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

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 α and β. 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 with 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 δu_α. 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

$$u_\alpha(l_k) \rightarrow u_\alpha(l_k) + \sum_\beta \mathcal{E}_{\alpha\beta}\, X_\beta^0(l_k),$$

where $X_\beta^0(l_k)$ 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

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

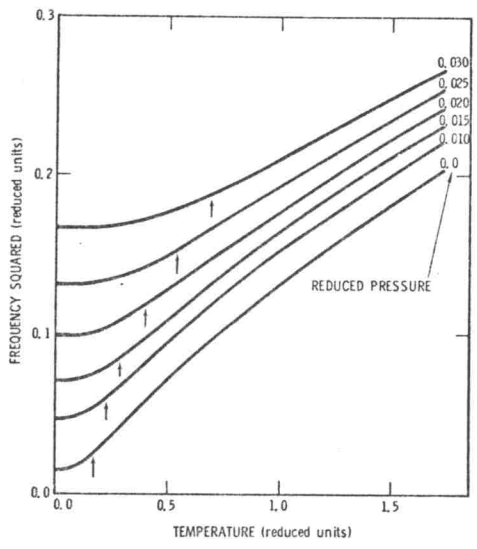

FIG. 1. Plot of the squared transverse optic mode frequency vs. temperature for different pressures. The arrows indicate the temperature T_1 below which the static dielectric constant deviates from a Curie–Weiss law. Squared frequencies are expressed in units of $\omega^{-2} = M_R^{-1}[2\pi(Z^*e)^2/r_0^3]$, 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 ϵ^{-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