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# Pressure-induced phase transition in $\beta$-LiIO$_3$

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We report the first observation of a pressure-induced phase transition in LiIO$_3$. A new phase appears when $\beta$-LiIO$_3$ is compressed hydrostatically at room temperature, beyond 50 kbar. This is a reversible first-order transition with negligible hysteresis. The new phase ($\delta$-LiIO$_3$) cannot be obtained by heating or cooling either $\alpha$- or $\beta$-LiIO$_3$ or by compressing the former. We observe the transition by studying the evolution of the Raman spectrum of $\beta$-LiIO$_3$ as a function of pressure (1 bar—95 kbar). We also report a detailed study of the pressure dependence of Raman frequencies for $\beta$-LiIO$_3$. The regularities observed in the mode-Grüneisen parameters and other pressure coefficients for the $\beta$ phase give insight into the probable structure of the high-pressure phase.

LiIO$_3$ is known to exist in three distinct crystalline modifications. Two of them, known as $\alpha$ and $\beta$ phases, belong to space groups $C_6^6$ ($P6_3$) and $C_{4h}^4$ ($P4_2/n$), respectively, and are stable at room temperature.[1-4] Another modification, the $\gamma$ phase, can be obtained by heating $\alpha$-LiIO$_3$, which goes through a reversible, first-order phase transition at about 220 °C. At higher temperature the material undergoes another phase transition into the $\beta$ phase, remaining in this phase all the way up to the melting point. Once the material is in the $\beta$ phase it remains in this phase even after it is cooled down to room temperature.[2,3,5] Interest in these phase transitions have led to a number of light scattering studies in $\alpha$-LiIO$_3$ where both temperature and pressure were varied.[6-8] In contrast, very little is known about the lattice dynamics of the other two phases. Recently,[9] we reported a complete study of the polarized Raman spectrum from single crystals of $\beta$-LiIO$_3$ at $T=10$ K. All but three of the 45 allowed Raman peaks were identified. In the present work we study the evolution of the room-temperature spectrum of $\beta$-LiIO$_3$ under hydrostatic pressure in the range 1 bar—95 kbar. The most interesting result from this study is the appearance of a discontinuous, reversible phase transition occurring at $P=50\pm1$ kbar. The high-pressure phase has a spectrum showing a greater number of lines in the region of the stretching modes of IO$_3^-$ ions.[9] These peaks show marked frequency shifts with increasing pressure. This behavior and those of the Raman frequencies in the $\beta$-phase as a function of pressure suggest that the high-pressure phase ($\delta$-LiIO$_3$) has a structure where oxygen atoms are more closely packed than in the $\beta$ phase.

Our samples were cut in slices from single crystals of $\beta$-LiIO$_3$, grown from aqueous solutions of the powdered material,[10] oriented by x-ray diffraction, and polished to a thickness of $\sim 50$ $\mu$m. Two types of platelets were used, with the tetragonal $c$ axis contained in or perpendicular to the polished face, respectively. Light scattering measurements were performed in the backscattering configuration, using the 5145-Å line of an argon-ion laser as exciting radiation. Scattering light was analyzed with a SPEX double spectrometer equipped with photon-counting electronics. The sample and a ruby chip, for pressure calibration, were placed inside a 300-$\mu$m-diam hole in a Cu-Be gasket. The pressure cell is of the opposed anvil type with one of the anvils made of sapphire.[11] A 4:1 mixture of methanol and ethanol was used as pressure-transmitting fluid. The optical arrangement and means of determining the pressure within the gasket are described elsewhere.[6,11] All measurements were performed at room temperature.

The factor group of $\beta$-LiIO$_3$ is $C_{4h}$, and its primitive cell contains eight formula units.[4] The Raman-active modes are divided among the irreducible representations of the factor group as[9]

$$\Gamma_R = 15A_g + 15B_g + 15E_g \ . \tag{1}$$

All but two modes of $A_g$ symmetry and one of $E_g$ symmetry were identified in the Raman spectrum at $T=10$ K. Some of these lines fuse into broader structures at higher temperatures, reducing the number of modes which can be studied at room temperature. Of these, some are too weak to be studied under pressure. In Table I we list the frequencies of all the observed[9] Raman lines in the spectrum at $T=10$ K and those of the lines which can be resolved at room temperature, or whose room-temperature frequency can be obtained by extrapolating the high-pressure results. Blank rows in Table I indicate the missing $A_g$ or $E_g$ modes in the regions of the spectrum where we feel they ought to be. For those lines that were studied under pressure we also list in Table I the coefficients $A_n$ obtained by a least-squares fit of the experimental data for $\omega$ vs $P$ ($P<50$ kbar) to a polynomial expression of the type

$$\omega = \omega_0 + \sum_n A_n P^n \ . \tag{2}$$

This fit is shown in Fig. 1 as a solid line, while circles, triangles, and squares represent experimental data.

Figure 1 shows that mode frequencies vary smoothly, and mostly linearly, as pressure increases up to $\sim 50$ kbar. At this point a discontinuous change takes place in the spectrum (Figs. 2 and 3): The number of peaks as well as the general shape of the spectrum is altered. For $P>50$ kbar the spectrum changes again in a continuous manner. In Fig. 2 the Raman spectrum is shown for different values of the applied pressure. Curves (a) and (b) show

TABLE I. Frequencies of the lines in the Raman spectrum observed both at $T=10$ and 400 K in order of increasing energy. Blank rows signify missing modes in regions of the spectrum where we feel they ought to appear. Coefficients $A_n$ from Eq. (3) and mode-Grüneisen parameters calculated using for the bulk modulus the value $B=243.1$ kbar estimated using Eq. (5). $E_g$ modes have only linear terms.

| $A_g$ | | | | | $B_g$ | | | | | $E_g$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\omega$ (cm$^{-1}$) 12 K | $\omega$ (cm$^{-1}$) 300 K | $A_1$ (cm$^{-1}$kbar$^{-1}$) | $10^2A_2$ (cm$^{-1}$kbar$^{-2}$) | $\gamma$ (estimated) | $\omega$ (cm$^{-1}$) 12 K | $\omega$ (cm$^{-1}$) 300 K | $A_1$ (cm$^{-1}$kbar$^{-1}$) | $10^2A_2$ (cm$^{-1}$kbar$^{-2}$) | $\gamma$ (estimated) | $\omega$ (cm$^{-1}$) 12 K | $\omega$ (cm$^{-1}$) 300 K | $A_1$ (cm$^{-1}$kbar$^{-1}$) | $\gamma$ (estimated) |
| 69.3 | | | | | 48.7 | 46.8 | 0.71 | −0.46 | 3.69 | 58.5 | 55.3 | | |
| 75.9 | 71.6 | 0.51 | −0.22 | 1.73 | 56.7 | | | | | 64.4 | 61.9 | 0.40 | 1.57 |
| 116.0 | 113.4 | 0.68 | −0.26 | 1.46 | 108.1 | 105.1 | 0.36 | | 0.83 | 82.4 | 82.0 | 0.35 | 1.04 |
| 126.3 | | | | | 125.1 | 119.8 | 1.04 | | 2.11 | 105.5 | 102.9 | | |
| 188.3 | 185.2 | 0.48 | −0.24 | 0.63 | 149.3 | 141.0 | 0.55 | −0.24 | 0.95 | 148.8 | 142.8 | 0.49 | 0.83 |
| | | | | | 232.0 | | | | | 227.2 | 222.0 | | |
| 249.1 | 246.0 | 0.39 | | 0.39 | 260.7 | 255 | 0.63 | | 0.60 | 260.7 | 254.5 | 0.63 | 0.60 |
| | | | | | 294.5 | | | | | 283.5 | | | |
| 308.5 | 308.4 | 0.35 | | 0.28 | 308.5 | 308.0 | 0.30 | | 0.24 | 308.5 | 308.2 | 0.32 | 0.25 |
| 322.5 | 319.0 | 0.36 | | 0.27 | 320.2 | 317.6 | 0.38 | | 0.29 | 330.6 | | | |
| 361.8 | 359.8 | 0.66 | −0.32 | 0.45 | 344.7 | 339.6 | 0.53 | | 0.38 | 386.5 | | | |
| 442.0 | | | | | 460.6 | 460 | 0.11 | | 0.058 | | | | |
| 763.8 | 765.0 | −0.22 | | −0.070 | 776.9 | | | | | 766.5 | 767.5 | −0.22 | −0.070 |
| 798.3 | 800.1 | −0.24 | 0.37 | −0.073 | 783.1 | 783.0 | −0.20 | | −0.062 | 783.7 | 780.0 | 0.39 | 0.12 |
| 816.3 | 811.0 | 0.64 | | 0.19 | 816.9 | 813 | | | | 825.7 | 823.2 | 0.36 | 0.11 |

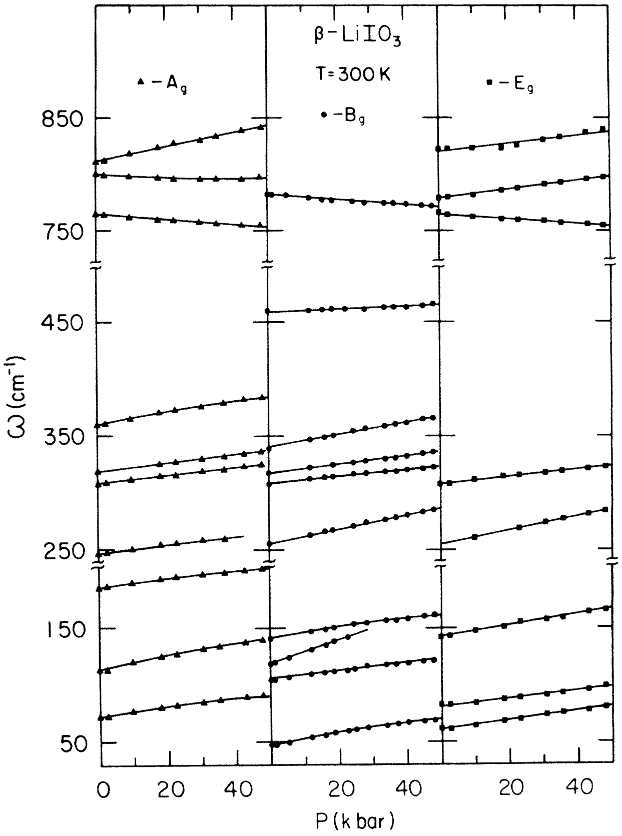

FIG. 1. Frequency vs pressure for most of the Raman-active modes of β-LiIO$_3$.

spectra of β-LiIO$_3$ at 2.6 and 48 kbar, respectively. In spite of the large pressure difference, both spectra are qualitatively similar. From curve (b) to curve (c) there is only a difference of 4 kbar. However, these two spectra are radically different both in general shape and in number and position of the Raman lines. From $P>50$ kbar onward the shape of the spectrum remains unaltered, as can be seen comparing curves (c) ($P=52$ kbar) and (d) ($P=95$ kbar) in Fig. 2. The abrupt change occurring at $P\sim50$ kbar is also shown in Fig. 3. Here we plot ω vs $P$ for the stretching modes[9] of the $IO_3^-$ ion. The smooth changes in ω vs $P$ at low pressures are abruptly interrupted at 50 kbar, where new peaks appear. From this point up to 95 kbar these peaks continue to change smoothly as pressure increases. This discontinuous change was seen to be reversible, to have negligible hysteresis, and to occur at $P=50\pm1$ kbar. The observations are consistent with the existence of a high-pressure phase (δ phase) with a first-order transition summarized by

$$\beta \underset{50\ \mathrm{kbar}}{\rightleftarrows} \delta \quad (T=300\ \mathrm{K}=\mathrm{const}) . \tag{3}$$

Furthermore, the δ phase cannot be obtained by compressing α$LiIO_3$ or by temperature changes in either α- or β-LiIO$_3$. To the best of our knowledge, this is the first observation of the phase transition described above.

The coefficients $A_n$ listed in Table I for the β phase can be used to calculate mode-Grüneisen parameters as

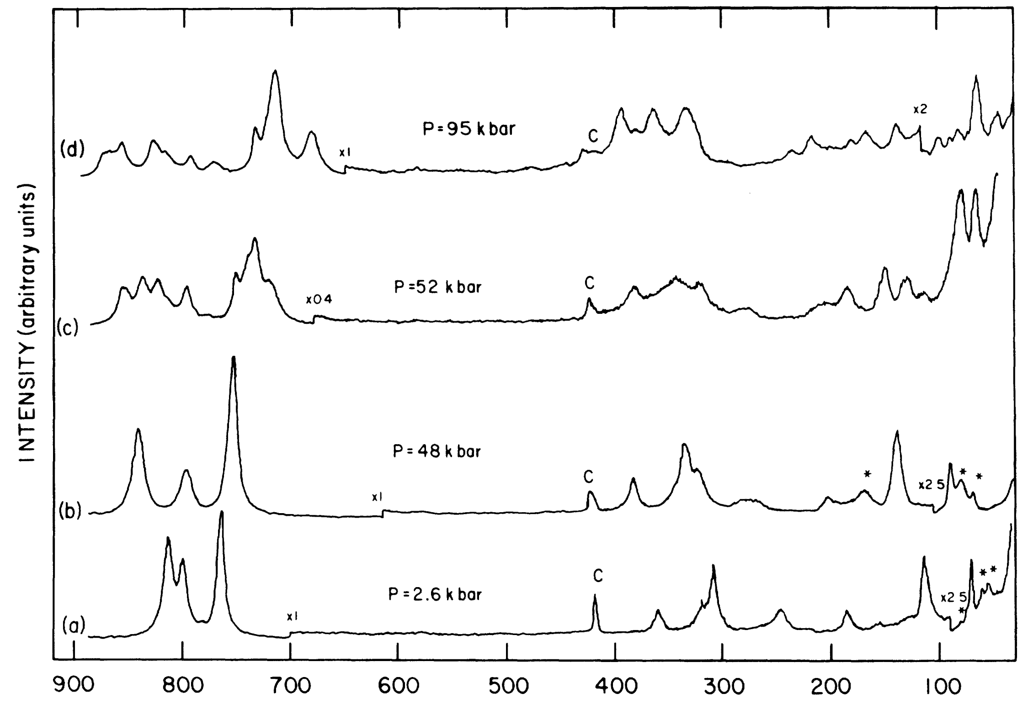

FIG. 2. Raman spectra of a sample which started as $\beta$-LiIO$_3$ taken at different pressures. For the (a) and (b) curves the scattering configuration is $x(zz)\bar{x}$, where $z$ corresponds to the tetragonal $c$ axis. Raman peaks from the sapphire window of the pressure cell are labeled $C$ (corundum).

$$\gamma_j = -\frac{d\ln\omega_j}{d\ln V} = \frac{A_1(j)B}{\omega_0(j)} , \tag{4}$$

where $B$ is the bulk modulus of the material. To the best of our knowledge, no experimental values of $B$ exist for $\beta$-LiIO$_3$. Hence we used an empirical rule, which has been shown to hold for families of related crystals and amorphous solids,[12,13] relating the bulk moduli and molecular densities of the two materials by

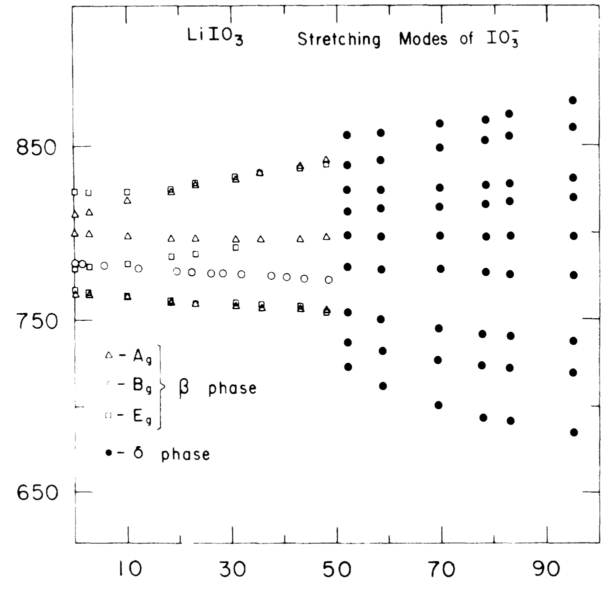

FIG. 3. Phonon frequency vs pressure for the highest-frequency modes in the Raman spectrum of $\beta$-LiIO$_3$.

$$\frac{B(2)}{B(1)} \simeq \left[\frac{\rho(2)}{\rho(1)}\right]^4 . \tag{5}$$

With the use of the bulk modulus of the $\alpha$ phase,[14] $B=319.5$ kbar, and the densities for both $\alpha$- and $\beta$-LiIO$_3$ given by Matsumura,[2] Eq. (5) predicts for $\beta$-LiIO$_3$, $B\simeq 243.1$ kbar. This value for the bulk modulus substituted into Eq. (4) yields the mode-Grüneisen parameters listed in Table I. These parameters are seen to decrease monotonically as the mode frequency increases. This trend is more readily appreciated in Fig. 4, where we plot the absolute value of the mode-Grüneisen parameter versus mode frequency in a log-log plot. The experimental points are more or less distributed about a straight line, which suggests an approximate dependence of $\gamma_j$ on $\omega_j$ of the type

$$|\gamma_j| \propto \omega_j^{-\eta} , \tag{6}$$

with $\eta \simeq 1.3$. In order to assess the significance of this behavior we shall briefly review the previously observed trends in a large variety of solids.[15] First, note that in a perfectly harmonic solid, phonon frequencies do not depend on unit-cell volume. Anharmonic terms in the ionic potential are responsible for this dependence in real crystals. The simplest assumption is that all mode frequencies scale with volume in the same way: $\omega_j \propto V^{-\gamma}$. This leads

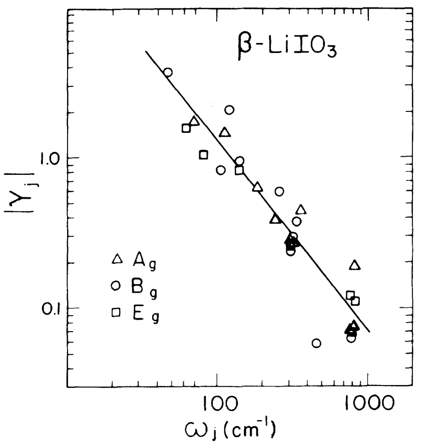

FIG. 4. Mode-Grüneisen parameter (absolute value) vs mode frequency.

to mode-Grüneisen parameters which are identical for all modes ($\gamma_j \simeq \gamma$ for all $j$). This assumption works fairly well for the optical modes of tetrahedrally coordinated semiconductors and simple ionic solids.[15] In molecular solids,[15] mode-Grüneisen parameters are seen to depend strongly on mode frequency, following an empirical law of the type given in Eq. (6) with $\eta \simeq 2$. This is explained on the basis of a simple linear chain model[15,16] in which a hierarchy of springs coexist (stiff springs responsible for internal modes and soft springs responsible for external modes) and where each spring constant $k_j$ scales with bond length $r_j$ in the same manner:

$$k_j \propto r_j^{-6\gamma}, \quad \gamma \simeq 1 \; . \tag{7}$$

Two extreme cases have simple solutions: (i) when all the spring constants are equal and (ii) when a hierarchy of spring constants exist such that $k_1 \gg k_2 \gg k_3 \gg \cdots$. In both these cases $\omega_j \propto k_j^{1/2}$, which leads to

$$\gamma_j = \gamma \left[ \frac{k}{k_j} \right] \left[ \frac{r}{r_j} \right] , \tag{8}$$

with

$$r = \sum_j r_j , \quad k^{-1} = \sum_j k_j^{-1} \; . \tag{9}$$

Assuming all bond lengths to be more or less the same, the equations above, for a chain with $n$ springs, reduce to

$$\gamma_j \simeq \begin{cases} \gamma \;\; \forall j \;\; \text{when } k_1 = k_2 = \cdots \\ n\gamma \left[ \dfrac{k_1}{k_2} \right] \propto \omega_j^{-2} \;\; \text{when } k_1 \gg k_2 \gg \cdots \; . \end{cases} \tag{10}$$

These results explain fairly well the trends observed in a large number of covalent, ionic, and molecular solids.[15] These trends can be summarized in a dependence of $\gamma_j$ on $\omega_j$ as given in Eq. (6) with $\eta = 2$ for the case where spring constants are very different ("true" molecular solids) and $\eta \simeq 0$ when they are very similar (three-dimensional networks with covalent or ionic bonding). For solids in which some "molecular" units can be identified, but where the difference between internal and external force constants is not very large, the reasoning above suggests a dependence of $\gamma_j$ on $\omega_j$ of the type given by Eq. (6) with $0 < \eta < 2$. A log-log plot of the data available[17] for TeO$_2$ confirms this hypothesis, yielding a value of $\eta \simeq 1$. LiIO$_3$ also shows this type of behavior, with $\eta = 2$ for the $\alpha$ phase[8] and $\eta = 1.3$ for the $\beta$ phase. In $\alpha$-LiIO$_3$ we could describe the optical modes in terms of internal vibrations of IO$_3^-$ pyramids and external modes where these groups displace rigidly.[8] The above discussion suggests that this description would be less accurate for $\beta$-LiIO$_3$. This is in consonance with crystallographic data,[4] which show that in the $\beta$ phase IO$_3^-$ pyramids are distorted and more interlinked than in $\alpha$-LiIO$_3$. Schulz[4] also points out that oxygen atoms in the $\alpha$ phase form a distorted hexagonal-closed-packed structure with a packing fraction larger than that found in $\beta$-LiIO$_3$. This accounts for two of our experimental observations: (i) $\beta$-LiIO$_3$ undergoes a phase transition under pressure (presumably to a more compact structure) while $\alpha$-LiIO$_3$ does not, and (ii) some of the "internal" (highest-frequency) modes in $\beta$-LiIO$_3$ are among the most strongly affected by pressure. If we assume that the δ phase corresponds to a rearrangement of oxygen atoms into a more compact structure, we would expect lattice modes involving motions of oxygen atoms in the $\beta$ phase to be more affected by pressure than all other modes, independent of mode frequency. Hence while in the $\alpha$ phase the coefficients $A_1$ of Eq. (2) decreased monotonically as the mode frequency increased,[8] we find in $\beta$-LiIO$_3$ (see Table I) high- and intermediate-frequency modes with $A_1$ coefficients as large as those of the lowest-frequency modes in the spectrum.

In conclusion, we report the existence of a pressure-induced phase transition in $\beta$-LiIO$_3$. This transition occurs at $P = 50 \pm 1$ kbar, is of first order, reversible, and shows negligible hysteresis. We also give a detailed study of the behavior of phonon frequencies under pressure ($P < 50$ kbar). The systematic dependence of pressure coefficients on mode frequency suggests that (i) the molecular-crystal approximation, which provided a good description[8] for the lattice dynamics of $\alpha$-LiIO$_3$, is not appropriate to describe the normal modes of the $\beta$ phase, and (ii) the high-pressure phase (δ-LiIO$_3$) corresponds to a structure where oxygen atoms are more closely packed. Detailed understanding of the new phase and of the mechanism of the $\beta \rightleftarrows \delta$ phase transition must await experimental measurements of x-ray diffraction under pressure and theoretical lattice-dynamics calculations. Such information is not available at the moment.

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