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# EFFECT OF PRESSURE ON THE DIELECTRIC PROPERTIES OF A PARAELECTRIC MATERIAL*

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Employing a self-consistent renormalization procedure for the treatment of the frequency spectrum of a model paraelectric, the essential features of the pressure dependence of the static dielectric constant of the incipient ferroelectric $KTaO_3$ are reproduced.

IN A PREVIOUS work[1] (hereafter referred to as I) self-consistent phonon techniques were applied to the treatment of the frequency spectrum of a model paraelectric. It was found that many of the qualitative features of the frequency spectrum of the paraelectric $KTaO_3$ could be reproduced, e.g., the temperature dependence of the mode coupling between the optic and acoustic branches of the same symmetry, as well as the temperature dependence of the soft zone center transverse optic mode frequency $\omega_{TO}(\Gamma)$. On the basis of an extension of that model, we examine in this note the effect of pressure on the frequency $\omega_{TO}(\Gamma)$. It is by now well established[2,3] that the temperature dependence of $\omega_{TO}^2(\Gamma)$ reflects a temperature dependence similar to that of reciprocal of the static dielectric constant $\epsilon^{-1}$. This has been demonstrated experimentally for the paraelectric $SrTiO_3$ by Cowley[4] and for the paraelectric $KTaO_3$ by Shirane, *et al.*[5] Similarly, one expects the pressure dependence of $\omega_{TO}^2(\Gamma)$ to follow closely the pressure dependence of $\epsilon^{-1}$. Indeed, our calculations of $\omega_{TO}^2(\Gamma)$ yield good qualitative agreement with recent pressure measurements be Abel[6] on the static dielectric constant of $KTaO_3$. In particular, the temperature $T_1$ at which $\epsilon^{-1}$ exhibits deviations from Curie–Weiss behavior increases with pressure. Furthermore, at fixed temperature $\omega_{TO}^2(\Gamma)$ is found to increase linearly with pressure up to a pressure $P_1$ beyond which deviations from linearity occur.

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The calculations in I were based on a model crystal of the rocksalt structure, with a nearest neighbor anharmonic short range interaction. The dipolar interaction was between rigid anions and cations and was treated in the harmonic approximation. It was shown that the parameters entering into the model could be scaled in such a way that the long wavelength properties were rendered relatively independent of the details of the dipolar interaction, the masses of the two types of ions, and the atomic volume. Thus, it was argued that the qualitative behavior of the zone center soft mode would mirror a similar behavior in a more complicated lattice such as the perovskite structure. This is indeed the case for the pressure dependence of the dielectric properties as we demonstrate below.

Following the procedure introduced in I, we indicate briefly the self-consistent procedure to be followed in treating the pressure dependence of the paraelectric soft mode. We introduce a trial free energy per particle of the form

$$F_t = \frac{1}{N} \mathrm{Tr}[\rho_t (H + \beta^{-1} \ln \rho_t)], \qquad (1)$$

where

$$\rho_t = e^{-\beta H_t} / \mathrm{Tr}\,(e^{-\beta H_t}), \quad \beta \equiv (K_B T)^{-1}. \qquad (2)$$

The canonical density matrix (2) is based on a trial harmonic Hamiltonian of the form

$$H_t = K + V_c^{(2)} + \frac{1}{2} \sum_{\substack{\alpha\beta \\ l\,l' \\ k\,k'}} u_\alpha\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right) \tilde{\phi}_{\alpha\beta}\left(\begin{smallmatrix} l\,l' \\ k\,k' \end{smallmatrix}\right) u_\beta\left(\begin{smallmatrix} l' \\ k' \end{smallmatrix}\right). \tag{3}$$

$K$ denotes the kinetic energy operator for the ions and $V_c^{(2)}$ is the harmonic dipolar interaction. The last term in (3) is a nearest neighbor short range interaction with force constants $\tilde{\phi}$ which are to be determined variationally. The lattice cells are labeled by $l$ and $l'$, the type of ion by $k$ and $k'$, and the Cartesian indices by $\alpha$ and $\beta$. The model Hamiltonian $H$ includes anharmonicity through a longitudinal short range interaction up to fourth order in the ion displacements.

$$H = K + V_c^{(2)} + \frac{1}{2} \sum \{\phi_L^{(2)} (\delta u_x)^2 + \phi_T^{(2)} [(\delta u_y)^2 + (\delta u_z)^2]\} + \sum \phi_L^{(3)} (\delta u_x)^3 + \sum \phi_L^{(4)} (\delta u_x)^4 . \tag{4}$$

The summations in (4) denote a sum over all lattice cells together wirh a six-fold sum over the octahedral environment of nearest neighbor ions, with the relative displacement between nearest neighbor $A$ and $B$ ion pairs being denoted by $\delta u_\alpha$. The local stability of the undistorted structure permits the tangential component of the harmonic short range interaction to be eliminated in terms of the static Coulombic energy per particle $V_c^{(0)}$. Indeed,

$$\phi_T^{(2)} = \frac{1}{3} (V_c^{(0)}/N).$$

The extension of the calculations to I to include strain is straightforward.[7] In (4) we merely make the replacement

$$u_\alpha\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right) \rightarrow u_\alpha\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right) + \sum_\beta \mathcal{E}_{\alpha\beta} X_\beta^0\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right),$$

where $X_\beta^0\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right)$ is a lattice vector of the unstrained lattice and $\mathcal{E}_{\alpha\beta}$ is the symmetric strain tensor appropriate to a homogeneous deformation. The trial free energy $F_t$, including strain, is easily evaluated. To obtain the self-consistent equations in the presence of a finite external pressure, we minimize the Gibbs free energy $G = F_t + PV$ with respect to $\mathcal{E}_{\alpha\beta}$ and the variational parameters $\tilde{\phi}$. The self-consistent determination of $\mathcal{E}_{\alpha\beta}$ and $\tilde{\phi}$ results from the coupled solutions of the equations

$$\frac{\partial G}{\partial \mathcal{E}_{\alpha\beta}} = 0, \quad \frac{\partial G}{\partial \tilde{\phi}_{\alpha\beta}\left(\begin{smallmatrix} l\,l' \\ k\,k' \end{smallmatrix}\right)} = 0.$$

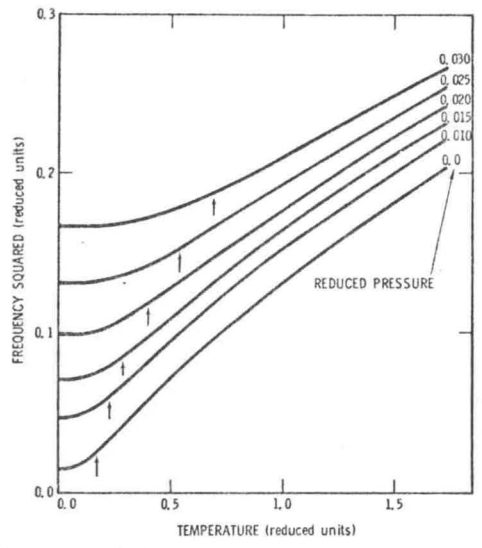


FIG. 1. Plot of the squared transverse optic mode frequency vs. temperature for different pressures. The arrows indicate the temperature $T_1$ below which the static dielectric constant deviates from a Curie–Weiss law. Squared frequencies are expressed in units of $\omega^{-2} = M_R^{-1}[2\pi(Z^*e)^2/r_0^3]$, where $M_R$ is the reduced mass of the ions, $Z^*$ is the effective ionic charge, and $r_0$ is the nearest neighbor distance. Temperature is measured in units of $(\hbar\omega/K_B)$ and pressure in units of Ry per unit cell volume.

The solution we are interested in corresponds to a uniform compression or expansion, so that $\mathcal{E}_{\alpha\alpha} = \mathcal{E}$ and $\mathcal{E}_{\alpha\neq\beta} = 0$.

In Fig. 1 the squared zone center TO mode frequency is plotted as a function of temperature at various pressures – the reduced units introduced in I are used throughout. With units appropriate to $KTaO_3$, the maximum temperature in Fig. 1 corresponds to ~400K and the maximum pressure to ~40 kbar. The most important qualitative feature of the plots in Fig. 1 is the fact that the temperature $T_1$ at which $\omega_{TO}^2(\Gamma)$ deviates from a linear temperature dependence increases with pressure. This mirrors the behavior observed by Abel in his measurements of $\epsilon^{-1}$ as a function of pressure and temperature. In view of the results of I, this behavior is to be expected. Indeed, in I we pointed out that the degree to which the linear temperautre dependence of $\omega_{TO}^2(\Gamma)$ extends into the low temperature regime depends critically on the density of long wavelength 'soft' modes with

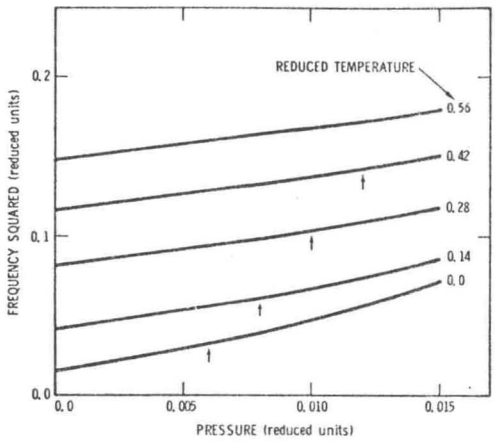


FIG. 2. Plot of the squared transverse optic mode frequency vs. pressure for different temperatures. Quantities are expressed in the reduced units of Fig. 1. The arrows indicate the pressure $P_1$ above which the static dielectric constant deviates from a linear dependence.

$(\hbar\omega/K_B T) < 1$. It is clear that as the pressure is increased the density of these modes decreases and, hence, $T_1$ increases. Figure 2 illustrates the behavior of $\omega_{TO}^2(\Gamma)$ vs. pressure for fixed temperature. For pressures less than 0.006(~8 kbar) it is clear that the dependence of $\omega_{TO}^2(\Gamma)$ on pressure is essentially linear at all temperatures, in agreement with the experimental measurements of Abel. However, we note that at high enough pressures deviations from a linear pressure dependence appear for pressures in excess of $P_1$, with $P_1$ increasing with temperature. This dependence of $\omega_{TO}^2(\Gamma)$ on pressure at fixed temperature is what one would expect on physical grounds. If we fix the temperature, then an increase in pressure will induce a corresponding increase in $\omega_{TO}^2(\Gamma)$ arising from the decrease in atomic volume. For small enough pressures, this change will be linear in the pressure, with deviations from linearity occurring at high pressure.

In summary, we emphasize that although our calculations were carried out on a model crystal of the NaCl structure for simplicity, the qualitative features of the results are essentially model independent and mirror similar behavior in the perovskite $KTaO_3$.

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Использовав самосогласованную методику перенормировки при обработке спектра частот модельного параэлектрика, мы воспроизводим существенные характеристики зависимости статического диэлектрического константа зарождающегося ферроэлектрика $KTaO_3$ от давления.

Utilisant une procédure de renormalisation auto-consistante pour le traitement du spectre de fréquence d'un paraélectrique modèle, les caractéristiques essentielles de la fonction de pression de la constante diélectrique statique de $KTaO_3$ ferroélectrique naissant sont reproduits.