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ELECTRIC FIELD DEPENDENCE OF OPTICAL-PHONON FREQUENCIES

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In electric-field–induced Raman-scattering experiments on the cubic perovskite $SrTiO_3$, a striking electric field shift and splitting of the "soft" optical phonon mode is observed. Experiments were done at temperatures ranging from 8 to 250°K and for electric fields between 0.2 and 12 kV/cm. We interpret the temperature and electric field dependence of the phonon frequency using Devonshire model of ferroelectricity and the Lyddane-Sachs-Teller relation.

In Cochran's theory of ferroelectricity,[1] soft-phonon modes are of central importance. As the transition temperature is approached from above (in the paraelectric phase) the phonon frequency tends toward zero. We have previously reported studies of the soft-phonon modes in $KTaO_3$[2] and $SrTiO_3$[3] in which an electric field was employed to induce Raman scattering from these odd-parity phonons. In this Letter we report the observation of striking electric field dependence of some optical-phonon frequencies in $SrTiO_3$. In particular, the lowest lying transverse optical phonon has been observed to shift in frequency by 400% and to split into two components polarized parallel and perpendicular to the applied field. Schaufele, Weber, and Silverman[4] have recently observed a small electric-field shift in the soft mode frequency at 77°K.

We have examined the induced Raman scattering at a variety of electric fields (between 0.2 and 12 kV/cm) and at temperatures between 8 and 250°K with the following general results: (1) With very small applied fields the soft-mode frequency varies with temperature from 11 cm^{-1} at 8°K to 85 cm^{-1} at 250°K, in good agreement with the predictions of the Lyddane-Sachs-Teller (LST) relation inserting Weaver's values of the dielectric constant.[5] (2) At low temperatures (<55°K) the spectrum of the field-induced scattering exhibits a field-dependent structure. Figure 1, taken at 8°K, shows that as the field is increased not only does the frequency of the soft mode shift from 11 to 45 cm^{-1}, but also three additional peaks become visible. Those labeled *B* and *C* are identified as components of the soft TO mode, polarized perpendicular and parallel to the applied field, respectively. Peaks *A* and *D* are not components of the soft mode, and appear as well in the intrinsic spectrum of $SrTiO_3$ [see Fig. 1(b)]. (3) The effects of electric field become increasingly strong as the temperature is lowered. This is true for the efficiency of the induced Raman scattering as well as for the shifting and splitting of phonon frequencies. (4) In contrast to the case of $KTaO_3$, we have observed in $SrTiO_3$ induced Raman scattering from the other TO modes at 170 and 550 cm^{-1}. We shall not discuss these results here except to say that these

mode frequencies exhibited neither temperature nor electric field dependence, and that the frequencies we observe are in good agreement with values obtained by other methods.[6,7]

We shall show below that our observations on the soft mode can be quantitatively accounted for in terms of a combination of simple thermodynamic theory and a slightly generalized LST relation.

The details of the experiment were essentially as in the earlier work[2] on $KTaO_3$ with the exception of the method of applying the electric field. To facilitate accurate measurements of field strength and to overcome possible problems with sample heating at low temperatures, we imposed repetitive square voltage pulses and synchronously detected the field-induced scattered light using a gated "boxcar" integrator. This method permitted discrimination against the strong background spectrum of intrinsic scattered light. By the intrinsic spectrum we mean the spectrum obtained by usual Raman techniques with no applied fields. Both the pulse width ($\leq$200 μsec) and the repetition rate (10 to 300/sec) were varied so as to prevent sample heating even when the peak field strength was increased substantially. Boxcar gate widths were typically one-fourth the voltage pulse width.

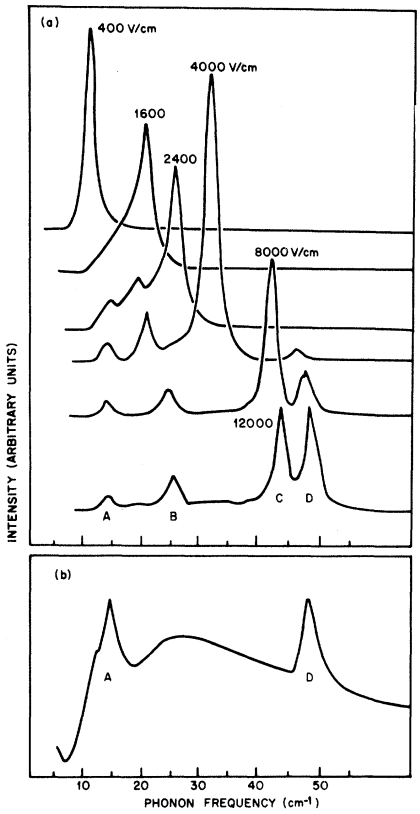

FIG. 1. (a) Electric-field–induced Raman spectrum in $SrTiO_3$ at 8°K. The spectra for different applied fields exhibit the large shift of the soft-phonon mode component C polarized paralled to the electric field, as well as the lesser shift for the soft-mode component B polarized perpendicular to the field. The components of the Raman-scattering tensor observed to be nonzero are α_{xz} for peaks A and B, and α_{xx} for peaks C and D. The electric field is applied in the x direction. The induced scattering intensity generally increased as the field increased and the vertical scales are not the same for spectra obtained at different field strengths. (b) The portion of the intrinsic (zero-field) spectrum of $SrTiO_3$ taken at 8°K and with the same slit settings as in (a). The sharp features A and D appear in both the induced and intrinsic spectra. In the intrinsic spectrum the nonzero Raman tensor components are α_{xz} for A and α_{xx} for D.

Cochran[1] and Anderson[8] first pointed out the implications of soft-phonon modes for the ferroelectric phase transition. The fundamental relation is that due to LST[9]:

$$\epsilon/\epsilon_\infty = \Pi_i(\omega_{Li}/\omega_{Ti})^2. \quad (1)$$

Here ω_{Li} and ω_{Ti} refer to the longitudinal and transverse optical phonon frequencies; ϵ_∞ is the high-frequency dielectric constant, and ϵ the low-frequency dielectric constant. Under the assumption that only the soft-mode frequency, ω_S, varies with temperature and that ϵ_∞ is insensitive to temperature, Eq. (1) reduces to $\omega_S^2\epsilon = \text{const.}$ (independent of T). Our result at very low fields on the soft-mode frequency in $SrTiO_3$ agree with this simplified form when the measured values of the dielectric constant[5] are inserted: $\omega_S^2\epsilon = 3.0\times10^6$ cm^{-2}, over the temperature range from 8 to 250°K.

To understand the behavior of the soft-mode frequency under the influence of electric fields, we assume that the LST relation remains valid in the presence of a field and use a simple phenomenological thermodynamic argument to obtain the field dependence of the dielectric response. Expressing the crystal's free energy per unit volume, A, in terms of the temperature, T, and the polarization, P, we have —ignoring tensor indices,[10] and assuming $\epsilon \gg 1$—

$$A(T,P) = \tfrac{1}{2}\chi(T)P^2 + \tfrac{1}{4}\xi(T)P^4 + \cdots \text{ (in mks units)}. \quad (2)$$

The derivatives of A are the useful quantities:

$$E = \partial A/\partial P = \chi(T)P + \xi(T)P^3 + \cdots \quad \text{(electric field)}, \quad (3)$$

$$\frac{1}{\epsilon_0\epsilon} = \frac{\partial^2 A}{\partial P^2} = \chi(T) + 3\xi(T)P^2 + \cdots \quad \text{(inverse dielectric constant)}, \quad (4)$$

where ϵ_0 is the permittivity of the vacuum. If care is taken to handle the approximations in a consistent manner one obtains the limiting relations

$$\frac{1}{\epsilon_0\epsilon} = \chi(T)\left[1 + \frac{3\xi(T)}{\chi^3(T)}E^2 + \cdots\right] \quad \text{(for small fields)}, \quad (5)$$

$$(\epsilon_0\epsilon)^{-1} = -\chi(T) + 3[\xi(T)E^2]^{1/3} + \cdots \quad \text{(for large fields)}. \quad (6)$$

The distinction between large and small fields is determined by which of the terms in Eq. (4) is dominant. Even for the largest fields encountered in our experiments, terms of higher order than P^4 in Eq. (2) are unnecessary to explain our experimental results. Both limits, Eqs. (5) and (6), have been used to obtain the nonlinear coefficient $\xi(T)$ from the temperature dependence of $\omega_S(E)$. In the high-field region (easily reached experimentally at 40°K and below), combination of Eq. (6) with the LST relation predicts

$$\omega_S^2(E) + \omega_S^2(E=0) = 3\times 10^6 \epsilon_0 \times [3\xi(T)E^2]^{1/3}. \quad (7)$$

This relationship [that is, a linear dependence of $\omega_S^2(E) + \omega_S^2(E=0)$ on $E^{2/3}$] has been verified experimentally at temperatures of 8, 27, and 40°K. The value of ξ obtained is $(1.2 \pm 0.3)\times 10^{10}$ in mks units and appears in this region to be independent of temperature. The value of ξ is larger by about a factor of 2 than that derived from measurements of Rupprecht, Bell, and Silverman[11] on the nonlinear dielectric constant of $SrTiO_3$ above 90°K and by about the same factor than the value found by Itschner from direct measurements of the dielectric constant[12] at low temperatures. Possible sources of this discrepancy include inaccuracy in precise determination of electric field and differences in dielectric response to dc and pulsed fields.

Figure 2 shows the temperature dependence of ω_S for various applied fields. While the field-induced frequency shift is indeed dramatic at low temperatures, the effect diminishes drastically as the temperature is increased; it is nearly unobservable above 80°K. We find a phonon frequency shift of only ~1.5 cm^{-1} for a field of 12 kV/cm at 77°K, which disagrees with the value 4 cm^{-1} of Schaufele, Weber, and Silverman.[4] This discrepancy arises from their interpretation of a peak in the intrinsic spectrum as the zero-field soft mode. This also leads them to conclude that the frequency shift is linear in field, whereas it is in fact quadratic, as expected from Eq. (5).

Peaks A and D appear in both the field-induced spectrum [Fig. 1(a)] and the intrinsic spectrum [Fig. 1(b)]. Their polarization properties are as follows: For incident light polarized parallel to the applied field (x direction), light scattered at peak A has Raman tensor component α_{xz}, while peak D has Raman tensor component α_{xx}. These peaks are unique in that no other features of the complicated intrinsic spectrum[13] of $SrTiO_3$ appear in the field-induced spectrum. A more detailed discussion of these peaks will not be given here, but their narrow width and their temperature and electric field behavior argue against their being due to strains, impurities, or two-phonon processes.

The large phonon frequency shifts induced by easily achievable electric fields suggest a number of interesting scientific and technological uses. At low temperatures the linewidth of the soft mode remains quite narrow (<2 cm^{-1}) even as the field is raised and the phonon frequency is swept from 11 to 45 cm^{-1}. This,

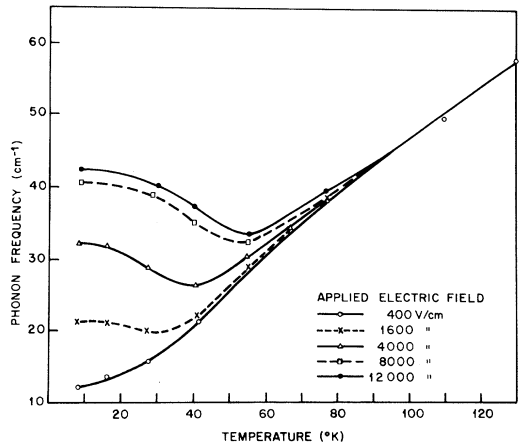

FIG. 2. Temperature dependence of the soft-mode frequency for various values of applied electric field. Only the C component is plotted here. Above 100°K the electric-field shift could not be seen, and so the curve does not continue to the highest temperatures we examined.

coupled with the large scattering efficiency induced by the field, makes the soft mode a prime candidate for an electric-field–tunable Raman laser. In addition, the natural infrared activity of the mode would provide radiation in the 10- to 100-cm^{-1} region of the spectrum. The knowledge of the soft-mode frequency and its variation with temperature and electric field should prove useful in other experiments. One example has already been given here by relating the variation in the phonon frequency to the dielectric properties of $SrTiO_3$. Many other physical parameters, such as thermal conductivity, depend upon the phonons for their microscopic origin. A movable phonon mode is a very useful probe for testing theories of optical, thermal, and mechanical properties of solids.

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ANOMALOUS TOTAL-ENERGY DISTRIBUTION FOR A MOLYBDENUM FIELD EMITTER

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The possibility of using field-electron microscopy to elucidate special features of bulk electronic band structure for metals has been proposed in previous theoretical[1,2] and experimental findings.[3,4] In a previous publication[3] an anomalous total-energy distribution (TED) from the ⟨100⟩ direction of tungsten, consisting of an enhanced emission (see Fig. 1) approximately 0.35 eV below the Fermi level E_F, was reported. Upon examination of theoretically and experimentally suggested band structures and Fermi surface shapes along the ⟨100⟩ of tungsten one could correlate the TED results with special bulk electronic features. Although molybdenum is nearly identical to tungsten both geometrically and electronically speaking, some notable differences along the ⟨100⟩ direction band structure, which might be manifested in TED measurements, motivated our undertaking of a similar investigation of Mo.

The expected electronic band structure for tungsten along the ⟨100⟩ direction (the ΓH direction in $\vec{k}$ space) is reproduced in Fig. 2 from a previous publication by Mattheiss.[5] Introduction of spin-orbit interactions (proportional to ξ_{5d}) results in a splitting of the Δ_5 degeneracy and removal of the Δ_7 crossing. Mattheiss points out that a value of $\xi_{5d} = 0.03$ Ry (0.4 eV) can account for the disappearance of the electron lenses along the ⟨100⟩ axes in tungsten, a result obtained by Sparlin and Marcus[6] from de Haas–van Alphen measurements. Thus, if the upper Δ_7 band does not dip below the Fermi level E_F [see Figs. 2(e) or 2(d)] one expects TED measurements of field-emitted electrons near E_F to be normal (i.e., obey the Sommerfeld model for field emission); however, at approximately 0.35 eV below E_F, emission