ELECTRIC-FIELD-INDUCED RAMAN EFFECT IN PARAELECTRIC CRYSTALS

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First-order Raman effect has been induced in the cubic perovskite, $KTaO_3$, by application of an external electric field. The normally infrared-active "ferroelectric" mode has thus been studied by Raman scattering at temperatures between 8 and 300°K.

In crystals possessing inversion symmetry at each atomic site, there is no first-order Raman effect because all the long-wavelength phonons have odd parity. Here we report the observation of first-order Raman scattering in a cubic perovskite crystal, $KTaO_3$, induced by an applied electric field which serves to remove the inversion symmetry of the crystal. Upon application of the electric field a large well-defined peak in the scattered light emerges. At 300°K the frequency of this line (~85 cm^{-1}) agrees well with that found by infrared (IR) studies of Miller and Spitzer[1] for the low-frequency TO mode. As the temperature was decreased from 300 to 8°K, the frequency of the induced scattering decreased as expected for the so-called "soft" or "ferroelectric" mode in $KTaO_3$.[2] The dependence of the observed scattering upon temperature and applied field, as well as the observation of both Stokes and anti-Stokes scattering, confirm that we have indeed made the "ferroelectric" mode in $KTaO_3$ Raman active.

For these experiments we employed an argon laser (4880 Å), a Spex double monochromator, and photoelectric detection. The incident light could be polarized either parallel or perpendicular to the applied field, and the polarization of the scattered light observed could also be selected. The $KTaO_3$ crystal (undoped) was provided with Ohmic electrodes of evaporated films of Cr and Au, clamped between In-faced Cu contacts and mounted on the cold finger of an optical Dewar. The electric field was applied in the (001) direction, while the incident and scattered light beams propagated in the (110) and $(1\bar{1}0)$ directions, respectively.

In the absence of applied field, the spectrum of light scattered from $KTaO_3$ is quite strong and rich in two phonon bands ranging in frequency from ~50 to ~800 cm^{-1} [see Fig. 1(a)]. Since the induced first-order scattering was expected to be much weaker than the natural second-order scattering, it was necessary to discriminate against the latter by imposing an alternating electric field (210 cps) and then searching for a scattered light signal modulated synchronously at twice the applied field frequency. The success of the technique is evident in Fig. 1(b). As the amplitude of the applied field, E_{ac}, is increased, the induced scattering (which appears at 47 cm^{-1} for $T \simeq 80$°K) increases as E_{ac}^2. We observed no other first-order scattering peaks in our experiments, even though our analysis indicates that in cubic perovskites all phonons are theoretically Raman active under the influence of an external field. However, the "ferroelectric" mode is expected to be the most strongly affected phonon for a given applied field.

The field dependence of the induced scattering intensity, I_1, can be understood from a simple perturbation theory. The lowest order non-

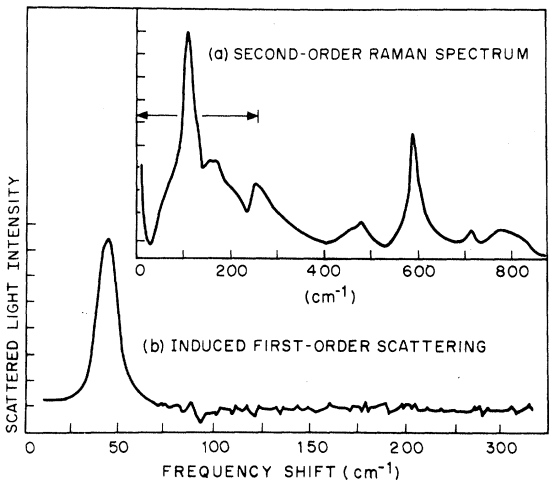

FIG. 1. Spectrum of light scattered from $KTaO_3$ at 77°K. (a) Intrinsic second-order spectrum taken with no applied electric field. Horizontal arrow indicates frequency range shown in Fig. 1(b). (b) Electric-field–induced scattering from the "ferroelectric" mode. The E_{ac} applied here was 10 000 V/cm at 210 cps. Scattered light modulated at 420 cps was detected. Discrimination against the strong second-order scattering is virtually complete. Note that the intensity scale in (b) is approximately 10 times as sensitive as that in (a).

vanishing matrix element, M, for induced scattering from a phonon of odd parity satisfies

$$M \propto \sum_{v'v''} \frac{\langle v'''|\vec{E}_1\cdot\vec{r}|v''\rangle\langle v''|\vec{E}_0\cdot\vec{r}|v'\rangle\langle v'|\vec{E}_{ac}\cdot\vec{r}|v\rangle}{(\omega''\pm\omega_{ac}\pm\omega_0)(\omega'\pm\omega_{ac})}, \quad (1)$$

where $|v\rangle$ is the initial state of the crystal; $|v'\rangle$ and $|v''\rangle$ are virtual excited states of odd and even parity, respectively; $|v'''\rangle$ is the initial state $|v\rangle$ plus one phonon; and E_0 and E_1, ω_0 and ω_1 are the field strengths and frequencies of the incident and scattered optical fields, respectively. The scattered intensity, I_1, is proportional to M^2 and thus to $E_{ac}{}^2$.

For a given applied field strength, the intensity of the scattered light was observed to increase when the temperature was lowered. This is primarily because in $KTaO_3$ the dielectric constant, ϵ_0, increases as T decreases,[3] thus increasing the response of the crystal to the field, E_{ac}. The integrated scattered intensity increases by a factor of about 10 in going from 300 to 80°K, and by about another factor of 10 between 80 and 8°K.

Comparing the integrated intensity of the induced scattering at 300°K and 14 000 V/cm with that of the 992-cm^{-1} line in liquid benzene, we find the latter to be about 20 times stronger. Since the absolute Raman cross section for the benzene line has been measured,[4] we can estimate the induced extinction coefficient for the ferroelectric mode in $KTaO_3$ under the above conditions to be 5×10^{-8} per cm of path length.

The more quantitative information derived from this experiment which pertains to the "ferroelectric" mode itself is summarized in Fig. 2, where the temperature dependence of the mode frequency is plotted. Except at the lowest temperatures this temperature dependence of the frequency is in quite good agreement with the Lyddane-Sachs-Teller relation[5]

$$\omega_{TO}{}^2/\omega_{LO}{}^2 = \epsilon_\infty/\epsilon_0, \quad (2)$$

where ω_{LO} and ϵ_∞ are assumed temperature independent and $\epsilon_0(T)$ has the temperature dependence measured by Wemple.[3] The dielectric constant above about 40°K has the paraelectric behavior $\epsilon_0 \propto (T-T_C)^{-1}$ which has been associated with a possible ferroelectric transition[2] at T_C. Below 40°K, ϵ_0 rises less rapidly than $(T-T_C)^{-1}$, and remains finite at the lowest temperatures. The solid line in Fig. 2 is a plot of $A/[\epsilon_0(T)]^{1/2}$. Very similar temperature dependence of this phonon frequency has been observed in neutron scattering by Shirane, Nathans, and Minkiewicz[6] and in infrared reflectivity by Perry and McNelly.[7] These experiments, though of lower resolution than ours as regards the phonon frequency, also reveal departure from Eq. (2) below about 15°K. This departure may be associated with a possible phase transition in the neighborhood of 15°K.[6]

Use of the induced Raman effect to study this phonon has enabled us to measure its linewidth more accurately than is possible with other techniques. The full width at half-height is 6 cm^{-1} at 8°K and increases roughly linearly with temperature at 24 cm^{-1} at room temperature. Our values of ω_{TO} are consistently lower by 3-4 cm^{-1} than those from neutron scattering[6] in the range 150-300°K.

The symmetry of the Raman tensor has been examined by studying the intensity of the scattering in the various polarization combinations available. The electric field distorts the O_h symmetry of the $KTaO_3$ unit cell into C_{4v}, where

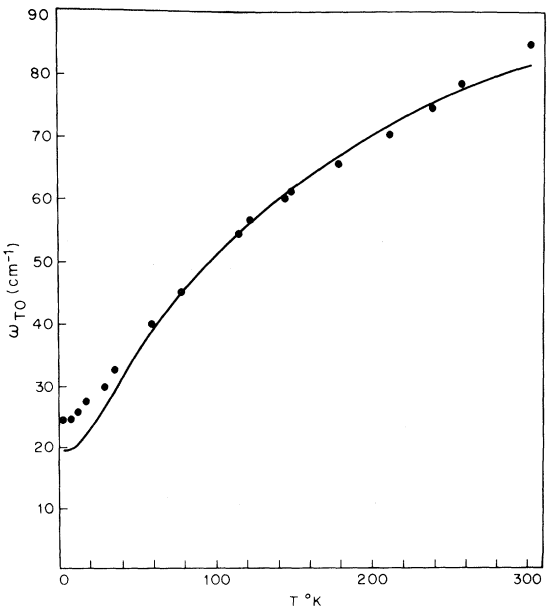

FIG. 2. Temperature dependence of the "ferroelectric" mode frequency. The solid line is a plot of $1.28\times10^3/[\epsilon_0(T)]^{1/2}$, where $\epsilon_0(T)$ was taken from Ref. 3.

the fourfold axis, z, is the direction of the applied field. The phonon generated in the scattering process propagates along the x axis, and may be (1) transversely polarized in the z direction, giving Raman-tensor elements α_{zz}, and $\alpha_{xx}=\alpha_{yy}$; (2) transversely polarized in the y direction, giving Raman-tensor elements $\alpha_{yz}=\alpha_{zy}$; or (3) longitudinally polarized, giving Raman-tensor elements $\alpha_{xz}=\alpha_{zx}$. We have observed α_{zz} and α_{zy} for the two degenerate low-frequency transverse phonons, and find $|\alpha_{zz}|^2 \cong 5|\alpha_{zy}|^2$; and $|\alpha_{xx}=\alpha_{yy}|^2 \approx 0$.

Finally, we mention the observation of some polarization saturation effects on the Raman scattering at low temperatures and high fields. Wemple[3] and Kahng and Wemple[7] have observed that the low-frequency polarization in $KTaO_3$ is not strictly proportional to applied field, but tends to saturate, the fields necessary for appreciable saturation being lower, the lower the temperature. Since ϵ_0 is so intimately connected with the frequency of the phonon studied here [see Eq. (2)], one expects high applied fields to affect the phonon and thus the spectrum of light scattered from it. We have observed such effects at low temperatures (8°K) and for fields in the range of 1000 to 10 000 V/cm. While these observations are preliminary, it is clear that the mode frequency shifts to higher values as the field is increased, and there appears to be a change in the line shape of the scattered light. However, our present field-modulation scheme is inappropriate for the detailed study of such effects and further work is being done with a modified apparatus.

We have shown that it is experimentally possible to study phonons which are not naturally Raman active with the help of external electric fields. This technique is capable of finer detail than IR reflectivity or neutron scattering in certain frequency ranges. The particular type of mode studied here can probably also be studied in several other paraelectric crystals, such as $SrTiO_3$ and $BaTiO_3$, for example. There the method should help resolve the question of possible anomalous first-order Raman lines recently reported for conventional Raman studies in these materials.[9]

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SCATTERING OF FAST ELECTRONS BY ORIENTED Ho^{165} NUCLEI*

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Many spherically symmetric nuclei have been investigated by the method of fast-electron scattering at Stanford in recent years.[1] A useful factor in determining the size of these nuclei is the well-pronounced diffraction structure of the measured differential scattering cross sections. However, nuclei with a large deformation do not exhibit such well-defined diffraction features and in such cases the accurate determination of the nuclear charge distribution is considerably more difficult.[2] Consideration was given to the possibility of obtaining more information about the deformed nuclei group by measuring the electron scattering cross sections for oriented nuclei.

The first experiment of this type was performed at Stanford University using the Mark III electron linear accelerator. The nucleus chosen for this experiment was Ho^{165} which has a large intrinsic electric quadrupole moment[3,4] of about