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Dielectric response spectrum of a damped one-dimensional double-well oscillator

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The characteristic features of the dielectric response spectrum associated with the condensation of a "soft" phonon mode during a ferroelectric phase transition can be reproduced by an oscillator moving in a damped linear double-well potential. The behavior of the response function below the transition temperature T_c can be simulated by introducing a linear mean-field coupling which destroys the symmetry of the well. Potentials derived from physically realistic parameters are shown to result in dielectric responses which are in order-of-magnitude agreement with experimental values.

I. INTRODUCTION

Ferroelectric materials can be characterized by the property that the electric polarization, which is present only below the transition temperature, can be reversed by placing the sample in an external electric field with a component opposite the direction of initial polarization. Moreover, in "displacive" ferroelectrics, the polarization is known to arise from a structural phase transition in which anions and cations are displaced in opposite directions from each other, relative to their equilibrium positions in the higher-symmetry, nonpolar lattice which exists above the transition temperature T_c. The reversal of the polarization due to the application of an external field, then, merely results in the reversal of the position vectors of the ions in the ferroelectric phase. This representation of a ferroelectric has led a number of workers[1] to model this class of transitions as an oscillator moving in a one-dimensional double well of potential energy. The displacement of the oscillator during the transition (or the polarization it produces) is then treated as an "order parameter" within the framework of Landau's theory[2] of structural phase transitions.

Further headway into the understanding of the nature of ferroelectric phase transitions was made when Cochran[3] and Anderson[4] introduced the concept that such transitions resulted from the condensation of a "soft mode", i.e., a low-frequency phonon in the spectrum of the paraelectric phase. This occurs because as the temperature is lowered toward T_c the restoring forces associated with the eigenvector of the "soft-mode" frequency disappear, thus "freezing in" the corresponding ionic displacements. Since the resulting structure involves antiphase displacements of anions and cations along a single direction within the lattice, the soft mode must be a transverse-optical, zone-center mode ($\mathbf{q}=0$). Raman and ir spectroscopy have shown that such mode softening does indeed occur. Moreover, the condensation process results in spectacular variations in the optical properties of the material, such as the reflectivity and the dielectric response, which diverges at $T=T_c$ and $\omega=0$.

In a great many ferroelectrics, the phase transition involves the appearance of a "central peak" in the imaginary component of the response function, which is a high-intensity peak which appears at very low frequencies as an additional response over and beyond the response due to regular phonon contributions. It is this peak which then dominates the spectrum and shifts rapidly toward zero, increasing rapidly in intensity near T_c. The real component shows typical anomalous dispersion, while also increasing in magnitude at low frequency, and, in some instances, may become negative near $\omega=0$. A number of mechanisms have been suggested to account for the central peak,[5] such as phonon density fluctuations, impurity relaxations, and domain-wall dispersion. In this paper we show that the behavior of the dielectric response function associated with a ferroelectric phase transition, including the formation of the central peak, can be emulated by a damped one-dimensional double-well oscillator with a linear mean-field coupling term. Further, by making use of available data dealing with the structure and polarization of known ferroelectrics and making simple, physically realistic assumptions, one can obtain amplitudes and a frequency dependence of the dielectric response in qualitative agreement with experiment.

In the following section we present the theory upon which the calculations are based, as well as the assumptions which were used in finding the physical parameters of the well. Section III contains a discussion of the calculations themselves, the results of which will be presented and discussed in Sec. IV.

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II. THEORY

Generally, mode softening and the development of the central peak have been discussed in terms of single-well oscillators with anharmonic terms and damping. Koehler and Gillis[6,7] suggested emulating ferroelectric phase transitions using a linear by coupled double-well Hamiltonian of the form

$$H=-\tfrac{1}{2}\lambda^2\frac{\partial^2}{\partial x^2}-Ax^2+Bx^4-\chi\langle x\rangle x \ , \tag{1}$$

where A and B are constants to be determined from the physical parameters of the energy. $\lambda=\hbar/\sqrt{M}$, where M is the oscillator mass, and χ may be regarded as a linear coupling between the oscillator and all other oscillators in the lattice which, in the mean-field approach, have an average position $\langle x\rangle$. (We note that such a term could include a constant external electric field as well; however, in the present study we assume that this term arises entirely from the crystal field.) Above T_c, the order parameter, $\langle x\rangle$, is zero and the potential function is temperature independent and symmetric about $x=0$, but below T_c the intercell coupling term (and the order parameter) become nonzero and the symmetry of the well is broken, one lobe becoming deeper than it was, and the other more shallow. Thus the mean-field approximation (MFA) is distinct from double-well treatments in which the well shape varies with temperature above and below the transition, but remains symmetric about $x=0$.[1]

It is not difficult to show that if E_b represents the "height" of the energy barrier and $\pm x_0$ the positions of the energy minima in the paraelectric phase, then the constants A and B in the Hamiltonian are given by

$$A=2.0E_b/x_0^2 \quad \text{and} \quad B=E_b/x_0^4 \ . \tag{2}$$

A general equation for the dielectric response of an oscillator system such as this has been given by Vaks, Galitskii, and Larkin,[8]

$$\epsilon=1+\frac{e_{\text{eff}}^2}{\varepsilon_0 V}\left[\frac{\pi(\omega,T)}{1-\chi(0)\pi(\omega,T)}\right] , \tag{3}$$

[where e_{eff} is the effective charge of the oscillator, V is the volume associated with each oscillator, ϵ_0 is the permittivity of free space, $\chi(0)$ is the response function of the oscillator at $q=0$ (since ferroelectric transitions involve long-wavelength phonons, near the Brillouin-zone boundary) and $\pi(\omega,T)$ is a sum over states. The form used in the present work is

$$\Pi(\omega,T)=\sum_{\alpha,\beta}\frac{(f_\alpha-f_\beta)|\langle\phi_\alpha|x|\phi_\beta\rangle|^2}{\omega-\omega_\alpha+\omega_\beta+i\gamma\omega} \ , \tag{4}$$

in which ω_α, ϕ_α, and f_α, respectively, the eigenfrequency, eigenvector, and the thermal weighting factor of the αth state, calculated for any given temperature using $f_\alpha=e^{-\varepsilon_\alpha/kT}/\sum_\beta e^{-\varepsilon_\beta/kT}$, where k is Boltzmann's constant. The imaginary terms in Eq. (4) provide for damping of the oscillator in ways to be described more fully below. This expression is valid for any potential well. However, in the case of a simple harmonic oscillator, the oscillator strengths in $\pi(\omega,T)$ would contain contributions only from pairs of adjacent energy levels, for which transitions are allowed. In the case of the potential of Eq. (1), the effect of the quadratic term is to break the degeneracy of the lower-energy levels of a symmetric quartic oscillator, resulting in sets of nearly degenerate energy levels below the barrier. It is the large matrix elements which exist between the relatively close energy levels in or just above the well which contribute large oscillator strengths to the sum in Eq. (4), and which, in turn, produce a large, frequency-dependent response as T_c is approached from above. Below T_c the linear term in the Hamiltonian breaks the symmetry of the double wells, causing the order parameter and the spacing between the two lowest-energy levels to increase. The eigenvectors ϕ_α and eigenfrequencies ω_α in Eq. (4) must then be recomputed self-consistently for each temperature for which the response is to be found. In this regime one expects the response peak to shift upward in frequency and diminish in amplitude, eventually "freezing in" at some frequency as the order parameter reaches its maximum value.

III. CALCULATIONS

In choosing the parameters for the double-well Hamiltonian, we have made use of the ideas set forth by Abrahams, Kurtz, and Jamieson,[9] in which they relate the transition temperature T_c to the displacement of the homopolar metal ion in the ferroelectric phase. If one further assumes, as they do, that the barrier height should be half of kT_c, and associates the displacement of the homopolar ion with x_0, one can obtain numerical values for the constants A and B from Eq. (2). It is interesting that when these criteria are applied to the ferroelectrics listed in Ref. 9, the value of A for nearly all of the ternary compounds lies in a range 4000–7700 K/bohr^2 (see Table I). We note that not all of the ferroelectrics listed are actually linear ferroelectrics, and these should, more properly, be treated in a multiwell formalism. We are, however, using this approach only to arrive at well parameters which are physically reasonable. A number of wells with A values in this range and with various well depths (and, therefore, transition temperatures) were examined. The general features were found to be the same for all of these. The results we will present here are for a well with $E_b=(200\ \text{K})k$ ($T_c=400$

TABLE I. Coefficient $A=T_c/x_0^2$ for a number of ternary ferroelectric compounds.

Compound	T_c (K)	x_0 (bohr)	A (K/bohr^2)
$PbTiO_3$	763	0.565	2390
$LiNbO_3$	1468	0.509	3830
SbSI	296	0.272	3990
$NaNbO_3$	73	0.113	5670
$BaTiO_3$	399	0.250	6410
$LiTaO_3$	891	0.372	6420
$KNbO_3$	708	0.302	7740

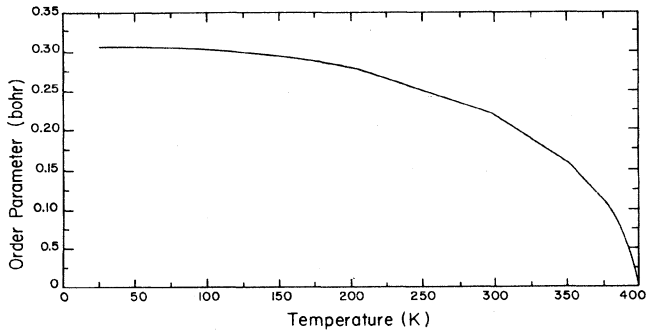

FIG. 1. Order parameter (i.e., oscillator equilibrium position) as a function of temperature.

K) and $x_0=0.258$ bohr, which gives $A=5000$ K/bohr^2. The mass of the oscillator was chosen to be 100 amu (close to that of Nb, for example). These are the only parameters which need to be specified in order to obtain the eigenvectors and eigenvalues of the double-well oscillator above T_c, and will therefore determine the general features of the response curve. The oscillator volume V and the effective charge, which enters into Eq. (3) will effect only the amplitude of the response and are not critical, since we are attempting to reproduce only the qualitative features of the dielectric response. We arbitrarily set the effective charge at three electronic charges and assumed the volume associated with the oscillator to be a cube 5 bohrs on each side.

Once E_b, x_0, and M are specified, Eq. (1) can be solved for the eigenvalues and eigenvectors of the system. This was done, as described in Ref. 6, by expanding the wave functions as sums of harmonic-oscillator wave functions for which the ground-state wave function was optimized to the specific double-well potential using a variational method. This results in a Hamiltonian matrix in the form of a band matrix with a width of nine elements. The matrix was truncated to a rank of 200 for the eigenvalue computation, and only the lowest 50 eigenvalues were retained in the sum over states in Eq. (4). $\chi(0)$ was determined by imposing the condition that the denominator of Eq. (2) be zero at $T=T_c$ and $\omega=0$. One can then use Eqs. (3) and (4) to find the real and imaginary parts of the dielectric response at any other frequency for temperatures above T_c. For temperatures below T_c, the well is no longer symmetric, and, as mentioned above, one must solve for the eigenvectors and eigenvalues of the asymmetric well which will result in a self-consistent parameter. This was done by specifying the desired value of the order parameter a few degrees below T_c, and then computing the value of the one-space coupling constant which would produce the proper order parameter. Hence, one can make the transition strongly first-order-like, by making the order parameter rise quickly below the transition, or second-order-like by letting it rise gradually. The main effect this has on the response curves is to change the rate with which the variations occur with respect to temperature. The transition used in the present work is fairly second order in nature, as can be seen from the curve for the order parameter as a function of temperature shown in Fig. 1. Once the coupling constant is found, Eqs. (3) and (4) can then be used, as before, to find the dielectric response.

As mentioned above, the sum over states contains a damping term linear in the frequency. This form was chosen as the simplest expression which would result in zero damping at $\omega=0$, and will undoubtedly become unphysical at higher frequencies, tending to broaden and suppress the features of the response curve. In the low-frequency regime, in which we are most interested, the effect of this term is to broaden the response peaks and shift them toward lower frequencies in order to simulate, at least qualitatively, the strongly overdamped characteristics of the response near T_c. It was found that a value of $\gamma=0.4$ produces curves which exhibit the characteristic features observed experimentally, although no attempt was made to reproduce curves for a specific material.

IV. RESULTS

The imaginary and real components of the dielectric response for the well described earlier, with $T_c=400$ K, are shown in Fig. 2 for a wide range of temperatures above T_c, and, in Fig. 3 for a wide range below T_c. We have included only the low-frequency range in order to enhance the soft-mode–central-peak phenomena. Higher-frequency peaks exist, but they show no temperature-dependent shifts and have very low ampli-

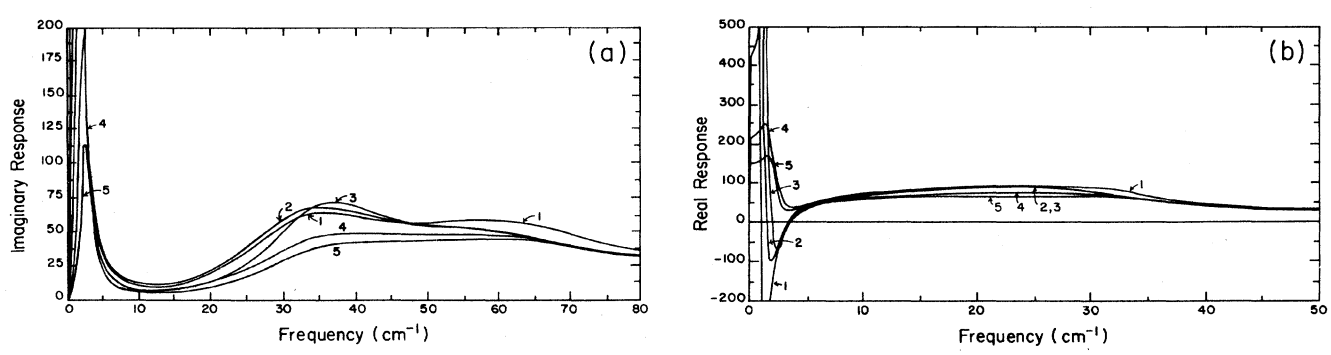

FIG. 2. Dielectric response as a function for temperatures far above $T_c=400$ K. (a) Imaginary component, (b) real component. Values of $|T-T_c|$ are 1, 10 K; 2, 25 K; 3, 50 K; 4, 100 K; 5, 150 K.

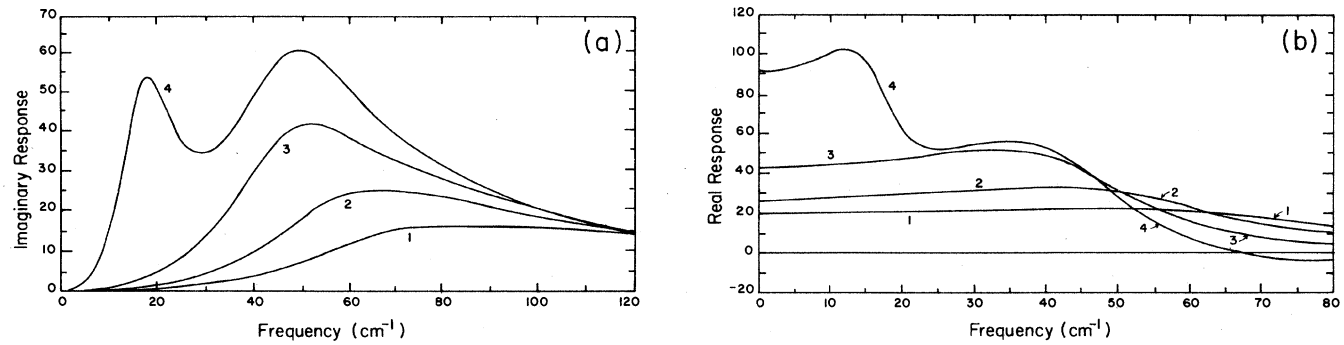

FIG. 3. Dielectric response as a function of frequency for temperatures far below $T_c = 400$ K. (a) Imaginary component, (b) real component. Values of $|T - T_c|$ are 1, 150 K; 2, 100 K; 3, 50 K; 4, 10 K.

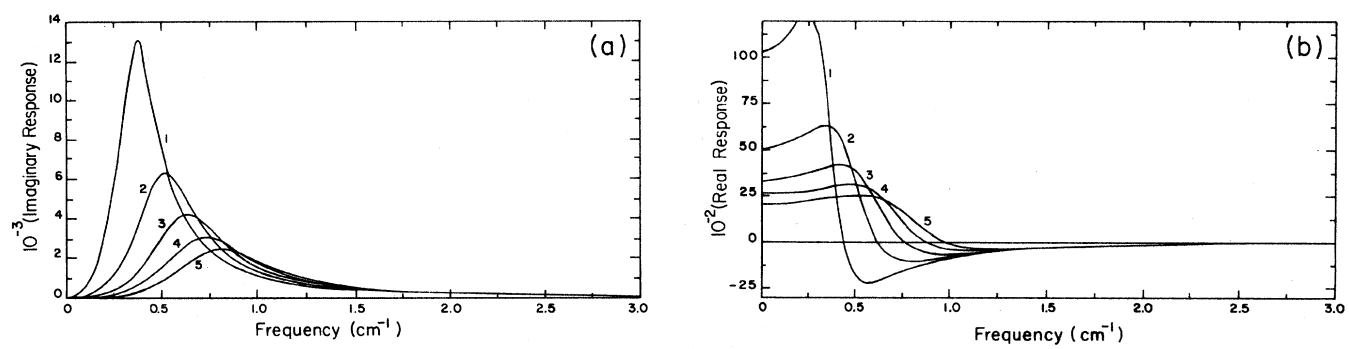

FIG. 4. Dielectric response as a function of frequency for temperatures just above $T_c = 400$ K. (a) Imaginary component, (b) real component. Values of $|T - T_c|$ are 1, 2 K; 2, 4 K; 3, 6 K; 4, 8 K; 5, 10 K.

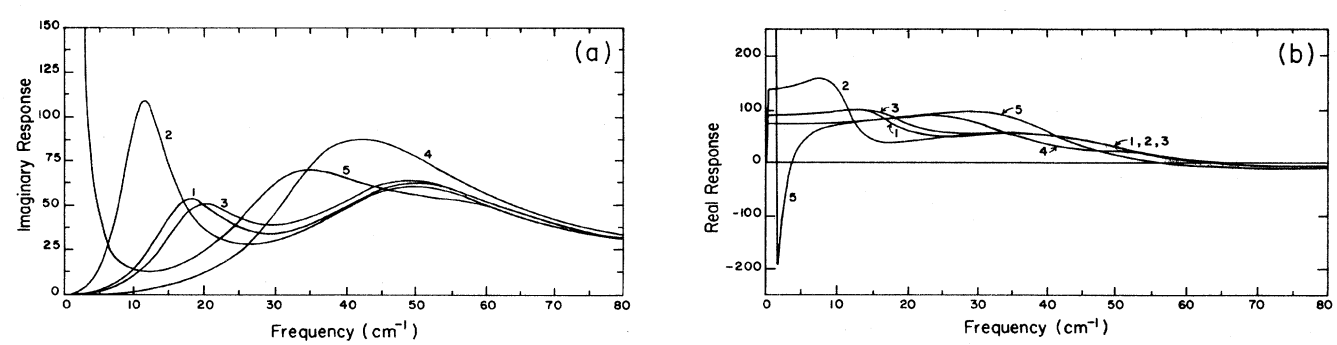

FIG. 5. Dielectric response as a function of frequency for temperatures just below $T_c = 400$ K. (a) Imaginary component (b) real component. Values of $|T - T_c|$ are 1, 10 K; 2, 8 K; 3, 6 K, 4, 4 K; 5, 2 K.

tudes due to the large damping term. Figure 2 clearly shows the downward shift of a low-frequency peak in the imaginary response, as temperature is lowered, with the concurrent increase in amplitude of a still lower frequency peak which appears in addition to the first. This peak shifts rapidly toward lower frequencies as T_c is approached from above, and ultimately diverges at $\omega=0$. (We note that the strong-damping term will tend to make the higher-frequency peak broader and lower in amplitude than it probably should be; however, the basic features of the curve will remain the same.) Below T_c the amplitude of this central peak diminishes rapidly and the peak itself shifts upward in frequency once more as temperature declines. The real component of the response undergoes the expected anomalous dispersion, with the zero-point shifting downward and amplitude increasing as T_c is approached from above.

These characteristics of the response spectrum arise due to large matrix elements between nearly degenerate energy levels near the bottom of the well, separated by about 4 cm^{-1} in this case. As T_c is approached from above, these levels will be the overwhelmingly dominant contributors to the sums over states [Eq. (4)], resulting in increasing intensity in the imaginary response function at lower frequencies. Once the mean-field coupling term comes into play, the symmetry of the well is destroyed, the energy levels begin to separate, and the equilibrium position of the oscillator (i.e., the order parameter in this case) shifts to the deeper of the two lobes of the well. Hence, the central peak is found to arise *quite naturally out of the existing frequency spectrum of the oscillator, as an additional peak to those arising from the normal phonon contributions.* Below the transition, the lower-energy levels are drastically altered, leading to the rapid disappearance of the central peak, whereas levels higher in the well (above the barrier) should remain fairly stable, as will the spectral lines arising from transitions between them.

Figures 4 and 5 show the transformation of the low-frequency dielectric response in more detail for a series of temperatures at 2-K intervals just above and below T_c. These figures demonstrate the rapid thermal rate of change of the response amplitude in the vicinity of the transition temperature. We point out that the frequency range has been reduced to 3 cm^{-1} in order to enhance the features of the central peak. The response scale has also been expanded 2 or 3 orders of magnitude in Fig. 4 for the response above T_c, so that even if the frequency scale had been expanded to include the second low-frequency peak, its amplitude, relative to that of the soft mode, would render it indiscernible. Of particular interest is a slight "retrograde" motion of the imaginary response over a narrow temperature range just below T_c; the peak shifts away from zero frequency, as expected, down to 396 K, then shifts *back toward zero* as the temperature is lowered to 392 K, before once again shifting away at still lower temperatures. The reason for this strange behavior becomes clear when one examines the variation in the energies of the three lowest levels as a function of temperature below T_c (Fig. 6). The spacing between the two lowest lines represents the undamped transition frequency between the two lowest levels, and that between the two upper lines represents transitions between the second and third levels. It is apparent that below the transition temperature the frequency of the previously dominant transition between levels 1 and 2 diverges rapidly, while that between the second and third levels actually decreases for a little while, going through a minimum at, in this case, about 392 K. It is this transition which becomes the low-frequency peak at temperatures only a few degrees below T_c, and the "retrograde" behavior cited above merely reflects the passing of this transition frequency through a minimum. The occurrence of this phenomena is undoubtedly dependent on the actual shape of the double well and the effects of damping, which, we reiterate, is being treated in a very simplistic fashion. Any attempt to accurately reproduce actual experimental results would undoubtedly require treating the damping and perhaps the well shape itself as temperature dependent. The main point is that this model can account for the presence of the central peak directly from a standard quantum-mechanical treatment of the frequency spectrum of the oscillator. With a proper treatment of damping and more sophisticated methods of fitting the various physical parameters in the Hamiltonian, it may be possible to accurately reproduce and, ultimately, predict the features of the dielectric response for "real," linear ferroelectric materials.

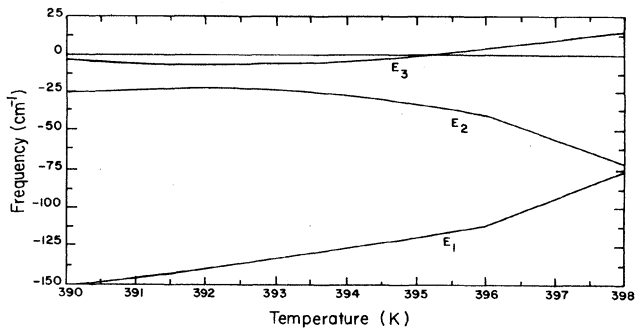

FIG. 6. Frequencies as a function of temperature of the three lowest-energy levels of the double well just below the transition.

ACKNOWLEDGMENTS

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