

Microwave Absorption in Cubic Strontium Titanate*

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An analysis of the temperature dependence of the microwave loss in SrTiO_3 is presented using the linear chain model of a ferroelectric as a basis for discussion. It is shown that a plausible explanation of the temperature dependence of the microwave loss tangent above liquid air temperature is possible if one considers the loss to be due to the damping of a virtual excitation out in the wing of a fundamental lattice absorption. The fundamental lattice absorption is associated with a low-frequency "ferroelectric" transverse optical mode of the material. The microwave loss tangent can be expressed by $\tan\delta = (T - T_c)^{-1}(A + BT + DT^2)$. The parameter A is a measure of the damping due to the presence of imperfections in the lattice. The parameters B and D are shown to arise from damping due to three- and four-phonon processes whose origin is attributed to the anharmonic interactions of the lattice.

I. INTRODUCTION

RECENTLY Rupprecht and Bell have measured the dielectric constant and loss tangent of single-crystal strontium titanate above liquid air temperature and at microwave frequencies.¹ Their results are presented in the preceding paper in this journal. In the present paper it will be shown that a plausible explanation of the origin of the temperature dependence of the microwave loss tangent is possible, if the paraelectricity of strontium titanate is regarded as originating from a low-lying temperature-dependent optical-mode frequency.² The relationship between this mode and the properties of the ferroelectric and paraelectric state has been previously discussed by Anderson,³ Landauer, Juretschke, and Sorokin,⁴ and Cochran.⁵

A transverse microwave radiation field will drive the low-lying transverse optical mode of the material in a forced vibration. Energy is transferred from the electromagnetic field to this lattice mode and is then degraded into other vibrational modes of the material. That this is the likely origin of the observed microwave loss can be shown by the following considerations. A uniform density N of viscously damped harmonic oscillators has a complex dielectric constant ϵ , given by

$$\epsilon - 1 = [(Nq^2/m)/\omega_0^2 - \omega^2 + i\omega\gamma]. \quad (1.1)$$

q is the charge on the oscillator, m is the oscillator mass, ω_0 is the resonant frequency, ω is frequency of the applied electric field, and γ is the damping constant. The real and imaginary parts of the dielectric constant

are

$$\begin{aligned} \epsilon' - 1 &= \left(\frac{Nq^2}{m} \right) \frac{(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}; \\ \epsilon'' &= - \left(\frac{Nq^2}{m} \right) \frac{\omega\gamma}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}. \end{aligned} \quad (1.2)$$

Imagine a situation for which

- (a) $\omega_0^2 \gg \omega^2$,
- (b) $Nq^2/m\omega_0^2 \gg 1$,
- (c) $\omega_0^2 \sim (T - T_c)$.

T is the absolute temperature and T_c a constant to be identified with the Curie temperature. The dielectric constant and loss tangent are then

$$\epsilon' \approx Nq^2/m\omega_0^2 \sim 1/(T - T_c), \quad \epsilon' \gg 1, \quad (1.3)$$

and

$$\tan\delta = -\epsilon''/\epsilon' \approx \omega\gamma/\omega_0^2 \sim \omega\gamma/(T - T_c). \quad (1.4)$$

Equations (1.3) and (1.4) describe the observed behavior of strontium titanate quite well.¹ The dielectric constant exhibits no relaxation at the highest microwave frequencies employed (35 kMc/sec). This is believed to result from the appreciable difference between the microwave frequency and natural frequency of the oscillator (condition a). The dielectric constant is very large when compared with the microwave or dc dielectric constant of other nonparaelectric crystalline materials, e.g., the alkali halides. This can be explained by an anomalously low natural frequency²⁻⁵ (condition b). These considerations show that the results of experiment roughly determine an upper and lower bound for the low-lying transverse optical-mode frequency. It must be sufficiently low compared with the frequencies found in nonparaelectric materials to yield a high dielectric constant; however, it must be sufficiently high compared with the microwave frequencies involved since no change from the dc dielectric constant is observed. The temperature dependence of this frequency leads to the Curie-Weiss behavior of the dielectric constant^{4,5} (condition c).

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¹ G. Rupprecht and R. O. Bell, preceding paper [Phys. Rev. 125, 1915 (1962)]. G. Rupprecht, Bull. Am. Phys. Soc. 6, 12 (1961); R. O. Bell and G. Rupprecht, *ibid.* 6, 12 (1961).

² B. D. Silverman, Bull. Am. Phys. Soc. 6, 12 (1961); G. Rupprecht, R. O. Bell, and B. D. Silverman, Phys. Rev. 123, 97 (1961).

³ P. W. Anderson (unpublished report).

⁴ R. Landauer, H. Juretschke, and P. Sorokin (unpublished report).

⁵ W. Cochran, Phys. Rev. Letters 3, 412 (1959); *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1960), Vol. 9, p. 387.

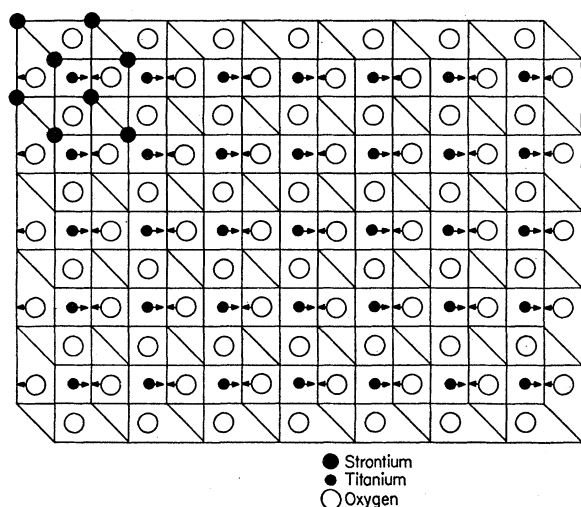


FIG. 1. Polarization mode displacements.

One contribution to the loss tangent of strontium titanate obeys a Curie-Weiss law as does the dielectric constant, (Figs. 1 and 5 in reference 1). It is seen that a temperature-independent damping constant gives a result in agreement with this observation. The possible origin of this damping will be discussed in Sec. IV. At higher temperatures the loss tangent deviates strongly from any Curie-Weiss type behavior. At the highest temperatures it increases linearly with temperature (Fig. 1 in reference 1). This behavior can be understood if one assumes that at these higher temperatures, lattice anharmonic interactions contribute appreciably to the observed loss. Specifically, a fourth-order anharmonic interaction treated in lowest-order or a third-order anharmonic interaction treated in next-to-lowest order may be held responsible for the observed temperature dependence of the damping constant γ . These interactions will produce a damping constant which is a quadratic function of temperature,

$$\gamma \sim T^2, \quad (1.5)$$

and therefore [using Eq. (1.4)]

$$\tan \delta \sim \omega T^2 / (T - T_c). \quad (1.6)$$

At temperatures high compared with T_c this gives a linear dependence of the loss tangent on temperature which is in agreement with observation. It is interesting to note that the temperature dependence of the damping constant of some alkali halides has been found to be proportional to the square of the temperature at high temperatures.⁶ The anharmonic damping in strontium titanate will be discussed in greater detail in Sec. V.

The preceding discussion in the main also applies to barium titanate in the paraelectric state. The observed loss tangent of barium titanate however is some orders

of magnitude larger than the strontium titanate value.⁷ Consequently, it is believed that anharmonic damping is not observed in a loss tangent vs temperature plot for this material since these interactions contribute a negligible amount to the loss over the entire temperature range of measurement. It is possible that the introduction of a chemical catalyst to facilitate a phase transformation from the hexagonal to perovskite modification is responsible for the large value of the loss tangent. Strain is another possibility to be considered.

The origin of conditions (a), (b), and (c) is essentially explained by a theory of the ferroelectric behavior of barium titanate proposed by Slater.⁸ Slater assumed that only the titanium ion can move and is therefore the only ion contributing a lattice part to the polarization of the medium. In Slater's theory the large value of the dielectric constant results from an almost complete cancellation of the short-range restoring forces on the titanium ion by the long-range Coulomb dipolar forces. This feature together with a slight linear temperature dependence of the short-range restoring force on the titanium ion leads to a Curie-Weiss behavior of the dielectric constant. To help make explicit some of the points presented in the preceding discussion, a simplified model of the perovskite structure will be introduced. This will make possible an investigation of certain aspects of the origin of the microwave loss. The non-irreversible properties of the model will be obtained in a manner analogous to that of Slater.

The model to be considered is as follows. The titanium and oxygen ions are coupled along chains in the $[100]$, $[010]$, and $[001]$ directions of the unit cell. The oxygen ions are constrained to move only perpendicular to the unit cell face on which they lie. The titanium ions are allowed a displacement in an arbitrary direction; however, the component of motion along one chain is taken to be uncoupled from motions along the other chains. In other words, shear forces are neglected. The strontium ions are assumed to be fixed in position and in the following treatment serve only to space the oxygen and titanium ions, and to constrain the motion in the manner described. This model will allow the motion of the titanium and oxygen ions to be described simply by a superposition of the modes of a linear chain. The origin of the microwave loss can then be discussed in terms of the damping of a linear chain. Figure 1 shows the $k=0$ optical mode displacements. This is just the mode in which a uniform polarization is generated and will subsequently be called the uniform or polarization mode. Only external fields applied along the $[100]$ direction will be considered. This will limit the analysis to the dynamics of one chain. The existence of the chains in the three directions will, however, yield a theory which is isotropic. The propagation vector κ

⁶ For an interesting discussion of this point see page 457 of a work by A. A. Maradudin and R. F. Wallis, *Phys. Rev.* **120**, 442 (1960).

⁷ T. S. Benedict and J. L. Durand, *Phys. Rev.* **109**, 1091 (1958); E. Stern and A. Lurio, *ibid.* **123**, 117 (1961).

⁸ J. C. Slater, *Phys. Rev.* **78**, 748 (1950).

of the transverse microwave radiation field is chosen to lie in the [001] direction. This field drives the transverse optical mode of the system in a forced vibration. The driven mode is composed of ionic displacements along the [100] direction since this is the direction of the electric field. The absolute value of the propagation vector $|\kappa|$ is sufficiently small to enable one to neglect the phase difference between the chains over a domain of dimensions large compared with the lattice parameter but small compared with the sample size. It is just over such domain that periodic boundary conditions are imposed on the chains. The investigation of the temperature dependence of the microwave loss tangent reduces essentially to an investigation of the damping of the $k=0$ mode of one of the chains.⁹ In other words, the microwave loss in SrTiO₃ will be investigated by considering the damping of a linear chain. The necessary three-dimensional aspect of the problem (the inclusion of the long-range dipolar interaction) is obtained by assuming that all the chains are driven in phase by the electric field over a small region of the crystal. The effect on the local field by the dephasing of the chains outside of this region is zero for a mode of transverse polarization.

For the very simple model we are to consider, the masses of the titanium and oxygen ions are chosen equal; the ionic charges of titanium and oxygen are taken to be equal in magnitude but opposite in sign; an equal electronic polarizability is attributed to each ion.

II. LOCAL FIELD

A uniform polarization developed along the [100] direction will contribute to the local electric field at each site. In what follows, contributions to the local electric field from oxygen ions not lying on the chains in the [100] direction will be neglected. The electronic dipole moment of each ion can be written in terms of the polarizability $\bar{\alpha}$ and the local fields:

$$p_{O^e} = \bar{\alpha} E_{loc}^O, \quad p_{Ti^e} = \bar{\alpha} E_{loc}^{Ti}. \quad (2.1)$$

The electronic polarization due to each of the ions is

$$P_{O^e} = (\bar{\alpha}/8d^3) E_{loc}^O, \quad P_{Ti^e} = (\bar{\alpha}/8d^3) E_{loc}^{Ti}; \quad (2.2)$$

$8d^3$ is the volume of the cubic unit cell, where d is the nearest-neighbor distance between oxygen and titanium ions. The local field at each of the sites can be written⁸

$$E_{loc}^O = E + \frac{1}{3\epsilon_0} P_O + \frac{b'}{3\epsilon_0} P_{Ti}, \quad (2.3)$$

$$E_{loc}^{Ti} = E + \frac{b'}{3\epsilon_0} P_O + \frac{1}{3\epsilon_0} P_{Ti}, \quad [b' = 8.182].$$

E is the macroscopic or average field, ϵ_0 is the permittivity of free space, and P is the polarization due to the ion designated by the subscript; this includes a lattice and an electronic part,

$$P = P^0 + P^e. \quad (2.4)$$

Consistent with the linear chain model, the lattice polarization of each sublattice and the local fields at the two different sites are equal. Equations (2.3) reduce to

$$E_{loc} = E + (a/\epsilon_0) P, \quad a = (1+b')/6. \quad (2.5)$$

Combining Eqs. (2.2), (2.4), and (2.5) the local field can be written in terms of the lattice polarization only,

$$E_{loc} = (1/b)[E + (a/\epsilon_0) P^0], \quad b = [1 - 2\bar{\alpha}a/8d^3\epsilon_0]. \quad (2.6)$$

The constant b characterizes the electronic contribution to the local field.

III. DIELECTRIC CONSTANT

The energy of a chain lying along the direction in which the field is applied is [using Eq. (2.6)]

$$H_0 = \frac{1}{2} m \sum_i \{ \dot{x}_i^2 + \dot{u}_i^2 \} + \frac{1}{2} K \sum_i \{ (x_i - u_{i+1})^2 + (x_i - u_{i-1})^2 \} + (ne/b)[Ee^{i\omega t} + (aP^0/2\epsilon_0)] \sum_i (x_i - u_i), \quad (3.1)$$

x_i and u_i are the displacements from equilibrium of the i th oxygen and titanium ions, respectively; n is the number of electronic charges on each ion; E is the amplitude of the applied field of frequency ω ; m is the mass of each ion; K is the spring constant coupling for nearest neighbors.

The Hamiltonian is next written in terms of the complex normal coordinates q_k :

$$x_i = (2Nm)^{-\frac{1}{2}} \sum_k (q_k^a - q_k^0) \exp(ikX_i^0);$$

$$u_i = (2Nm)^{-\frac{1}{2}} \sum_k (q_k^a + q_k^0) \exp(ikU_i^0) \quad (3.2)$$

$$-\pi/2d \leq k \leq \pi/2d.$$

X_i^0 and U_i^0 are the equilibrium positions of the oxygen and titanium ions, respectively.

Substituting Eq. (3.2) into Eq. (3.1), we obtain

$$H_0 = \frac{1}{2} \sum_k [p_k^a p_{-k}^a + (\omega_k^a)^2 q_k^a q_{-k}^a] + \frac{1}{2} \sum_{k \neq 0} [p_k^0 p_{-k}^0 + (\omega_k^0)^2 q_k^0 q_{-k}^0] + \frac{1}{2} [(p_0^0)^2 + \omega_T^2 (q_0^0)^2] - (ne/b) E e^{i\omega t} (2N/m)^{\frac{1}{2}} q_0^0, \quad (3.3)$$

with

$$\omega_T^2 = (\omega_0^0)^2 - \frac{1}{4} (ne)^2 a / \epsilon_0 m d^3 b, \quad (3.4)$$

$$\omega_k^a = (4K/m)^{\frac{1}{2}} \sin(kd/2),$$

$$\omega_k^0 = (4K/m)^{\frac{1}{2}} \cos(kd/2). \quad (3.5)$$

⁹ To be precise, this mode which is coupled directly to the radiation field is not the $k=0$ mode. It is a mode for which $k \approx 0$. To distinguish between longitudinal and transverse mode frequencies, one must take into consideration the finite wavelength of this mode. Once this distinction is made, however, the mode can be treated as the $k=0$ mode since its wavelength is very large compared with all the other modes of interest. For a more detailed discussion of this point see E. W. Kellerman, Phil. Trans. Roy. Soc. 238, 513 (1940); T. H. K. Barron, Phys. Rev. 123, 1995 (1961).

p_k is the momentum conjugate to q_k . Equation (3.5) is just the usual dispersion relation for a monotonic chain with only nearest-neighbor coupling. The separation into acoustical and optical modes is performed merely to assist in interpreting the results of this analysis. The more familiar Brillouin zone of wave vector interval π/d has been folded about the value $\pi/2d$. Modes of wave vector less than $\pi/2d$ are called acoustical. Modes of wave vector greater than $\pi/2d$ are called optical. For a diatomic chain these two branches are separated since there is a discontinuity at $\pi/2d$.

It is seen that the dipolar field reduces the frequency of the $k=0$ optical mode [Eq. (3.4)]. This is the mode in which the two different type ions move 180° out of phase and produce a uniform lattice polarization. In general the dipolar field will modify the frequencies of all the modes. Our treatment does not include this feature—only the modification of the $k=0$ optical mode appears. This occurs since the local field has been taken to be proportional to the polarization. Only the $k=0$ optical mode has a nonzero polarization associated with it, since cyclic boundary conditions have been imposed on the ionic motion.

A transition to the ferroelectric state occurs when the polarization mode becomes unstable ($\omega_T \rightarrow 0$). This is believed due to the cancellation of the short-range repulsive forces by the dipolar forces. Cochran has discussed this point in detail in a recent article.⁵

Using the Hamiltonian [Eq. (3.3)] one can solve for the motion of the system to obtain the polarization and in turn the dielectric constant

$$\epsilon = 1 + \frac{2\bar{\alpha}}{8d^3b\epsilon_0} + \frac{(ne)^2}{4md^3b^2\epsilon_0} \frac{1}{(\omega_T^2 - \omega^2)}. \quad (3.6)$$

Only the uniform mode is involved in determining the dielectric constant since all the modes are uncoupled in the harmonic approximation. The first two terms on the right of Eq. (3.6) are the square of the optical index of refraction. The third term is the lattice contribution to the dielectric constant which vanishes at infinite frequency.

To obtain a Curie-Weiss behavior of the dielectric constant we make use of an effective temperature-dependent spring constant,

$$\left. \frac{4K}{m} \right|_{\text{eff}} = \frac{(ne)^2 a}{4\epsilon_0 m d^3 b} [1 + c(T - T_c)]. \quad (3.7)$$

This relation is obtained (Appendix II) by including the effects of anharmonic interactions on the spring constant of the linear theory. The derivation presented in Appendix II follows the work of Slater⁸ very closely. As the temperature is increased the ions experience an increased restoring force or stiffer spring.

From Eqs. (3.4) and (3.7) we obtain

$$\omega_T^2 = \frac{(ne)^2 ac}{4\epsilon_0 m d^3 b} (T - T_c). \quad (3.8)$$

This temperature dependence of the polarization mode frequency has been proposed previously^{4,5} and is implicit in the work of Slater. A choice of the generalized Lorentz factor a enables one to determine b and c from experiment. The numerical determination of these constants is discussed in Appendix I. The frequency of the temperature-dependent polarization mode, written in terms of the number of electronic charges per ion, is

$$\omega_T = 8.5 \times 10^{11} n (T - T_c)^{1/2}. \quad (3.9)$$

For $n=1$, the wavelength of the radiation field required to excite this mode is recorded for liquid air¹⁰ and room temperature:

$$\begin{aligned} 320\mu & \text{ at } 77^\circ\text{K}, \\ 140\mu & \text{ at } 298^\circ\text{K}. \end{aligned}$$

The optical value of the dielectric constant is small compared with the microwave or dc value, essentially condition b, Sec. I and, therefore, Eq. (3.6) is written

$$\epsilon = \frac{(ne)^2}{4md^3b^2\epsilon_0} \frac{1}{(\omega_T^2 - \omega^2)}. \quad (3.10)$$

For all microwave pump frequencies whose square is small compared with the square of the polarization mode frequency (condition a, Sec. I) the dielectric constant obeys a Curie-Weiss law,

$$\epsilon = C/(T - T_c), \quad C = 1/abc. \quad (3.11)$$

This is obtained from Eqs. (3.8) and (3.10). A comparison of the two frequencies involved can now be made under the least favorable conditions for the verification of condition a of Sec. I. We write the square of the polarization mode frequency at liquid air temperature (77°K) and the square of the highest microwave frequency employed (35 kMc/sec),

$$\omega^2 \approx 5 \times 10^{22} / \text{sec}^2,$$

$$\omega_T^2 \approx 5 \times 10^{25} / \text{sec}^2,$$

and therefore

$$\omega^2 / \omega_T^2 \approx 10^{-3}.$$

So we conclude—if the large value of the dielectric constant of SrTiO_3 is associated with a low-lying optical mode frequency it is not surprising that no relaxation of the dielectric constant has been observed in the microwave range.

IV. IMPERFECTION DAMPING

One contribution to the loss tangent of strontium titanate obeys a Curie-Weiss law (Figs. 1 and 5 in reference 1). It has been shown in the introduction that this behavior can be understood if the damping of the polarization mode is assumed to be temperature

¹⁰ Since a phase transformation has been observed at about 110°K by various investigators one is not certain as to the validity of the present treatment below this temperature. For published evidence concerning this phase transformation see K. A. Muller, *Phys. Rev. Letters* **2**, 341 (1959).

independent—the case for which the damping constant γ is independent of temperature [Eq. (1.4)]. This suggests that the damping is due to the presence of imperfections in the lattice, e.g., impurities, dislocations, local strains, etc. These imperfections will couple the polarization mode to other modes and provide a mechanism for the scattering of energy out of the driven mode.

A specific model for the damping will be introduced to illustrate in greater detail the general features of the loss mechanism which lead to a temperature independent damping constant. By no means do we suggest that the actual mechanism responsible for the observed loss is understood. The results of the analysis to be presented will show however, the possibility of explaining the order of magnitude of the observed loss tangent even though the measurements are performed at a frequency for which the dielectric constant exhibits no relaxation.

Let us assume that a number of springs along a chain have modified spring constants K_1 due to the presence of interstitials or local strain. These modified springs are located randomly along a chain. The change in the Hamiltonian due to the presence of these springs is

$$H_{\text{imp}} = \frac{1}{2} K' \sum_{i, \text{imp}} (x_i - u_{i+1})^2 + \frac{1}{2} K' \sum_{j, \text{imp}} (x_j - u_{j-1})^2, \quad K' = K_I - K. \quad (4.1)$$

Only the first term on the right in Eq. (4.1) will be considered since both terms will damp the uniform mode independently. The calculation presented here and in Sec. V is similar in procedure to that of Blackman¹¹ who treated the damping of a diatomic chain by lattice anharmonic interactions. Equation (4.1) is written in terms of the complex normal modes [Eq. (3.2)] where only terms contributing to the damping of the polarization mode in lowest order are retained:

$$H_{\text{imp}} = -\frac{K'}{Nm} \sum_k D(k) q_k^a q_0^0, \quad D(k) = \sum_{i, \text{imp}} \exp(ikX_i^0) (1 - e^{ikd}). \quad (4.2)$$

The total Hamiltonian is

$$H = H_0 + H_{\text{imp}}, \quad (4.3)$$

where H_0 is given by Eq. (3.3). The Hamiltonian is next written in terms of the creation-destruction operators a_{kj} and then transformed to the interaction representation (see Appendix III),

$$H = \frac{1}{2} [(\dot{p}_0^0)^2 + \omega_T^2 (q_0^0)^2] - \frac{ne}{b} E e^{i\omega t} \left(\frac{2N}{m} \right)^{\frac{1}{2}} q_0^0 - \frac{K'}{Nm} \sum_{k,j} D(k) a_{kj}^a \exp(i\omega_{kj}^a t) q_0^0. \quad (4.4)$$

¹¹ M. Blackman, Z. Physik **86**, 421. (1933).

The equations of motion for the system are

$$\begin{aligned} \dot{q}_0^0 &= p_0^0, \\ \dot{p}_0^0 &= -\omega_T^2 q_0^0 + \frac{ne}{b} E e^{i\omega t} \left(\frac{2N}{m} \right)^{\frac{1}{2}} \\ &\quad + \frac{K'}{Nm} \sum_{k,j} D(k) a_{kj}^a \exp(i\omega_{kj}^a t), \\ \dot{a}_{kj}^a &= -i \frac{K'}{2Nm} \frac{D(-k) q_0^0}{\omega_{k,j}^a} \exp(i\omega_{k-j}^a t). \end{aligned} \quad (4.5)$$

If we let $q_0^0 = q_0^0(0) e^{i\omega t}$, the set of Eqs. (4.5) can be combined simply to yield the equation of motion for a damped driven oscillator,

$$\ddot{q}_0^0 + (\omega_T^2 + i\Gamma) q_0^0 = (ne/b) E e^{i\omega t} (2N/m)^{\frac{1}{2}}, \quad (4.6)$$

with

$$\Gamma = \frac{1}{2} \left(\frac{K'}{Nm} \right)^2 \sum_{k,j} \frac{D(k) D(-k) \sin[(\omega + \omega_{k-j}^a) t]}{\omega_{kj}^a (\omega + \omega_{k-j}^a)}. \quad (4.7)$$

(Note that $\Gamma = \omega\gamma$; where γ has been defined in Sec. I.)

The damping constant Γ can be evaluated by going to the limit of a chain of infinite length. The damping constant is found to be

$$\Gamma = (4K'/m)^2 (n/2N) [\omega/(\omega_0^0)^3], \quad (4.8)$$

$(n/2N)$ is the line density of modified springs. The damping arises since phonons of microwave pump frequency virtually excited in the polarization mode are scattered into an acoustic mode whose frequency is equal to the microwave pump frequency.¹² Crystalline momentum is not conserved in the process. In general the polarization mode phonon is scattered into any mode whose frequency is equal to the microwave frequency.

From Eqs. (4.6) and (4.8) the loss tangent may be written

$$\tan \delta = \Gamma/(\omega_T^2 - \omega^2) \approx \Gamma/\omega_T^2 \sim \omega/(T - T_C). \quad (4.9)$$

Use has been made of conditions (a), (b), and (c) of Sec. I. Part of the observed loss tangent of strontium titanate is in agreement with Eq. (4.9) (Figs. 1 and 5 in reference 1). The temperature dependence of the loss tangent is a reflection of the temperature dependence of the frequency of the transverse polarization mode. This temperature dependence will be the same for any temperature independent damping process. High-loss polycrystalline samples of barium-strontium

¹² This is not quite true. Since the damping constant γ is of the order of the microwave pump frequency, polarization mode phonons are virtually excited in a band of width comparable to the microwave frequency. These phonons are therefore scattered into a band of acoustic frequencies. The treatment of the damping in this section is still well defined since the width of the band is small compared with the range of frequencies of the acoustic branch. These considerations also apply to Sec. V.

titanate mixtures¹³ and single-crystalline samples of barium titanate⁷ exhibit loss tangents that are described quite well by Eq. (4.9). The loss tangent of crystalline SrTiO₃ increases linearly with temperature at the higher temperatures (Fig. 1 in reference 1). It will be shown in the next section that the damping of microwaves due to lattice anharmonic interactions may be held responsible for this behavior.

An interesting question to consider is the following one. Is the order of magnitude of the SrTiO₃ loss tangent reasonable for pump frequencies at which no relaxation of the dielectric constant is observed? We will show that the order of magnitude of the loss tangent can be obtained with reasonable values for the parameters of the preceding analysis. Using Eqs. (4.8) and (4.9) one can write

$$\tan\delta \approx (4K'/m)^2 (n/2N) [\omega/(\omega_0^0)^3 \omega_T^2]. \quad (4.10)$$

Let us assume that the change in the spring constant K' is of the same order as the spring constant K .

Since $(\omega_0^0)^2 = 4K/m$ [Eq. (3.5)], one can write

$$\tan\delta \approx (n/2N) [\omega \omega_0^0 / \omega_T^2]. \quad (4.11)$$

Since $\tan\delta$, ω , ω_0^0 , and ω_T are either known or can be estimated, one can obtain an order-of-magnitude estimate for $(n/2N)$:

$$n/2N \approx 10^{-3}.$$

A three-dimensional treatment of the damping would lead one to interpret $(n/2N)$ as the volume density of modified springs. This result shows that it is not unreasonable to attribute the observed microwave loss to some type of imperfection damping of the polarization mode. It is emphasized once more that the actual detailed origin of the damping is still to be determined.

A word should be said about the frequency dependence of the loss tangent. The frequency dependence of the loss tangent for all the samples studied to date is linear.¹ The damping mechanism considered in this section was chosen specifically for this reason. Had we chosen pairs of modified springs (symmetric about a given ion) distributed randomly, the loss tangent would have been proportional to the cube of the pump frequency. It can be argued that any damping mechanism which gives rise to a loss tangent with a stronger than linear dependence on frequency would not be observed. Any extra power of ω in the numerator of Eq. (4.10) would of necessity introduce a factor of ω_0^0 in the denominator of this expression (for dimensional reasons). Since $\omega/\omega_0^0 \approx 10^{-3}$ at K band, it seems unlikely that any nonlinear dependence of the loss tangent on frequency would be observed.

¹³ L. Davis, Jr., and L. G. Rubin, J. Appl. Phys. **24**, 1194 (1953); A. von Hippel, Revs. Modern Phys. **22**, 221 (1950); J. G. Powles and W. Jackson, Proc. Inst. Elec. Engr. **III**, **96**, 383 (1949).

V. ANHARMONIC DAMPING

The loss tangent of a single crystal of SrTiO₃ increases linearly with temperature at the highest temperatures (Fig. 1 in reference 1). This increase in loss is not believed due to bulk electronic semiconduction for several reasons.¹ The measured value of the conductivity is too small to account for the observed loss. The frequency dependence of the loss tangent is linear. One would expect a reciprocal dependence on frequency if the loss was due to electronic conduction. The temperature dependence of the loss does not appear to be exponential. In this section it will be shown that a third- or fourth-order anharmonic interaction may be held responsible for the observed behavior of the loss tangent.

First we consider the damping of microwaves due to third-order anharmonic interactions. Many years ago Pauli¹⁴ calculated the effect of a third-order anharmonic interaction on the damping of a linear chain of equal masses. The calculation described here is similar to the calculation of Pauli except for one feature—that is the temperature dependence of the polarization mode frequency. The notation and treatment to be presented is similar to a calculation of Blackman¹¹ concerning the damping of a linear diatomic chain.

The third-order anharmonic energy of a chain is

$$H_{\text{anh}} = \frac{1}{3}\alpha \sum_i [(x_i - u_{i-1})^3 - (x_i - u_{i+1})^3], \quad (5.1)$$

where α is the third-order coupling coefficient. The total Hamiltonian of the system is

$$H = H_0 + H_{\text{anh}}, \quad (5.2)$$

where H_0 is given by Eq. (3.3). The Hamiltonian [Eq. (5.2)] is then written in terms of the creation-destruction operators and transformed to the interaction representation¹⁵ (see Appendix III).

$$H = \frac{1}{2}[(p_0^0)^2 + \omega_T^2 (q_0^0)^2] - (ne/b) E e^{i\omega t} (2N/m)^{\frac{1}{2}} q_0^0 + \frac{1}{N^{\frac{1}{2}}} \sum_{k,k'} F(k,k') q_0^0 a_{k,j}^0 a_{k',j'}^0 \times \exp[i(\omega_{k,j}^0 + \omega_{k',j'}^0)t] \Delta_{(k+k')}, \quad (5.3)$$

$$F(k,k') = [4\alpha/(2m)^{\frac{3}{2}}] [(1 + e^{-ikd})(1 - e^{-ik'd}) + \text{c.c.}],$$

and

$$\Delta_{(k+k')} = 0 \quad \text{for } k+k' \neq 0, \\ = 1 \quad \text{for } k+k' = 0.$$

¹⁴ W. Pauli, Verhandl. deut. physik. Ges. **6**, 10 (1925).

¹⁵ We use the language of quantum mechanics to describe essentially a classical calculation. Quantum-mechanical results can be obtained simply by keeping track of the commutation relations and by assuming the initial oscillator states to be populated in accord with Bose-Einstein statistics. This is not necessary at temperatures sufficiently high so that a significant number of the states involved in the scattering are populated in accordance with classical statistics.

Only terms contributing to the damping of the polarization mode in lowest order have been retained. The equation of motion for the polarization mode coordinate is

$$\ddot{q}_0^0 + (\omega_T^2 + i\Gamma)q_0^0 = (ne/b)Ee^{i\omega t}(2N/m)^{1/2}, \quad (5.4)$$

where

$$\Gamma = \frac{kT}{4N} \sum_k \frac{|F(k, -k)|^2}{(\omega_k^0)^2 (\omega_k^a)^2} (\omega_k^0 - \omega_k^a) \times \frac{\sin[(\omega - \omega_k^0 + \omega_k^a)t]}{(\omega - \omega_k^0 + \omega_k^a)}, \quad (5.5)$$

$$\Gamma = [64(2)^{1/2} \alpha^2 kT / m^3 (\omega_0^0)^5] \omega,$$

and

$$\tan \delta = \Gamma / \omega_T^2 \sim [T / (T - T_C)] \omega. \quad (5.6)$$

For $T \gg T_C$ this will contribute a temperature-independent part to the loss tangent. The third-order damping essentially arises since a polarization mode phonon virtually excited by the electromagnetic field is destroyed with the simultaneous destruction of an acoustic phonon and the creation of an optical phonon. The linear temperature dependence of the damping constant results from the assumption that the acoustical and optical modes are populated in accordance with classical statistics. The anharmonic damping of microwaves presented here is somewhat artificial since the small microwave energy separation required between the acoustical and optical branches is achieved solely due to the choice of the spectrum of a monotonic chain. This small separation occurs near the edge of the zone. No anharmonic damping of the type described would result from the treatment of a diatomic chain since the separation between the acoustical and optical branches of the frequency spectrum would be of the order of optical frequencies. The work of Cochran,⁵ however, suggests that the low-lying transverse optical branch crosses the longitudinal acoustic branch at some point within the Brillouin zone. If the modes are populated in accordance with classical statistics near the crossover, one might expect some anharmonic damping of the type described. In the real crystal, other third-order damping processes are possible. A polarization mode phonon can decay into two acoustic phonons. The decay can also occur with the scattering of phonons between different acoustic branches. It is difficult to estimate the relative importance of the various processes until a more realistic picture of the lattice vibrational spectrum of SrTiO_3 is available. With similar reservations we proceed to calculate the microwave loss tangent due to fourth-order anharmonic interactions.

The fourth-order anharmonic energy of a chain is

$$H_{\text{anh}} = \frac{1}{4} \beta \sum_i [(x_i - u_{i-1})^4 + (x_i - u_{i+1})^4]. \quad (5.7)$$

The total Hamiltonian of the system,

$$H = H_0 + H_{\text{anh}}, \quad (5.8)$$

is written in terms of the creation-destruction operators a_{kj} and then transformed to the interaction representation

$$\begin{aligned} H = & \frac{1}{2} [(\dot{p}_0^0)^2 + \omega_T^2 (q_0^0)^2] \\ & - (ne/b) E e^{i\omega t} (2N/m)^{1/2} q_0^0 \\ & + \frac{1}{N} \sum_{k, k', k''} F(k, k', k'') q_0^0 a_{kj}^0 a_{k'j'}^a a_{k''j''}^a \\ & \times \exp[i(\omega_{k,j}^0 + \omega_{k',j'}^a + \omega_{k'',j''}^a)t] \\ & \times \Delta_{(k+k'+k'')}, \\ F(k, k', k'') = & \frac{3}{2} (\beta/m^2) [(1 + e^{-ikd})(1 - e^{-ik'd}) \\ & \times (1 - e^{-ik''d}) + \text{c.c.}]. \end{aligned} \quad (5.9)$$

The equations of motion for the system are

$$\dot{q}_0^0 = \dot{p}_0^0, \quad (5.10)$$

$$\begin{aligned} \dot{p}_0^0 = & -\omega_T^2 q_0^0 + \frac{ne}{b} E e^{i\omega t} \left(\frac{2N}{m} \right)^{1/2} \\ & - \frac{1}{N} \sum_{k, k', k''} F(k, k', k'') a_{kj}^0 a_{k'j'}^a a_{k''j''}^a \\ & \times \exp[i(\omega_{k,j}^0 + \omega_{k',j'}^a + \omega_{k'',j''}^a)t] \Delta_{(k+k'+k'')}, \end{aligned} \quad (5.11)$$

$$\begin{aligned} \dot{a}_{k,j}^0 = & \frac{i}{2N} \sum_{k', k''} \frac{F(-k, k', k'')}{\omega_{k,j}^0} q_0^0 a_{k'j'}^a a_{k''j''}^a \\ & \times \exp[i(\omega_{-k,j}^0 + \omega_{k',j'}^a + \omega_{k'',j''}^a)t] \\ & \times \Delta_{(-k+k'+k'')}, \end{aligned} \quad (5.12)$$

$$\begin{aligned} \dot{a}_{k',j'}^a = & \frac{i}{N} \sum_{k, k''} \frac{F(k, -k', k'')}{\omega_{k',j'}^a} q_0^0 a_{kj}^0 a_{k''j''}^a \\ & \times \exp[i(\omega_{k,j}^0 + \omega_{-k',j'}^a + \omega_{k'',j''}^a)t] \\ & \times \Delta_{(k-k'+k'')}. \end{aligned} \quad (5.13)$$

These equations are solved by assuming

$$a_{kj}(t) = b_{kj} + c_{kj}(t), \quad (5.14)$$

where the b_{kj} are diagonal in the noninteracting phonon representation and the $c_{kj}(t)$ are considered to be small compared with the b_{kj} . If we assume an harmonic time variation of the polarization mode coordinate,

$$q_0^0 = q_0^0(0) e^{i\omega t},$$

Eqs. (5.12) and (5.13) can be integrated.

$$\begin{aligned} c_{k,j}^0 = & \frac{i}{2N} \sum_{k', k''} \frac{F(-k, k', k'')}{\omega_{k,j}^0} q_0^0(0) b_{k'j'}^a b_{k''j''}^a \\ & \times \frac{\{\exp[i(\omega + \omega_{-k,j}^0 + \omega_{k',j'}^a + \omega_{k'',j''}^a)t] - 1\}}{i(\omega + \omega_{-k,j}^0 + \omega_{k',j'}^a + \omega_{k'',j''}^a)} \\ & \times \Delta_{(-k+k'+k'')}, \end{aligned} \quad (5.15)$$

$$c_{k',j',a} = \frac{i}{N} \sum_{k,k''} \frac{F(k, -k', k'')}{\omega_{k',j',a}} q_0^0(0) b_{kj^0} b_{k'',j'',a} \\ \times \frac{\{\exp[i(\omega + \omega_{kj^0} + \omega_{-k'-j',a} + \omega_{k'',j'',a})t] - 1\}}{i(\omega + \omega_{kj^0} + \omega_{-k'-j',a} + \omega_{k'',j'',a})} \\ \times \Delta_{(k-k'+k'')}. \quad (5.16)$$

Using Eqs. (5.10) to (5.16) and the relation

$$|b_k|^2 \equiv kT/2\omega_k^2, \quad (\text{equipartition law}), \quad (5.17)$$

the equation of motion for the polarization mode coordinate q_0^0 is

$$\ddot{q}_0^0 + (\omega_T^2 + i\Gamma)q_0^0 = (ne/b)Ee^{i\omega t}(2N/m)^{1/2}, \quad (5.18)$$

where

$$\Gamma = \frac{(kT)^2}{4N^2} \sum_{k,k'} \frac{|F(k, k' - k - k')|^2}{(\omega_k^0)^2 (\omega_{k',a})^2 (\omega_{k+k',a})^2} \\ \times (\omega_k^0 - \omega_{k',a} - \omega_{k+k',a}) \\ \times \frac{\sin[(\omega - \omega_k^0 + \omega_{k',a} + \omega_{k+k',a})t]}{(\omega - \omega_k^0 + \omega_{k',a} + \omega_{k+k',a})}, \quad (5.19)$$

and

$$\tan\delta = \frac{\Gamma}{\omega_T^2} \sim \frac{T^2}{T - T_C} \omega. \quad (5.20)$$

The fourth-order damping described here is essentially due to the decay of a polarization mode phonon with the simultaneous destruction of two acoustic phonons and the creation of an optical phonon. At temperatures high compared with T_C , the loss tangent [Eq. (5.20)] increases linearly with temperature. This is in agreement with the experimental results (Fig. 1 in reference 1). The linear frequency dependence of Eq. (5.20) is also in agreement with observation. The quadratic temperature dependence of the damping constant can also result from two successive third order anharmonic scatterings. The first scattering could destroy the polarization mode phonon along with an acoustic phonon and create an optical phonon. Except for conservation of energy, this is similar to the third order process treated in the beginning of this section. The second scattering would destroy another acoustic phonon along with the optical phonon previously created and then create yet another optical phonon. These successive three-phonon processes are equivalent to the four-phonon process discussed previously. Another four-phonon process contributing to the damping of the linear chain is one which involves two optical phonons and one acoustic phonon. This has not been considered explicitly but can be treated by the same procedure described in this section. The contribution to the loss tangent from this process is of the same form as Eq. (5.20). Damping due to one four-phonon process or to two successive three-phonon processes does not

require a close approach (to within the order of microwave frequencies) or crossover of the optical and acoustical branches as does the damping due to a three-phonon process. A significant fraction of the modes involved, however, must be populated in accordance with classical statistics. In the real crystal other four-phonon processes are possible. The polarization mode phonon can decay into three acoustic phonons. The decay can also occur with the scattering of phonons between different acoustic branches. These processes will also contribute loss tangents with a temperature dependence given by Eq. (5.20).

VI. CONCLUSION

Figure 5 in the preceding paper shows a plot of $(T - T_C) \tan\delta$ vs temperature for crystalline SrTiO_3 doped with Gd^{3+} and Fe^{3+} . The solid curve has been fitted to the data by using the following expression:

$$(T - T_C) \tan\delta = [A + BT + DT^2].^* \quad (6.1)$$

The fitted curve agrees with the data over the measured temperature range above 110°K to within the experimental accuracy.¹⁰ The work of Rupprecht and Bell indicates that the parameters B and D are intrinsic properties of the sample unaffected by the quantity of Fe^{3+} or Gd^{3+} added to the lattice. They also conclude that the parameter A is dependent on the impurity content of the material. Figure 1 in the preceding paper indicates that above the transition temperature, the sample of pure crystalline SrTiO_3 has a negligible contribution to its loss tangent from imperfection scattering. The parameters B and D , however, have the same values as the doped material. These experimental results are in agreement with the explanation proposed in this paper and elsewhere.²

APPENDIX I

Identifying the square of the optical index of refraction, n , with the first two terms in Eq. (3.6), we write

$$b = 2\bar{\alpha}/8d^3\epsilon_0(n^2 - 1) \quad (\text{AI.1})$$

Using (AI.1) and the definition of b [Eq. (2.6)] we find

$$2\bar{\alpha}/\epsilon_0 = 8d^3/[1/(n^2 - 1) + a]. \quad (\text{AI.2})$$

Since n^2 and d are known from experiment, a choice of the constant a will determine the average electronic polarizability $\bar{\alpha}$ and the constant b . a is determined in Sec. II.

$$a = (1 + 8.182)/6 = 1.53.$$

This value is slightly large since we have neglected contributions to the local field from the strontium ions and oxygen ions not lying on a chain. For simplicity we chose $a = 1$. This determines an enhancement factor

$$3a/b = 15,$$

which is in rough agreement with Slater's⁸ enhancement

factor of 16. Using $a=1$, $8d^3=59.6\times 10^{-30}$ m³, and $n^2-1=3.961$, one obtains

$$b=0.202, \quad \bar{\alpha}/\epsilon_0=23.8\times 10^{-30} \text{ m}. \quad (\text{AI.3})$$

Next the frequency of the transverse polarization mode is determined. We had [Eqs. (3.8) and (3.11)]

$$\omega_T^2 = \frac{(ne)^2 ac}{4\epsilon_0 md^3 b} (T - T_C), \quad (\text{AI.4})$$

$$\epsilon = C/(T - T_C), \quad C = 1/abc.$$

A knowledge of the Curie constant C determines c

$$C = 8.25 \times 10^4 \text{ }^\circ\text{K}, \quad c = 6.00 \times 10^{-5} \text{ }^\circ\text{K}^{-1}.$$

We will also use

$$m = 2m_0 m_{\text{Ti}} / (m_0 + m_{\text{Ti}}) = 4.03 \times 10^{-26} \text{ kg}.$$

Substituting these values in (AI.4) results in

$$\omega_T = 8.45 \times 10^{11} n (T - T_C)^{\frac{1}{2}}. \quad (\text{AI.5})$$

To determine the second- and fourth-order coupling constants, we write [Eqs. (AII.12) and (AII.13)]

$$4K/m = (ne)^2 a / 4\epsilon_0 md^3 b, \quad (\text{AI.6})$$

$$48\beta k / m^2 (\omega_0^0)^2 = (ne)^2 ac / 4\epsilon_0 md^3 b, \quad (\text{AI.7})$$

where k is Boltzmann's constant.

Dividing (AI.7) by (AI.6), we obtain

$$48\beta k / m^2 (\omega_0^0)^4 = c. \quad (\text{AI.8})$$

Using (AI.6), the spring constant is found to be

$$K = 1.2 \times 10^2 n^2 \text{ joule/m}^2. \quad (\text{AI.9})$$

(AI.8) determines the fourth-order coupling constant

$$\beta = 2.1 \times 10^{22} n^4 \text{ joule/m}^4. \quad (\text{AI.10})$$

When one of the ions is moved a lattice distance, the lattice energy expansion in powers of the displacement should diverge, contributions from each order roughly becoming equal.⁸ Setting the harmonic contribution to the energy equal to the fourth-order contribution,

$$Kd^2 \approx (\beta/2)d^4,$$

the number of electronic charges per ion is found to be $n \approx 0.5$.

APPENDIX II

The free energy of a chain will be calculated to first order in the fourth-order anharmonic coupling constant β . The free energy F is written

$$-F/kT = \ln Z_0 - (Z_1/Z_0), \quad (\text{AII.1})$$

$$Z_0 = \frac{1}{h^{2N}} \int_{\text{phase space}} e^{-H_0(p,q)/kT} dp dq, \quad (\text{AII.2})$$

$$Z_1 = \frac{1}{(kT)h^{2N}} \int e^{-H_0(p,q)/kT} H_{\text{anh}}(p,q) dp dq,$$

$$H_0 = \frac{1}{2} \sum_k [p_k^a p_{-k}^a + (\omega_k^a)^2 q_k^a q_{-k}^a] + \frac{1}{2} \sum_k [p_k^0 p_{-k}^0 + (\omega_k^0)^2 q_k^0 q_{-k}^0] - neE_0(2N/m)^{\frac{1}{2}} q_0^0, \quad (\text{AII.3})$$

$$H_{\text{anh}} = \frac{3\beta}{Nm^2} \sum_k |1 - e^{ikd}|^2 (q_k^a q_{-k}^a + q_k^0 q_{-k}^0) (q_0^0)^2. \quad (\text{AII.4})$$

To eliminate the term bilinear in the applied field and polarization mode coordinate we perform the following transformation.

$$q_0^0 \rightarrow q_0^0 + [neE_0/(\omega_0^0)^2] (2N/m)^{\frac{1}{2}}. \quad (\text{AII.5})$$

Next, the real coordinates, α_k^a and α_k^0 are introduced:

$$\begin{aligned} \alpha_k^a &= [1/(2)^{\frac{1}{2}}] (q_k^a + q_{-k}^a), \\ \alpha_k^0 &= [1/(2)^{\frac{1}{2}}] (q_k^0 + q_{-k}^0), \\ \alpha_{-k}^a &= [1/i(2)^{\frac{1}{2}}] (q_k^a - q_{-k}^a), \\ \alpha_{-k}^0 &= [1/i(2)^{\frac{1}{2}}] (q_k^0 - q_{-k}^0), \end{aligned} \quad (\text{AII.6})$$

(note: α_k and α_{-k} are independent of each other). After the transformation (AII.5) and (AII.6) the Hamiltonian is

$$\begin{aligned} H &= \frac{1}{2} \sum_k [(\dot{\alpha}_k^a)^2 + (\omega_k^a)^2 (\alpha_k^a)^2] + \frac{1}{2} \sum_k [(\dot{\alpha}_k^0)^2 + (\omega_k^0)^2 (\alpha_k^0)^2] \\ &+ \frac{6\beta (ne)^2 E_0^2}{m^3 (\omega_0^0)^4} \left\{ \sum_k |1 - e^{ikd}| (\alpha_k^a)^2 + \sum_k |1 + e^{ikd}|^2 (\alpha_k^0)^2 \right\} - \frac{(ne)^2 E_0^2 N}{m (\omega_0^0)^2}. \end{aligned} \quad (\text{AII.7})$$

The free energy can be obtained to first order in the fourth-order anharmonic coupling constant by using (AII.1), (AII.2), (AII.7). Integrations are performed over the phase space of real coordinates. One obtains

$$\begin{aligned} F &= - \frac{(ne)^2 E_0^2 N}{m (\omega_0^0)^2} - 2NkT \ln \left(\frac{kT}{h\bar{\omega}} \right) \\ &+ \frac{48\beta kT (ne)^2 E_0^2 N}{m^3 (\omega_0^0)^6}, \end{aligned} \quad (\text{AII.8})$$

$\bar{\omega}$ is the geometrical mean of all the frequencies (neglecting of course the $k=0$ acoustical frequency). The

line polarization of a chain is

$$P_{\text{oh}} = -\frac{\partial F}{\partial E_0} = \frac{2(ne)^2 E_0 N}{m(\omega_0^0)^2} - kT \frac{96\beta (ne)^2 E_0 N}{m^3 (\omega_0^0)^6}, \quad (\text{AII.9})$$

which may be written as

$$P_{\text{oh}} = \frac{2(ne)^2 E_0 N}{m(4K/m)_{\text{eff}}},$$

with

$$\left(\frac{4K}{m}\right)_{\text{eff}} = \frac{4K}{m} + \frac{48kT\beta}{m^2(\omega_0^0)^2}. \quad (\text{AII.10})$$

We had assumed [Eq. (3.8)] that

$$\left(\frac{4K}{m}\right)_{\text{eff}} = \frac{(ne)^2 a(1-cTc)}{2\epsilon_0 m d^3 b} + \frac{(ne)^2 ac}{2\epsilon_0 m d^3 b} T. \quad (\text{AII.11})$$

Identifying the terms of (AII.10) and (AII.11), we obtain the following two relations:

$$\frac{4K}{m} = \frac{(ne)^2 a(1-cTc)}{2\epsilon_0 m d^3 b}, \quad (\text{AII.12})$$

$$\frac{48\beta k}{m^2(\omega_0^0)^2} = \frac{(ne)^2 ac}{2\epsilon_0 m d^3 b}. \quad (\text{AII.13})$$

Equation (AII.12) determines the spring constant K , and states essentially that the long-range dipolar interaction cancels the effect of the short-range repulsion to roughly one part in a thousand. Equation (AII.13) relates the fourth-order coupling constant to the Curie constant.

APPENDIX III

The complex normal coordinates and momenta are related to the creation-destruction operators by the following expressions:

$$q_k^a = a_{k,1}^a + a_{k,-1}^a = \sum_j a_{k,j}^a,$$

$$q_k^0 = a_{k,1}^0 + a_{k,-1}^0 = \sum_j a_{k,j}^0,$$

$$p_k^a = i\omega_{k,1}^a (a_{-k,1}^a - a_{-k,-1}^a),$$

$$p_k^0 = i\omega_{k,1}^0 (a_{-k,1}^0 - a_{-k,-1}^0);$$

where $j = \pm 1$ and

$$[a_{-k-j}, a_{k',j'}] = \delta_{kk',jj'} \hbar/2\omega_{jk}.$$

The harmonic part of the Hamiltonian is

$$H_0 = \sum_j \sum_k (\omega_{kj}^a)^2 a_{kj}^a a_{-k-j}^a + \sum_j \sum_{k \neq 0} (\omega_{kj}^0)^2 a_{kj}^0 a_{-k-j}^0 \\ + \frac{1}{2} [(p_0^0)^2 + \omega_T^2 (q_0^0)^2] - (ne/b) E e^{i\omega t} (2N/m)^{1/2} q_0^0.$$

In the interaction representation this becomes

$$H_{\text{int}} = \exp(iH_0' t/\hbar) H_0 \exp(-iH_0' t/\hbar) - H_0' \\ = \frac{1}{2} [(p_0^0)^2 + \omega_T^2 (q_0^0)^2] - (ne/b) E e^{i\omega t} (2N/m)^{1/2} q_0^0,$$

where

$$H_0' = \sum_j \sum_k (\omega_{kj}^a)^2 a_{kj}^a a_{-k-j}^a + \sum_j \sum_{k \neq 0} (\omega_{kj}^0)^2 a_{kj}^0 a_{-k-j}^0.$$

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