ment with the observed one.[20] It seems not improbable from an examination of the published plot of the energy levels as a function of Dq [20] and from observations made in this work that a good fit to the observed energies could be made by using reduced electrostatic f-d parameters and a larger value of Dq. Of course, this is mere speculation and intensity and eigenvalue calculations are both needed. It would certainly be instructive to reexamine these two cases, particularly since they are much simpler two-particle problems and complete diagonalization of the Hamiltonian, including all electronic interactions, can be done.

Recent calculations on the MCD of CaF_2: Tm^{2+} have also supported the model of coupling the crystal field split $5d$ orbitals to the f^{n-1} core terms.[21] It may be possible to account for the observed bandwidths by including the Coulomb f-d interaction. It is certainly of interest to know how the $5d$ electron is affected by, and interacts with, the other electrons in the crystal, and we believe that future studies along the lines discussed will shed much light on the problem.

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Pressure Dependence of Acoustic-Mode–Soft-Optic-Mode Interactions in Ferroelectric $BaTiO_3$†

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Measurements of the pressure dependence of the Raman and Brillouin spectra of tetragonal $BaTiO_3$ at 296 K have shown that the frequency separation between the two branches of the coupled acoustic-mode–soft-optic-mode system increases and the mode coupling decreases with increasing pressure. The results yield independent quantitative support for the model recently discussed by Fleury and Lazay and demonstrate the utility of pressure studies as a unique means of investigating coupled-mode interactions.

We report the first measurements of the effect of hydrostatic pressure on the coupled acoustic-optic modes in ferroelectric $BaTiO_3$. These experiments provide a direct measurement of the pressure dependence of the acoustic- and optic-mode frequencies and dampings and yield the pressure dependence of the coupling between the soft TO mode and the acoustic mode of the same symmetry. The results quantitatively support the harmonically coupled acoustic-mode–optic-mode description for this important ferroelectric. In addition, these results demonstrate the importance of pressure as a general variable for investigating coupled-mode interactions of this type.

Barium titanate is a well-known ferroelectric[1] and extensive studies have been made of its properties. As a function of temperature, the crystal exhibits four phases, of which three are ferroelectric. At room temperature, $BaTiO_3$ is ferroelectric with tetragonal (C_{4v}) symmetry and undergoes a ferroelectric-ferroelectric phase transition to orthorhombic symmetry (C_{2v}) at $T \simeq 7\,^{\circ}C$. This transition is driven by the softening of a zone-center transverse optic mode. Initial measurements of the soft optic mode by Raman scattering techniques were made by DiDomenico *et al.*,[2] who analyzed the spectra assuming a single damped-harmonic-oscillator form for the mode. Several authors[3–5] have shown, however, that the long-wavelength acoustic and optic modes interact in ferroelectric crystals if the optic-mode frequency approaches the acoustic-mode frequency, and Dvorák[5] has shown that the interaction between the long-wavelength acoustic and soft TO modes is large in tetragonal $BaTiO_3$ due to the strong piezoelectric effect and the low frequency of the soft optic mode in this material.

The mode coupling in tetragonal $BaTiO_3$ was very recently observed by Fleury and Lazay,[6] who made a detailed study of the temperature dependence of the Brillouin and Raman spectra.[7] The Brillouin spectra were found to be anomalously temperature dependent near the 7 °C phase transition due to changes in the mode coupling and the decrease in the soft-mode frequency with decreasing temperature. Hydrostatic pressure causes a large increase in the frequency of the soft optic mode[8] and the coupling between the acoustic and optic modes can be expected to decrease as the frequency separation of the two branches increases with pressure. Since the coupling parameter involves quantities that can be measured independently, the direct measurements of the pressure dependence of this parameter provides a sensitive test of the model for the coupled modes. We have therefore investigated the pressure dependence of the Brillouin and Raman scattering to determine the effect of pressure on the coupled-mode system. Combined with our earlier results on the pressure dependences of the spontaneous polarization and dielectric constant, the present results allow a quantitative assessment of the model.

The data were taken using conventional Raman and Brillouin spectrometers. The pressure cell had three optic windows to provide a 90° scattering geometry and the sample (~ 0.05 cm^3), which was a single-domain single crystal, was immersed in the pressure fluid (Isopar H, Humble Oil Co.) to ensure a completely hydrostatic-pressure environment. The spectra were excited with the 4880-Å line of a single-mode argon laser with incident power from 50 to 100 mW. Only data taken at room temperature (296 K) are discussed here; the pressure measurements at other temperatures are currently in progress.

Data taken at 1 bar with the sample in the pressure cell are shown in Fig. 1; the lower trace is the combined Raman-Brillouin spectrum taken with a double-grating spectrometer while the insert is the Brillouin region of the spectrum taken in the first order of a Fabry-Perot interferrometer. The combined spectrum exhibits the pronounced interference minima near the acoustic modes previously noted[6,9] in acoustic-mode–soft-optic-mode interactions. The background near $\omega = 0$ in the Brillouin spectrum is produced by scattering from the soft optic mode which extends to $\omega = 0$ because of the heavy damping of the mode. The Brillouin data shown in Fig. 1 were taken in first order to illustrate the general features of the scattering; data presented in the remainder of the paper were taken in higher order to afford greater accuracy in determining the frequency and linewidth changes in the acoustic branch of the spectrum.

The spectral response $S(\omega)$ of the coupled system is given by

$$S(\omega) = (-1/\pi)\,[\mathrm{Im}\chi(\omega)]\,[n(\omega)+1]\,, \tag{1}$$

where $n(\omega) = (e^{\hbar\omega/kT} - 1)^{-1}$ and $\chi(\omega)$ is the susceptibility which derives from the equations of motion of the coupled system. These equations of motion are obtained from the generalized potential-energy density[5] and are given by[6]

$$\begin{aligned} &(\omega_o^2 - \omega^2 + 2i\Gamma_o\omega)P + aq(K/4\pi)X = F_P\,, \\ &(\omega_a^2 - \omega^2 + 2i\Gamma_a\omega)X + (aq/\rho)P = F_X\,, \end{aligned} \tag{2}$$

where $\omega_o(\omega_a)$ and Γ_o (Γ_a) are the optic (acoustic) frequency and damping; P, X, q, and ρ are the polarization, strain, phonon wave vector, and density, respectively; $a = a_{15}$ is the relevant piezoelectric constant which couples the optic and acoustic phonons, while F_X and F_P are the normalized driving forces. The parameter K relates the temperature-dependent frequency $\omega_o(T)$ to the clamped dielectric constant $\epsilon_a'(T)$ in the Lyddane-Sachs-Teller relation and is defined by

$$\omega_o^2(T) = K/\epsilon_a'(T)\,. \tag{3}$$

Assuming the coupled system is driven by polarization fluctuations (F_P) in this experiment, so that F_X is negligible, solution of Eqs. (2) yields the susceptibility $\chi(\omega)$ [6]:

$$\chi(\omega) = \frac{\chi_o^{(o)}(\omega)}{1 - A^2\chi_o^{(o)}(\omega)\chi_a^{(o)}(\omega)}\,, \tag{4}$$

where the $\chi_j^{(o)}(\omega) \equiv (\omega_j^2 - \omega^2 + 2i\Gamma_j\omega)^{-1}$ are the uncoupled susceptibilities and $A^2 \equiv a^2q^2K/4\pi\rho$ is the coupling constant. Of the parameters which comprise A^2, q is determined by the experiment, while

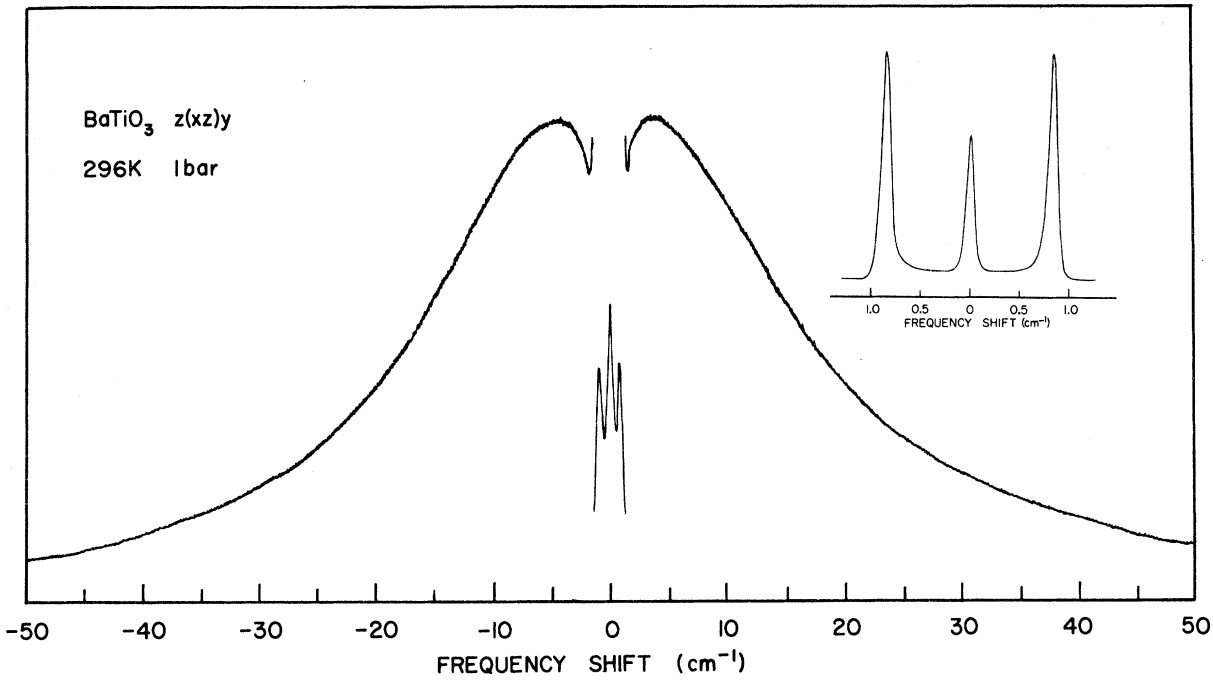

FIG. 1. Combined Raman-Brillouin spectra of $BaTiO_3$ at 1 bar (lower trace). The insert shows the Brillouin region of the spectra taken in first order of the Fabry-Perot.

a, K, and ρ are known at atmospheric pressure from independent measurements.[1]

The large effect of the mode coupling can be illustrated by examining the response of the coupled system for $\omega \approx \omega_a \ll \omega_o$.[7] In this limit the coupled frequency $\omega_a(c)$ and damping $\Gamma_a(c)$ of the low-frequency branch of the system are

$$\omega_a^2(c) \cong \omega_a^2 - \frac{A^2}{\omega_o^2}, \qquad \Gamma_a(c) \cong \Gamma_a + \frac{\Gamma_o A^2}{\omega_o^4}. \tag{5}$$

The effect of hydrostatic pressure increases ω_o, which will therefore increase $\omega_a(c)$ and decrease $\Gamma_a(c)$ ($A^2 < \omega_o^2$). The optic-mode damping Γ_o is expected to be pressure dependent, and the coupling constant A^2 was found by Lazay and Fleury[7] to be temperature dependent and is also expected to be strongly pressure dependent.

The measured frequency increase and linewidth decrease for the acoustic branch of the *coupled* system as a function of pressure are shown in Fig. 2. To evaluate these data, we require the pressure dependence of ω_a, Γ_a, ω_o, Γ_o, and A^2. In principle, the pressure dependence of each of these parameters could be determined from the measured pressure dependence of the Brillouin and Raman spectra; however, such a procedure would result in large uncertainties for the values of the parameters. Therefore, the value of A^2 at 1 bar is determined from other measurements of the parameters which comprise A^2 and the pressure dependence of ω_o is obtained from the measured pressure dependence of ϵ_a.[10] With this information, the pressure dependences of A^2 and Γ_o are obtained from a computer fit to the Brillouin and Raman spectra. It should be noted that the pressure dependences of ω_a and Γ_a also enter the pressure dependence of $\chi(\omega)$; however, the pressure dependences of the other acoustic modes were found to be small. Furthermore, for the entire pressure range investigated, the spectra could be well fit assuming the atmo-

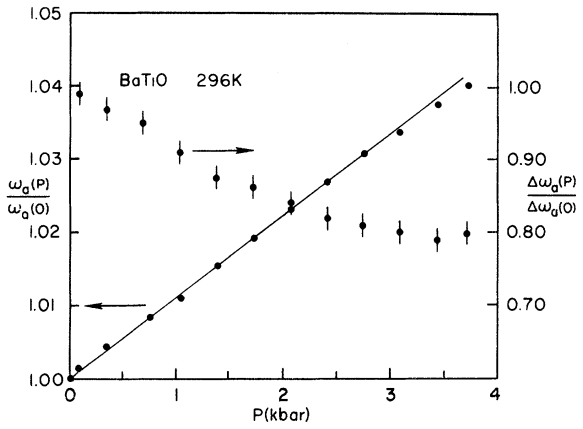

FIG. 2. Pressure dependence of the low-frequency (Brillouin) branch of the *coupled*-mode system.

spheric pressure values of $\omega_a = 1.060\ \mathrm{cm}^{-1}$ and $\Gamma_a = 0.002\ \mathrm{cm}^{-1}$ and these values were used at all pressures. These results are consistent with the lack of temperature dependence observed for these parameters.[7]

Table I summarizes the measured pressure dependences of the parameters. As indicated above, not all of the parameters are independent; rather, $d\ln\omega_o/dP$ is given by $d\ln\epsilon_a/dP = -2d\ln\omega_o/dP$. The pressure dependence of A^2 should be discussed in more detail. The procedure used to obtain $d\ln\omega_o/dP$ assumes K is pressure independent. Thus the decrease in A^2 reflects only changes in a_{15}, q, and ρ. From the volume compressibility,[8] we have $d\ln\rho/dP = 0.00078$/kbar. The change in q arises from the change in the refractive index n with pressure. If we take the change in n as approximately that of $SrTiO_3$, then $d\ln n/dP \cong -0.00005$/kbar. Both of these contributions to A^2 are small compared to the measured $d\ln A^2/dP = -0.0323$/kbar, so that $d\ln A^2/dP \cong d\ln a_{15}^2/dP$. Relating a_{15} to the spontaneous polarization through the equation

$$a_{15} = Q_{44} P_s , \tag{6}$$

where Q_{44} is the electrostrictive constant which is essentially temperature independent,[1] and neglecting the pressure dependence of Q_{44}, gives

$$\left(\frac{d\ln a_{15}}{dP}\right)_T = \left(\frac{d\ln P_s}{dP}\right)_T . \tag{7}$$

From the above discussion we then have

$$\left(\frac{d\ln a_{15}}{dP}\right)_T \cong \frac{1}{2}\left(\frac{d\ln A^2}{dP}\right)_T \cong \left(\frac{d\ln P_s}{dP}\right)_T , \tag{8}$$

so that a comparison can be made between our measurements of the pressure dependence of A^2 and the previously reported measurements of the pressure dependence of P_s. From Ref. 10, $d\ln P_s/dP = -1.37\%$/kbar, which is to be compared with $\frac{1}{2}(d\ln A^2/dP)_T = -1.61\%$/kbar. In view of the approximations made in arriving at Eq. (8), the agreement is quite good. Including the decrease in n and the increase in ρ reduces $\frac{1}{2}(d\ln A^2/dP)_T$ to -1.57%/kbar; the remaining difference between $(\frac{1}{2}d\ln A^2/dP)_T$ and $(d\ln P_s/dP)_T$ may be due either to the neglected pressure variation of K and Q_{44} or to the observed variation of $(d\ln P_s/dP)_T$ between different samples.[10]

TABLE I. Values of various parameters and their pressure derivatives for $BaTiO_3$ at 296 K.

Parameter	Value (x)	$(1/x)dx/dP$ (%/kbar)
ϵ	2660	−2.63
ω_0	35.0 cm^{-1}	1.32
Γ_0	44 cm^{-1}	1.25
ω_a	1.060 cm^{-1}	...
Γ_a	0.002 cm^{-1}	...
A^2	361 cm^{-4}	−3.23

In conclusion, the present results show that the coupling between the modes is essentially through the piezoelectric interaction at room temperature, and they demonstrate the utility of hydrostatic pressure as an important variable for evaluating coupled-mode interactions. Extension of these measurements to temperatures very near the 7 and 133 °C phase-transition temperatures should provide a more detailed picture of the nature of the mode coupling, the phase transitions, and ferroelectric properties of $BaTiO_3$.

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