

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 crystals¹ 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 $P63 (C_6)$ 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 following⁵: symmetrical stretch $\nu_1=779 \text{ cm}^{-1}$, asymmetric stretch $\nu_3=826 \text{ cm}^{-1}$, 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 asymmetric 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: $A(\text{TO})=784 \text{ cm}^{-1}$, $A(\text{LO})=810 \text{ cm}^{-1}$, $E_1(\text{TO})=762 \text{ cm}^{-1}$, and $E_1(\text{LO})=838 \text{ cm}^{-1}$. From this data we see that the $A_{\text{TO-LO}}$ long-range electrostatic splitting is 26 cm^{-1} , the E_1 TO-LO electrostatic splitting is 76 cm^{-1} , the $A_{\text{TO-}E_{1\text{TO}}}$ anisotropy splitting is 22 cm^{-1} , and the $A_{\text{LO-}E_{1\text{LO}}}$ anisotropy splitting is 28 cm^{-1} . This crystal thus seems to be an intermediate case between Loudon's⁶ case (I) ($\omega_{\text{LO}}^{\text{I}}-\omega_{\text{TO}}^{\text{I}} \gg \omega_{\text{TO}}^{\text{II}}-\omega_{\text{TO}}^{\text{I}}$ or $\omega_{\text{LO}}^{\text{II}}-\omega_{\text{LO}}^{\text{I}}$), i.e., when the electrostatic interaction dominates over anisotropy splitting, and case (II) ($\omega_{\text{TO}}^{\text{II}}-\omega_{\text{TO}}^{\text{I}}$ and $\omega_{\text{LO}}^{\text{II}}-\omega_{\text{LO}}^{\text{I}} \gg \omega_{\text{LO}}^{\text{I}}-\omega_{\text{TO}}^{\text{I}}$ or $\omega_{\text{LO}}^{\text{II}}-\omega_{\text{TO}}^{\text{II}}$), 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,

⁵ W. E. Dasent and T. C. Waddington, J. Chem. Soc. 2429 (1960).

⁶ R. Loudon, Advan. Phys. 13, 423 (1964).

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¹ T. C. Damen, S. P. S. Porto, and B. Tell, Phys. Rev. 142, 570 (1966); C. A. Arguello, D. L. Rousseau, and S. P. S. Porto, *ibid.* 181, 1351 (1969).

² J. F. Scott and S. P. S. Porto, Phys. Rev. 161, 903 (1967); L. Couture-Mathieu, J. A. A. Ketelaar, W. Vedder, and J. Fahrenfort, J. Chem. Phys. 20, 1492 (1952).

³ A. Rosenzweig and B. Morosin, Acta Cryst. 20, 758 (1966).

⁴ W. Ottaguro, S. P. S. Porto, and C. Arguello (unpublished).

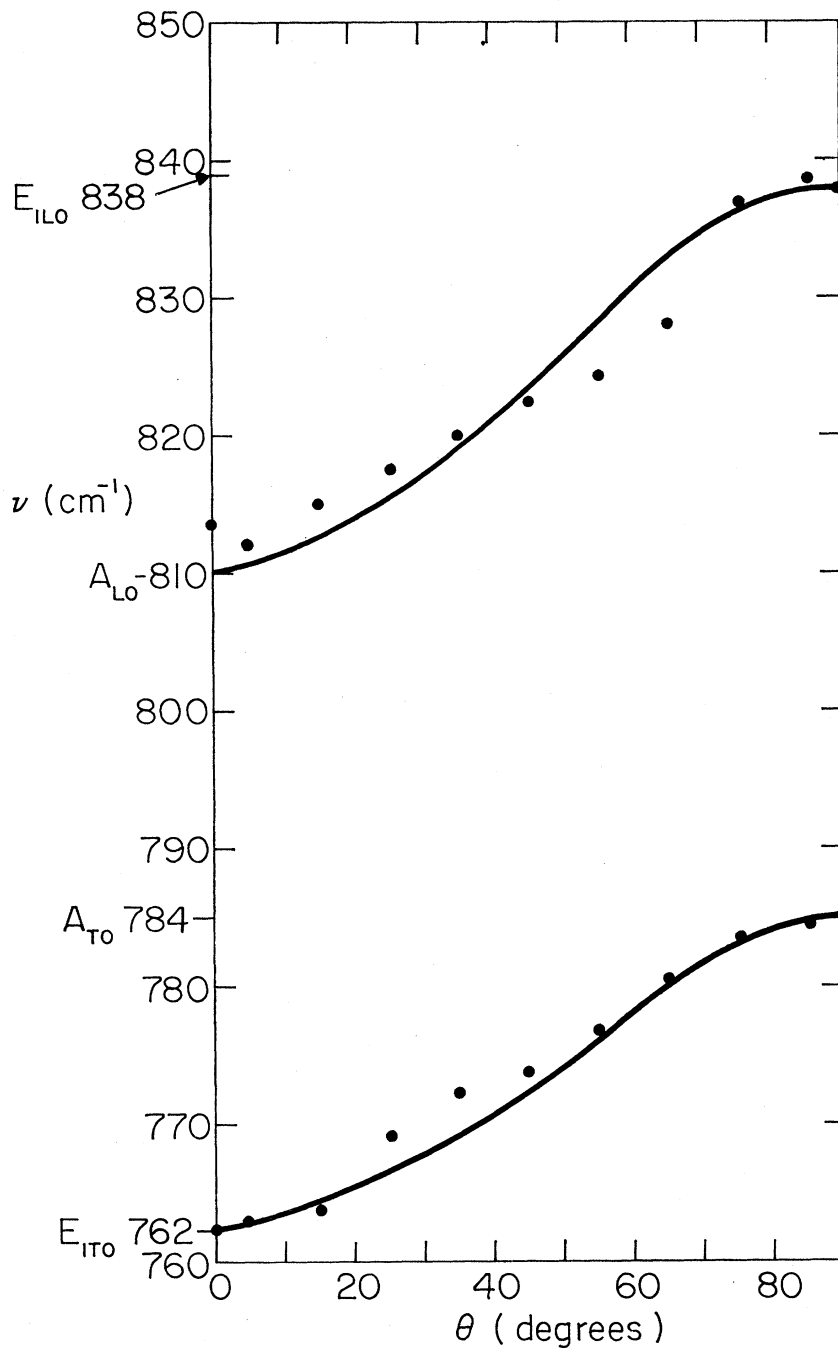


FIG. 1. *A* and *E*₁ phonon frequency versus phonon propagation direction. The points are the experimental data and the solid curves are the theoretical curves calculated from Eq. (1).

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 θ=0 (**k** propagating along the *z* axis) to θ=90° (**k** propagating along the *x*

axis). The frequency of the phonons follows the relations

$$\begin{aligned} \omega_{LO}^2 &= \omega_{A-LO}^2 \cos^2\theta + \omega_{E_1-LO}^2 \sin^2\theta, \\ \omega_{TO}^2 &= \omega_{A-TO}^2 \sin^2\theta + \omega_{E_1-TO}^2 \cos^2\theta, \end{aligned} \quad (1)$$

where θ is the angle formed between the phonon prop-

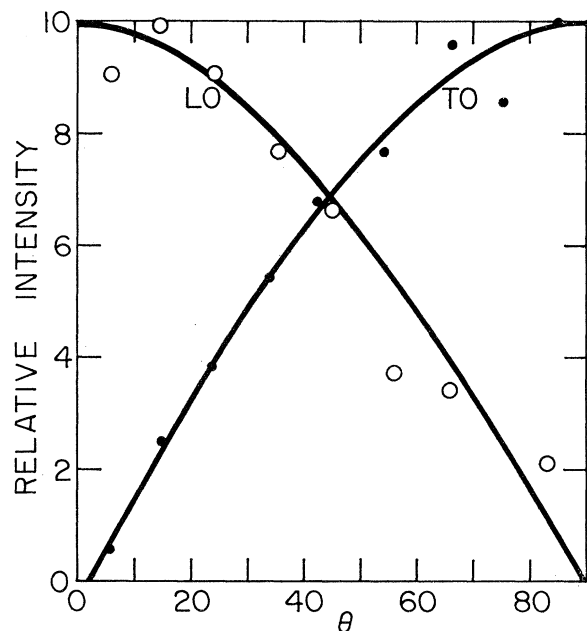


FIG. 2. Relative cross section of the A polarizability component versus phonon propagation direction. The points are the experimental data and the solid curves are the theoretical curves calculated from Eq. (2).

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

$$\begin{aligned} I_{LO} &= I_{A_{LO}} \cos\theta + I_{E_1-LO} \sin\theta, \\ I_{TO} &= I_{A_{TO}} \sin\theta + I_{E_1-TO} \cos\theta. \end{aligned} \quad (2)$$

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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