

Superconductivity in Lithium, Potassium, and Aluminum under Extreme Pressure: A First-Principles Study

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Extreme pressure strongly affects the superconducting properties of “simple” elemental metals, such as Li, K, and Al. Pressure induces superconductivity in Li (as high as 17 K) while suppressing it in Al. We report first-principles investigations of the superconducting properties of dense Li, K, and Al based on a recently proposed, parameter-free, method. Our results show an unprecedented agreement with experiments, assess the predictive power of the method over a wide range of densities and electron-phonon couplings, and provide predictions for K, where no experiments exist so far. More importantly, our results help uncover the physics of the different behaviors of Li and Al in terms of phonon softening and Fermi surface nesting in Li.

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The effect of high pressure on phonon-mediated superconductors has been the subject of many investigations. These studies revealed a strong material dependence: While applied pressure suppresses superconductivity in some materials, it favors it in others [1]. Even in simple metals, the physics underlying pressure effects on the superconducting properties can be very complicated. For example, Li [1–9] and Al [10–13] behave in many circumstances like nearly free-electron gases, but they exhibit very different behaviors under pressure, still only partially understood within the Eliashberg theory [14]. At ambient pressure, Al is a superconductor with $T_c = 1.18$ K [10]. Pressure rapidly reduces T_c , bringing it down to 0.075 K at 6.2 GPa [10]. Lithium, on the other hand, is a rather complex material: Below 77 K and at zero pressure, it shows a martensitic transition to energetically competing closed packed structures [15]; from 7.5 to 70 GPa, it undergoes several structural transitions [2] which suggest the presence of strong electron-phonon (e -ph) interactions. No sign of a transition to a superconducting state above 4 K was found up to ≈ 20 GPa, while, at higher pressures, Li becomes a superconductor [3–6]. In the range 20–38.3 GPa, where Li crystallizes in an fcc structure, experiments by Shimizu *et al.* [4], Struzhkin *et al.* [5], and Deemyad and Schilling [6] found that T_c increases rapidly with pressure, reaching values around 12–17 K (the highest T_c observed so far in any elemental superconductor). Also, K undergoes several phase transitions and is stable in the fcc phase between 11.6 and 23 GPa [16].

The pressure dependence of T_c for Al, Li, and K has been calculated by Dacorogna *et al.* [12], by Christensen and Novikov [7,17], and by Shi *et al.* [18], respectively. For Al, Dacorogna *et al.* [12] obtained a nearly satisfactory agreement with experiments [10,11]. In the case of Li, Christensen *et al.* [7] used a rigid-muffin-tin approximation

for the e -ph coupling constant λ and $\mu^* = 0.13$. Because of the empirical scaling of phonon frequencies [17], they obtained a much too high T_c (45–75 K) unless the “non-standard” value of $\mu^* \approx 0.22$ or an additional term modeling spin fluctuations was used. For K, Shi *et al.* [18] obtained $T_c = 9$ K at 13.5 GPa, using $\mu^* = 0.13$.

Note that, in these reports, as in most other Eliashberg-based calculations, the electron-electron (e - e) repulsion was treated semiempirically through the Morel-Anderson pseudopotential μ^* . The validity of this procedure for the case of low density solids such as Li has been questioned by Richardson and Ashcroft [19]. Building on the seminal work of Oliveira, Gross, and Kohn [20], and on further developments [21], some of us recently introduced an alternative approach to Eliashberg theory: an extension of the density functional theory to the superconducting state (SCDFT) [22]. This theory is fully *ab initio* and is capable of describing correctly the superconducting properties of several elements [23] and compounds [24]. In the present Letter, we explore this very promising method to study the superconducting properties of Li, K, and Al under pressure. Furthermore, we provide a detailed description of the subtlety of superconductivity in Li, where the incipient phase transitions produce a phonon softening and a very strong electron-phonon coupling, thus enhancing T_c up to values unusually large for simple elemental metals. Our results for Li and K confirm that a full treatment of electronic and phononic energy scales is required, in agreement with previous arguments [19]. We predict K to be superconducting, with a T_c up to ≈ 2 K in the experimental stability range of the fcc structure and up to ≈ 11 K in the range of stable calculated phonon frequencies.

Ground-state calculations were performed using the pseudopotential-based code PWSCF [25] within the local density approximation (LDA) to the density functional

theory. The validity of the pseudopotential approach at high pressures was verified by comparison with all-electron methods. Phonon frequencies and e -ph couplings were obtained from density functional perturbation theory. The electron-phonon coupling spectral function $\alpha^2F(\omega)$ and \mathbf{q} -dependent phonon linewidth were evaluated through a careful integration over the Fermi surface. The implementation of SCDFT has been reported elsewhere [22,23]. All systems were considered in the fcc structure in their experimental ranges of stability.

The LDA underestimates the equilibrium volume of Li and Al, as it can be observed by calculating the equation of state $P(V)$ using Murnaghan's formula. To compensate for this systematic error, we apply a positive pressure shift of about 3.5 and 2 GPa for Al and Li, respectively. This is the amount required to match the experimental equation of state [2,26,27]. Note that these shifts will always be included in the values given in the following. No shift is necessary for K.

In Fig. 1, we compare the calculated pressure dependence of T_c for Al, K, and Li with available experimental results. For Al, SCDFT calculations match exactly the experimental zero pressure $T_c = 1.18$ K and reproduce the rapid decrease of the transition temperature. In the same figure, we report the estimation of T_c by means of McMillan's formula (using $\mu^* = 0.13$, in agreement with previous studies [12]).

In the case of Li (lower panel in Fig. 1), despite the poor agreement among the four sets of experimental data, the most recent experiments [5,6] agree in: (i) Li is not superconducting at ambient pressure; (ii) T_c is lower than 4 K up to 20 GPa; and (iii) T_c then increases with pressure, reaching 14 K at about 30 GPa. The only exception to this behavior is the early report by Lin and Dunn [3]. In this pressure range, the results of Struzhkin *et al.* [5] and of Deemyad and Schilling [6] are quite similar, while Shimizu *et al.* [4] find lower values of T_c . At even higher pressures, experiments show a quite complex behavior (see below). Within this scenario, our calculated SCDFT results are in excellent quantitative agreement with the most recent experiments [5,6] up to about 30 GPa. We find that Li is not superconducting up to 8 GPa and that T_c shows two different trends with pressure, a first region (8–20 GPa), in which T_c increases at a rate of ~ 0.3 K/GPa, and a second region (20–30 GPa) at ~ 1.3 K/GPa.

K shows a behavior quite similar to Li: Beyond a pressure threshold (20 GPa), T_c rises rapidly. In the range where phonons were found to be stable, it reaches ≈ 11 K at 29 GPa; the experimentally observed instability of the fcc phase, however, limits this value to ≈ 2 K at 23 GPa.

The differences between Al and Li can be understood by looking at the e -ph coupling as a function of pressure. In Al, the phonon frequencies increase as the pressure rises (this corresponds to the normal stiffening of phonons with

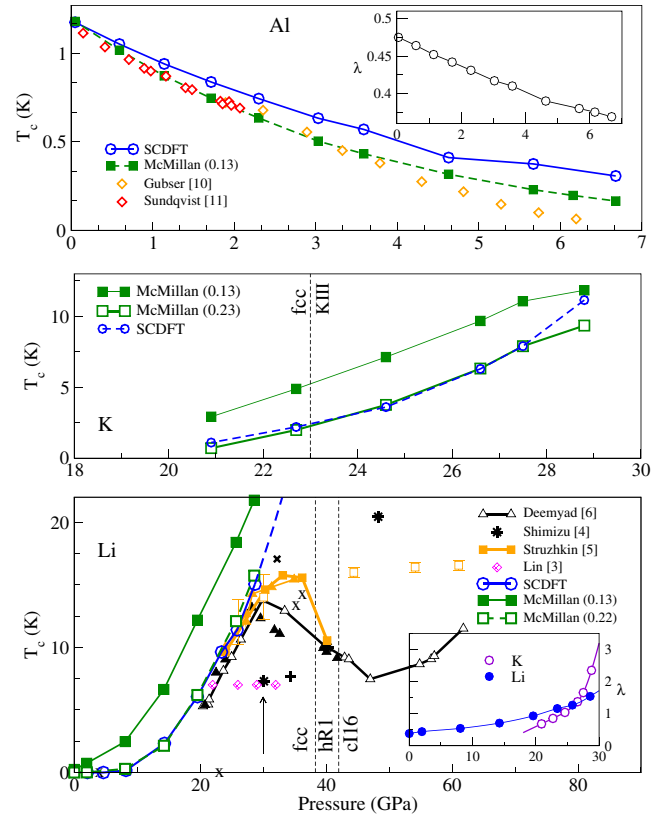


FIG. 1 (color online). Comparison between calculated and experimental critical temperatures for fcc-Al (upper panel), K (middle panel), and fcc-Li (lower panel). Numbers in parentheses after “McMillan” indicate the μ^* value. Different symbols with the same color refer to the same experimental report using different setups. Vertical dashed lines indicate the experimental structural transition pressures for Li and K. The insets depict λ vs pressure in GPa. The dashed line in the lower panel (Li) represents the calculation above the dynamical instability pressure.

increased pressure). In addition, the Eliashberg spectral function $\alpha^2F(\omega)$ shows a high-frequency peak whose height decreases as a function of pressure. These factors contribute to the decrease of λ (see the inset in Fig. 1) and, consequently, of the critical temperature T_c .

In Li, on the other hand, the phonon frequencies exhibit a quite different behavior. In Fig. 2, we present the phonon dispersion of the lowest branch along the X - K - Γ line of the Brillouin zone. For pressures up to 8 GPa, there is an increase of the phonon frequencies, as in the case of Al. However, as the pressure is raised further, the phonons near the K point start to soften. The softening continues up to 33 GPa, when this frequency becomes imaginary. A closer inspection of Fig. 2 reveals that, already at around 30 GPa, a phonon mode close to the Γ point develops an imaginary frequency. We believe that this marks the transition to the hR1 (rhombohedral symmetry) phase, but further analysis would be required to fully validate this assumption. Although diffraction experiments performed at 180 K [2]

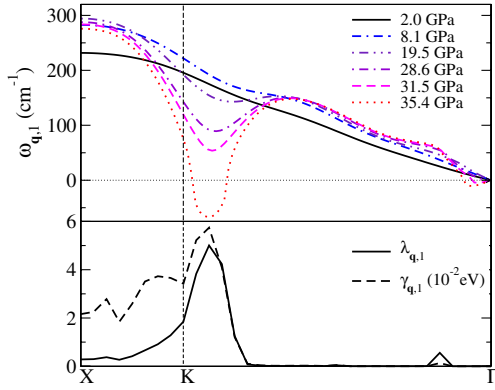


FIG. 2 (color online). Upper panel: Phonon dispersion of Li along the X - K - Γ line, at different pressures, for the lower frequency mode (frequencies below the zero axis denote imaginary values). Lower panel: Electron-phonon coupling $\lambda_{q,1}$ and phonon linewidth $\gamma_{q,1}$ calculated at 28.6 GPa.

set the structural phase transition at 39 GPa (up to 42 GPa), it was observed recently that T_c has a maximum at 30–33 GPa and drops drastically beyond that pressure [5,6]. This latter finding, so far unexplained, is consistent with our theoretical prediction of a complete phonon softening at around 30 GPa.

In Fig. 2, we plot for the lowest frequency phonon the linewidth $\gamma_{q,\nu}$ [the Fermi surface (FS) average of the e -ph coupling matrix elements] and the corresponding \mathbf{q} -dependent electron-phonon coupling $\lambda_{q,\nu}$, at $P = 28.6$ GPa. The quantity $\gamma_{q,\nu}$ shows a peak close to K and a broad maximum between K and X . This peak suggests the presence of FS nestings. To demonstrate this idea, we plot in Fig. 3 a cut of the FS parallel to the (110) plane which includes the L point. We clearly recognize nesting vectors (indicated by arrows) connecting fairly flat and parallel lines. The effects of nesting are remarkably enhanced by the strong e -ph matrix elements. In Fig. 3(c), we show the isosurface $\lambda_{q,\nu=1} = 5$. As can be seen, the extremely high-coupling regions form tubular structures oriented parallel to the Cartesian axes and centered around \mathbf{q} values along the (110) direction, matching the FS nesting vectors indicated above. The observed phonon softening as a function of pressure is a direct consequence of the presence of the FS nesting. In turn, the progressive FS nesting with the increase of pressure is a consequence of the FS topological transition from a spherical free-electronlike to a distorted anisotropic shape (see Fig. 3). This topological transition is a manifestation of an “ s - p ” transition of the electronic states near E_F [2,7,28]. In particular, we can see in Fig. 3(a) that the k -resolved Δ_k is maximum on the rings of the FS around the L , arising from mostly p -like and strongly covalently bonded states. An analogous “ s - d ” transition occurs in K . Also, the electron localization function (ELF), which progressively increases with pressure, indicates the departure from the free-electron picture towards more “covalent” phases. This produces strong

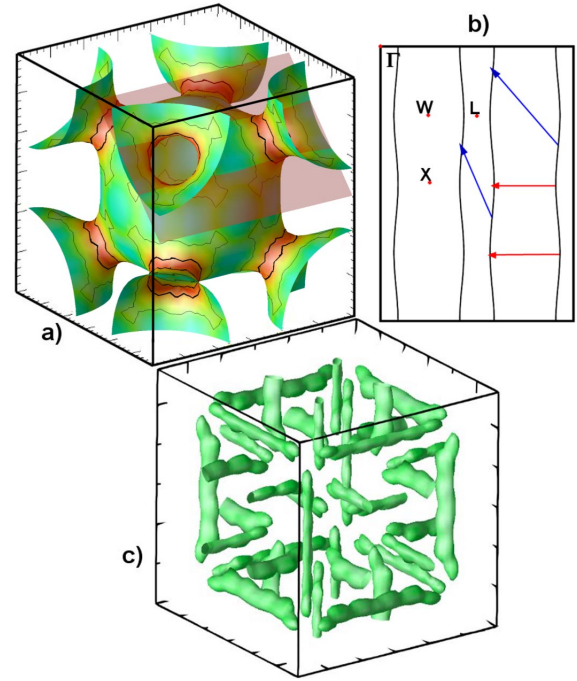


FIG. 3 (color online). (a) 3D view of the Fermi surface of Li, at 28.6 GPa, with a color scale indicating the value of Δ_k . The red color indicates high values of Δ . (b) The FS cut on the plane of (a), including the L point and parallel to the (110) plane, brings into evidence the FS nesting. The arrows represent nesting vectors. (c) Isosurface of $\lambda_{q,\nu=1} = 5$. Γ is at the vertices and at the center of the cube; X is at the centers of the faces.

electron-phonon coupling that leads to the symmetry-breaking phase transitions at high pressure [2] and to the “paired bonded” structures close to 100 GPa [28].

Our calculation of $\alpha^2 F(\omega)$ for Li leads to a value of $\lambda = 0.38$. Using this number and the standard value $\mu^* = 0.13$ inside McMillan’s formula, we obtain $T_c = 0.25$ K at zero pressure, which is lower than the previously reported one [7] but in agreement with more recent calculations [17]. However, it is in complete disagreement with our SCDFT results and with experiments, both giving $T_c = 0$ K. In order to obtain this latter result from McMillan’s equation, we need to use $\mu^* \approx 0.22$. This value also describes quite well the behavior of T_c with pressure. The same physical result was found for K (Fig. 1), where a very similar value $\mu^* \approx 0.23$ has to be used to bring McMillan and SCDFT results into agreement for all pressures [29]. According to Richardson and Ashcroft [19], a large value of μ^* is justified by the fact that the e - e interaction becomes unusually large at such densities. These authors pointed out that, in this density range, a full treatment of electrons and ions on the same footing is required. This is exactly what our method [22,23] achieves: The different energy scales of Coulomb repulsion and phonon-mediated attraction are fully included without any *ad hoc* modeling.

In order to further investigate the effect of the Coulomb repulsion, we solved the SCDFT gap equation in Li using

for the e - e repulsion both the actual matrix elements of the Thomas-Fermi screened potential and the approximate functional $\mathcal{K}^{\text{TF-SK}}$ introduced in Ref. [23]. While this latter approximation failed for the localized σ orbitals in MgB_2 , it works very well for Li over the pressure range considered. Thus, while the strong e -ph coupling and the ELF indicate that covalency is becoming progressively more important, the Coulomb repulsion can still be modeled as if electrons were delocalized. Then why μ^* does have to be so large? We can try to answer this question using SCDF. By making a comparative analysis between Al and Li, we found that the FS average of the Coulomb potential multiplied by $N(E_F)$ (which can be directly related to μ) is $\approx 40\%$ larger in Li than in Al, mostly because of the van Hove peak in the density of states of Li. This effect is present even after taking into account the renormalization of the Coulomb repulsion due to retardation effects. Thus, our results clearly demonstrate a larger value of the Coulomb repulsion in Li than in Al. Since our functional, based on the Thomas-Fermi screened Coulomb repulsion, does not include spin fluctuations, we can clearly rule out that spin fluctuations are required to explain the large Coulomb contributions and the anomalously high value of μ^* . Further investigations at $T = 0$ indicate that the gap function is very sensitive to changes of the density of states at all energies, once again showing the difficulty to reduce the complexity of the Coulomb interaction into a single numerical parameter.

In summary, the recently introduced SCDF method allowed us to calculate the superconducting transition temperature of Al, K, and Li under high pressure from first principles. The results obtained for Al and Li are in very good agreement with experiment and account for the opposite behavior of these two metals under pressure. Furthermore, the increase of T_c with pressure in Li is explained in terms of the strong e -ph coupling, which is due to changes in the topology of the Fermi surface and is responsible for the observed structural instability. Finally, our results for K provide predictions intriguing enough to suggest experimental work on this system.

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Note added.—During the reviewing process of this Letter, two reports appeared, confirming phonon softening [30] and Fermi surface deformation [31] in Li under pressure.

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