Origin of the anomalous semiconducting behaviour in dense lithium

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Experimentally, it is known that lithium undergoes a metal to semiconductor transition at about 80 GPA and a reentrant semiconductor to metal transition near 120 GPA. This unusual behaviour has been attributed to the formation of high-pressure electrides in the Li-Aba$^2$ phase. Using the accurate wave function based quantum Monte Carlo (DMC) method, we show that the valence charge distribution of the Li-Aba$^2$ phase is incompatible with an insulating or semiconducting ground state. At DMC level, the most stable phase at 100 GPA is an orthorhombic oP24 structure with Pbca symmetry whose valence charge density shows an electride paired distribution, in correspondence with the theoretical predictions of Neaton and Ashcroft [Nature 00, 141 (1999)]. Here, we propose the electride pairing in the oP24-(Pbca) phase as the origin of the semiconducting behaviour observed in diamond anvil cell experiments.

Under high pressure lithium exhibits an exotic and often counterintuitive chemistry. It shows an anomalous melting curve, isotope effects, and a Fermi surface that becomes progressively anisotropic with increasing pressure. In 1999, Neaton and Ashcroft predicted that at high pressures lithium should undergo a metal-to-insulator (or semiconductor) transition to a paired structure, similar to a condensed molecular solid as observed in dense hydrogen. This theoretical prediction was confirmed experimentally ten years later by Matsuoka and Shimizu who observed a metal to semiconductor transition at about 80 GPA, and four years later, a reentrant semiconductor to metal transition near 120 GPA.

Several theoretical studies based on density-functional theory (DFT) have proposed the (Aba$^2$, oC40) phase (hereinafter referred to as Aba$^2$) as the most plausible candidate for the semiconducting regime. In this phase the valence electrons separate from all atoms and tend to occupy interstitial regions, leading to the formation of high-pressure electrides. Both DFT and many-body GW calculations predict the existence of a semiconducting band gap in the Li-Aba$^2$ phase. However, it has been pointed out that some of the interstitial sites are singly occupied. This phase should be metallic. However, this fundamental contradiction may be alleviated if two neighboring interstitial quantum orbitals actually form covalent bonds (i.e., a quasimolecule) and, therefore, a gap opens up between their bonding and antibonding states, as recently proposed by Miao and co-workers.

In this Letter, we investigate the origin of the semiconducting behaviour experimentally observed in dense lithium. We study the high-pressure Li-Aba$^2$ structure, which has been identified previously as the best candidate for the semiconducting phase of Li, by combining DFT and many-body GW calculations with the highly accurate diffusion quantum Monte Carlo (DMC) method. The topology of the valence electron distribution of the Li-Aba$^2$ phase reveals the existence of partially covalent multi-center bonds centered on interstitial electrides. Moreover, our DMC results indicate that the most stable structure at 100 GPA is an orthorhombic oP24 structure with Pbca symmetry, whose valence charge distribution shows the existence of electride-electride pairs at interstitial sites, being consistent with an insulating or semiconducting ground state as described by Kohn.

In 2011, the high-pressure Li-Aba$^2$ structure was identified in two computational studies. Marqués et
al.\textsuperscript{14} and Lv \textit{et al.}\textsuperscript{13} reported a Li-\textit{Aba2} structure as the lowest-enthalpy phase in the pressure range of 67-91.3 GPA and 60-80 GPA, respectively. These results are in good agreement with x-ray diffraction data,\textsuperscript{2} which suggests a C-face centred orthorhombic structure having 40 atoms per unit cell (oC40) as the most stable phase between \( \sim 70 \) and \( \sim 100 \) GPA. Guillaume \textit{et al.}\textsuperscript{2} reported the existence of a transition from this phase to an orthorhombic structure near 100 GPA at 77 K, which has 24 atoms per unit cell and seems to be stable at least 130 GPA. Moreover, as Li-\textit{Aba2} is the only known competitive structure showing a semiconducting gap in DFT calculations, it has been systematically associated in the literature with the semiconducting phase experimentally observed in the pressure range of 80-120 GPA. Naumov and Hemley,\textsuperscript{23} assuming a weakly correlated system, suggested that the opening a band gap in the Li-\textit{Aba2} phase results from a strong s-p orbital mixing near the Fermi level. Miao \textit{et al.}\textsuperscript{20} suggested that its semiconducting nature could be due to the formation of bonding and antibonding states (\textit{quasimolecules}) between two neighbouring interstitial electrides.

We first investigate the electronic structure of the \textit{Aba2} phase at 60 GPA within the quasiparticle self-consistent \textit{GW} approximation (\textit{QSGW}), which is known to provide an accurate description of the electronic structure of solids.\textsuperscript{24-26} Our calculations were performed using the ABINIT code,\textsuperscript{27} with full details provided in the Supplementary Information. Figure 1 shows the quasiparticle band structure of the Li-\textit{Aba2} phase at 60 GPA. We found the existence of a direct gap of 1 eV at the \( \Gamma \) point, thereby confirming the semiconducting character of this phase as predicted by previous DFT calculations.

In addition, we have found that both band edges are derived from interstitial electrides. In Figure 1, the blue bands in the valence-band are mainly derived from electrides with a predominant s-like character, whereas the red bands at the bottom of the conduction-band are derived from electrides that are a mixture of s- and p-like states. The charge density isosurfaces corresponding to the valence-band maximum (VBM) and the conduction-band minimum (CBM) are plotted in Figure 2. It is worth to mention that the electrides that form the band edges could be seen as periodic arrays of quantum dots,\textsuperscript{17} whose wave functions strongly overlap due to their high concentration and close proximity,\textsuperscript{28-30} giving rise to delocalized bands in reciprocal space.

The semiconducting nature of Li-\textit{Aba2} is in disagreement with experimental observations, which indicate that Li is metallic in the range of 70-80 GPA.\textsuperscript{11,12} However, the Pauli exclusion principle that prevents short-range interactions may play a crucial role in determining the electronic properties of the Li-\textit{Aba2} phase. If the Pauli repulsion is strong enough, the valence charge density could be rejected from the position of the s-like electrides that form the top of the valence-band (blue bands in Figure 1) and be partially transferred to the high energy electrides of mixed s- and p-like character that form the bottom of the conduction-band (red bands in Figure 1), thus avoiding the overlap between the negatively charged s-like electrides and the core 1s electrons of the neighboring Li nuclei. Moreover, if the electrides that form the top of the valence-band are primarily 1s in character (as is the case of sodium near 200 GPA)\textsuperscript{32} the possibility of a charge transfer between the two classes of electrides should be strongly increased. To investigate this hypothesis, we used the accurate wave function based diffusion quantum Monte Carlo method\textsuperscript{33,34} to obtain the valence electron charge distribution of the Li-\textit{Aba2} phase at 60 GPA. The DMC method is in principle an exact technique to solve the imaginary time dependent Schrödinger equation. It has been successfully applied in the study of the high-pressure phase diagram of solid molecular hydrogen,\textsuperscript{35} the high-pressure properties of silica,\textsuperscript{36} and the stability of square 2D ice under pressure.\textsuperscript{37} We have used a trial wave function of the Slater-Jastrow form,\textsuperscript{38} in which a determinant of single-particle orbitals obtained from a DFT calculation is multiplied by a Jastrow correlation factor. In order to make the wave function depend explicitly on the particle separations, we used a three-term Jastrow factor that includes an electron term, an electron-nucleus term, and an electron-electron-nucleus term.
According to Kohn,\textsuperscript{22} the insulating behavior is a strict consequence of the localization of the electronic wave function in the many-particle configuration space. This characterization includes conventional insulators, in which the ground state is isolated from the exited states by a finite energy gap, as well as Mott insulators,\textsuperscript{28,39,40} which are usually described as metals by one-electron band theory. Figure 3(a) shows the valence charge distribution of the Li-\textit{Aba}2 phase at 60 GPA obtained from quantum Monte Carlo calculations. The DMC result, in which correlations were explicitly included through a Jastrow correlation factor, is consistent with our previous analysis. The valence density is mostly delocalized and exhibits several local maxima centered at interstitial positions. We observe a large degree of delocalization between the basins and wide regions in which the electron distribution is relatively flat, being consistent with metallic behavior.\textsuperscript{41} Moreover, the topology of the electron distribution indicates a multicenter bonding situation similar to that previously reported for the metallic Li-cI16 phase.\textsuperscript{42} In addition, DMC shows that the valence electrons percolate through the space forming a three-dimensional connected network, as shown in Supplementary Figure 2(b). These findings seem to be incompatible with the formation of isolated covalently bonded \textit{quasi-molecules} in the Li-\textit{Aba}2 phase, as recently proposed in Ref. \textsuperscript{20}.

It is illustrative to compare the DMC valence charge distributions of Li-\textit{Aba}2 and Li-cI16, as the latter phase is well-known to be metallic and is also characterized by the formation of high-pressure electrides.\textsuperscript{21,43} The calculated valence charge distribution of the metallic Li-cI16 phase is shown in Figure 3(b). The more delocalized character in the Li-\textit{Aba}2 phase (Figure 3(a)) is clear. Thus, the appearance of a finite energy gap seems to be incompatible with the Kohn’s description of the insulating state.

Finally, we performed DFT calculations to obtain the static (i.e., neglecting the zero-point motion) low temperature phase diagram of Li between 50 and 140 GPA, including the most competitive crystal structures previously proposed in the literature.\textsuperscript{14,15,44,45} Our results are shown in Figure 4. We found that the Li-\textit{Aba}2 structure is the most stable phase in the range of 68.5–90.5 GPA, in agreement with previous theoretical works.\textsuperscript{13–15} Furthermore, we chose 100 GPA as a representative pressure for the experimentally observed semiconducting regime. At this pressure, we identify three distinct structures nearly degenerate in enthalpy: a local three-coordinated oC24 (\textit{Cmca}) structure (proposed by Rousseau et al.),\textsuperscript{44} an orthorhombic oP24 (\textit{Pbca}) structure, and an oC24 structure with \textit{Aba}2 symmetry. All of these are electride phases, showing valence charge localization at interstitial positions.

We performed DMC calculations to compare their relative enthalpies at a higher level of theory and found that Li-oP24 (\textit{Pbca}) is the most stable phase at 100 GPA. The second most stable phase, higher 9.77 meV/atom in enthalpy, is Li-oC24 (\textit{Cmca}) which is closely followed by Li-oC24 (\textit{Aba}2), just 1.79 meV/atom higher in enthalpy. We should note that the enthalpy of insulating phases is expected to be lowered at DMC level with respect to metallic phases.\textsuperscript{10} This is due to a downshift in the absolute position of the valence-band that lowers the total energy. In metallic phases, there are no such
downshifts and DFT is expected to be sufficiently accurate. We can obtain the correction to the valence-band of the Li-oC24 phase by comparing the ionization potential (IP) obtained by PBE and DMC calculations. The IP can be approximated as, IP = E_0 − E_+, where E_0 is the total energy of the ground state and E_+ is the total energy of the positively charged state.\(^4\) We found a correction of −0.27 eV for the valence-band. Similarly, the correction to the conduction-band can be approximated by computing the electron affinity (EA) given by, EA = E_- − E_0, where E_- is the total energy of the negatively charged state. We found a correction of 0.32 eV for the conduction-band by comparing the PBE and DMC results.

Figure 5(a) shows the electronic band structure of the Li-oP24 phase at 100 GPA, in which DMC corrections of 0.32 eV and −0.27 eV were applied to the conduction-band and the valence-band, respectively. Figure 5(b) shows the DMC valence charge distribution plotted in the Miller index plane (002). We find that the distribution is mostly localized showing electride-electride pairs or quasimolecules centered at interstitial sites. These findings are in good agreement with the theoretical predictions of Neaton and Ashcroft,\(^9\) suggesting that electride pairing in the Li-oP24 phase could be the origin of the semiconducting behaviour observed in diamond anvil cell experiments.\(^11,12\)

Moreover, the calculated lattice parameters at 115 GPA are a = 4.249 Å, b = 4.236 Å, and c = 7.581 Å, in good agreement with the experimentally found values of a = 4.213 Å, b = 4.205 Å, and c = 7.482 Å.\(^2\)

In summary, our calculations exclude the formation of high-pressure electrides in the Li-Aba2 phase as the origin of the semiconducting behavior experimentally observed in compressed lithium. Our DMC results, in which electron correlations are explicitly taken into account, show that the most stable crystal structure at 100 GPA is a paired orthorhombic oP24 structure with Pbca symmetry. Thus, we propose the electrode-electride pairing in this phase as the origin of the semiconducting behaviour experimentally observed in the range of 80-120 GPA.

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