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Long-wavelength soft modes, central peaks, and the Lyddane-Sachs-Teller relation

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A derivation of the Lyddane-Sachs-Teller relation is presented which depends only on the broad requirements of statistical mechanics. Mode frequencies are introduced as peaks in the dielectric response to avoid the introduction of a Hamiltonian. Using this approach the modes may be very anharmonic, may be coupled, and may have a central-peak character and yet be precisely entered into the Lyddane-Sachs-Teller relation. The number of such modes need not conform to the number predicted by the usual group-theoretic methods applied to the symmetry of the solid. Examples are given of several types of spectra and the requirements of mode softening are discussed.

I. INTRODUCTION

Lyddane *et al.*[1] were the first to derive the relationship between the dielectric constants of a crystal $\epsilon(0)$ (the dielectric constant at low frequencies) and $\epsilon(\infty)$ (the dielectric constant at high frequencies), and the long-wavelength lattice vibration frequencies ω_l and ω_t:

$$\epsilon(0)/\epsilon(\infty) = \omega_l^2/\omega_t^2 . \tag{1}$$

They derived Eq. (1) by a fairly detailed argument which involved introduction of a microscopic charge in each unit cell and a consideration of the difference between the macroscopic field and the local field and the use of a Lorentz cavity. After some manipulations, they obtained the surpising result given by Eq. (1). It is surprising in the sense that the reduced mass of the ions, the effective charge, and the cell parameter which were introduced have all disappeared in the final result. We note that $\epsilon(0)$ and[2] $\epsilon(\infty)$ are macroscopic quantities, unlike the microscopic parameters effective charge, force constant, etc. We also regard the vibrational frequencies ω_l and ω_t as macroscopic quantities following the discussion by Born and Huang.[3]

Kurosawa[4] and Cochran and Cowley[5] have derived Eq. (1) by using a specific model for the lattice vibrations at long wavelengths. They set up an energy expression which is harmonic and which depends on macroscopic ion displacement and electric fields. Using this approach there is considerable algebra necessary concerning the mass density, force constant, and charge matrices, which parameters all vanish in the final result which is written in the form

$$\frac{\epsilon(0)}{\epsilon(\infty)} = \prod_{j=4}^{N} \frac{\omega_{lj}^2}{\omega_{tj}^2} . \tag{2}$$

The product on the right-hand side of Eq. (2) extends over all the optically active modes allowed by group theory, but omits the three low-frequency modes which have acoustic character.[5]

It is our viewpoint that the Lyddane-Sachs-Teller (LST) relation is a macroscopic relation which can be derived from the general principles of statistical mechanics. The introduction of a harmonic Hamiltonian or energy expression is unnecessary. The use of force constants and masses, etc., in the theories described above was only necessary so that some quantity related to the square root of a (force constant)/mass could be called a frequency. If we give up the introduction of a harmonic Hamiltonian, we will have to define macroscopic lattice frequencies in a different way. At the same time we note that we will not be restricted to the product $j=4, N$ for the number of modes to be included in Eq. (2). Because of this it will be possible for what are commonly known as combination bands and also for central peaks to enter the LST relation, as we intuitively feel they must.

Barker[6] derived an extended LST relation which held for many modes and included damping. This was accomplished by introducing equations of motion which had damping terms and hence were not derived from a conservative Hamiltonian. That work stressed that the parameters on the right-hand side of Eq. (2) are the poles and zeros[7] of the dielectric constant. Once this was recognized, the derivation became an exercise in polynomial algebra with no need to introduce masses, force constants, or charges which are later eliminated. The same approach was extended to cover the very broad mode found in some ferroelectrics at low frequencies with the Debye dispersion form.[8] Lax and Nelson have derived a slightly more-general form of the LST relation for an anisotropic dielectric which shows that only zeros of a certain function of the dielectric tensor determine the ratio on the left-hand side of (2) for arbitrary mode propagation directions.[7,9]

Since anharmonicity is extremely important in ferroelectric crystals, and appears to be important in theories which attempt to predict a central peak in the fluctuation spectra, it appears reasonable to develop an approach which does not start from a harmonic Hamiltonian. We develop such an approach below and give pictorial examples of specific spectra to show various kinds of modes and how they enter the LST relation. We then show how the macroscopic theory of phase transitions requires mode softening (i.e., $\omega_t \to 0$) at a ferroelectric transition.

II. IMPLICATIONS OF STATISTICAL MECHANICS

In this section we follow the notation and much of the treatment given by Landau and Lifshitz in their discussion of fluctuations.[10] A solid is pictured as possessing macroscopic coordinates $Q_1, Q_2, \ldots$. For a theory of dielectrics we take these to correspond to optically active long-wavelength lattice vibrations. If one of these coordinates is set vibrating, there are present in the crystal frictional processes which gradually bring the motion to a halt. The kinetic energy connected with Q has been dissipated in the form of heat. We next introduce an external force E which acts on the coordinates. The time dependence of E can be expanded by a Fourier integral to a set of components with time dependence $e^{-i\omega t}$. Using the language of dielectrics,[11] we take the external force to be the macroscopic electric field so that the perturbation which results from E is the electric displacement D,

$$D(\omega) = \epsilon(\omega) E(\omega) . \tag{3}$$

Since the time dependence of the coordinates Q_j must be real functions, it follows that $\epsilon(\omega)$ is the Fourier transform of a real function of time.[10] Since the power dissipation must be positive definite and is connected with the imaginary part of $\epsilon(\omega)$, we find that the latter is always positive for positive ω. These fairly general statements are, in fact, all we need to derive our results. Specifically, they are enough to show that $\epsilon(\omega)$ is a complex function of frequency whose imaginary part is positive and approaches zero as frequency approaches infinity, and that

$$\epsilon(-\omega) = \epsilon^*(\omega^*) , \tag{4}$$

$$\epsilon = \epsilon' + i\epsilon'' , \quad \epsilon^* = \epsilon' - i\epsilon'' , \quad \epsilon'' > 0 . \tag{5}$$

In addition, the real and imaginary parts of ϵ denoted by ϵ' and ϵ'' must obey the Kramers-Kronig relations. These integral relations follow from causality arguments.[10] The Kramers-Kronig relation we will need below is

$$\epsilon'(\omega) - \epsilon(\infty) = \frac{2}{\pi} \int_0^\infty \frac{x \epsilon''(x)\, dx}{x^2 - \omega^2} , \tag{6}$$

where the variable of integration x is taken along the real frequency axis.[2] Note that since ϵ'' vanishes at infinite frequency, a prime is not necessary on $\epsilon(\infty)$.

III. LST RELATION FROM KRAMERS-KRONIG INTEGRAL

The LST relation may be obtained by examining the Kramers-Kronig integral given in Eq. (6) at two special frequencies. We must first specify a certain minimum amount of information about ϵ''. If we specify nothing, *a priori* then we know only that ϵ'' falls off at high frequencies as required by statistical mechanics. By not specifying any information we are essentially not specifying any mode structure (peaks) in ϵ'' and it is natural that we would not be able to obtain any information to fill in the right-hand side of Eq. (1).

We will start with the simplest possible assumption, namely that ϵ'' goes to zero at zero frequency and has a peak at a frequency ω_t. The special case where ϵ'' does not go to zero at low-frequencies must from physical reasoning correspond to a metal or a material with free carriers. This case is treated in a subsection below. To summarize, we specify that the spectrum of ϵ'' has one peak located at a frequency ω_t. Equation (6) is first evaluated at low frequencies

$$\epsilon'(0) - \epsilon(\infty) = \frac{2}{\pi} \int_0^\infty \frac{\epsilon''(x)\, dx}{x} . \tag{7}$$

Equation (7) tells us essentially how much the peak in ϵ'' contributes to the low-frequency dielectric constant. Next, Eq. (6) is evaluated at a special frequency to which we will give the name ω_l, and which we will provisionally call the longitudinal mode frequency. The special characteristic of ω_l is that here $\epsilon'(\omega)$ is zero.[12] Evaluating Eq. (6) at ω_l, we obtain

$$-\epsilon(\infty) = \frac{2}{\pi} \int_0^\infty \frac{x \epsilon''(x)\, dx}{x^2 - \omega_l^2} . \tag{8}$$

Finally, use is made of the fact that the spectrum of ϵ'' is sharply peaked near ω_t. If the spectrum is strongly peaked, the integral in Eq. (8) may be approximated in the following way:

$$-\epsilon(\infty) \approx \frac{2}{\pi} \frac{\omega_t^2}{\omega_t^2 - \omega_l^2} \int_0^\infty \frac{\epsilon''(x)\, dx}{x} . \tag{9}$$

Note that this approximation, bringing out some of the frequency dependence in front of the integral sign, is exact and trivial in the case that ϵ'' has a δ-function spectrum centered at the frequency ω_t.

The integral which appears in Eqs. (7) and (9) may be eliminated between these equations to obtain

$$\epsilon(0)/\epsilon(\infty) = \omega_l^2/\omega_t^2 . \tag{10}$$

This is the desired result.[13] This LST relation contains the starting information, that is, the dielectric constant at high and low frequencies; it contains the frequency ω_t which we specified as a region where the absorption was peaked; and it contains a frequency ω_l which was defined as the frequency where the dielectric constant is zero. For the discussion in this section only, we will content ourselves with the definitions[13]

$$\omega_t = \text{transverse-optic-mode frequency} = \text{frequency where } \epsilon'' \text{ peaked}, \tag{11a}$$

$$\omega_l = \text{longitudinal-optic-mode frequency} = \text{frequency where } \epsilon' = 0 . \tag{11b}$$

The reader who wishes to assure himself that these are reasonable definitions is referred to the discussion of response functions by Barker and Loudon.[14] The reader who is unhappy with these definitions and would like to see ω_t related, for example, to the time dependence of some actual coordinate as it oscillates after being given an initial impulse must realize that the definitions of Eq. (11) are the price we pay for having given up the detailed and restrictive harmonic Hamiltonian approach. The system we envisage here may have any amount of anharmonicity. If a single coordinate is given an impulse at $t=0$, the energy may couple very strongly to some or all other modes, and individual motions need not be even approximately sinusoidal.

One problem remains in regarding Eqs. (7)–(11) as a general derivation of the LST relation. ω_l was introduced as the frequency where the real part of the dielectric constant was zero, allowing Eq. (8) to be written. For very broad modes, ϵ' may not be zero anywhere on the real frequency axis. We will find that the longitudinal mode resonance is properly regarded as a complex frequency and that the LST relation still exists, but the absolute value of this complex number is required. In the remainder of this paper, we consider such cases using algebraic methods, which have intuitive appeal and more significance for spectroscopists. Integral methods could be used as was done in the above equations, but these become tedious for paths of integration in the complex frequency plane other than along the real frequency axis.

IV. LST RELATION FOR SOME SPECIFIC SPECTRAL FUNCTIONS

In this section we will examine some specific dielectric functions including classical oscillators, Debye dispersion, frequency-dependent damping, coupled modes, and central peaks. We also examine the problems mentioned earlier of free carriers which lead to ϵ'' having a nonvanishing value as the frequency approaches zero.

A. Classical oscillator modes

Assume the spectrum of ϵ'' is given by the formula

$$\epsilon''(\omega) = \omega S \omega_t^2 \gamma / [(\omega_t^2 - \omega^2)^2 + \omega^2\gamma^2] . \tag{12}$$

This is the form of a classical oscillator mode of strength S and damping γ. The dielectric response of a solid is completely specified by Eq. (12) and the additional parameter $\epsilon(\infty)$ in the frequency range of interest here. By Kramers-Kronig analysis of Eq. (12) (or by inspection) we find that the complete dielectric function is

$$\epsilon(\omega) = \epsilon(\infty) + S\omega_t^2/(\omega_t^2 - \omega^2 - i\omega\gamma) . \tag{13}$$

At this stage we have a spectrum defined by four parameters including $\epsilon(\infty)$. ω_t is the frequency where ϵ'' is peaked, as long as γ is not too large. We therefore have all the ingredients of Sec. III except ω_l.

The equation

$$\epsilon(\omega) = 0 \tag{14}$$

must now be solved. We denote the roots of Eq. (14) by ω_l. There are two roots given by

$$\omega_l = \pm[\omega_t^2\epsilon(0)/\epsilon(\infty) - \tfrac{1}{4}\gamma^2]^{1/2} - i(\tfrac{1}{2}\gamma) . \tag{15}$$

We define ω_l given by Eq. (15) to be the longitudinal-optic-mode frequency. This ω_l is not identical to the ω_l appearing in Eq. (8), which was a real number. The present ω_l is complex. Eq. (14) is the exact definition of the longitudinal-optic-mode frequency we will use for the remainder of this paper. If γ is not too large (compared with ω_t), then the entire derivation given in Sec. III goes through for the classical oscillator dispersion of Eq. (13). To derive the LST relation directly from Eq. (13) we merely consider the absolute value squared of ω_l given above

$$|\omega_l|^2 = \omega_t^2\epsilon(0)/\epsilon(\infty) . \tag{16}$$

This is the LST relation for the classical oscillator. Figure 1 shows interrelation of frequencies and the peaks in the dielectric spectrum. At the top of the figure the ϵ'' spectrum is displayed; it possesses a peak near the frequency ω_t. The poles and zeros of $\epsilon(\omega)$ [Eq. (13)] are plotted in the lower part of the figure. Since the absolute value of a complex number is just the distance from the origin to that number, we are able to label this distance in Fig. 1. A separate calculation of the location of the poles of $\epsilon(\omega)$ shows that in fact the parameter ω_t is really similar to ω_l, i.e., it is also the distance from the origin to, in this case, the pole. Therefore, it is also the absolute value of some complex number. It is only an accident that the standard way of writing the classical oscillator, Eq. (13), uses this parameter rather than the separate real

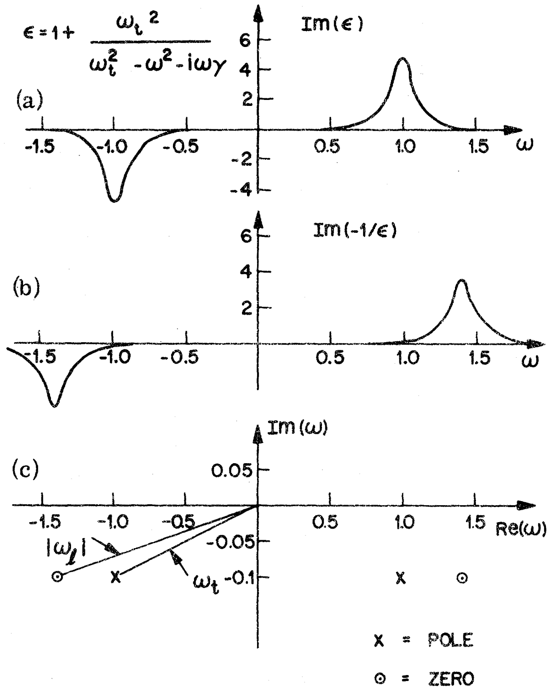

FIG. 1. Classical oscillator dispersion. (a) Dielectric spectrum Im(ε) plotted for real frequency. (b) Dielectric spectrum Im(−1/ε) plotted for real frequency; ω_t is chosen to be 1.0 here. (c) Location of poles and zeros in the complex frequency plane. Note that the peaks in (a) and (b) lie near the projections of the poles and zeros on the real frequency axis. Poles and zeros occur in pairs mirrored in the imaginary frequency axis.

and imaginary parts of the pole frequency. For reasonably low damping the poles and zeros occur in pairs which are reflections in the imaginary frequency axis. This is guaranteed by Eq. (4). For much larger damping the poles and then the zeros approach the imaginary frequency axis and finally lose their real part entirely. This behavior has been discussed before in Ref. 8.

Parts a and b of Fig. 1 show the spectra which contain the usual information that is available to an experimentalist concerning these poles and zeros lurking in the imaginary frequency plane. The ϵ'' spectrum contains information on long-wavelength fluctuations of the polarization which have transverse character.[14] Note that the peak comes near the projection of the pole on the real frequency axis. The Im(− 1/ε) spectrum contains the details of polarization fluctuations of longitudinal character. We note that the peak in this spectrum comes near the projection of ω_l on the real frequency axis. Both Im(ε) and Im(− 1/ε) are odd functions of frequency along the real frequency axis. This is another result following from Eq. (4). The significance of the two spectra shown in Fig. 1 is that they may be obtained from infrared experiments on a solid (or liquid or gas). The thermal fluctuations of the polarization are also completely determined by these spectra[14] so that a scattering experiment can, under certain conditions, also yield the spectra. The spectra completely determine the dielectric function; once determined, they can be manipulated to check that they fit Eq. (13), and if they do, the parameters ω_l and ω_t may be put in Eq. (16) to determine the ratio of dielectric constants. If the spectra do not fit the form of Eq. (13), we then have a problem. We hope to clarify this situation in the following sections. However, we note here that there has been a tendency by some writers in that situation to immediately state that the LST relation has "broken down." Since our arguments have shown that the LST relation breaks down only when statistical mechanics or causal behavior breaks down, we reject such a viewpoint.[15]

The extension of the LST relation to the case of a sum of classical oscillator modes for Eq. (12) uses the same methods and has been presented earlier.[6,8] The result is

$$\epsilon(0)/\epsilon(\infty) = |\omega_{l1}|^2 |\omega_{l2}|^2 \cdots / \omega_{t1}^2 \omega_{t2}^2 \cdots , \qquad (17)$$

where the product is taken over all the poles and zeros, i.e., peaks in the spectral functions which occur in the spectrum. Note that since we have not set up a harmonic Hamiltonian or system of equations with a definite number of coordinates, we cannot say how many terms there should be in the product. For a simple well-behaved solid like NaCl, group theory predicts one long-wavelength optic mode. It seems reasonable, in that case, that the product in Eq. (17) should have only one transverse and one longitudinal frequency on the right-hand side. This in fact holds to an accuracy [in ε(0)] of about 2% at 300 K. To higher accuracy more terms must be multiplied together on the right-hand side. These terms would be classical oscillator modes used to represent low-frequency combination bands, for example, which are known to exist in the ϵ'' spectrum of NaCl. The LST relation has not broken down and is exact as long as we include all modes on the right-hand side of Eq. (17) in the sense of accounting for all peaks in the spectrum of ϵ''. This is because our derivation (Sec. III) depends on the spectrum of ϵ'' and on all the peaks it contains. It does not depend on any kind of mode-counting scheme which arises from a harmonic Hamiltonian and the application of group theory.

To summarize this section, we obtained the LST relation [Eq. (17)] for a material whose ϵ'' spectrum can be represented by a sum of classical oscillators. The mode frequencies which appear on the right-hand side are precisely defined in terms of the poles and zeros associated with the two primary spectra which determine the transverse- and longitudinal-optic fluctuations and which can be measured experimentally. Since any spectrum can be decomposed into a sum of classical oscillator terms, it would appear that Eq. (17) would be a good place to stop. However, the appearance of other types of simple spectra, for example, the Debye dispersion, show that we must investigate these forms separately. A Debye dispersion can be represented quite accurately by a sum of, say, ten classical oscillators. Such a procedure would yield an LST relation involving 20 frequencies. In fact, we will find that we can fit this dispersion with two frequencies exactly.

B. Debye dispersion

One Debye mode. The dielectric spectrum for a single Debye mode is given by

$$\epsilon(\omega)=\epsilon(\infty)+(S/1-i\omega\tau)\,, \tag{18}$$

where S is the strength of the mode and τ is the relaxation time associated with the mode. The time dependence of a system which has the spectrum given by Eq. (18) will be discussed below, together with the time dependence of classical oscillator systems and frequency-dependent damping systems. Materials which exhibit the Debye spectrum are discussed in standard textbooks on dielectrics. The right-hand side of Eq. (18) may be collected over a common denominator to give the form

$$\epsilon(\omega)=\epsilon(\infty)[(\omega_l-\omega)/(-i\omega_t-\omega)]\,, \tag{19}$$

where

$$\omega_t=1/\tau\,,$$
$$\omega_l=-i[\epsilon(\infty)+S]/\epsilon(\infty)\tau\,. \tag{20}$$

The definitions given by Eq. (20) parallel those for the classical oscillator. ω_l is the complex frequency where the zero of $\epsilon(\omega)$ occurs, and ω_t is the absolute value of the frequency where the pole occurs. By writing the dielectric spectrum to exhibit explicitly the poles and zeros, we may obtain the LST relation by taking the zero frequency limit of Eq. (19). The LST relation is therefore

$$\epsilon(0)/\epsilon(\infty)=|\omega_l|/\omega_t\,. \tag{21}$$

The pole and zero frequencies enter the LST relation linearly rather than quadratically for the Debye spectrum, Figure 2 shows an example of a Debye spectrum illustrating the two spectral functions and the locations of the poles and zeros.

Two Debye modes. If the current in a material is carried by two separate mechanisms which each obey the Debye dispersion, we have the spectrum

$$\epsilon(\omega)=\epsilon(\infty)+S_1/(1-i\omega\tau_1)+S_2/(1-i\omega\tau_2)\,. \tag{22}$$

The poles and zeros of such a function are easily obtained. Note that they no longer occur as pairs mirror-imaged in the real frequency axis, but all lie on the pure imaginary frequency axis. Using algebraic methods like those of Ref. 6 we find the LST relation

$$\epsilon(0)/\epsilon(\infty)=|\omega_{l1}|\,|\omega_{l2}|/\omega_{t1}\omega_{t2}\,. \tag{23}$$

The poles are located at $-i/\tau_1$ and $-i/\tau_2$. The zeros are obtained by solving a simple quadratic. Figure 3 shows the spectra and the locations of the poles and zeros. Note that the poles and zeros alternate along the imaginary frequency axis. For some purposes the spectra shown in Fig. 3 could be approximated by a single Debye mode. However, for exact results, two modes are necessary, and the LST relation must contain the four frequencies of Eq. (23).

Debye mode plus classical oscillator mode. In the above paragraphs we have seen how Debye modes are characterized by poles and zeros on the imaginary frequency axis. Such modes enter the LST relation linearly rather than quadratically. Some solids are known to possess both sharp phonon modes and Debye dispersion. The latter is

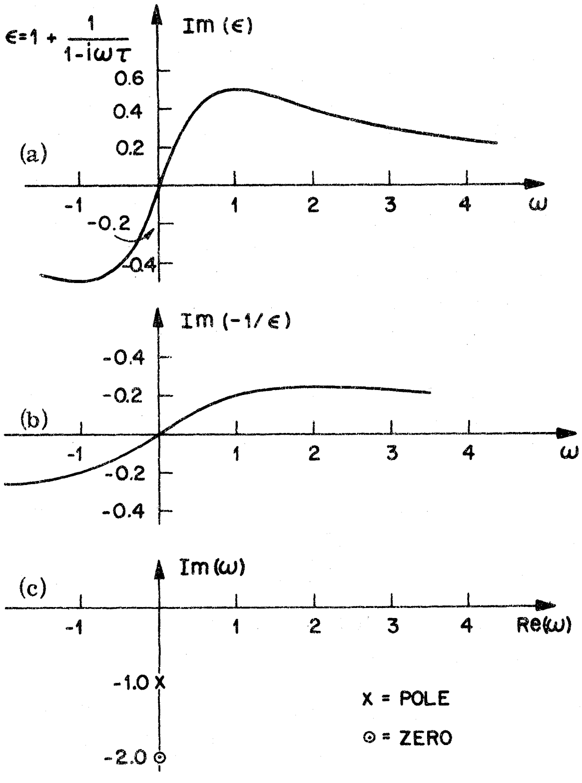

FIG. 2. Debye dispersion. In (a) and (b) the two primary (transverse and longitudinal) dielectric spectra are plotted as in Fig. 1. τ has been chosen to be 1.0. (c) shows the location of the pole and zero on the imaginary frequency axis.

sometimes associated with hindered rotation of a chemical subgroup in each unit cell. Figure 4 shows the spectra for such a case. Equations (13) and (18) have been added and $\epsilon(\infty)$ has been set equal to 2.0. The actual parameters are listed in the figure. We find three poles and three zeros. Two of each are mirror images, as was seen in Fig. 1, and these are obviously to be associated with the classical oscillator mode.[16] Note that the Debye mode has had some effect on the oscillator. The zero is pushed down compared with the pole. The LST relation is

$$\epsilon(0)/\epsilon(\infty) = |\omega_{l1}|\,|\omega_{l2}|^2/\omega_{t1}\omega_{t2}^2 , \tag{24}$$

where ω_{l1} and ω_{t1} are the zero and pole on the imaginary frequency axis. These enter linearly, as was found above. To find the zeros, a cubic equation must be solved in this case. For the parameters used in Fig. 4, $\epsilon(0)$ is 5.0. If a spectroscopist can measure only in the frequency range 10–25, and can determine the spectra to 10% accuracy, he might assume that the oscillator peak describes all the dispersion in this material. He would conclude $\epsilon(0)=3$, approximately, from the LST relation Eq. (1). Low-frequency capacitor measurements would show $\epsilon(0)=5.0$. The results are brought into agreement only by including the extra linear frequency factors in the LST associated with the Debye dispersion. The LST relation has not broken down; rather, the spectra were not completely determined.

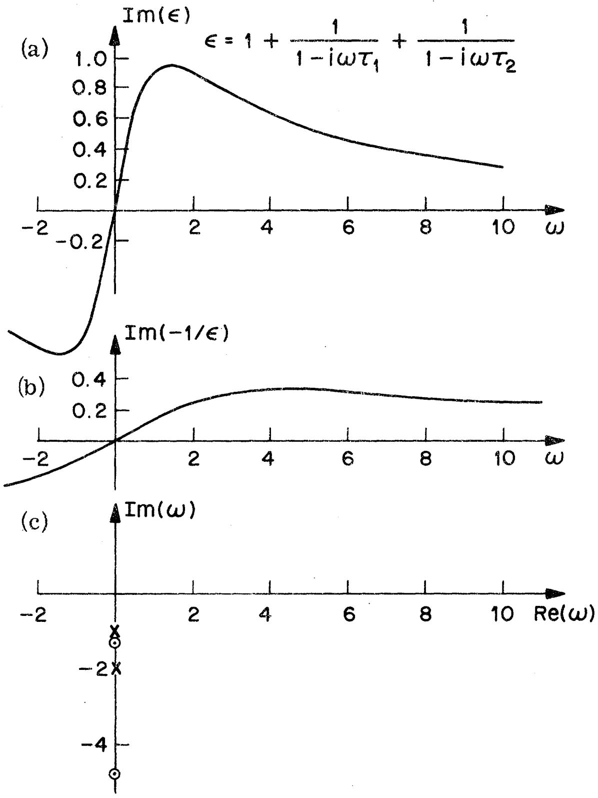

FIG. 3. Sum of two Debye modes. (a) and (b) show the transverse and longitudinal spectra plotted against real frequency as in the preceding figures. τ_1 and τ_2 have been chosen as 1.0 and 0.5, respectively. The spectra suggest that a single Debye mode with $\tau \simeq 0.67$ would be a reasonable approximation. In (c) the two poles and zeros are shown on the imaginary frequency axis.

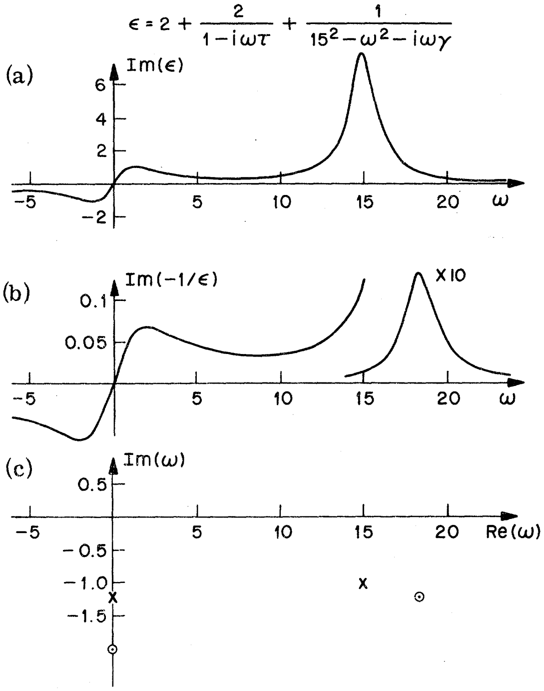

FIG. 4. Debye mode plus classical oscillator mode. (a) and (b) show the spectra for real frequency. As in preceding figures these are odd functions of frequency. They show the broad Debye mode and the higher-frequency oscillator peak. τ is 0.833 and γ is 0.2 in the units used here. (c) shows the pole zero pair on the imaginary frequency axis and the other poles and zeros which lie in the plane and have mirror images off the figure to the left.

C. Central peaks

The polarization fluctuations of transverse character at long wavelength are given by

$$\langle P^2\rangle_\omega = (k_B T/\hbar\omega)\,\mathrm{Im}[\epsilon(\omega)] , \tag{25}$$

while those of longitudinal character are given by

$$\langle P^2\rangle_\omega = (k_B T/\hbar\omega)\,\mathrm{Im}[-1/\epsilon(\omega)] , \tag{26}$$

where k_B is Boltzman's constant and classical statistics have been employed.[14] The weighting factor $1/\omega$ in these spectra can cause a pronounced "central" (zero frequency) peak for dielectric spectra with sufficient weight at low frequencies. Figure 5 shows the polarization fluctuation spectrum for the same dielectric response used in Fig. 4. The presence of the low-lying pole and zero which enter the LST relation are emphasized in this type of spectra. The occurrence of a central peak does not imply Debye-type dispersion. Any dielectric spectrum with suitable low-frequency form can show a central peak when Eqs. (25) and (26) are evaluated. It is clear from the Debye example, however, that a central peak will have associated with it low frequency poles and zeros which must be included in the LST relation. The contribution of the central peak alone to $\epsilon(0)$ may be evaluated in two ways. Equation (7) may be used with the upper limit of integration replaced by some frequency well above the central peak but well below all other resonances. The second (and equivalent) method involves evaluation of the LST relation both with and without the lowest frequency modes included, and comparing the results. We will comment on the importance of such central peaks in a paraelectric material near a ferroelectric transition in a section below.

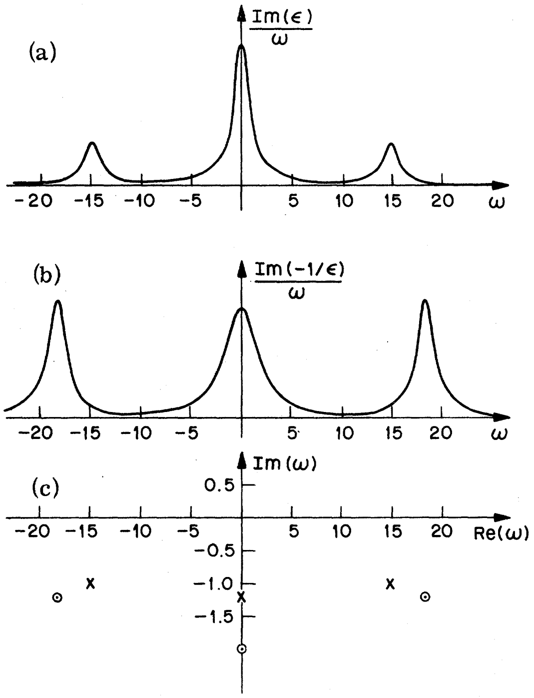

FIG. 5. Fluctuation spectra corresponding to Fig. 4. (a) Spectrum of transverse fluctuations. (b) Spectrum of longitudinal fluctuations. Poles and zeros are shown again here in (c) for convenience. Note that (a) and (b) are even functions and show a large central peak feature.

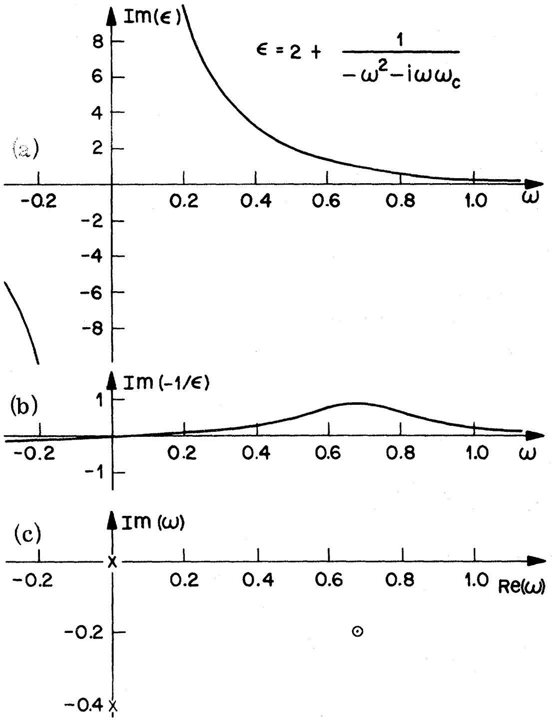

FIG. 6. Dielectric spectra for quasifree carriers. (a) and (b) show the spectral functions for real frequency for the formula given in the figure. $\omega_c = 0.4$ and the plasma frequency is $|\omega_l| = 0.707$. (c) shows the two poles of ϵ on the imaginary frequency axis and one zero. Second (mirror-image) zero is off the figure to the left.

D. Free carriers

Equation (4) shows that for real frequencies ϵ'' must be an odd function of frequency. In the above sections we have discussed dielectrics which have ϵ'' proportional to frequency at low frequency. The simplest and probably only significant case where ϵ'' does not vanish at zero frequency is the case of free carriers where ϵ'' is proportional to $1/\omega$. The dielectric spectrum for quasifree carriers is given by

$$\epsilon(\omega) = \epsilon(\infty) + \omega_n^2/(-\omega^2 - i\omega\omega_c) \; . \tag{27}$$

Here ω_c is the carrier collision frequency and ω_n is related to the carrier density by the relationship

$$\omega_n^2 = 4\pi n e^2/m \; , \tag{28}$$

where n is the carrier density and the m the effective mass (cgs units are being used). For this type of spectrum the dielectric constant at low frequencies does not reach a limiting value. The imaginary part increases without limit, while the real part levels off at a negative value. There are two poles for this spectrum which occur at zero and $i\omega_c$. That is, they are both on the imaginary frequency axis. The zeros for reasonably small ω_c occur as a pair of reflections in the imaginary frequency axis.[16] The zeros are located at

$$\omega_l = \pm\, \omega_n \left(\frac{1 - \epsilon(\infty)\omega_c^2/(4\omega_n^2)}{\epsilon(\infty)} \right)^{1/2} - \tfrac{1}{2} i\omega_c \; . \tag{29}$$

Figure 6 shows the location of the poles and zeros. By using the absolute value of the frequency of the zero, we may establish two different relations, either one of which is comparable to the LST relation of a dielectric. These relations are

$$1/\epsilon(\infty) = |\omega_l|^2/\omega_n^2 \tag{30}$$

and

$$\epsilon'(0)/\epsilon(\infty) = |\omega_l|^2/\omega_c^2 . \tag{31}$$

Note that the low-frequency dielectric constant must now have a prime to make clear that we mean the real part. The longitudinal fluctuation spectrum which is related to part b of Fig. 6 has a peak near ω_l. In metals this longitudinal resonance is called the plasma frequency.

E. Frequency-dependent damping

Frequency dependence and LST relation. We will start with a particular form of frequency-dependent damping and justify this form and indeed the concept of frequency-dependent damping somewhat later. Consider the dielectric function

$$\epsilon(\omega) = \epsilon(\infty) + \frac{S\omega_t^2}{\omega_t^2 - c\omega_t^2/(1-i\omega\tau) - \omega^2} . \tag{32}$$

S is a dimensionless mode strength and ω_t is a restoring force, as usual [cf., Eq. (13)]. The second term in the denominator, which has the frequency-dependence characteristic of Debye dispersion, can be thought as a correction to the restoring force or first term. At very high frequencies it approaches zero, but at low frequencies it has significant real and imaginary parts which affect the total denominator. These modifications are caused by interactions of the primary oscillator (whose strength is given by S) with other phonons. In this case the interactions have significant frequency dependence and cause damping and force constant shifts. A fourth term can be added to the denominator of the form $i\omega\gamma$ [cf., Eq. (13)] to provide a constant damping term in addition to the frequency-dependent damping, without affecting any of the conclusions of this section. The parameter c is used to suggest a coupling coefficient which governs this strength of the interaction of the primary phonon with the other phonons which contribute to the damping. Figure 7 shows the spectra for a particular choice of parameters. Note that the form of the spectra and the location of the poles are rather similar to Fig. 4. However, there are significant differences and the spectra are not equivalent. There are three poles and three zeros as shown in part c of Fig. 7. The LST relation must include all three; it has the form of Eq. (24). This form is easily derived using the same algebraic methods as had been used before to find the roots of $\epsilon(\omega)$. Thus we find that Eq. (32), which appears to have one degree of freedom [one term besides $\epsilon(\infty)$], actually simulates a system with two degrees of freedom such as was considered for Fig. 4. The peak near 15 in Fig. 7(a) corresponds to a resonance near ω_t, while the broad peak at low frequencies corresponds to driving all the coupled phonons via the effective charge of the principle mode (i.e., the effective charge that enters the parameter S). Essentially, S is spread over both peaks and the parameter c controls the fraction of S which appears in each. If Eq. (32) describes a soft-mode paraelectric material, and if the spectra are examined only in the region of the high-frequency peak, it is quite easy to miss the true soft-mode behavior. The divergence of $\epsilon(0)$ near a ferroelectric phase transition may consist entirely of the low-frequency pole on the imaginary axis of Fig. 7(c) moving towards the origin, that is, the high-frequency peak in the spectrum may not soften.

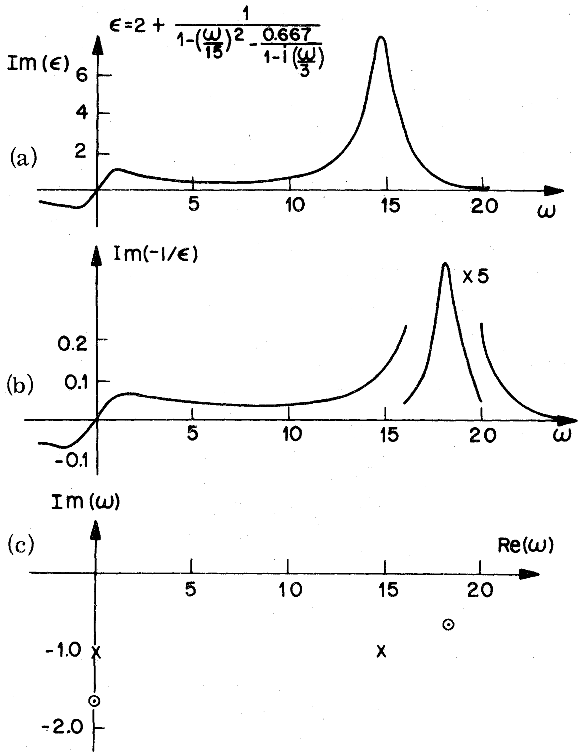

FIG. 7. Dielectric spectra for a mode with frequency-dependent damping. Equation is given in the figure and corresponds to $\omega_t = 15$, $\tau = 0.33$, and coupling $c = 0.667$ in Eq. (32). (a) and (b) show the spectra for real frequency. (c) shows the locations of the poles and zeros.

Time dependence. In this section we briefly consider the origin of the frequency-dependent damping such as given by Eq. (32). Lax[17] has considered the problem of the motion of a selected lattice vibration coordinate when it is coupled to a reservoir consisting of all the remaining lattice vibrations. The general result is that the classical oscillator form of Eq. (3) is appropriate, but with the damping $i\omega\gamma$ replaced by a frequency-dependent term which depends on various anharmonic coefficients. This term has real and imaginary parts which must obey the Kramers-Kronig relations. The form used in Eq. (32) was chosen to satisfy this general requirement and to have ϵ'' positive. Therefore this dispersion spectrum is satisfactory from the viewpoint of obeying the general requirements of statistical mechanics.

To gain a little more insight we may consider the equations of motion

$$m_1\ddot{x}_1 = -k_1x_1 - k_{12}(x_1 - x_2) - \gamma_1\dot{x}_1 + z_1E \, , \tag{33}$$

$$m_2\ddot{x}_2 = -k_2x_2 - k_{12}(x_2 - x_1) - \gamma_2\dot{x}_2 \, . \tag{34}$$

The particles described by m_1 and m_2 are coupled, vibrate in one dimension, and have restoring force k_1 and k_2 and damping γ_1 and γ_2. Only particle 1 is coupled to the electric field E via the effective charge z_1. The equations are now specialized to the case of particular interest here by setting m_2 and γ_1 equal to zero to obtain simpler forms. The motion of particle 1 is given by

$$x_1 = \frac{z_1E}{k_1 + k_{12} - m_1\omega^2 - k_{12}/(k_2 + k_{12} - i\omega\gamma_2)} \, . \tag{35}$$

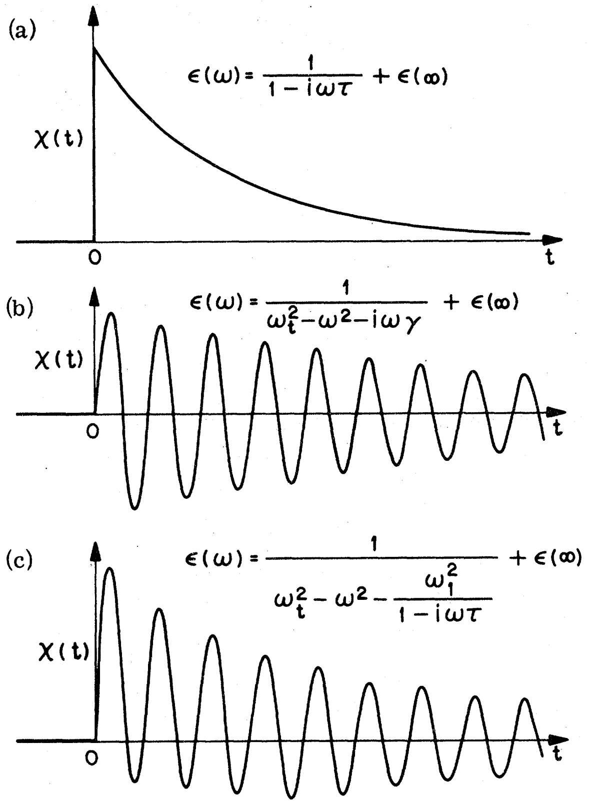

FIG. 8. Time dependence of an optic-mode coordinate after an electric field impulse. Three mode types are considered, with the dielectric constant formulas displayed in the figure; (a) Debye mode, (b) classical oscillator mode, and (c) mode with frequency-dependent damping. Note the separate decay of the amplitude of oscillation and of the mean value of the coordinate.

The dispersion form given by Eq. (32) is immediately obtained by evaluating first the polarization and then the dielectric constant in the usual way, and by redefining some groups of constants. This simple model suggests that frequency-dependent damping of the form of Eq. (32) arises when the electric field couples to an optic mode (the particle x_1) which in turn is coupled to an optically inactive mode or group of modes, described in this case by the single coordinate x_2. In a real solid the group of modes described by Eq. (34) may be a two-phonon band. The coupling coefficient k_{12} may therefore be temperature dependent. Cowley has considered a specific model of a paraelectric material and derived Eq. (32) by considering the anharmonic phonon processes in detail.[18] With this amount of motivation for the frequency-dependent damping equation we now turn to the time dependence. Figure 8 shows the time dependence of a coordinate x for a particle corresponding to the optic mode coordinate described by various dielectric constants. A δ-function impulse of electric field is applied at $t = 0$. In Fig. 8(a), the response corresponding to the Debye mode is shown with its characteristic exponential decay from the initial position which was achieved by infinite velocity at the time the impulse was applied. In part b the characteristic time dependence for a classical oscillator is shown following the same impulse at $t = 0$. In part c we have taken the Fourier transform of the frequency-dependent damping spectrum [Eq. (32)] to obtain the time dependence of this particular type of response function. Note that in contrast to parts a and b of the figure, in part c there are two characteristic decay times. One has to do with the decrease in amplitude of the oscillations similar to part b while the other is connected with the approach of the mean position of oscillation to the origin, which is reminiscent of part a. Note that part c is not obtained by the addition of parts a and b, although it appears to approximately follow the sum of these two time dependences. This result correspond exactly to the point made earlier that Fig. 7 is not exactly the result of adding two oscillators as was done in Fig. 4, although the result is roughly the same in some respects. Silverman[19] and others have derived frequency-dependent damping by considering the time response as a memory function. It might be pointed out for those unfamiliar with frequency-dependent damping that since the 1930's most automobiles have had so-called variable-rate-damping shock absorbers to improve the response of the automobile after a sudden impulse. The use of frequency-dependent damping is therefore not entirely academic, nor is it restricted to unusual and rare circumstances.

To summarize the results of the present section, the LST relation has been derived for a particular form of frequency-dependent damping. For sufficient coupling strength c the spectrum of Fig. 7 will show a central peak when plotted as a fluctuation spectrum, as was done in Fig. 5. A strong central peak here is associated with low-lying poles and zeros on the imaginary axis close to the origin, which must be included in the LST relation. Equations (33) and (34) represent one form of mode coupling of the type discussed by Barker and Hopfield.[20] In all cases of mode coupling even a mode with zero effective charge in an uncoupled representation must be included in the LST relation if it couples significantly to an active mode.

F. Band-gap absorption

In the preceding sections response functions have been examined which contained simple poles and zeros. We now consider a case with a different type of singularity, the branch cut. Standard works on semiconductors show that interband absorption across a direct gap has the functional form

$$\epsilon''(\omega) = \pm A(|\omega| - \omega_g)^{1/2}/\omega^2 , \quad |\omega| > \omega_g , \qquad (36)$$

where ω_g is the frequency associated with the energy gap, and where the positive sign on this square root is associated with positive frequencies and the negative sign is taken for negative frequencies. Equation (36) can be shown to hold near the band gap for parabolic bands; however, some modifications set in at higher frequencies. We neglect such effects here. Figure 9(a) shows the dielectric spectrum with the characteristic square-root threshold at ω_g. Fluctuations of a transverse character follow the form of Fig. 9(a) [modified by the factor given in Eq. (25)]. Figure 9(b) shows the spectrum which corresponds to longitudinal fluctuations, and in part c the singularities are indicated. The electronic excitations contribute to $\epsilon(0)$ just as the optic phonon excitations do. The problem in obtaining an LST relation consists of picking suitable frequencies to be used in the expression. The branch cut shown in Fig. 9(c) has one natural frequency associated with it, namely ω_g. It is difficult to find a second frequency because the analytic forms of $\epsilon(\omega)$ and of $1/\epsilon(\omega)$ are extremely cumbersome. A possible form to expect for the LST relation would be

$$\epsilon(0)/\epsilon(\infty) = \omega_l^{3/2}/\omega_g^{3/2} . \qquad (37)$$

Since the integral of Eq. (7) yields a $\frac{3}{2}$ power dependence on ω_g, it is reasonable that such a relation exists. For the spectra of Fig. 9, $\omega_l = 1.72$. Unfortunately, ω_l is not simply related to the spec-

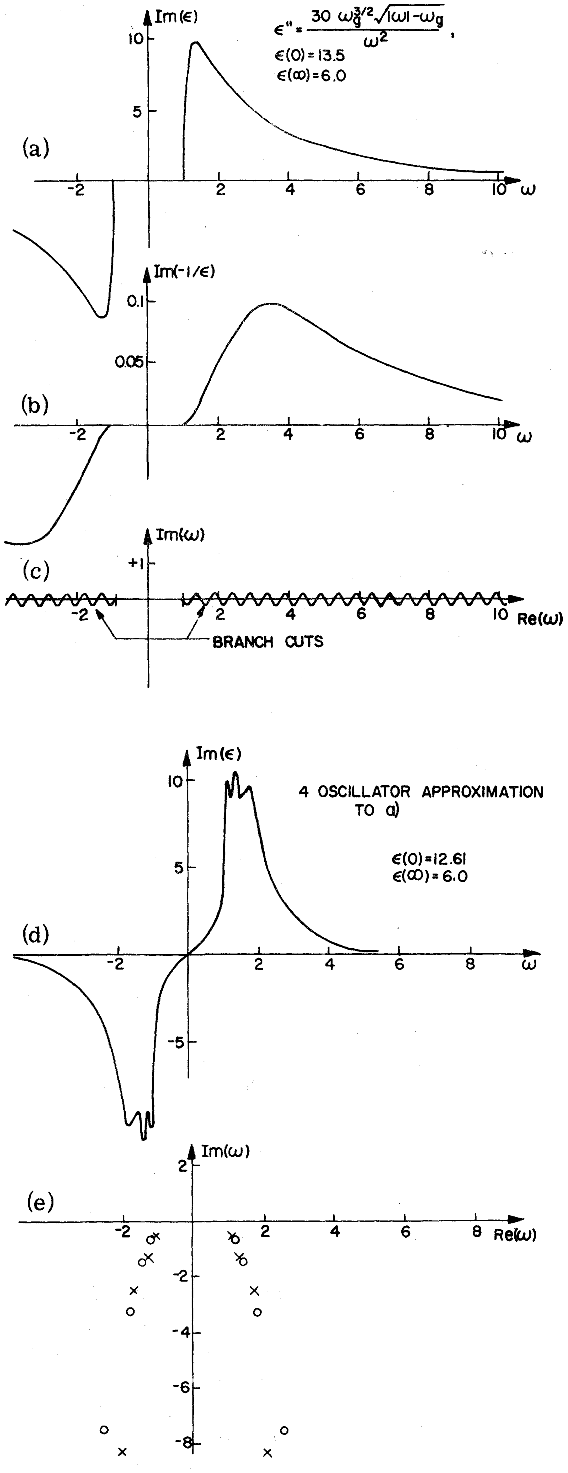

FIG. 9. Dielectric spectra for band-gap excitations. Form of ϵ'' is given in the figure. ω_g is 1.0 and ω_l [Eq. (37)] is 1.72. (a) and (b) show the spectra for real frequency and (c) shows the location of the singularity in the complex frequency plane. (d) Four-oscillator approximation to the spectrum of (a). (e) Poles and zeros in the complex frequency plane for the four oscillators of part (d).

tra of Fig. 9.[21] This means that the LST relation becomes merely a definition of ω_l rather than an independent usable relationship. The reason for the difficulty in obtaining ω_l from the spectra is directly related to the type of singularity involved. The pole and zero singularities, even with considerable damping, could be associated with damped simple harmonic time dependence and thus thought of as elementary excitations. The time dependence is much more complicated here; the spectra involve a series of excitations, and part of the shape comes from the density of states near the band edges. We conclude that there is an LST relation for this case, but it has little direct use. The introduction of a longitudinal mode frequency can be avoided by avoiding the ratio of dielectric constants used in the LST relation. Taking this approach, the more useful relation

$$\epsilon(0)=\epsilon(\infty)+A/4\omega_g^{3/2} \tag{38}$$

is obtained by using Eq. (7).

Finally, it is instructive to examine an approximation to the band-gap absorption of Eq. (36). Figure 9(d) shows an approximation consisting of the use of four classical oscillators. There is a sharp rise in absorption near $\omega=1$; however, a finite number of oscillators can never exactly reproduce the sharp edge shown in Fig. 9(a). Figure 9(e) shows the location of the four poles and zeros used in this approximation. To obtain a better approximation even more poles and zeros are added, and individual damping terms may be decreased so that the poles and zeros move closer to the real frequency axis. In the limit of an infinitely dense cluster of poles and zeros they of course move right up to the location of the branch cut shown in Fig. 9(c). The LST relation for this four-oscillator approximation has four transverse frequencies and four longitudinal frequencies as described in Sec. IV A. The actual value of $\epsilon(0)$ obtained is 12.61, as opposed to the correct value of 13.5 shown in Fig. 9(a).

The approximate representation by four (or some other number of) oscillators can be useful in situations where a simple analytic form for $\epsilon(\omega)$ is required. We recognize, however, that the poles and zeros shown in Fig. 9(e) have little significance individually. Their combined weight, when entered on the right-hand side of the LST relation, will, however, give an approximation to the dielectric-constant ratio.

G. Flat absorption band

In this section we consider briefly the case of a wide frequency region consisting of featureless or flat absorption. Figure 10(a) shows an example of such a spectrum which stretches over six decades in frequency. As with the band-gap absorption, we find that this absorption is not described by simple poles and zeros, and we find no unique frequency or mode to associate with the longitudinal spectrum [shown in Fig. 10(c)]. Just as we did above, we can avoid the introduction of a longitudinal mode frequency by assessing the contribution of the mode structure to $\epsilon(0)$. The result for a spectrum stretching from frequency ω_1 to ω_2 of strength $\epsilon''=A$ is given by Eq. (7)

$$\epsilon(0)=\epsilon(\infty)+(2/\pi)A\ln(\omega_2/\omega_1)\ . \tag{39}$$

Note that the result depends only on the ratio of ω_2 to ω_1. This exact result obtains for a spectrum that turns on sharply with a step function at ω_1 and similarly drops to zero with a step function at ω_2. Such sharp steps cause logarithmic singularities in ϵ'. In the physical situations we have in mind we expect no such sharp steps and have shown rounded edges on the spectra in Fig. 10. Equation (39) is still correct; however, ω_1 and ω_2 are less well defined. For suitably shaped edges on the spectrum, these frequencies correspond to the midway point with value $\frac{1}{2}A$. A spectrum with $\epsilon''=$ Const. corresponds to the situation where the real part of the conductivity varies linearly with frequency. Such spectra can arise from the hopping of a charged particle as discussed by Mott and Davis.[22]

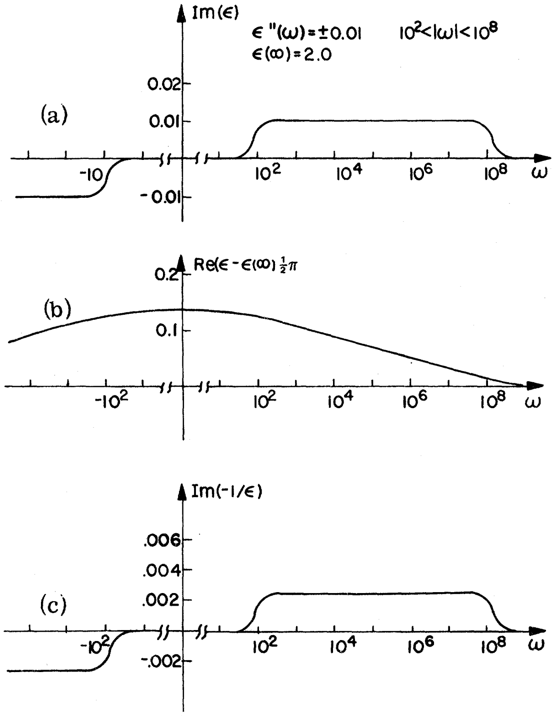

FIG. 10. (a) Imaginary part of the dielectric constant plotted against real frequency for a flat absorption band. (b) Real part of the dielectric constant corresponding to (a). (c) Imaginary part of the reciprocal dielectric constant corresponding to the spectrum in (a).

We consider here the case where the spectrum is weak in the sense that the second term of Eq. (39) is much smaller than the first term. Such spectra are important in certain semiconductors at low temperatures, and in certain disordered solids. Such spectra may also be important in almost any solid if it is measured with sensitivity sufficient to detect the presence of rather minor impurities which move in a hindered fashion. We believe such spectra to be important also in certain ferroelectrics. Note that the fluctuation spectrum given by Eq. (25) will have a central peak which rises as $1/\omega$ for frequencies approaching ω_1 from above. The exact behavior at $\omega = 0$ depends, of course, on the shape of the tail of ϵ'' at $\omega = 0$.

Figure 10(b) shows the behavior of ϵ'. It falls smoothly in a logarithmic fashion over the entire spectral region where the absorption occurs. For the case we consider where $\epsilon(\infty)$ is very large, the longitudinal spectrum shown in Fig. 10(c) mimics the transverse spectrum shown in Fig. 10(a).

In the case of a solid which has an infrared active mode at frequency ω_t which can be approximated by a classical oscillator, Eq. (39) must be altered. As a concrete example, we might imagine a paraelectric with a soft mode at ω_t which lies above the spectral region shown in Fig. 10(a). Equation (39) must have $\epsilon(\infty)$ replaced by the contribution of this soft mode. The relation becomes

$$\epsilon(0) = (2/\pi) A \ln(\omega_2/\omega_1) + \epsilon(\infty) |\omega_l^2| / \omega_t^2 , \qquad (40)$$

where $\epsilon(\infty)$ is, of course, the dielectric constant at frequencies well above both the flat absorption and the soft-mode frequencies, and ω_l corresponds to the zero in the dielectric constant. For the present example of a soft mode well above the flat spectrum, ω_l may be calculated by ignoring the flat spectrum contribution to $1/\epsilon(\omega)$.

V. MODE SOFTENING

Devonshire was the first to construct a detailed phenomenological theory of the phase transition in ferroelectrics.[23] This was a thermodynamic theory which dealt only with the static or low-frequency properties of ferroelectrics. Devonshire did not discuss optic modes; however, his result that the dielectric constant must diverge at the ferroelectric transition in certain materials is directly connected with mode softening through the LST relation. Devonshire expanded the free energy in the form

$$F(T, P) = F_0(T) + AP^2 + BP^4 + CP^6 , \qquad (41)$$

where P is the polarization, T is the temperature, and A, B, and C are phenomenological coefficients to be determined by general principles or by fitting to a particular compound. For a second-order phase transition, Devonshire found that B and C are positive while A is temperature dependent and goes to zero at the phase transition. Landau and Lifshitz obtain exactly the same result in their discussion of second-order phase transitions.[10] By taking derivatives of the free energy it is easily established that

$$\epsilon(0) = 1 \Big/ \left(\frac{\partial^2 F}{\partial P^2} \right)_{P=0} = \frac{1}{2A} . \qquad (42)$$

The vanishing of A at a second-order phase transition causes therefore a divergence in $\epsilon(0)$ at the phase transition. Using reasonable models, Devonshire established that even for a first-order transition A is temperature dependent and decreases to a considerable extent, though not to zero. The usual assumption is that A varies linearly with temperature near the phase transition,[23-25] that is

$$A = a(T - T_0) . \qquad (43)$$

Scott has briefly reviewed the thermodynamic theories and commented on the expected temperature dependence for A.[24] The concept of $\epsilon(0)$ becoming infinitely large near a phase transition may now be applied to our various LST relations. First, in Eq. (1) we note that the left-hand side will increase as $\epsilon(0)$ increases, since $\epsilon(\infty)$ consists of temperature-independent polarizations, i.e., polarization which is not included in the Devonshire expression, Eq. (41). Looking at the right-hand side of Eq. (1), we note that the equation is satisfied if there is mode softening of ω_t, i.e., if ω_t approaches zero. The other obvious possibility, of ω_l approaching infinity, must be rejected by arguments outside the general thermodynamic approach. We may follow Cochran's discussion, which considers a specific lattice-dynamic model.[25] Briefly, the result is that mode frequencies cannot approach infinity since masses cannot approach zero nor force constants approach infinity. It is easy, however, to construct situations in which a frequency *can* approach zero, since there is no reason that force constants cannot be zero due to cancellations of long- and short-range components or harmonic and anharmonic components. With this somewhat sketchy background we conclude that Eq. (43) predicts a mode softening of ω_t in Eq. (1). Using the same reasoning we find that one or more transverse modes must approach zero in the situation covered by Eq. (2) as the ferroelectric transition is approached. Following the discussion which lead to Eq. (17), we conclude that this result holds with the interpretation (see Fig. 1) that the pole of the dielectric constant approaches the origin. The method of approach is immaterial as long as the distance from the origin continues to decrease as the temperature approaches the phase transition temperature. Considering next the Debye mode dispersion [Eqs. (21) and (23)], we conclude that again a pole must approach the origin as $T \rightarrow T_0$, but in this case along the imaginary frequency axis. For the central peak shown in Fig. 5, regardless of whether it arises from frequency-dependent damping or the sum of two independent modes, the LST relation Eq. (24) was obtained. The divergence in $\epsilon(0)$ near the phase transition may now be caused by either the central peak or the higher-frequency peak approaching zero. The most likely situation would be for the high-frequency peak to decrease in frequency to some extent, but for this effect to increase the coupling c in Eq. (32), so that the low-frequency mode which contributes to the central peak takes over and dominates the spectrum as the temperature approaches the transition temperature. From Eq. (38) for the case of band-gap absorption we note that the divergence of $\epsilon(0)$ can be associated with the band gap ω_g going to zero.

Finally, for the case of the flat absorption spectrum with $\epsilon(0)$ given by Eqs. (39) or (40), we have the possibility of ω_1 approaching zero or the spectral density A approaching infinity at the phase transition. As was mentioned above, a weak flat-band spectrum may be present in many solids owing to a small contamination by impurities. If the spectrum arises from Debye-type hopping over a distribution of barriers which are governed by short-range forces, we might expect this distribution to be rather temperature independent. If the hopping takes place in a region of large local electric field which is connected with the polarization of a higher-lying soft mode, there can be considerable enhancement of the hopping polarization. A simple model of such local field enhancement shows that the parameter A in Eq. (40), which is related to the number of hopping centers and their effective charge, varies as $1/\omega_t^2$. Such a model predicts therefore that if ω_t is soft, both terms in the dielectric constant [Eq. (40)] diverge together. More subtle considerations might of course cause one of the diverging terms to win out over the other as T approaches the transition temperature. For all of these types of dispersion therefore the LST relation predicts that a mode softens as the ferroelectric transition temperature is approached. For the model of flat-band absorption mentioned above, the parameter ω_1 may not soften, but the divergence in the dielectric constant will cause a divergence in the strength of the central peak associated with the absorption.

VI. CONCLUSIONS

In the above sections we have derived the LST relation for several kinds of dielectric response functions. Some of the response functions contained a central peak when plotted in the appropriate way and comments were made on other response functions which contained mode coupling. The general result obtained was that when the dielectric constant diverges near a phase transition, the mode frequencies must change according to the LST relation. Using a fairly general lattice-dynamical model it can be established that in many cases the longitudinal-mode frequency is relatively stable, and it is the transverse-mode frequency which softens or approaches zero near the phase transition. It was stressed that the number of modes need not agree with the group-theory result for the ideal crystal.

Mode softening may occur in a central-peak type mode which may or may not correspond to any of the modes obtained in the harmonic approximation of lattice dynamics. The central peak can be intrinsic to the material, resulting from coupling of allowed and forbidden modes, or it may be due to impurities. An example has been given of a broad flat absorption band arising from an impurity with a distribution of barrier heights in its hopping dynamics.

The derivation of the LST relation depended only on the principles of macroscopic physics, that is, statistical mechanics and the principle of causality. Using this viewpoint one is seldom justified in checking whether the LST relation holds. What one is checking is whether all of the modes which contribute to $\epsilon(0)$ have been found, or perhaps whether $\epsilon(0)$ has been measured correctly. We note finally that even one part of the requirements for an LST relation can be abandoned if one wishes to discuss modes with negative oscillator strength. For example, in the classical oscillator equation (13) S can be negative. Such negative oscillator strengths result from transitions which are being pumped by some outside agency. In this situation there is still an LST relation; however, now ω_l lies at lower frequencies than ω_t in the case of, for example, a single oscillator mode. As the pumping is increased so that S becomes even more negative, we can have the longitudinal-mode frequency approach zero while the transverse-mode frequency remains fixed. As with the cases described above, the basic LST relation here results directly from the application of the Kramers-Kronig integral.

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[1] R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. 59, 673 (1941).

[2] We make the assumption which is usual in lattice dynamics that the spectra are separable into components well-separated in frequency. All high-frequency electronic absorption processes have their influence lumped into $\epsilon(\infty)$, and any Kramers-Kronig integrals which have infinity as an upper limit may actually be terminated at a frequency well above all lattice absorption but below the electronic absorption.

[3] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University, London, 1954), Chap. 2.

[4] T. Kurosawa, J. Phys. Soc. Jpn. 16, 1298 (1961).

[5] W. Cochran and R. A. Cowley, J. Phys. Chem. Solids 23, 4471 (1962).

[6] A. S. Barker, Jr., Phys. Rev. 136, A1290 (1964).

[7] In anisotropic crystals the optic modes may not correspond separately to poles and zeros, but all to poles or all to zeros of special functions. This situation is discussed in Ref. 9 and in Ref. 14.

[8] A. S. Barker, Jr., in *Ferroelectrics*, edited by E. F. Weller (Elsevier, Amsterdam, 1967), p. 213.

[9] M. Lax and D. F. Nelson, Phys. Rev. B 4, 3694 (1971).

[10] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, London, 1969).

[11] For other systems an LST relation is still possible. For example, in a paramagnetic system the magnetic field H replaces E and magnetic permeability replaces the dielectric constant.

[12] While we have made the most natural choice, other frequencies may be defined here. The frequency where the dielectric constant is -1 could be used, for example. This frequency corresponds to polar surface modes ω_s which can be used in the LST relation. The relation becomes $[\epsilon(0)+1]/[\epsilon(\infty)+1]=(\omega_s/\omega_t)^2$. Similarly the frequency where the dielectric constant is $+1$ can be used to obtain a slightly different LST relation, This frequency corresponds to the reflectivity being zero, which is convenient for the spectroscopist. It does not correspond to a mode excitation frequency for bulk samples of simple shape.

[13] The approximate equality of Eq. (9) may be made exact by a suitable choice of ω_t. Usually this involves choosing ω_t some small fraction of the linewidth above or below the frequency of the peak in ϵ''. An exact definition of ω_t is given in following sections.

[14] A. S. Barker, Jr., and R. Loudon, Rev. Mod. Phys. 44, 18 (1972).

[15] Our viewpoint is that the LST relation is between the dielectric constants and mode structure. Lyddane *et al.* discovered one manifestation of it using a harmonic model. Similar manifestations were discovered in Refs. 4–6, 8, and 9. The real breakdown is the use of the number of modes given by group theory, assuming a harmonic lattice, or the use of mode frequencies derived from experimental spectra fit by classical oscillator modes. Either one or both of these procedures can be wrong for a particular solid.

[16] For very large damping even the oscillator mode singularities cease to be mirror-image pairs as has been discussed in Ref. 8.

[17] M. Lax, J. Phys. Chem. Solids, 25, 487 (1964).

[18] R. A. Cowley, J. Phys. Soc. Jpn. Suppl. 28, 239 (1970).

[19] B. D. Silverman, Phys. Rev. B 11, 1768 (1975).

[20] A. S. Barker, Jr., and J. J. Hopfield, Phys. Rev. 135, A1732 (1964).

[21] A different approach to defining the longitudinal-mode frequency is to evaluate moments. Instead of searching in the complex plane for singularities, weighted integrals (moments) of ϵ or $1/\epsilon$ can be evaluated along the real frequency axis and an appropriate average frequency defined. This method has been used to derive mode frequencies for model Heisenberg antiferromagnets by P. C. Hohenberg and W. Brinkman [Phys. Rev. B 10, 128 (1974)].

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[23] A. F. Devonshire, Philos. Mag. 40, 1040 (1949); Philos. Mag. Suppl. 3, 85 (1954).

[24] J. F. Scott, Rev. Mod. Phys. 46, 83 (1974).

[25] W. Cochran, Adv. Phys. 9, 387 (1960).