Anomalous Static Electronic Screening in Compressed Lithium

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\textbf{Abstract.} Lithium has long been considered a simple metal. However, under pressure lithium departs radically from this simple behavior, as it strongly enhances its superconducting transition temperature before phase transitions to complex structures emerge. Interestingly, these features are not unique of lithium, as have been also observed in other simple elements, but lithium becomes a good system to characterize their physical origin. In this article we will analyze anomalies arising in the static electronic susceptibility of lithium under pressure, where clear connections between anisotropies in the Fermi surface, phonon instabilities, and enhanced electron-phonon coupling will be shown.

1. Introduction

At normal conditions of pressure and temperature lithium adopts a compact and highly symmetric \textit{bcc} structure, and main physical properties can be characterized within the nearly free electron-like model. However, under pressure the contribution associated to the non-local character of the pseudopotential rises\cite{1, 2}, the nearly free electron-like approximation breaks and lithium undergoes several phase transitions to more complex structures\cite{3, 4}: \textit{bcc} to \textit{fcc} at 8 GPa, \textit{fcc} to \textit{hR1} at 39 and \textit{hR1} to \textit{cI16} (with 16 atoms per unit cell) at 41 GPa.

In spite of lithium at normal conditions superconducts at the very low $T_c = 0.4$ mK \cite{5, 6}, the transition temperature to the superconducting state increases up to around 17 K when the applied pressure rises to 30 GPa \cite{7, 8, 9}, becoming the element with one of the highest transition temperature\cite{10}, which even rises the interest in characterizing physical properties of compressed lithium. Interestingly, this complex behavior is not only characteristic of lithium, but has been also observed in other simple elements\cite{11}. However, considering the more simple electronic configuration of lithium, it becomes a good system to understand in detail the physical origin of these quite general features arising under pressure.

In this article we will analyze anomalies arising in the static electronic susceptibility of lithium under pressure, where clear connections between anisotropies in the Fermi surface, phonon instabilities, and enhanced electron-phonon coupling will be shown. Section 2 describes the
computational methods that we have used in this study. In Section 3 we present our results and, finally, conclusions are presented in Section 4.

2. Computational Methods
We have used a plane-wave implementation of Density Functional Theory (DFT) within the Local Density Approximation (LDA), as implemented in the Vienna Ab Initio Simulation Package (VASP) [12, 13]. Although at high pressure an important core overlap is observed, we have checked that the Projector Augmented Wave (PAW) approximation [14], which fully treats all the electrons, and ultrasoft pseudopotentials [15] give similar results. Figures of three dimensional Fermi surfaces have been generated by XCrySDen [16] and phonon frequencies have been computed with Density Functional Perturbation Theory (DFPT), as implemented in the plane-wave self-consistent field (PWscf) code [17]. Generally, a sample of the Brillouin zone (BZ) with a Monkhorst-Pack mesh of $20 \times 20 \times 20$ has been demonstrated to be enough to reach electronic convergence. However, a $60 \times 60 \times 60$ mesh has been required to calculate electron-phonon linewidths and a much denser grid ($96 \times 96 \times 96$) is considered for the non interacting electronic susceptibility. At the same time, energetic convergence has been achieved by implementation of a $430$ eV energy cutoff.

3. Results
An essential feature determining electronic properties of any metal is the topology of the Fermi surface (FS). Although at ambient pressure lithium is well described by a nearly free electron model, which is reflected by its almost perfect spherical FS, as a result of the increasing non-local character of the pseudopotential, it deforms significantly under compression [18, 19, 20]. Fig. 1 shows the Fermi surface of fcc lithium at $30$ GPa and the analysis of its cross sections along several planes. Although the cross section of the FS along the $\Gamma K X$ plane shows an almost perfect circle, it becomes highly distorted in the $\Gamma L$ and $\Gamma W$ planes, with cooper-like necks along $\Gamma L$ and well defined nestings in the $\Gamma X$, $\Gamma K$ and $\Gamma W$ directions. Hence, a high number of valence electrons will be coupled with a momentum transfer of $2k_F$ along these directions and Peierls distortions might be favored.

The interaction between the BZ boundary and the FS develops extended necks along the fcc $\Gamma L$ direction where a pseudogap opens and, therefore, reduces the overall electronic energy. In fact, the electronic band structure strongly deviates from the nearly free electron-like behavior, and lithium shows a remarkable covalent character associated to the increasing electronic localization at atomic interstitials (Fig. 2). For example, the occupied bandwidth along $\Gamma X$ is almost constant under pressure ($3.93$ eV at $8$ GPa and $4.1$ eV at $30$ GPa) and even decreases along $\Gamma L$ ($3.67$ eV at $8$ GPa and $3.5$ eV at $30$ GPa), whereas the bandgap at $L$ considerably increases ($4.8$ eV at $8$ GPa and $7$ eV at $30$ GPa).

In order to deeper analyze the influence of the Fermi surface deformation on the physical properties of compressed lithium, we have calculated diagonal contributions to the ab initio static electronic susceptibility matrix of the non interacting electron system:

$$\chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) = \frac{1}{\Omega} \sum_{\mathbf{k}} \sum_{n,n'} \frac{f_{\mathbf{k}n} - f_{\mathbf{k}n'+\mathbf{q}}}{\varepsilon_{\mathbf{k}n} - \varepsilon_{\mathbf{k}+\mathbf{q},n'}}$$

$$\times \langle \psi_{\mathbf{k}n}| e^{-i(\mathbf{q}+\mathbf{G}) \cdot \mathbf{r}} | \psi_{\mathbf{n}',\mathbf{k}+\mathbf{q}} \rangle$$

$$\times \langle \psi_{\mathbf{k}+\mathbf{q},n'}| e^{i(\mathbf{q}+\mathbf{G}') \cdot \mathbf{r}} | \psi_{\mathbf{k},n} \rangle.$$

Here $\mathbf{k}$ is a wave vector belonging to the first BZ, $f_{nk}$ represents the Fermi-Dirac distribution function, $\Omega$ is the normalization volume, $\mathbf{G}$ and $\mathbf{G}'$ are reciprocal-lattice vectors, and if $\mathbf{k}+\mathbf{q}$ lies
outside the first BZ, it gets folded back into the first BZ by addition of the appropriate reciprocal lattice vector. The first summation in Eq. (1) was performed with the use of $96 \times 96 \times 96$ k-mesh, which correspond to 442368 points in the BZ. The second sum runs over the occupied and all unoccupied valence bands up to an energy of 50 eV above Fermi level.

Fig. 3 displays the static electronic susceptibility along $\Gamma X$, $\Gamma K$ and $\Gamma W$ directions in comparison with the electron gas approximation (Lindhard function). Screening corresponding to the ab initio calculation becomes less effective than in the electron gas approximation. The main reason of this difference is associated to the lowering under pressure of the occupied bandwidth [2, 3] and the opening of a pseudogap at $N$ (necks in the FS). Additionally, although we have not seen any special feature on the static susceptibility along the $\Gamma K$ direction, interesting kinks emerge at $q_{nest}^\Gamma = 2\pi/a(4/3, 2/3, 0)$ and $q_{nest}^\Gamma = 2\pi/a(19/14, 0, 0)$ corresponding to the above mentioned nestings along $\Gamma W$ and $\Gamma X$, respectively.

In order to analyze the effect of these kinks in the phonon spectra, Fig. 4 shows the phonon frequencies of fcc lithium at 30 GPa along high symmetric directions. While longitudinal phonon frequencies increase with pressure, a remarkable softening is observed in the lowest transverse mode ($T_1$), specially along $\Gamma K$, where it becomes unstable at $\tilde{q}_{anom}^\Gamma = 2\pi/a(-2/3, 2/3, 0)$. Interestingly, this instability is connected to the kink in the electronic susceptibility at $q_{nest}^\Gamma$. In order to compare both momenta we have to take into account that $\tilde{q}_{anom}^\Gamma$ extends out from the first BZ, which after folding it back with the reciprocal lattice vector $G = 2\pi/a(-2, 0, 0)$ results to be $q_{nest}^\Gamma$: $q_{nest}^\Gamma = q_{nest}^\Gamma + G$. On the other hand, it is also interesting to analyze the remarkable Kohn anomaly in the longitudinal mode along the $\Gamma X$ direction at $q_{nest}^\Gamma = 2\pi/a(-9/14, 0, 0)$, which can be also associated to the kink in the electronic susceptibility at $q_{nest}^\Gamma = 2\pi/a(19/14, 0, 0)$. As $q_{nest}^\Gamma$ also extends out from the first BZ, in order to compare both momenta we need to fold it back by adding an adequate reciprocal lattice vector. Considering $G = 2\pi/a(-2, 0, 0)$, $q_{nest}^\Gamma + G = q_{nest}^\Gamma$.

As shown in Fig. 5, these two anomalies in the phonon spectra are also manifested in the electron-phonon linewidth, where the observed maxima in each direction correspond to these anomalous features. The maximum of the electron-phonon linewidth corresponding to the transverse mode at $\tilde{q}_{anom}^\Gamma$ already has been well characterized and consider to be the main responsible of the observed enhanced superconducting transition in lithium under pressure[21, 22, 23, 24, 25]. However, the observed maximum along $\Gamma X$ associated to the longitudinal mode, exactly located at $q_{anom}^\Gamma$, has not been considered before, because, among other things, in this case a very dense mesh ($60 \times 60 \times 60$) has been required to reach the convergence and properly include nesting features in the Fermi surface.

On the other hand, although the kink at $q_{nest}^\Gamma$ in the electronic susceptibility is enough to explain the strong Kohn anomaly in the longitudinal mode at $q_{anom}^\Gamma$, besides the correlation between the kink at $q_{nest}^\Gamma$ and the observed phonon instability in the transverse branch at $q_{anom}^\Gamma$, this phonon instability cannot be completely explained by this kink, but without considering crystal local-field effects a divergent behavior of the electronic susceptibility would be required. Phonon frequencies can be related to the dielectric matrix, $c_{\alpha\beta}(q)$, via the Pick-Cohen-Martin formula[26]:

$$D_{\alpha\beta}(q) = \tilde{D}_{\alpha\beta}(q) - \tilde{D}_{\alpha\beta}(0),$$

$$\tilde{D}_{\alpha\beta}(q) = \sum_{G,G'} |q + G|^2 V_c(q + G)(q + G)_\alpha 
\times c_{G,G'}^{-1}(q) V_c(q + G')(q + G')_\beta,$$

$$V_c(q) = 4\pi/|q|^2$$

being the Coulomb potential, $D_{\alpha,\beta}(q)$ is the dynamical matrix and $\alpha, \beta$ are...
Cartesian indices. The dielectric matrix in Eq. (2) includes umklapp processes via the so-called crystal local-field effects. In terms of the full electronic susceptibility, \( \chi_{G,G'}(q) \), the dielectric matrix is given by the following expression:

\[
\epsilon^{-1}_{G,G'}(q) = \delta_{G,G'} + V_c(q + G)\chi_{G,G'}(q),
\]

and within the random phase approximation (RPA), where exchange and correlation effects between the electrons are neglected, \( \chi \) can be obtained from the non-interacting electronic susceptibility, \( \chi^0 \):

\[
\chi_{G,G'}(q) = \chi^0_{G,G'}(q) + \sum_{G''} \chi^0_{G,G''}(q)V_c(q + G'')\chi_{G'',G'}(q).
\]

It is clear that an eigenvalue of the dynamical matrix in Eq. (2) can soften, and eventually go to zero, even if the macroscopic dielectric function, \( \epsilon(q) = \frac{1}{\epsilon^0(q)} \), or the diagonal contribution to the non-interaction electronic susceptibility, does not diverge[27]. Although a detailed understanding of the contribution associated to crystal local-field effects will require a deeper analysis, Fig. 6 shows the effect of including umklapp processes in the diagonal contribution of the full electronic susceptibility matrix of fcc lithium at 30 GPa along ΓW. Interestingly, even though these diagonal elements just include crystal local-field effects through the inverse of the determinant associated to \( \chi^0_{G,G'}(q) \) required to obtain the full \( \chi \) matrix in Eq. (4), their contribution becomes specially relevant at \( q_{\Gamma W}^{\text{nest}} \). Actually, this important contribution of crystal local-field effects associated to the non diagonal elements in the electronic susceptibility can be also explained in terms of the increasing covalent character of lithium under pressure.

Another important difference between both phonon anomalies is their polarization. While at \( q_{\Gamma X}^{\text{anom}} \) just the longitudinal mode is involved, the instability at \( q_{\Gamma K}^{\text{anom}} \) corresponds to one of the transverse modes. This difference can be associated to the required reciprocal lattice vector, \( G \), to fold back \( q_{\text{nest}}^{\Gamma X} \) and \( q_{\text{nest}}^{\Gamma W} \) into the first BZ. While \( q_{\text{nest}}^{\Gamma X} \) is parallel to \( G \) this is not the case of \( q_{\text{nest}}^{\Gamma W} \), which also contributes to increase the influence associated to non-diagonal elements in Eq. (2), mainly characterizing features associated to the transverse modes.

4. Conclusions

Fermi surface of lithium becomes highly distorted under pressure, which is characterized by extended nestings. These nestings originate peaks in the static electronic susceptibility. As a result of the enhancement of crystal local-field effects associated to the increasing electronic inhomogeneity under pressure, phonon spectra of compressed fcc lithium is characterized by a well defined transverse phonon softening along ΓK correlated to the nesting associated kink in the electronic susceptibility at \( q_{\text{nest}}^{\Gamma W} \). This softening, besides preluding the observed transition to complex structures, increases the electron-phonon coupling under pressure. Interestingly, a similar transverse soft-mode has been also observed in other simple elements correlated to their superconducting transition under pressure (e.g., P, Ca, Ga, S, and Y). On the other hand, the observed nesting along ΓX induces a well defined Koh anomaly in the longitudinal mode at \( q_{\text{nest}}^{\Gamma X} \), which also enhances the electron-phonon coupling. Additionally, band structure deformation of lithium under pressure not only modifies the static but also the dynamic response function is expected to be strongly pressure dependent (for example, a new low energy long-lived interband collective mode has been predicted to arise[28]).
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Figure 1. (a) Fermi surface of fcc lithium at 30 GPa and its cross sections (solid lines) along (b) ΓKX (100), (c) ΓKL (110) and (d) ΓWX (210) planes. Brillouin zone boundary is represented by dotted lines. The cross section along the ΓKX plane shows an almost perfect circle, whereas both in the ΓKL and ΓWX planes present clear nestings in the ΓX, ΓK and ΓW directions.
Figure 2. Electronic charge density of fcc lithium at P=30 GPa. Yellow areas represent minimum electronic charge density around the atoms, whereas the maximum electronic charge density (purple) locate at the interstitials, as a consequence of the increasing covalent character of lithium under pressure.
Figure 3. Diagonal contribution of the static non-interacting susceptibility, $\chi_{0,0}(q)$, along $\Gamma X$ (dotted line), $\Gamma K$ (dashed line) and $\Gamma W$ (solid line) directions at $P=30$ GPa, and (dashed-dotted line) the free electron gas approximation (Lindhard function) calculated with the \textit{ab initio} effective mass, $m^* = 2m_e$, so that both different approximations present the same value at $q = 0$. For clarity, the location of $X$, $W$ and $K$ points in the BZ are shown in the figure and, although no special feature is seen along $\Gamma K$, both kinks emerge along $\Gamma X$ and $\Gamma W$ with the nesting momenta, $q_{\Gamma X}^{\text{nest}}$ and $q_{\Gamma W}^{\text{nest}}$, extending out from the first BZ. On the other hand, band effects are shown to decrease the electronic screening compared to the electron gas approximation.

Figure 4. Phonon frequencies of \textit{fcc} lithium at $P=30$ GPa. Besides the general softening of the transverse $T_1$ branch, it is remarkable the well defined instability of the $T_1$ branch along $\Gamma K$ $q_{\Gamma K}^{\text{anom}}. The longitudinal branch along $\Gamma X$ also shows a well defined Kohn anomaly at $q_{\Gamma X}^{\text{anom}}$. Both anomalous features are connected to the above mentioned nesting induced kinks in the electronic susceptibility.
Figure 5. Electron-phonon linewidth of fcc lithium at 30 GPa along ΓK and ΓX directions. Blue (black) color corresponds to the longitudinal (transverse) mode. In order to correctly capture features in the Fermi surface and get the results converged, a 60 × 60 × 60 Γ-centered grid has been required.

Figure 6. (a) Diagonal contribution of the static ab initio full electronic susceptibility, $\chi_{0,0}(q)$, of fcc lithium at 30 GPa along ΓW with (solid line) and without (dashed line) including crystal local field effects. (b) Relative difference between both approximations, the maximum relative contribution associated to crystal local-field effects being located at $q_{\text{nest}}^{\Gamma W}$. 