Superconductivity and Crystal Structure of Lithium under High Pressure

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Abstract. The superconductivity and structural properties of lithium under high pressure are investigated by simultaneous measurements of X-ray diffraction and electrical resistance at low temperature below 25 K. The structural transitions fcc − hR₁ − cI₁₆ near 40 GPa and the possible structural transition to higher pressure phases were observed above 70 GPa. The superconducting transition temperature \( T_c \) increases with applied pressure and has maximum in fcc phase. At higher pressures, \( T_c \) decreases in hR₁ phase and increases again in cI₁₆ phase. We did not observe \( T_c \) above 9 K for pressures above 70 GPa. Superconductivity possibly disappears in high pressure phases above 70 GPa.

1. Introduction
Lithium undergoes several structural transitions under high pressure. The structural sequence bcc to fcc at around 7 GPa and fcc to cI₁₆ structure via intermediate hR₁ structure at around 40 GPa has been reported from X-ray diffraction works at near 180 K [1][2]. Above 60 GPa, the crystal structure is still unknown.

We found Li to be a superconductor at 7 K and 30 GPa [3]. Recently, superconductivity of Li was observed below 0.4 mK at ambient pressure [4]. The superconducting transition temperature \( T_c \) rises with applied pressure and reaches 20 K (38 GPa), the second highest observed \( T_c \) for elemental superconductors [3][5][6]. Deemyad and Schilling reported the detailed superconducting phase diagram of lithium under nearly hydrostatic pressure obtained by ac-susceptibility measurements [6]. The \( T_c \) of Li rise with applied pressure and had a maximum at 30 GPa and 14 K. Above 30 GPa, it went down to 7 K at 50 GPa and showed increase. Above 60 GPa, the \( T_c \) was not observed above 4 K.

Both the structural phase transition and relatively high \( T_c \) of Li are considered to be driven by the softening of phonon and electron-phonon interaction enhanced along with the shift in electronic character \( s \) to \( p \) under high pressure[1][2][3][5][6][7]. The relationship between the superconducting properties and structures is fundamental interest. Detailed properties of crystal structure and superconductivity will provide the essential information in understanding the superconductivity of alkaline metals, which shows relatively high-\( T_c \) under high pressure. Simultaneous measurements of the electrical resistance and X-ray diffraction in low-temperature region crossing the superconducting phase enable the direct comparison of the pressure dependence of the \( T_c \) and the crystal structures of Li.
2. Experimental
Experiments were performed at BL10XU of SPring-8 using a diamond anvil cell in the combination with monochromatic synchrotron radiation (wavelength 0.410 Å) and imaging plate detection. Figure 1 shows the experimental set-up. Electrical resistance was measured by four points contact method using the deposited fine electrodes on the surface of the diamond anvil (Figure 1a). Cu was employed for the material to reduce the contact resistance between the sample and the electrodes [7]. The thicknesses of the deposited electrodes were roughly less than 1 µm. We didn't see any contribution of Cu to the diffraction patterns.

The Li sample (99.999%, Johnson-Matthey) was loaded into the sample chamber in a DAC under well controlled Ar gas atmosphere. We used the gasket made of diamond powder mixed with epoxy resin. The possibility of chemical reaction between Li and epoxy resin has been concerned, however contamination of the sample was negligible at low temperatures below 25 K where experiments were performed, judging from the color and the value of the electrical resistance at fixed pressure and temperature. Pressure was estimated from the first-order Raman spectra of diamond anvil [8]. To avoid chemical reaction and the failure of diamond anvils [1][2][4], the DAC was, for all pressures above 4 GPa, kept below 25 K in a cryostat.

![Figure 1](image)

**Figure 1.** Experimental set-up on DAC for the simultaneous measurement of resistance and X-ray diffraction (a) Photograph of lithium sample and deposited electrodes at 4 GPa. The top surface of anvil is 150 µm in diameter. Scale bar is 50 µm. (b) Schematic drawings of the cross section. The deposited electrodes were connected to the platinum foil electrodes placed on the insulator gasket made of the mixture of diamond powder and epoxy resin. Experiments were performed below 25 K using a refrigerator. Diffraction patterns were recorded on an imaging plate.

3. Results and Discussion
Figure 2 shows the obtained X-ray diffraction patterns of Li at 25 K at various pressures. The diffraction peaks from the diamond powder gasket are noted by the mark "g". We observed fcc phase up to 34 GPa and hR1 phase at 46 GPa. Li transformed to cI16 structure with admixture of hR1 phase at 56 GPa. Although there are small difference in transition pressures, the obtained result is in good agreement with previous works performed at around 180 K [1][2]. At 69 GPa, adding to the diffraction peaks from cI16 phase, a peak (closed circle) appeared, indicating the transition to a higher pressure phase. At 86 GPa, a different spectrum was obtained. We named these two phases as hp-I and hp-II respectively. These two high pressure phases can be considered to be corresponding to the possible broken symmetry phases that have been reported by Goncharov et al. [9].
We observed superconducting transition at 29 GPa (fcc), 34 GPa (fcc), 46 GPa (hR1) and 69 GPa (cI16 + hp-I). $T_c$ was determined as the onset temperature where the resistance curve starts to deviate from the linear dependence to the temperature. At 56 GPa (hR1 + cI16) and 86 GPa (hp-II), the superconducting transition was not observed above 8.5 K which is the minimum temperature reached in this work.

Figure 3 shows the pressure dependence of $T_c$ and the structural sequence of Li obtained in this work. Dashed line shows the data reported by Deemyad and Schilling [6]. Similar pressure dependence of $T_c$ was obtained in both experiments. The difference between these data in pressure and $T_c$ might be due to the pressure condition; hydrostatic condition with helium pressure medium in ac-susceptibility experiments and non-hydrostatic condition without pressure medium in resistance measurements. We can see $T_c$ of Li increases with applied pressure and has maximum in fcc phase. In hR1 phase, $T_c$ decreases. At 56 GPa in cI16 phase, superconducting transition was not observed above 8.5 K. It can be considered that the $T_c$ of cI16 increased from low temperature to 10 K at pressures between 56 GPa and 69 GPa. Above 70 GPa, the superconducting transition was not observed. Superconductivity possibly disappears in high pressure phases hp-I and hp-II.

What is the nature of the unique pressure dependence of the $T_c$ of Li in fcc phase? We compare the obtained results with the theoretical calculation of $T_c$ shown with open-squares in figure 3 [10]. Experimental results and theoretical data showed quite good agreement in fcc phase. Maheswari et al. performed ab-initio calculation of lattice dynamics and found the fcc structure shows phonon instability around 40 GPa and turn over of the $T_c$ just before reaching this pressure. The increase in $T_c$ is attributed to the lattice softening causing an increase in electron-phonon coupling constant. The decrease in $T_c$ is from the decrease of the logarithmic-averaged phonon frequency, which proportionally contributes to the $T_c$ in Allen-Dyne’s formula for the superconducting transition [11], just before the phase becomes unstable towards to hR1 phase.

![Figure 2](image.png)

**Figure 2.** X-ray diffraction patterns of Li under high pressure at 25 K. Above 69 GPa, the changes of diffraction patterns were observed. The peaks of high pressure phase I and II (hp-I, hp-II) are shown with closed circle and triangles respectively. The mark ‘g’ denotes the peaks from gasket diamond powder.
4. Conclusion
Simultaneous measurements of the X-ray diffraction and the electrical resistance of Li revealed that the $T_c$ increases with applied pressure and shows maximum in fcc phase. The $T_c$ shows increase again in $cI16$ phase with pressure. Crystal phase transition above 70 GPa from $cI16$ to high pressure phases, hp-I and hp-II were observed. Superconducting transition was not observed above 70 GPa and 9 K, which may indicate that the superconducting phase does not exist in high pressure phases above 70 GPa.

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