

## Spectroscopic evidence for broken-symmetry transitions in dense lithium up to megabar pressures

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We report optical spectroscopic studies of <sup>7</sup>Li and <sup>6</sup>Li at variable temperatures to 123 GPa. The optical reflectivity decreases above 40 GPa (25 GPa at room temperature). The Raman spectra reveal a broad mid-frequency band that we assign as a maximum in the phonon density of the states. Interpretation is consistent with the theoretical calculations for the observed crystal structures. The observed changes in Raman spectra and optical properties correlate with those reported previously from x-ray and superconductivity studies and attributed to structural transitions. Above 60 GPa new Raman bands appear that we ascribe to a theoretically predicted symmetry breaking transition associated with changes in bonding.

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### I. INTRODUCTION

In spite of the illusive simplicity of the alkali metals, there is growing evidence that these materials exhibit unexpectedly complex behavior at high densities.<sup>1,2</sup> In particular, lithium has been predicted to form a paired-atom structure,<sup>3</sup> with intriguing similarities to another light element—hydrogen. Optical properties of lithium change above 20–25 GPa at room temperature.<sup>4,5</sup> These observations suggest a change in the electronic structure of Li under pressure, but no firm conclusions could be drawn so far just on the basis of the optical observations (but see Ref. 2). The crystal structure of lithium at 40–50 GPa was found to be complex,<sup>2</sup> but no sign of the changed electronic structure was reported. A sharp increase in the electrical resistance<sup>6,7</sup> observed for shock and statically compressed Li at densities of 1.2–1.4 g cm<sup>-3</sup> appears to be related to the structural changes reported in Ref. 2. Vibrational spectroscopy provides a straightforward way of probing the bonding in complex phases at very high pressures, because it is particularly sensitive to changes in local atomic environment. Here we report spectroscopic studies of <sup>7</sup>Li and <sup>6</sup>Li to 123 GPa at 180 K. Raman spectra reveal new bands above 60–70 GPa, which we interpret as resulting from a gradual transformation to a broken-symmetry state with a different charge distribution.

The high-pressure properties of simple low-Z metals are of fundamental interest. Theoretical calculations predict a departure of the electronic structure from the free-electron behavior<sup>2</sup> and development of an optical gap.<sup>3,8</sup> Moreover, possible high-temperature superconductivity has attracted particular attention to low-Z elements.<sup>9</sup> Solid metallic and possibly superconducting phases have also been predicted for hydrogen (e.g., Ref. 10), but these have not been realized experimentally. Recently, superconductivity has been found in Li experimentally;<sup>11–13</sup> the variation in  $T_c$  with pressure data suggests a complex high-pressure phase diagram<sup>12,13</sup> in qualitative agreement with x-ray data.<sup>2</sup> Previously, use of diamond anvil cells was seriously impaired by the reactivity of Li with diamonds and because of sample leakage through

the diamond-gasket interface.<sup>11</sup> Special loading techniques<sup>5,11,13</sup> and use of low temperature<sup>2</sup> have solved some of these problems.

### II. EXPERIMENTAL DETAILS

We performed optical studies in diamond anvil cells, and sample preparation methods for these experiments are described in Refs. 4 and 12. For the Raman studies we used cells especially designed for obtaining very weak Raman signals from poorly scattering materials such as metals and high-temperature superconductors.<sup>14</sup> The cell was placed in a continuous flow cryostat, maintaining the temperature at 173–178 K (cf., Ref. 2). Our Raman setup has been described previously.<sup>14</sup> The Raman spectra were excited by 488 and 514.5 nm lines of an Ar laser. The Raman spectra were analyzed by a single-stage spectrograph with a multichannel CCD detector. The spectrograph is equipped with two gratings—for low- and high-dispersion mode operation. The first one is convenient for collection of broad spectra in a wide spectral range, while the second one (with higher spectral resolution but typically lower signal-to-noise ratio) is necessary when narrow bands are measured or overlapping bands need to be separated. Pressure was measured using standard ruby fluorescence techniques.

Lithium samples of 99.9% purity with natural isotopic abundances (referred to as <sup>7</sup>Li) and <sup>6</sup>Li samples with the light isotope atomic fraction of 0.95 with the stated purity 99.99% were used. Lithium was loaded into the cell in a glove box in an oxygen-free Ar atmosphere using Re as a gasket material. No visible trace of material chemical degradation was observed at these conditions for hours. No pressure medium was used in the Raman experiment. Thus, the sample was in direct contact with the culet of a diamond anvil forming a surface of optical quality, which improves coupling of the excitation laser beam to a material that is difficult to polish and preserve a good flat optical surface under pressure. This technique was used before for Fe (Refs. 15 and 16) and Co (Ref. 17), which are also (as well as Li—see below) very weak Raman scatterers. Examples of

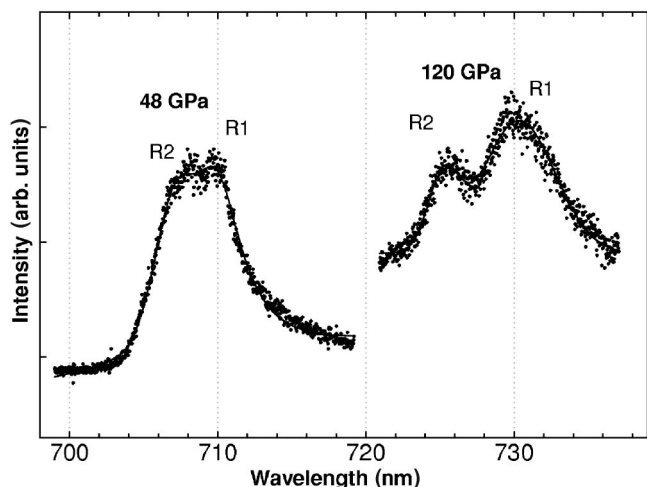


FIG. 1. Examples of the ruby fluorescence spectra measured in the course of our experiment. Points are experimental data; lines correspond to phenomenological two-peak fits.

using Raman spectroscopy to study metals in quasihydrostatic conditions are very rare and so far are limited to the materials with relatively large Raman cross sections such as Zn (Ref. 18) and Re (Ref. 14). Since no medium was used, our ruby spectra (Fig. 1) indicate the presence of deviatoric stresses as much as 8% (based on the magnitude of the  $R_1$ - $R_2$  splitting) and pressure gradients up to 6% of the nominal (uniform) hydrostatic component of the stress tensor in the sample chamber (based on measurements of different ruby sensors). The presence of deviatoric stresses and pressure gradients may affect the pressure dependencies of the Raman frequencies<sup>14,18</sup> or even phase transformations (see, e.g., Ref. 19) as will be discussed below.

In the results of experiments reported here, no traces of chemical reaction between Li and gasket or diamonds were observed. The latter is supported by optical microscopy and Raman spectroscopy of the diamonds (cf., Ref. 4). We also report here the results of optical studies including direct visual observations, reflectivity, and transmission spectroscopy in visible and near IR extending the work reported in abstract form.<sup>4</sup> Altogether more than ten experiments were performed in a variety of transmitting media (e.g., mineral oil) over a range of pressures to 70 GPa at room temperature.

### III. RESULTS

Representative Raman spectra of Li at high pressures are shown in Fig. 2. The spectra do not match those of conceivable Li-containing materials produced by possible chemical reactions or contamination. Indeed, the most probable contamination would result from contact with the atmosphere, mostly  $N_2$ ,  $O_2$ ,  $H_2O$ , and  $CO_2$ . Contact with diamonds can introduce carbon, if there is substantial reactivity between Li and carbon in diamond. The atmosphere of the glove box can have trace amounts of hydrogen (used as a regeneration additive to argon during regeneration process). Thus, the effects of N, O, C, and H can be considered either as elements or compounds. One possible compound,  $Li_3N$ , has a single

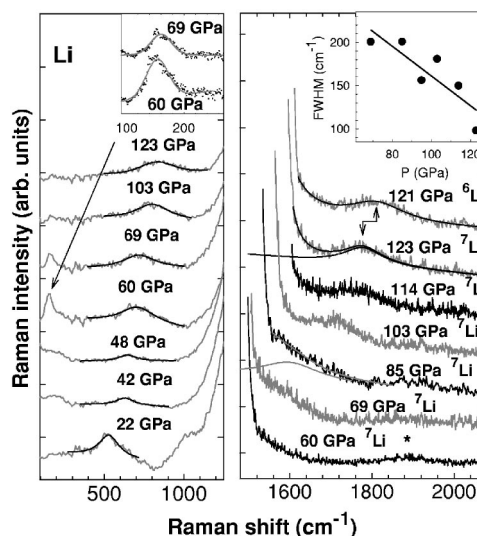


FIG. 2. Raman spectra of Li at elevated pressures and 173–176 K (spectra are shifted vertically for clarity). The points are the experimental data; the lines are phenomenological fits. The Raman character of all bands was verified by use of two different excitation energies. Left and right panels correspond to spectral windows below and above the first-order scattering from the stressed diamond anvils; the spectra in different panels are reduced to the same intensity scale (see text for details). The lower-frequency spectra were collected in the low dispersion mode, which results in better signal-to-noise ratio compared to the spectra taken in the high dispersion mode (right panel), but worse spectral resolution. The difference in the spectral resolution is mainly responsible for the different rate of rise of the signal towards the diamond first-order peak. The difference in the spectra collection conditions for the two panels results in a relative scale ratio of approximately 10 (if intensities are reduced to the same collection time) for the left to the right panel. The left panel inset shows the details of the low-frequency spectra measured in a high dispersion mode (see text). The spectra were corrected for the optical transmission of the notch filters used to reject elastically scattered radiation. The arrows indicate the positions of a new Raman band that appears under pressure for different isotopes. The asterisk corresponds to a weak diamond second-order peak, corresponding to the 2TA overtone (Ref. 20). The right panel inset shows the pressure dependence of the linewidth of the new band for the  $^7Li$  isotope sample, indicating that this mode becomes less anharmonic with pressure (see text).

first-order Raman band at  $600\text{ cm}^{-1}$  and two second order bands at  $\sim 350$  and  $\sim 1010\text{ cm}^{-1}$ .<sup>21</sup> The first-order band at  $600\text{ cm}^{-1}$  (which is close in frequency to the low-frequency band in our experiment) involves motion of N, and therefore should have a reduced isotope effect in contrast to what we observed. LiOH has a strong OH band at  $3607\text{ cm}^{-1}$  and a weak band at  $500\text{ cm}^{-1}$ .<sup>22</sup> The Raman spectrum<sup>23</sup> of LiH has many more bands than are measured in our spectra.

The Raman signal from Li is extremely weak, consistent with the metallic or semimetallic nature of the material (Fig. 2). Below 50 GPa, the dominant Raman feature is a broad band at  $600\text{--}650\text{ cm}^{-1}$  that shifts to higher energies with pressure. A weaker band at  $1000\text{ cm}^{-1}$  could only be observed at 22–35 GPa, being masked by the Raman signal from diamond at higher pressures. At 60 GPa a sharp low-

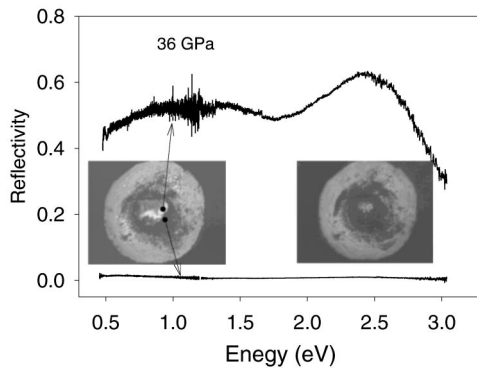


FIG. 3. The visible near-IR reflectivity spectra of Li at 22 GPa measured from a “shining” and a “dark” part of the sample in a transition region (see text). The “shining” area on the sample persisted to 36 GPa and disappeared at 46 GPa.

frequency band appears, but it loses intensity at the next pressure point and disappears completely with further increase in pressure. No such feature was observed for the  $^6\text{Li}$  sample, which can be related to different high-pressure ordering schemes for Li isotopes (cf., hydrogen.<sup>24</sup>). At this pressure (69 GPa) one can see a weak shoulder on the high-energy side of the Raman band associated with the stressed diamond. At higher pressures, this band increases intensity and shifts to higher energies, such that it becomes totally resolved from the Raman signal of the stressed anvil. The latter gives rise to a well-known Raman peak, the position of which can be used for pressure determination inside the pressure chamber.<sup>25</sup> The pressure determined from the spectral position of this peak is in good agreement with the direct ruby pressure measurements. Thus, the observed broad high-frequency band clearly corresponds to Raman scattering from the sample. It is important to note that the left and right panels in Fig. 2 represent measurements taken in the low- and high-dispersion modes, respectively (see above). The new high-frequency Li band can be resolved spectrally much better in the latter mode of operation at the expense of some reduction in signal-to-noise. The spectra are plotted with the same relative intensities in both panels; this was determined from the ratio of integrated intensities of the low- and high-frequency Li bands, measured in the same spectral window in the low-dispersion mode. The Raman spectra are totally reversible on pressure release (checked for  $^7\text{Li}$  isotope to 50 GPa).

Optical spectroscopy experiments were also carried out at room temperature in conjunction with the Raman studies. These measurements show a change of reflectivity around 22 GPa. The corresponding near-IR and visible spectra are featureless, revealing just an overall drop in reflectivity and the presence of the two-phase region (Fig. 3). The two-phase region was observed up to 36 GPa (at 42 GPa the sample area became completely dark). Room temperature measurements are complicated by many factors, including the possibility of chemical interaction between Li and diamond at these pressures,<sup>2</sup> however, our observations correlate with increasing resistivity in Li samples observed in earlier experiments by Lin and Dunn.<sup>7</sup> In Raman measurements carried out at 180 K we also observed that the sample changes

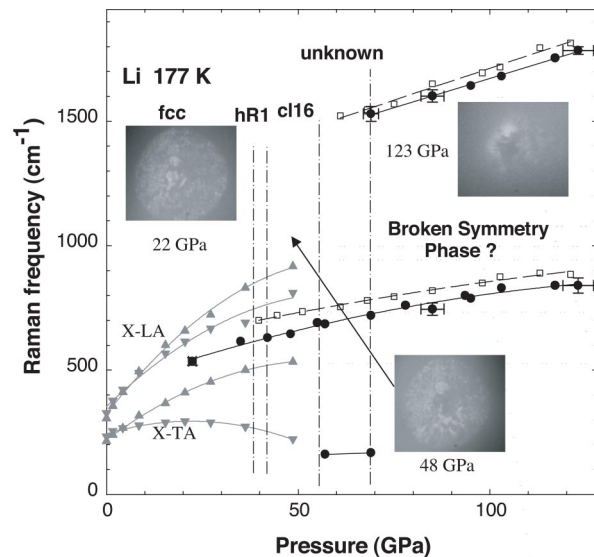


FIG. 4. The pressure dependence of the measured Raman frequencies in comparison with theoretical calculations (Ref. 27). The full circles and solid lines (open squares and dashed lines) correspond to experimental data for the  $^7\text{Li}$  ( $^6\text{Li}$ ) isotope from this study. The gray triangles pointing up and down are X-TA and X-LA phonon frequencies calculated from elastic constants and by the “supercell” frozen-phonon method, respectively (Ref. 27). The experimental equation of state (Refs. 2 and 28) was used to present theoretical data as a function of pressure. The vertical lines correspond to phase transformations, reported in Ref. 2 to 50 GPa and proposed from the results of this work (see text). The error bars are only shown for selected experimental points. The microphotographs illustrate the change of the optical properties of Li above 40 GPa. The sample at 123 GPa looks dim at the edges because of diamond anvil cupping.

appearance from shiny to black in reflected light (Fig. 4), which is also consistent with recent observations to 80 GPa (K. Syassen, private communication). Our experiments demonstrate that the loss of reflectivity becomes more pronounced at megabar pressures.

#### IV. DISCUSSION

According to x-ray diffraction measurements,<sup>2</sup> the crystal structure of Li below 38 GPa is *fcc*. Thus, no first-order Raman signal is expected. We observe the broad Raman band at  $600\text{ cm}^{-1}$ , which can be assigned to either a maximum of the phonon density of states activated by disorder (e.g., stacking faults) or second-order scattering.<sup>26</sup> The position of this peak is in fair agreement with available theoretical calculations of the phonons in *fcc* Li.<sup>27</sup> The Raman peak nearly coincides with the calculated maximum in the phonon density of states corresponding to longitudinal modes (Fig. 4). An x-ray diffraction study reports a transformation of *fcc* Li to the hR1 and then to the cI16 phase at 38 and 41 GPa, respectively.<sup>2</sup> Within our measurement precision, no change is observed in the Raman spectra at these pressures, but some band broadening and reduction of the Raman intensity occur. This supports our assignment of the broad Raman peak at



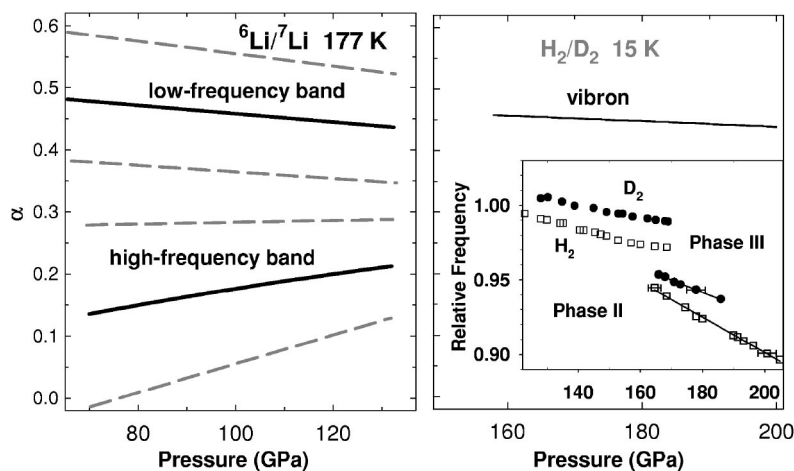


FIG. 5. The isotope effect on the vibron frequency of hydrogen and the high- and low-frequency modes of  ${}^6\text{Li}/{}^7\text{Li}$  (left panel). Long-dashed gray lines indicate the confidence interval for Li determined from the experimental errors of the frequencies. The solid gray line is the result of the similar analysis for the Raman vibrons in hydrogen (Ref. 33) and deuterium (Ref. 34) (right panel). The inset shows the pressure dependencies of the Raman frequencies (normalized to the 0 GPa values) in the vicinity of the II-III phase transition. The pressure dependencies of the vibrons in phase III of  $\text{H}_2$  and  $\text{D}_2$  were approximated by linear dependencies (see the right panel inset, the error bars for the frequencies are smaller than the symbol size). This interpolation procedure resulted in approximately linear dependence of  $\alpha$ . The uncertainty of  $\alpha$  for  $\text{H}_2/\text{D}_2$  is estimated not to exceed  $\pm 0.04$ .

$600\text{ cm}^{-1}$  to a maximum in the density of the phonon states. Since only a minor volume change (less than 1%) has been observed at these transitions,<sup>2</sup> one would not expect the spectral position of the Raman band to change substantially. No first-order Raman scattering is expected for the hR1 phase (one atom per unit cell), while group theory predicts five Raman-active modes ( $A_1+2E+2T_2$ ) for the cI16 structure. We do not observe an abrupt change in the Raman spectra at 41 GPa, which may be explained by band overlap, broadening, and/or low intensity. The fact that the Raman response in the cI16 phase does not seem to contain first-order scattering is interesting. It may mean that the Raman response is affected by a strong electron-phonon coupling,<sup>2,27</sup> as in the case of  $\text{MgB}_2$  (see Ref. 29), which is indirectly supported by the presence of the peak just below  $E_F$  in the electronic density of states,<sup>2</sup> but this suggestion requires additional work to be confirmed.

No x-ray diffraction measurements have apparently been reported above 50 GPa. The observation of the low-frequency band at about 60 GPa in  ${}^7\text{Li}$  suggests a phase transformation to an unknown intermediate phase [the increased intensity of the low-frequency mode at approximately  $165\text{ cm}^{-1}$  can be explained by coupling to the soft mode (see, e.g., Ref. 30)]. Overall, the Raman and optical data (Figs. 2 and 4) at 180 K correlate favorably with the results of x-ray<sup>2</sup> and superconductivity<sup>13</sup> studies. Indeed, the structural transformation to the cI16 phase at 42 GPa and the abrupt change in  $T_c(P)$  at 45 GPa correlate with the change of the visible reflectivity of our sample. Our data suggest the presence of an intermediate phase at 55–69 GPa, which is consistent with monotonous increase of  $T_c$  in this pressure range in Ref. 13. Superconductivity disappears from the accessible temperature range above 62 GPa, while our Raman data show the appearance of the new Raman band at 69 GPa. We conclude that in spite of different stress conditions in our work and Ref. 13, the results of both studies are quite consistent.

The appearance of the high-frequency band above 69 GPa is intriguing and may indicate a new interaction or bonding scheme between Li atoms at high densities in a broken-symmetry phase (see Ref. 3). It should be noted that the frequency of this band is very close to a doubled frequency of the lower energy broad band. This fact makes it possible to consider the high-frequency band as an overtone of the disorder-induced  $650\text{ cm}^{-1}$  band. In an attempt to unambiguously assign this band we have made measurements on two different Li isotopes.

The isotope effect on the vibrational frequencies of Li can be characterized by  $\alpha = -\log(\nu_6/\nu_7)/\log(6.05/6.941)$ , where  $\nu_6$  and  $\nu_7$  are the Raman frequencies of the light and heavy isotope, respectively.  $\alpha$  is close to the ideal value 0.5 for the low-frequency band, however, the calculated isotope shift of the higher frequency band is much lower than the ideal value. In Fig. 5 we plot  $\alpha$ 's for the high-frequency modes of  ${}^6\text{Li}/{}^7\text{Li}$  in comparison to that for the low-frequency modes and the  $\text{H}_2/\text{D}_2$  vibron frequencies at high pressures. The drastically reduced isotope effect is observed for the high-frequency mode, while the low-frequency one shows almost ideal isotope effect. This fact could be explained by strongly anharmonic potential (e.g., a double-well potential) for a corresponding normal coordinate, which favors the interpretation of this band as a Li—Li vibration in the “paired” phase (i.e., with different bonding) close to the phase stability line,<sup>31</sup> although other anharmonic effects cannot be ruled out. Because of the large zero-point motion for Li atoms, a quantum-mechanical treatment is necessary to explain such a large deviation from the ideal case.<sup>32</sup>

The deviation from the ideal  $\alpha$  could also indicate that the band arises from a coupled Li-impurity vibration; however, a consideration of the possible impurities suggests this interpretation is unlikely. We considered the possibility of a Li-X vibration for  $\text{Li}_2\text{O}$ ,  $\text{LiOH}$ ,  $\text{Li}_2\text{C}_2$ , and other possible impurities and reaction products. Comparison of the experi-

mentally obtained  $\alpha$  with the calculation of the isotope effect for the reduced mass of Li- $X$  gives a possible range of atomic masses for  $X$  of 1.7 to 4.2 a.u. Thus, it may be compatible with deuterium (or tritium, which has too little abundance to be considered) impurities, which are highly unlikely to be incorporated into our sample. On other hand, the reduced isotope effect can be explained by a combination band that includes Brillouin zone boundary modes. In this case, the second highest frequency component should correspond to the light atom, having the atomic mass  $m_x = 1.3 \pm 0.4$ , close to the mass of the hydrogen atom, which is not very likely (see above).

We also point out that the relative intensity and narrow linewidth of the high-frequency mode are inconsistent with its assignment to a combination band. Notably, the isotope effect approaches the ideal value on compression, which may imply stabilization of the BS phase under pressure. It should be noted that the linewidth of the high-frequency band decreases with pressure accordingly (see also Fig. 2). For comparison, the isotope shift in H<sub>2</sub> (D<sub>2</sub>) decreases with increasing pressure, which is a signature of increasing anharmonicity and destabilization of the paired state in high-density hydrogen.<sup>31</sup>

Given the arguments presented above, we consider the high-frequency band as a fundamental of the Li—Li stretching vibrations. Assuming this interpretation, the unusually high frequency of the mode and its anomalous isotope effect have implications for the charge distribution around the Li atoms in the high-pressure phase. According to Neaton and Ashcroft,<sup>3</sup> both Li atoms within the so-called “pair” have a large core consisting of 1s electrons, with the outer 2s electrons pushed out of the core region ( $s$ - $p$  $\pi$  hybridization). This arrangement is unique in the sense that there is actually no 2s electron density between Li atoms, and the interaction between them may be substantially determined by core-core repulsion, making the frequency of Li—Li vibration quite high. Also, since the structure of Li above 50 GPa is not known, it is useful to point out that it can be an incommensurate host-guest type, as observed in other simple metals.<sup>35,36</sup> In this case, the distances between metal atoms in

the incommensurate “guest” chains may be substantially shorter than expected, causing an increase of the phonon frequency because the host modulates the “guest” atom positions. As it has been already noted, the change in the pressure dependence of  $T_c$  at 55 GPa reported in Ref. 13 correlates well with the appearance of the low-frequency band in our spectra, indicating possible phase change. These results seem to agree with each other and with available x-ray data<sup>2</sup> in spite of the different temperatures and stress conditions.

## V. CONCLUSIONS

We report optical spectroscopic evidence for transformation of compressed lithium to a broken-symmetry phase above 70 GPa. At lower pressure, the changes in Raman spectra correlate well with the phase transitions reported from x-ray measurements<sup>2</sup> and the reported pressure dependence of the superconducting transition temperature.<sup>11–13</sup> Loss of visible and near-IR reflectivity is also consistent with these observations and also with an increase of resistivity in normal state.<sup>6,7</sup> The reduced isotope shift of the high-frequency mode suggests an anharmonic potential for Li—Li stretching vibration; however, the observed frequency is higher than that predicted by calculations.<sup>3</sup> The reported results should stimulate further theoretical and experimental work on the complex bonding in Li at high densities.

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