L. Ginzburg, Usp. Fiz. Nauk. **77**, 621 (1962) [English transl.: Soviet Phys.—Usp. **5**, 649 (1963)].

⁴ P. W. Anderson, in *Fizika Dielektrikov*, edited by G. I. Skanavi (Akademicheskii Nauk S.S.S.R. Fizicheskii Inst. im P. N. Lebedeva, Moscow, 1960), in Russian.

⁵ R. A. Cowley, Phys. Rev. Letters **9**, 159 (1962).

⁶ A. J. Bosman and E. E. Havinga, Phys. Rev. **129**, 1593 (1963).

⁷ B. D. Silverman, Bull. Am. Phys. Soc. **9**, 84 (1964).

⁸ M. Born, Festschr. Akad. Wiss. Göttingen Math.-Physik K. **1**-16 (1951); Nachr. Akad. Wiss. Göttingen Math.-Physik K. **6**, 1-3 (1951); M. Born, Compt. Rend. 2^e Réunion Chim. Phys., pp. 334-337 (1952); M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Appendix VIII.

general nuclear potential function when the electronic ground state is far removed from the excited states. This treatment is more general than the Born-Oppenheimer⁹ procedure, since one need not expand the potential in powers of nuclear displacements from equilibrium positions at the start. After elimination of the electronic coordinates one then obtains a general nuclear potential function which can include harmonic instabilities and the possibility that a unique equilibrium position of the ions does not actually exist. This potential is then expanded in powers of displacements from mean atomic positions and the Hamiltonian written in the familiar Born and Huang notation:

$$\begin{aligned}
 H = & \sum_{lk\alpha} \frac{\hat{p}_\alpha^2(k)}{2m_k} + \frac{1}{2!} \sum_{\substack{lk\alpha \\ l'k'\beta}} \Phi_{\alpha\beta}(\substack{l' \\ k'k'}) \mu_\alpha(k) \mu_\beta(k') \\
 & + \frac{1}{3!} \sum \Phi_{\alpha\beta\gamma}(\substack{l' \\ k'k'k''}) \mu_\alpha(k) \mu_\beta(k') \mu_\gamma(k'') \\
 & + \frac{1}{4!} \sum \Phi_{\alpha\beta\gamma\delta}(\substack{l' \\ k'k'k''k'''}) \mu_\alpha(k) \mu_\beta(k') \mu_\gamma(k'') \mu_\delta(k''') \\
 & + \dots
 \end{aligned} \quad (2.1)$$

Periodic boundary conditions are next imposed and the displacements are Fourier analyzed.

Following the suggestion of Anderson,⁴ the Hamiltonian is written as a sum over contributions from each wave vector \mathbf{y} .

$$\begin{aligned}
 H = & \sum_{\mathbf{y}} \left\{ \frac{1}{2} \sum_{k\alpha} |\dot{w}_\alpha(k|\mathbf{y})|^2 + \frac{1}{2} \sum_{\substack{k\alpha \\ k'\beta}} D_{\alpha\beta}(\substack{-\mathbf{y} \\ k'k'}) w_\alpha(k|\mathbf{y}) \right. \\
 & \times w_\beta(k'|\mathbf{y}) + \frac{1}{2\sqrt{N}} \sum_{\mathbf{y}'\mathbf{y}''\neq\mathbf{y}} \sum_{k\alpha k'\beta k''\gamma} D_{\alpha\beta\gamma}(\substack{-\mathbf{y}'-\mathbf{y}'' \\ k'k'k''}) \\
 & \times w_\alpha(k|\mathbf{y}) w_\beta(k'|\mathbf{y}') w_\gamma(k''|\mathbf{y}'') \Delta(\mathbf{y}+\mathbf{y}'+\mathbf{y}'') \\
 & + \frac{1}{4N} \sum_{\mathbf{y}'\neq\mathbf{y}} \sum_{\substack{k\alpha, k'\beta \\ k''\gamma, k'''\delta}} D_{\alpha\beta\gamma\delta}(\substack{\mathbf{y}-\mathbf{y}' \\ k'k'k''k'''}) w_\alpha(k|\mathbf{y}) \\
 & \left. \times w_\beta(k'|\mathbf{y}') w_\gamma(k''|\mathbf{y}'') w_\delta(k'''\mathbf{y}''') + \dots \right\}, \quad (2.2)
 \end{aligned}$$

where

$$\begin{aligned}
 D_{\alpha\beta}(\substack{\mathbf{y} \\ k'k'}) &= \sum_l D_{\alpha\beta}(\substack{l \\ k'k'}) e^{-2\pi i \mathbf{y} \cdot \mathbf{X}(l)}, \\
 D_{\alpha\beta\gamma}(\substack{\mathbf{y}\mathbf{y}' \\ k'k'k''}) &= \sum_{m,n} D_{\alpha\beta\gamma}(\substack{om \ n \\ k'k'k''}) \\
 & \times e^{-2\pi i \{\mathbf{y} \cdot \mathbf{X}(m) + \mathbf{y}' \cdot \mathbf{X}(n)\}}, \quad (2.3)
 \end{aligned}$$

$$\begin{aligned}
 D_{\alpha\beta\gamma\delta}(\substack{\mathbf{y}\mathbf{y}'\mathbf{y}'' \\ k'k'k''k'''}) &= \sum_{m,n,r} D_{\alpha\beta\gamma\delta}(\substack{om \ n \ r \\ k'k'k''k'''}) \\
 & \times e^{-2\pi i \{\mathbf{y} \cdot \mathbf{X}(m) + \mathbf{y}' \cdot \mathbf{X}(n) + \mathbf{y}'' \cdot \mathbf{X}(r)\}}.
 \end{aligned}$$

This procedure is adopted since we wish to determine

⁹ M. Born and R. Oppenheimer, Ann. Physik **84**, 457 (1927).

the average effect that all other modes have on the modes of wave vector \mathbf{y} . It should be noted that certain terms have been neglected, e.g., third-order terms with two or more wave vectors equal to \mathbf{y} and fourth-order terms with three or more wave vectors equal to \mathbf{y} . These terms will not contribute to the set of effective harmonic equations to be derived and hence will not contribute to the effective frequency. Before an effective harmonic equation of motion can be obtained for the modes of wave vector \mathbf{y} , terms linear in the third-order coupling coefficient must be eliminated. The following normal mode decomposition is introduced which, in general, is to be determined later on.

$$w_\alpha(k|\mathbf{y}) = \sum_j e_\alpha(k|j^y) Q(j^y). \quad (2.4)$$

This is then substituted for all modes other than the ones of interest. The Hamiltonian is then written.

$$\begin{aligned}
 H = & \sum_{\mathbf{y}} \left\{ \sum_{k\alpha} |\dot{w}_\alpha(k|\mathbf{y})|^2 + \frac{1}{2} \sum_{\substack{k\alpha \\ k'\beta}} D_{\alpha\beta}(\substack{-\mathbf{y} \\ k'k'}) w_\alpha(k|\mathbf{y}) w_\beta(k'|\mathbf{y}) \right. \\
 & + \frac{1}{2\sqrt{N}} \sum_{\substack{\mathbf{y}'\mathbf{y}'' \\ \mathbf{y}'\mathbf{j}' \\ \mathbf{y}''\mathbf{j}''}} \sum_{k\alpha} F_\alpha(k, \mathbf{y}; \substack{\mathbf{y}'\mathbf{y}'' \\ \mathbf{j}'\mathbf{j}''}) Q(\mathbf{j}') Q(\mathbf{j}'') \\
 & \times \Delta(\mathbf{y}+\mathbf{y}'+\mathbf{y}'') w_\alpha(k|\mathbf{y}) + \frac{1}{4N} \sum_{\mathbf{y}'\mathbf{j}'} \sum_{k\alpha k'\beta} G_{\alpha\beta}(k, k'; \mathbf{y}; \mathbf{j}') \\
 & \left. \times Q(\mathbf{j}') Q(\substack{-\mathbf{y}' \\ \mathbf{j}'}) w_\alpha(k|\mathbf{y}) w_\beta(k'|\mathbf{y}') \right\} \quad (2.5)
 \end{aligned}$$

with

$$\begin{aligned}
 F_\alpha(k, \mathbf{y}; \substack{\mathbf{y}'\mathbf{y}'' \\ \mathbf{j}'\mathbf{j}''}) &= \sum_{k'\beta k''\gamma} D_{\alpha\beta\gamma}(\substack{-\mathbf{y}'-\mathbf{y}'' \\ k'k'k''}) \\
 & \times e_\beta(k'|\mathbf{y}') e_\gamma(k''|\mathbf{y}''), \quad (2.6)
 \end{aligned}$$

$$\begin{aligned}
 G_{\alpha\beta}(k, k'; \mathbf{y}; \mathbf{j}') &= \sum_{k''\gamma k'''\delta} D_{\alpha\beta\gamma\delta}(\substack{\mathbf{y}-\mathbf{y}' \\ k'k'k''k'''}) \\
 & \times e_\gamma(k''|\mathbf{y}') e_\delta(k'''\mathbf{y}'').
 \end{aligned}$$

The term linear in the third-order coupling coefficient F is next eliminated by a canonical transformation

$$e^{-iS} H e^{iS} = H + i[H, S] - \frac{1}{2} [[H, S], S] + \dots \quad (2.7)$$

The transformation operator S is given by

$$\begin{aligned}
 S = & \frac{1}{\sqrt{N}} \sum_{\mathbf{y}, \mathbf{n}} g_\alpha(k, \mathbf{y}; \substack{\mathbf{y}'\mathbf{y}'' \\ \mathbf{j}'\mathbf{j}''}) w_\alpha(k, \mathbf{y}) Q(\mathbf{j}') \\
 & \times P(\substack{-\mathbf{y}'' \\ \mathbf{j}''}) \Delta(\mathbf{y}+\mathbf{y}'+\mathbf{y}''). \quad (2.8)
 \end{aligned}$$

$g_\alpha(k, \mathbf{y}; \substack{\mathbf{y}'\mathbf{y}'' \\ \mathbf{j}'\mathbf{j}''})$ is chosen so that the commutator of the harmonic part of the Hamiltonian with S just cancels the term linear in F . One then obtains

$$g_\alpha(k, \mathbf{y}; \substack{\mathbf{y}'\mathbf{y}'' \\ \mathbf{j}'\mathbf{j}''}) = \frac{F_\alpha(k, \mathbf{y}; \substack{\mathbf{y}'\mathbf{y}'' \\ \mathbf{j}'\mathbf{j}''})}{\hbar[\omega^2(\substack{\mathbf{y}'' \\ \mathbf{j}''}) - \omega^2(\substack{\mathbf{y}' \\ \mathbf{j}'})]}. \quad (2.9)$$

After evaluating the other commutators, one can then write an effective harmonic Hamiltonian $H(\mathbf{y})$ for a mode of wave vector \mathbf{y} by thermally averaging over all other modes.

$$\begin{aligned}
 H(\mathbf{y}) = & \frac{1}{2} \sum_{k\alpha} |\dot{w}_\alpha(k|\mathbf{y})|^2 + \frac{1}{2} \sum_{\substack{k\alpha \\ k'\beta}} \left\{ D_{\alpha\beta}(\bar{k}|\mathbf{y}) \right. \\
 & - \frac{1}{N} \sum F_\alpha(k, \mathbf{y}; \substack{y' y'' \\ j' j''}) F_\beta(k' - \mathbf{y}; \substack{-y' -y'' \\ j' j''}) \\
 & \times \frac{1}{[\omega^2(y'_{j'}) - \omega^2(y'_{j''})]} \langle Q(y'_{j'}) Q(\bar{y}'_{j'}) \rangle \Delta(\mathbf{y} + \mathbf{y}' + \mathbf{y}'') \\
 & \left. + \frac{1}{2N} \sum G_{\alpha\beta}(k, k'; \mathbf{y}; \substack{y' \\ j'}) \langle Q(y'_{j'}) Q(\bar{y}'_{j'}) \rangle \right\} \\
 & \times w_\alpha(k|\mathbf{y}) w_\beta(k'|\mathbf{y}), \quad (2.10)
 \end{aligned}$$

and the effective harmonic equation of motion for a mode of wave vector \mathbf{y} is

$$\begin{aligned}
 \omega^2(\mathbf{y}) w_\alpha(k|\mathbf{y}) = & \sum_{k'\beta} \left\{ D_{\alpha\beta}(\bar{k}|\mathbf{y}) - \frac{1}{N} \sum F_\alpha(k, -\mathbf{y}; \substack{y' y'' \\ j' j''}) F_\beta(k', \mathbf{y}; \substack{-y' -y'' \\ j' j''}) \right. \\
 & \times \frac{1}{[\omega^2(y'_{j'}) - \omega^2(y'_{j''})]} \langle Q(y'_{j'}) Q(\bar{y}'_{j'}) \rangle \Delta(\mathbf{y} + \mathbf{y}' + \mathbf{y}'') \\
 & \left. + \frac{1}{2N} \sum G_{\alpha\beta}(k, k'; \mathbf{y}; \substack{y' \\ j'}) \langle Q(y'_{j'}) Q(\bar{y}'_{j'}) \rangle \right\} \\
 & \times w_\beta(k'|\mathbf{y}). \quad (2.11)
 \end{aligned}$$

Effects of higher order anharmonic terms can be included if so desired. For the case of strong anharmonic coupling one has a complicated set of integral equations to solve. In general, the solution of these equations can be attempted in a self-consistent manner. One chooses the set of eigenvectors $e_\alpha(k|\mathbf{y})$ and the corresponding eigenfrequencies $\omega^2(\mathbf{y})$, then calculates the coupling parameters F and G , and the averages over the product of normal mode coordinates. Next, the set of effective harmonic equations is solved and the solution obtained is then compared with the starting set of polarization vectors and frequencies. Hooton¹⁰ has attempted such a procedure in a consideration of the lattice vibrational properties of solid helium. Such a complicated procedure, however, does not appear necessary to obtain the qualitative behavior of strontium titanate and barium titanate. Anderson⁴ has stated that the temperature variation of the parameters in the effective Hamiltonian [Eq. (2.10)] should be controlled by modes which are not sensitive to any changes caused by the ferroelectric transition. This suggests that in the nonpolar phase the temperature-dependent frequencies arise from averages over only the spectrum of relatively

temperature-independent modes. Since the strong temperature dependence of the long-wavelength transverse optical mode results from a near cancellation between driving (long-range) and restoring (short-range) forces in the lattice, it is reasonable that the only strongly temperature-dependent branch of the spectrum is the branch to which this mode belongs.¹¹ The frequencies of all other branches should be relatively temperature independent, being determined essentially by the harmonic forces between the ions. Averages over the acoustic branches are probably responsible for the major contribution to the observed temperature-dependent frequencies of the optical branch since a large fraction of the acoustic modes are populated classically. In the high-temperature limit, the averaged square of the normal mode coordinate is proportional to the temperature. This then enables one to define effective coupling parameters between the ions (for a given mode of wave vector \mathbf{y}) which have a small linear temperature dependence. The effective harmonic equations of motion can then be written.

$$\begin{aligned}
 \omega^2(\mathbf{y}) w_\alpha(k|\mathbf{y}) = & \sum_{k'\beta} \{ D_{\alpha\beta}(\bar{k}|\mathbf{y}) + D_{\alpha\beta}'(\bar{k}|\mathbf{y}) T \} w_\beta(k'|\mathbf{y}), \quad (2.12)
 \end{aligned}$$

with

$$\begin{aligned}
 D_{\alpha\beta}'(\bar{k}|\mathbf{y}) = & \frac{k_B}{2N} \sum_{y' j'} G_{\alpha\beta}(k, k'; \mathbf{y}; \substack{y' \\ j'}) \frac{1}{\omega^2(y'_{j'})} \\
 & - \frac{k_B}{N} \sum_{\substack{y' j' \\ y'' j''}} F_\alpha(k, -\mathbf{y}; \substack{y' y'' \\ j' j''}) F_\beta(k', \mathbf{y}; \substack{-y' -y'' \\ j' j''}) \\
 & \times \frac{\Delta(\mathbf{y} + \mathbf{y}' + \mathbf{y}'')}{[\omega^2(y'_{j'}) - \omega^2(y'_{j''})] \omega^2(y'_{j'})}. \quad (2.13)
 \end{aligned}$$

Sums over the modes in Eq. (2.13) can be considered to represent sums over acoustic modes that are classically populated. Coupling of the temperature-dependent optical modes to higher optical branches is probably weak due to the relatively small number of phonons in these high-frequency modes. Equation (2.12) is then one of a set of effective harmonic equations. For a given wave vector \mathbf{y} , the coupling between atoms consists of a temperature-independent part resulting from the harmonic interactions, and a small part linear in temperature resulting from fourth- and third-order anharmonic interactions.

The frequencies of the temperature-dependent branch are written

$$\begin{aligned}
 \omega^2(\bar{y}) = & T \sum_{\substack{k\alpha \\ k'\beta}} e_\alpha^*(k|\bar{y}) D_{\alpha\beta}'(\bar{k}|\bar{y}) e_\beta(k'|\bar{y}) \\
 & + \sum_{\substack{k\alpha \\ k'\beta}} e_\alpha^*(k|\bar{y}) D_{\alpha\beta}(k|\bar{y}) e_\beta(k'|\bar{y}). \quad (2.14)
 \end{aligned}$$

¹⁰ D. J. Hooton, *Phil. Mag.* **46**, 422, 433, 485 (1955).

¹¹ B. D. Silverman, *Phys. Rev.* **128**, 638 (1962).

Now, if as we have argued, each temperature-dependent frequency is, so to speak, renormalized by the spectrum of relatively temperature-independent frequencies, $D_{\alpha\beta}'(k_r)$ is relatively temperature-independent and $\omega^2(\frac{0}{F})$ will then vary as $T-T_C$ if (1) the harmonic contribution or second term on the right is negative, (2) the first term on the right of Eq. (2.14) is positive, (3) the eigenvector of the soft mode $e_\alpha(k|\frac{0}{F})$ has only a slight linear temperature dependence associated with it. Condition (1) results from the harmonic instability of the long-wavelength modes of the low-lying optical branch. Condition (2) is a reflection of the temperature-dependent behavior of the dielectric constant at constant volume.⁶ Condition (3) results from the relatively low frequency of the long-wavelength modes. This last condition will be understood more clearly after the discussion of the properties of the triatomic linear chain model (Sec. III).

As the value of the wave vector increases, driving forces become less predominant and the second term in Eq. (2.14) becomes positive. At large wave vectors (zone edge) the anharmonic contribution to the frequency is a small fraction of the total contribution, and hence, the frequencies are relatively temperature-independent. This qualitative description, however, should not hold for an antiferroelectric material in the nonpolar phase. Again, the relatively large temperature-dependent frequency in the vicinity of zero wave vector will reflect the Curie-Weiss behavior of the dielectric constant; however, there should be a large temperature dependence of certain frequencies with wavelength on the order of the lattice parameter.

Therefore, given a general potential between ions, one could, in principle, solve for the eigenfrequencies and eigenvectors of the harmonic system. One would get a

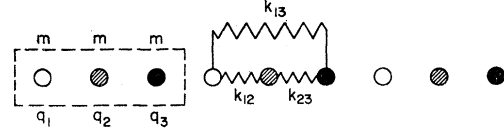


FIG. 1. Triatomic linear chain model.

number of positive roots of the secular equation, corresponding to the frequencies of the acoustic and optical branches which in the actual crystal are relatively temperature-independent. These values are then used to calculate the effective coupling constants [Eq. (2.13)]. The effective equations of motion [Eq. (2.12)] are then solved to obtain the frequencies and displacements of the modes of the temperature-dependent branch.

III. LINEAR CHAIN MODELS

A. Triatomic Linear Chain

To illustrate in as simple a manner as possible the temperature dependence of the eigenvector associated with the soft ferroelectric mode, we turn to the consideration of a triatomic linear chain model. At zero wave vector, this model will yield a low-lying temperature-dependent frequency and a higher relatively temperature-independent frequency. Since the third frequency (the acoustic frequency) is zero, one can obtain the frequencies of this model by solving a quadratic secular equation and hence gain some insight into the temperature dependences associated with the various quantities with a minimum of effort. The model is shown in Fig. 1. The sum of the charges are equal to zero. The masses are chosen equal for simplicity. The equations of motion for the zero wave vector modes are

$$\begin{pmatrix} m\omega^2 - k_{12} - k_{13}, & k_{12}, & k_{13} \\ k_{12}, & m\omega^2 - k_{12} - k_{23}, & k_{23} \\ k_{13}, & k_{23}, & m\omega^2 - k_{13} - k_{23} \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ X_3 \end{pmatrix} = 0. \quad (3.1)$$

k_{12} , k_{13} , k_{23} represent the zero wave vector couplings between the inequivalent sublattices. Each coupling can be considered to be composed of a temperature-independent or harmonic part plus a small linear temperature-dependent part arising from anharmonic interactions, as previously discussed. The X 's are ionic displacements from mean positions.

The two optical frequencies are given by

$$m\omega^2 = (k_{12} + k_{13} + k_{23}) \pm [(k_{12} + k_{13} + k_{23})^2 - 3(k_{12}k_{13} + k_{12}k_{23} + k_{13}k_{23})]^{1/2}. \quad (3.2)$$

A low frequency will arise if the second term under the root is small compared with the first term. Let us assume that this small term results from the near cancellation of harmonic forces. Expanding in powers of this

small term we obtain

$$m\omega^2 = (k_{12} + k_{13} + k_{23}) \pm (k_{12} + k_{13} + k_{23}) \times \left\{ 1 - \frac{3(k_{12}k_{13} + k_{12}k_{23} + k_{13}k_{23})}{2(k_{12} + k_{13} + k_{23})^2} + \frac{9(k_{12}k_{13} + k_{12}k_{23} + k_{13}k_{23})^2}{8(k_{12} + k_{13} + k_{23})^4} \dots \right\}. \quad (3.3)$$

The negative sign gives the low-lying mode.

$$m\omega_1^2 = \frac{3(k_{12}k_{13} + k_{12}k_{23} + k_{13}k_{23})}{2(k_{12} + k_{13} + k_{23})} - \frac{9(k_{12}k_{13} + k_{12}k_{23} + k_{13}k_{23})^2}{8(k_{12} + k_{13} + k_{23})^3}. \quad (3.4)$$

Assuming that driving forces predominate over restoring forces in the harmonic approximation and that the slight linear temperature-dependent contributions are responsible for the stability of the system, one can write

$$\frac{3}{2m} \frac{(k_{12}k_{13} + k_{12}k_{23} + k_{13}k_{23})}{(k_{12} + k_{13} + k_{23})} = A(T - T_c), \quad (3.5)$$

and therefore

$$\omega_1^2 = A(T - T_c) \left\{ 1 + O\left(\frac{A(T - T_c)}{2k/m}\right) \right\} \approx A(T - T_c), \quad (3.6)$$

where $k = k_{12} + k_{13} + k_{23}$. $A(T - T_c)/(2k/m)$ is the ratio of the square of the soft mode frequency to the square of the relatively temperature-independent frequency de-

termined mainly by harmonic interactions. $O(x)$ indicates a quantity of the order of x .

The higher frequency which is relatively temperature-independent is given by the positive sign in Eq. (3.3).

$$m\omega_2^2 = 2(k_{12} + k_{13} + k_{23}) - \frac{3}{2} \frac{(k_{12}k_{13} + k_{12}k_{23} + k_{13}k_{23})}{(k_{12} + k_{13} + k_{23})}, \quad (3.7)$$

$$\omega_2^2 = (2/m)(k_{12} + k_{13} + k_{23}) - A(T - T_c) \approx (2/m)k.$$

The eigenvector or displacements associated with each mode are

$$\frac{X_1}{X_3} = \frac{-k_{13}m\omega^2 + k_{12}k_{13} + k_{12}k_{23} + k_{13}k_{23}}{m^2\omega^4 - (2k_{12} + k_{13} + k_{23})m\omega^2 + k_{12}k_{13} + k_{12}k_{23} + k_{13}k_{23}}, \quad (3.8)$$

$$\frac{X_2}{X_3} = \frac{-k_{23}m\omega^2 + k_{12}k_{13} + k_{12}k_{23} + k_{13}k_{23}}{m^2\omega^4 - (2k_{12} + k_{13} + k_{23})m\omega^2 + k_{12}k_{13} + k_{12}k_{23} + k_{13}k_{23}}.$$

The high-frequency mode displacements are

$$X_1 = -\frac{k_{13}}{\sqrt{2}(k_{13}^2 + k_{23}^2 + k_{13}k_{23})^{1/2}} \left\{ 1 + O\left(\frac{A(T - T_c)}{2k/m}\right) \right\},$$

$$X_2 = -\frac{k_{23}}{\sqrt{2}(k_{13}^2 + k_{23}^2 + k_{13}k_{23})^{1/2}} \left\{ 1 + O\left(\frac{A(T - T_c)}{2k/m}\right) \right\}, \quad (3.9)$$

$$X_3 = \frac{(k_{13} + k_{23})}{\sqrt{2}(k_{13}^2 + k_{23}^2 + k_{13}k_{23})^{1/2}} \left\{ 1 + O\left(\frac{A(T - T_c)}{2k/m}\right) \right\}.$$

The low-frequency displacements are

$$X_1 = \frac{k_{13} - 2(k_{12} + k_{23})}{\sqrt{6}(4k_{12}^2 + k_{13}^2 + k_{23}^2 + 2k_{12}k_{13} + 2k_{12}k_{23} - k_{13}k_{23})^{1/2}} \left\{ 1 + O\left(\frac{A(T - T_c)}{2k/m}\right) \right\},$$

$$X_2 = \frac{k_{23} - 2(k_{12} + k_{13})}{\sqrt{6}(4k_{12}^2 + k_{13}^2 + k_{23}^2 + 2k_{12}k_{13} + 2k_{12}k_{23} - k_{13}k_{23})^{1/2}} \left\{ 1 + O\left(\frac{A(T - T_c)}{2k/m}\right) \right\}, \quad (3.10)$$

$$X_3 = \frac{4k_{12} + k_{13} + k_{23}}{\sqrt{6}(4k_{12}^2 + k_{13}^2 + k_{23}^2 + 2k_{12}k_{13} + 2k_{12}k_{23} - k_{13}k_{23})^{1/2}} \left\{ 1 + O\left(\frac{A(T - T_c)}{2k/m}\right) \right\}.$$

Hence, the low-frequency displacements are relatively temperature-independent even though the frequency is significantly temperature-dependent. To lowest order the eigenvector is given by the zero-frequency eigenvector. This illustrates that the eigenvector of the harmonically unstable problem will not be much different from the eigenvector obtained after the frequency renormalization has been performed. In other words, the eigenvector of the low-lying mode is not very different whether one chooses it to be the eigenvector of the

harmonically unstable problem

$$\bar{X} = \bar{X}_{T=T_c} \left\{ 1 + O\left(-\frac{AT_c}{2k/m}\right) \right\},$$

the zero frequency eigenvector

$$\bar{X} = \bar{X}_{T=T_c},$$

or the eigenvector of the effective temperature-depend-

ent mode

$$\bar{X} = \bar{X}_{T=T_c} \left\{ 1 + O\left(\frac{A(T-T_c)}{2k/m}\right) \right\}.$$

B. Diatomic Linear Chain

To illustrate the behavior of the temperature-dependent optical branch in the simplest possible way, let us consider the diatomic linear chain shown in Fig. 2. This is a chain of alternating plus and minus charges interacting with a nearest-neighbor harmonic coupling k_1 and a next-nearest-neighbor harmonic coupling k_2 . The masses, m , have been again chosen equal for simplicity. The equations of motion for this system are

$$m d^2 X_i / dt^2 = -2(k_1 + k_2)X_i + k_1(X_{i+1} + X_{i-1}) + k_2(X_{i+2} + X_{i-2}). \quad (3.11)$$

The frequency spectrum is given by

acoustic branch

$$\omega_a^2(y) = \frac{4k_1}{m} \sin^2 \frac{yd}{2} + \frac{4k_2}{m} \sin^2 yd, \quad (3.12)$$

$$0 \leq y \leq \pi/2d$$

optical branch

$$\omega_o^2(y) = \frac{4k_1}{m} \cos^2 \frac{yd}{2} + \frac{4k_2}{m} \sin^2 yd. \quad (3.13)$$

The frequency of the zero wave vector optical motion is completely determined by the nearest-neighbor coupling k_1 , since for this mode plus and minus sublattices are individually undistorted and just move out of phase with one another. If we choose k_1 small and negative, we build an instability into the system in the vicinity of zero wave vector. In the real crystal this would correspond to the slight predominance of the harmonic driving forces (long range) over the harmonic restoring forces (short range) for certain long-wavelength transverse optical motions. Choosing k_2 large and positive stabilizes the system at wave vectors away from zero. Figure 3 shows the square of the frequency spectrum in the harmonic approximation as a function of wave vector. The uppermost branch is the acoustic branch which will remain essentially as shown even after anharmonic interactions have been introduced. The lower branch is the "optical branch" where in the vicinity of zero wave vector there is a range of imaginary frequencies. The similarity of this branch with the one

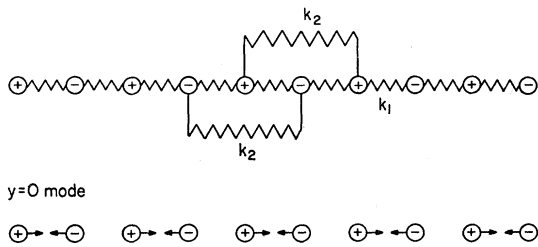


FIG. 2. Diatomic linear chain model.

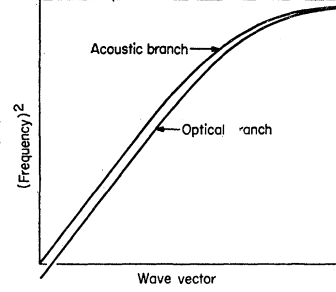


FIG. 3. Frequency spectrum in the harmonic approximation.

appearing in Anderson's paper⁴ is to be noted. The Hamiltonian can be written in terms of the "normal modes" of the harmonically unstable system.

$$H_0 = \frac{1}{2} \sum_y \{ p_y^a p_{-y}^a + \omega_a^2(y) q_y^a q_{-y}^a \} + \frac{1}{2} \sum_y \{ p_y^o p_{-y}^o + \omega_o^2(y) q_y^o q_{-y}^o \}. \quad (3.14)$$

Next, a fourth-order anharmonic interaction is introduced between nearest neighbors.

$$H' = \frac{\beta}{4!} \sum_i (X_{i+1} - X_i)^4. \quad (3.15)$$

β is a fourth-order coupling constant. Writing this in terms of the normal mode coordinates and picking out just the most important terms leading to the frequency renormalization we get

$$H' = \frac{4\beta}{Nm^2} \sum_y \left\{ \sum_{y'} \sin^2 \frac{y'd}{2} q_{y'}^a q_{-y'}^a \right\} \times \cos^2 \frac{yd}{2} q_y^o q_{-y}^o + \dots \quad (3.16)$$

Here we have assumed that coupling to the acoustic branch is most important in determining the effective temperature-dependent frequencies. This has been discussed in Sec. II. An effective harmonic Hamiltonian can be written by averaging over the product of coordinates in the curly brackets in Eq. (3.16).

$$H_0^E = \frac{1}{2} \sum_y \{ p_y^a p_{-y}^a + \Omega_a^2(y) q_y^a q_{-y}^a \} + \frac{1}{2} \sum_y \{ p_y^o p_{-y}^o + \Omega_o^2(y) q_y^o q_{-y}^o \}, \quad (3.17)$$

with

$$\Omega_o^2(y) = \left(\frac{8\beta}{Nm^2} \sum_{y'} \sin^2 \frac{y'd}{2} \langle q_{y'}^a q_{-y'}^a \rangle + \frac{4k_1}{m} \right) \cos^2 \frac{yd}{2} + \frac{4k_2}{m} \sin^2 yd, \quad (3.18)$$

$$\Omega_a^2(y) = \left(\frac{8\beta}{Nm^2} \sum_{y' \neq y} \sin^2 \frac{y'd}{2} \langle q_{y'}^a q_{-y'}^a \rangle + \frac{4k_1}{m} \right) \sin^2 \frac{yd}{2} + \frac{4k_2}{m} \sin^2 yd. \quad (3.19)$$

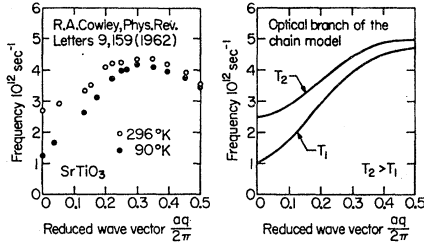


FIG. 4. Low-lying temperature-dependent optical branch from neutron inelastic scattering data compared with optical branch of the diatomic chain model.

The major contribution to the acoustic branch frequencies arises from the second term in Eq. (3.19), the term involving k_2 , and hence these frequencies are relatively temperature insensitive. Therefore, a good first approximation is to average over the harmonic acoustic spectrum in the expression [Eq. (3.18)] for the frequencies of the optical branch. Using

$$\langle q_y^a q_{-y}^a \rangle \approx \frac{k_B T}{\omega_a^2(y)} \approx \frac{k_B T}{(4k_2/m) \sin^2 y d}, \quad (3.20)$$

and the assumption that the major contribution to the frequency renormalization comes from the linear region of the spectrum, i.e., $\sin y d \approx y d$, one obtains

$$\Omega_0^2(y) = \left(\frac{\beta k_B}{2m k_2} T - \frac{4|k_1|}{m} \right) \cos^2 \frac{y d}{2} + \frac{4k_2}{m} \sin^2 y d. \quad (3.21)$$

The presence of the anharmonic term therefore stabilizes the system at temperatures above the Curie-Weiss temperature T_C , where

$$T_C = 8|k_1|k_2/\beta k_B. \quad (3.22)$$

The optical branch can now be plotted as a function of wave vector at two temperatures and compared with the results of inelastic neutron scattering. This comparison is shown in Fig. 4. It is seen that this simple model does represent the salient features of experiment quite well. The anharmonic contribution to the frequency is most evident in the vicinity of zero wave vector of the optical branch where it stabilizes the modes and provides the relatively strong temperature-dependent frequencies. For larger wave vectors the anharmonic interaction contributes less to the frequency than harmonic interactions, and hence, in this region, the branch is less temperature-dependent. Had there been a harmonic instability of modes at the edge of the Brillouin zone ($y = \pi/2d$), one might then expect strong temperature-dependent frequencies in the vicinity of the zone edge and the possibility of the material making a transition to an antiferroelectric state.¹¹

IV. CONCLUSION

In Sec. II we have derived an effective harmonic equation for the modes of a given wave vector \mathbf{y} [Eq.

(2.11)]. It was then shown that if each relatively temperature-dependent frequency arose from averages over only that part of the spectrum that was relatively temperature-independent (acoustic branches), the solution of the set of equations was simplified considerably. The neglect of the coupling between the modes with relatively temperature-dependent frequencies led to a set of linear equations. With the further assumption that the major contribution to the effective harmonic couplings resulted from averages over modes that are classically populated, it was shown that each effective harmonic coupling could be written as a sum of a temperature-independent (harmonic) coupling plus a small coupling (arising from the anharmonic interactions) linear in the temperature. The temperature dependence of the long-wavelength frequency previously discussed [Eq. (1.1)] then arises from a close cancellation between harmonic forces in the lattice for certain long-wavelength transverse optical modes. The temperature-dependent branch arises from the relatively large contributions anharmonic interactions make to the frequencies of this branch. Higher than fourth-order anharmonic interactions were neglected since they do not contribute to the linear temperature dependence of the square of the temperature-dependent long-wavelength effective frequencies [Eq. (1.1)]. These higher order anharmonic interactions were also assumed to contribute negligibly to the other frequencies of the low-lying branch. The polarization vector associated with the temperature-dependent frequency was shown to be relatively temperature-independent and not much different from the polarization vector describing the harmonic instability.

The procedure presented in this paper is essentially equivalent to the approach adopted in the calculation of the dielectric response.^{1,2} In the previous work it was assumed that the anharmonic Hamiltonian was represented in terms of the polarization vectors of the harmonically unstable problem. The long-wavelength mode with harmonic imaginary frequency was then coupled only to the modes with relatively temperature-independent frequencies leading to results equivalent to those presented in this paper.

The previous discussion is a simplification of, in general, a very complicated system. Ferroelectric and antiferroelectric materials exhibit a Curie-Weiss behavior of the dielectric constant over only a restricted interval of temperature above the transition temperature. At low temperatures SrTiO_3 and KTaO_3 deviate from this behavior due to what are believed to be quantum mechanical effects. Whether SrTiO_3 ever actually becomes spontaneously polarized is still open to dispute. At high temperatures one might expect deviations from Eq. (1.1) as higher order anharmonic effects become important. The present treatment is proposed as a qualitative explanation of the behavior of these materials for just the region $T > T_C$ for which Eq. (1.1) is expected to apply.

A quantitative description of a particular material must entail a very complete description of the interatomic forces since the temperature-dependent frequencies arise from a close cancellation between harmonic forces. Effects of thermal expansion must be considered. Any slight temperature dependence of ionic charges due to changes in bonding as a function of temperature could contribute to these frequencies. The electronic contribution to the lattice frequencies (neglected in the present discussion since our qualitative conclusions are unaffected by its presence) must also be taken into account. In view of this complexity and the state of knowledge concerning interatomic forces, there exists little possibility at present to calculate effective lattice couplings from first principles.

Applications of shell-model-type calculations¹² to the present problem also have their associated difficulties. The perovskite structure has a relatively large number (five) of atoms per primitive unit cell. Any attempted realistic model must of necessity introduce a large number of constants. If these constants cannot be determined from first principles but are chosen to fit experimental data, one may not be certain that the fit obtained is unique (having a physical basis) or is merely the result of introducing a sufficient number of undetermined parameters to obtain such a fit. This objection has been pointed out by Janovec and Dvorak.¹³ Also, while one might attempt to understand the qualitative features of the SrTiO₃ spectrum, the significance of a more detailed interpretation of the present neutron data is questionable. SrTiO₃ exhibits a phase transition at about 110°K.¹⁴ The material is cubic above 110°K and tetragonal below. Since measurements of the temperature-dependent optical branch have been made on both

sides of this transition, one must not only include effects of thermal expansion in a quantitative theory, but also any effects that might arise from the presence of the phase transformation. While there is no dielectric anomaly at the 110°K transition, systematic deviations of the dielectric constant from a Curie-Weiss behavior appear in the vicinity of this temperature,¹⁵ which might reflect the effect of the transition on the long-wavelength modes and/or the onset of quantum mechanical effects. The effect of the transition on the modes of shorter wavelength is unknown. It would be of value if the spectrum of SrTiO₃ were measured as a function of temperature over a region above 110°K. KTaO₃ also seems a likely choice for investigation since it is cubic above approximately 13°K¹⁶ and large single crystals of this material are easily prepared.

In conclusion, the temperature-dependent frequency spectrum of a paraelectric material has been discussed with use of an effective harmonic lattice equation of motion. For a given wave vector, the effective couplings between atoms are written as a sum of a temperature-independent part, arising from harmonic interactions, and a part linear in the temperature, arising from fourth- and third-order anharmonic interactions. The conditions required for the observed Curie-Weiss behavior of the dielectric constant and associated temperature dependence of certain long-wavelength transverse optical frequencies have been examined. It has been shown that the salient features of the temperature-dependent low-lying optical branch in SrTiO₃ can be understood by considering the effects of anharmonic interactions at constant volume.

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¹⁶ J. K. Hulm, B. T. Matthias, and E. A. Long, *Phys. Rev.* **79**, 885 (1950).