Crystal Structures of Dense Lithium: A Metal-Semiconductor-Metal Transition


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Ab initio random structure searching and single-crystal x-ray diffraction have been used to determine the full structures of three phases of lithium, recently discovered at low temperature above 60 GPa. A structure with C2mb symmetry, calculated to be a poor metal, is proposed for the oC88 phase (60–65 GPa). The oC40 phase (65–95 GPa) is found to have a lowest-enthalpy structure with C2cb symmetry, in excellent agreement with the x-ray data. It is calculated to be a semiconductor with a band gap of ~1 eV at 90 GPa. oC24, stable above 95 GPa, has the space group Cmca, and refined atomic coordinates are in excellent agreement with previous calculations.

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Lithium is the simplest metal in the periodic table, and its electronic structure is well explained by the nearly free-electron model. However, at high pressures in simple metals, the free-electron picture breaks down, through reduced valence volume, pseudogap opening at the Fermi surface, or electride formation [1–4]. This implies lowered crystal symmetry and electrical conductivity, and diffraction studies [5] have revealed a sequence of phases with increasing complexity, up to c16 a soft-mode distortion of bcc with a 16 atom unit cell [2]. Density functional theory (DFT) showed that a 24-atom orthorhombic structure (Cmca-24) has lower enthalpy than the c16 phase above 88 GPa [6] or 100 GPa [7]. A subsequent study using diffraction and electrical resistance measurements at 25 K, along with visual observations, revealed two further structural transitions at ~70 and ~80 GPa at 25 K, first to a metallic Li-VI phase and then to a semiconducting Li-VII phase [8].


Our recent x-ray diffraction studies mapped out the lithium phase diagram in a wide pressure and temperature range [12]. At 200 K, the study located the transitions from c16 to Li-VI and then to Li-VII at 60 and 65 GPa, and also found a further transition to a previously unreported Li-VIII phase at 95 GPa. Li-VI, VII, and VIII were reported to have C-face centered orthorhombic structures with 88, 40, and 24 atoms (denoted oC88, oC40, and oC24), respectively, on the assumption of continuity of atomic volume through the sequence of phase transitions. However, due to the difficulty associated with collecting high-quality data at low temperatures, the detailed structures were not determined on a purely experimental basis. Also, the large size of the oC88 and oC40 unit cells means that previous calculations have been unable to identify these structures correctly.

In this Letter, we combine ab initio random structure searching (AIRSS) [13] and analysis of single-crystal diffraction data to investigate the structures and natures of these three phases. For the description of the experimental and theoretical techniques involved in this study we refer the reader to Refs. [12,14,15] and supplemental online materials [16]. A schematic representation of the P-T space and sequence of the solid phases involved in this study is shown in Fig. 1.

We start by considering the 24-atom structure. Experimentally, all the reflections for the oC24 structure at 125 GPa and 300 K were indexed with lattice parameters \(a = 7.424(3) \text{ Å}, b = 4.175(4) \text{ Å}, \) and \(c = 4.214(3) \text{ Å}\) and showed systematic absences corresponding to Cmca or C2cb space group symmetry, as also found at 105 GPa [16]. Least-squares refinement yielded a structure corresponding to the Cmca-24 structure of Rousseau et al. [6,10] with atomic coordinates in excellent agreement with the calculated values. Our calculations detected the same Cmca, C2cb, and Pbca candidates as previous works; these diverge in enthalpy only in a small pressure region, calculated as 90–95 GPa. Details of the space group determination, structure refinement, and calculations are given in supplemental material [16].

Li-VII (oC40) is the only known phase of lithium showing pronounced semiconducting behavior (see below and Refs. [8,12]). Single crystals of Li-VII (at 75 GPa and 240 K) were of poorer quality than those obtained for...
The space group was determined as either Cmca or C2cb, resulting in broader, weaker reflections (see [16]). The space group was determined as either Cmca or C2cb, and least-squares fitting of reflection d spacings gave lattice parameters of a = 4.942(4) Å, b = 8.026(10) Å, and c = 6.784(3) Å. Searches for possible aC40 structures were initially conducted using a 20-atom primitive cell with space group P2_1/c (a subgroup of Cmca). The initial lattice parameters were chosen as the experimental values, but allowed to change during the optimizations. After searching 250 possible structures, the lowest-enthalpy candidate structure with Cmca symmetry was found to have only a small range of stability against c16 (see [16]). We then performed 600 further trials with 20-atom structures with three lower-symmetry space groups: P6c (subgroup of both Cmca and C2cb space groups); randomly selected space groups with 4 and 2 symmetry operations; and symmetry reduced to P1. From these we found a still-lower enthalpy structure with noncentrosymmetric space group C2cb and five nonequivalent Li atoms located on 8b sites (labeled Li1-5, see [16]).

Calculations of the zone center (Γ) phonons for the calculated Cmca-40 structure revealed an imaginary frequency for a B1u mode, the first-order parameter for the Cmca-40 to C2cb-40 group-subgroup distortion. Detailed enthalpy calculations (Fig. 2) show that the C2cb-40 structure also has considerably lower enthalpy than the monoclinic C2-24 structure previously reported to be stable in this pressure range [9]. The predicted C2cb-40 to Cmca-24 transition pressure is 91.3 GPa, in agreement with the experimental value of 95 GPa at 200 K. In fact, our calculations predict that the C2cb-40 structure would transform to the P2ca-24 structure at 90.5 GPa, then C2cb-24 at 94 GPa, and finally Cmca-24 at ~110 GPa. But, the enthalpy differences responsible for the stability of P2ca-24 and C2cb-24 with respect to the high-symmetry Cmca-24 phase are smaller than our calculational accuracy (less than 1 meV/atom).
ELF attractors \[\text{Fig.4(b)}\] are located on distorted layers 0.896, respectively. As with the atomic arrangement, the B layer, while the other two layers, \(\text{M}1\) and \(\text{M}3\), contain both \(\text{C}0\) and \(\text{D}0\), similar to the direct band gap of 1.03 eV at \(\text{EF}\). Integrating the electron density within the ELF attractor basins of Li are connected (Fig. 5), generating "pseudoanions" holding \(\sim 6\) electrons \([\text{Fig. 5(d)}]\) within which the ELF never drops below 0.83.

These ELF basins do not span space; they are separated by regions with ELF values as low as 0.4. Although interstitial electron localization has been observed for other proposed Li phases \([9]\), the fact that all the ELF basins hold electron pairs, in analogy with the electride behavior of the \(\text{M}1\) and \(\text{M}3\) ELF attractors merge into a single \(\text{M}1\)-\(\text{M}3\)-\(\text{M}1\) superbasin containing \(\sim 6\) electrons \([\text{Fig. 5(d)}]\) within which the ELF never drops below 0.83. A complicated framework. In particular, the \(\text{M}1\) and \(\text{M}3\) ELF attractors do not span space; they are separated by regions with ELF values as low as 0.4. Although interstitial electron localization has been observed for other proposed Li phases \([9]\), the fact that all the ELF basins hold electron pairs, in analogy with the electride behavior of the \(\text{M}1\)-\(\text{M}3\)-\(\text{M}1\) superbasin containing \(\sim 6\) electrons \([\text{Fig. 5(d)}]\) within which the ELF never drops below 0.83.

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Although a case can be made for electron pairs lying in $M^2$-$M'$ superbasins (ELF = 0.88), the metallic character seems to be related to a fractional occupancy of the ELF basins. So, in the metallic $Cmca$-24 phase at 125 GPa we identify two basins centered on $8d$ (ELF = 0.91) and $8f$ (ELF = 0.89) sites containing 1.28 and 1.60 electrons, respectively. Fractional occupancy means that Li-VIII is a metal, but the high ELF value of the basins, and the considerably lower values in between, implies poor conduction and atypical metallic behavior [17].

This real-space analysis complements the $k$-space picture of Fermi-surface–Brillouin-zone interactions, also leading to commensurate charge density modulation. Alternate pictures include projection of the electrons onto atom-centered or two-centered molecular orbitals. The projection onto $s$ and $p$ states in Fig. 3(a) shows that complex behavior occurs at an energy where $2p$ orbitals can hybridize with $2s$, and appears to show that both the valence and conduction bands’ edges have strong $p$ character. However, given that the electron density lies primarily in the interstitial regions, the value of an interpretation in terms of atom-centered projections seems limited. Previous work has also attributed the interstitial charge density to “pairing” of atoms into “dilithium” molecules, or to $p\pi$ bonding extending into the interstitial regions [1,6]. Although the wave functions can be expanded in such basis sets, these pictures contrast strongly with our ELF-based electride picture of well-defined Lewis pairs centered on interstitial sites.

Finally, we address the most complex phase—$oC88$ (Li-VI). Systematic absences determined the space group as either $Cmma$ or $C2mb$, and the lattice parameters at 65 GPa and 240 K refined to $a = 8.445(5)$ Å, $b = 9.175(11)$ Å, and $c = 8.280(6)$ Å. We have carried out AIRSS, constrained by the experimental information, with 44 atoms per primitive cell. The lowest-enthalpy structure identified by AIRSS had space group $Cmma$ with 44 atoms per primitive cell. The lowest-enthalpy $Cmma$ space group were found, and is in good agreement with observed intensities estimated (as for $oC40$) on a scale of strong, medium and weak and unobserved, comparable to the fit obtained for $oC40$. For details of the calculated atomic coordinates, density of states, and a drawing of the structure, see [16].

The shortest Li-Li distance is 1.77 Å. The density of states is low at the Fermi energy but shows no band gap, in agreement with the observed metallic nature of this phase [8]. This structure is the second most stable of the phases calculated at 0 K and in the Li-VI experimental pressure range, from 60 to 65 GPa, Li-V ($c116$) has lower enthalpy (Fig. 2). The difference is small, and the inclusion of dynamical effects, both zero-point and finite-temperature, could stabilize this $oC88$ structure against $c116$. Thus AIRSS has revealed the structure, but some additional physics is needed to explain the thermodynamic stability of $oC88$. A peculiarity of the observed $oC88$ phase at very low temperature is the reported huge increase of resistivity at 25 K (4 orders of magnitude) across its narrow range of stability, interpreted as a phase mixture [8]; no such mixture is observed in our experiment, albeit at higher temperatures, and we cannot exclude the possible instability of $oC88$ to a soft-phonon transition at very low temperatures.

In summary, we have shown that $oC88$ is metallic with a large, complex structure with probable $C2mb$ symmetry; $oC40$ has a $C2cb$-40 structure not observed previously, which is nonmetallic with a larger band gap than any previously found or proposed for Li at any pressure; and the $oC24$ phase has the $Cmca$-24 structure proposed by Rousseau et al. [6]. All of these phases are characterized by the valence electrons occupying interstitial regions, which may become disjoint leading to semiconducting electride phases. This invites further investigation of the role of interstitial electron density in these systems [18].

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Note added in proof.—After our Letter was submitted a paper by Lv et al. [19] was submitted to Physical Review Letters describing a similar calculation of the $oC40$ phase.

[11] The authors refer to the conventional setting $Aba2$ (space group 41). We use the alternative $C2cb$ setting where $abc - \overline{cba}$ to be consistent with the $oC40$ notation.