Comments and Addenda

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Mixing of Internal Modes of Different Molecular Symmetry in $LiIO_3$†

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We present experimental data which show that there is a smooth and continuous frequency and polarization variation with phonon propagating directions in single-crystal $LiIO_3$, which implies a mixing of phonon symmetries at $\mathbf{k}=0$ and continuous mixing of internal vibrational modes of the IO_3^- ion.

POLARIZATION and frequency dependence on phonon propagating directions in single-crystal $LiIO_3$ were made. They showed that as the phonon propagation direction is changed, there is a continuous frequency and polarization variation with propagation direction which implies a mixing of phonon symmetries of the internal modes of the IO_3^- ion in the crystal.

It is well known that phonons which are both infrared- and Raman-active can have direction-dependent phonon frequency and polarization. Such a phenomenon has been described for simple wurtzite-type crystals[1] and quartz.[2] We report such a direction-dependent mixing for the case of the "molecular" crystal $LiIO_3$ which can only be understood as a direction-dependent mixing of the ν_1 (symmetrical stretch) and ν_3 (asymmetrical stretch) internal modes of the IO_3^- ion.

Crystalline $LiIO_3$ belongs to the P63 (C_6^6) space group with two molecules per unit cell.[3] Group theory predicts optical phonons belonging to the following irreducible representations: $4A+5B+4E_1+5E_2$. A complete infrared and Raman analysis of those modes is forthcoming.[4] The A and E_1 symmetry phonons are both Raman- and infrared-active with the A-phonon polarization in the z direction (parallel to the C_6 axis) and with the E_1 phonon polarization in the (xy) plane. The E_2 phonons are only Raman-active, and the B phonons both Raman- and infrared-inactive. The frequency of the internal modes of the IO_3^- ion obtained from IO_3^- ion solutions are the following[5]: symmetrical stretch $\nu_1=779\ \mathrm{cm}^{-1}$, asymmetric stretch $\nu_3=826\ \mathrm{cm}^{-1}$, while the symmetrical and asymmetrical bending modes ν_2 and ν_4 occur at 390 and 330 cm^{-1}. When the IO_3^- ions are in the $LiIO_3$ crystals, the factor group analysis results in an A and a B mode corresponding to the ν_1 symmetrical in-phase and out-of-phase stretches of the IO_3^- ion and an E_1 and E_2 mode corresponding to the in-phase and out-of-phase ν_3 asymetric internal stretches of the IO_3^- ion. Since both the A and E_1 modes are infrared- and Raman-active, they will be split by the long-range electrostatic forces into transverse and longitudinal optic modes. Performing the usual Raman-scattering experiments using different geometries combined with polarized infrared reflectivity, the following modes were observed: $A(\mathrm{TO})=784\ \mathrm{cm}^{-1}$, $A(\mathrm{LO})=810\ \mathrm{cm}^{-1}$, $E_1(\mathrm{TO})=762\ \mathrm{cm}^{-1}$, and $E_1(\mathrm{LO})=838\ \mathrm{cm}^{-1}$. From this data we see that the $A_{\mathrm{TO\text{-}LO}}$ long-range electrostatic splitting is 26 cm^{-1}, the E_1 TO-LO electrostatic splitting is 76 cm^{-1}, the A_{TO}-$E_{1\mathrm{TO}}$ anisotropy splitting is 22 cm^{-1}, and the A_{LO}-$E_{1\mathrm{TO}}$ anisotropy splitting is 28 cm^{-1}. This crystal thus seems to be an intermediate case between Loudon's[6] case (I) ($\omega_{\mathrm{LO}}{}^{\perp}-\omega_{\mathrm{TO}}{}^{\perp}\gg\omega_{\mathrm{TO}}{}''-\omega_{\mathrm{TO}}{}^{\perp}$ or $\omega_{\mathrm{LO}}{}''-\omega_{\mathrm{LO}}{}^{\perp}$), i.e., when the electrostatic interaction dominates over anisotropy splitting, and case (II) ($\omega_{\mathrm{TO}}{}''-\omega_{\mathrm{TO}}{}^{\perp}$ and $\omega_{\mathrm{LO}}{}''-\omega_{\mathrm{LO}}{}^{\perp}\gg\omega_{\mathrm{LO}}{}^{\perp}-\omega_{\mathrm{TO}}{}^{\perp}$ or $\omega_{\mathrm{LO}}{}''-\omega_{\mathrm{TO}}{}''$), where anisotropy splitting dominates over the long-range electrostatic field.

When propagating the phonon in the xz plane and measuring the (yy), A polarizability tensor component,

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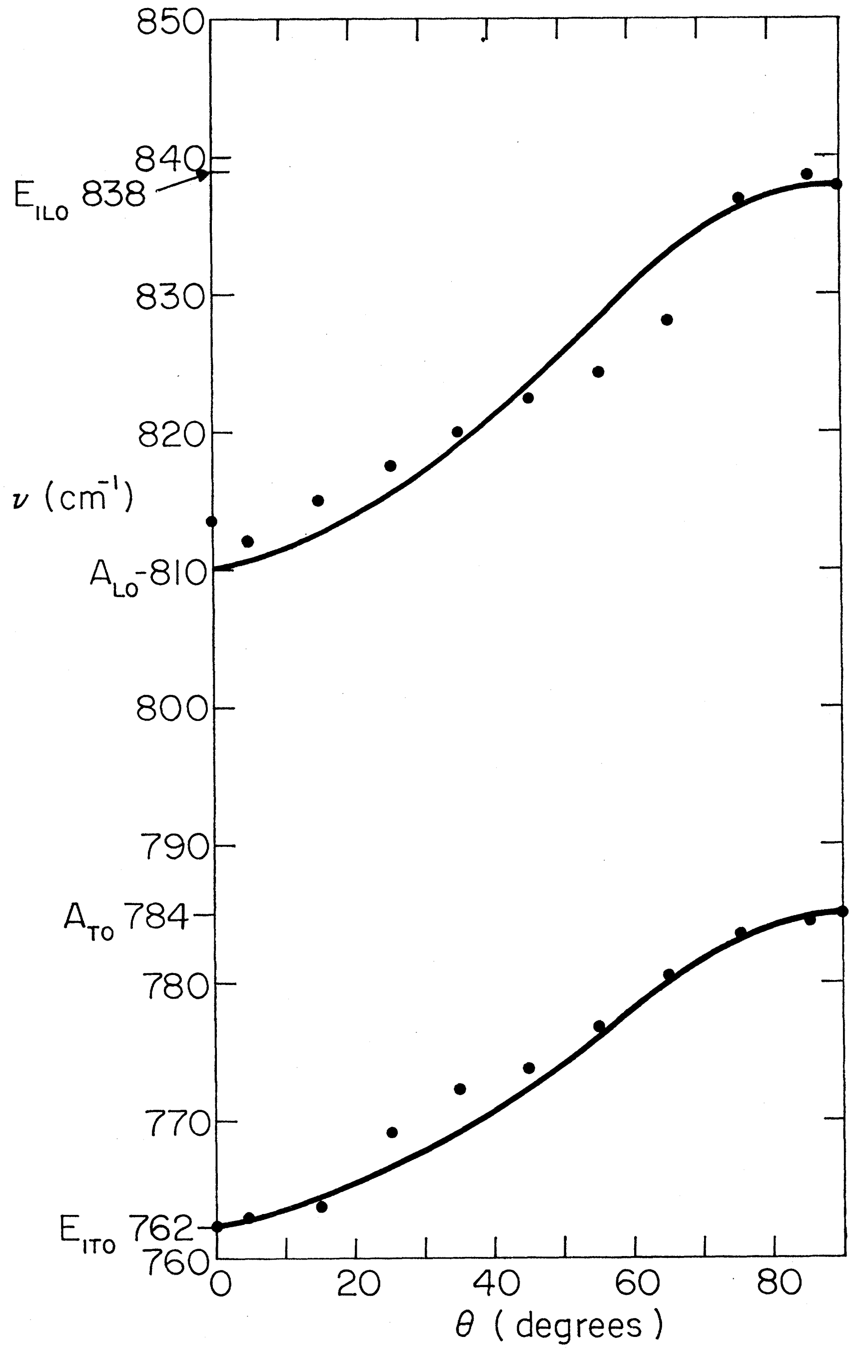

FIG. 1. A and E_1 phonon frequency versus phonon propagation direction. The points are the experimental data and the solid curves are the theoretical curves calculated from Eq. (1).

and the (zy), E_1 polarizability tensor component, we observe that in the 762–784-cm^{-1} and 814–838-cm^{-1} regions of the spectrum, there is always a single phonon whose frequency and polarizability tensor changes continuously while going from $\theta=0$ (**k** propagating along the z axis) to $\theta=90°$ (**k** propagating along the x axis). The frequency of the phonons follows the relations

$$\begin{aligned}\omega_{\mathrm{LO}}^2&=\omega_{A\text{-LO}}^2\cos^2\theta+\omega_{E_1\text{-LO}}^2\sin^2\theta\,,\\ \omega_{\mathrm{TO}}^2&=\omega_{A\text{-TO}}^2\sin^2\theta+\omega_{E_1\text{-TO}}^2\cos^2\theta\,,\end{aligned}\tag{1}$$

where θ is the angle formed between the phonon prop-

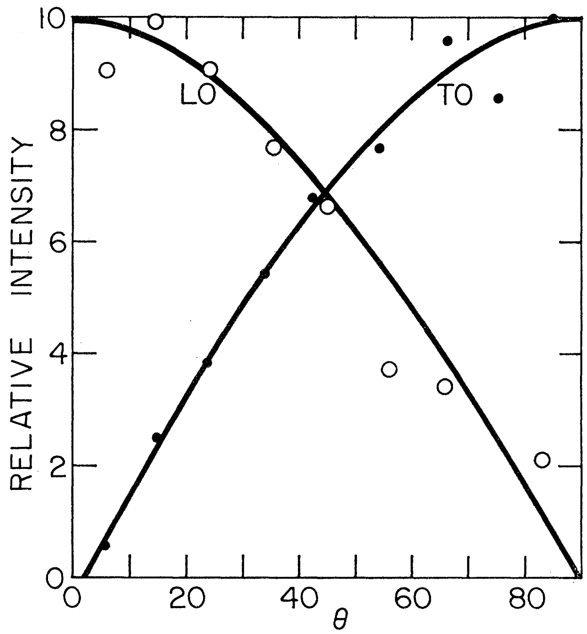

FIG. 2. Relative cross section of the A polarizability component versus phonon propagation direction. The points are the experimental data and the solid curves are the theoretical curves calculated from Eq. (2).

agation direction and the z axis. Figure 1 shows a comparison between the experimentally measured phonon frequencies and those predicted by Eq. (1). Figure 2 shows the relative cross section of the (yy), A polarizability tensor component, for each phonon frequency as a function of the propagation direction θ. We see from Figs. 1 and 2 that a phonon propagating at an angle θ to the z axis will have a frequency given by Eq. (1) and mixed A-E_1 symmetry. The A and E_1 intensities of this mixed phonon as a function of θ are given by

$$\begin{aligned} I_{\mathrm{LO}} &= I_{A_{\mathrm{LO}}} \cos\theta + I_{E_1\text{-LO}} \sin\theta , \\ I_{\mathrm{TO}} &= I_{A_{\mathrm{TO}}} \sin\theta + I_{E_{1\mathrm{TO}}} \cos\theta . \end{aligned} \tag{2}$$

The results show that

(1) the A and E_1 modes (although originating from different internal normal modes of the IO_3 ion) mix;

(2) the phonon mechanical polarization is always either transverse or longitudinal, showing the existence of a long-range macroscopic electric field which dominates over all other designations (A or E_1, internal or external of the phonons).

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