Lithium Pushed to its Limit:

a simple metal not superconducting above 5 mK at ambient pressure, to a 20 K superconductor at 50 GPa. Lithium is now the highest $T_c$ superconducting element.
Superconductivity and Lattice Instability in Compressed Lithium: Fermi Surface Hot Spots

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Acknowledgements to: S. Y. Savrasov, K. Koepernik, A. K. McMahan
Outline of the Presentation

• Experimental data from three groups & formalism for calculation of $T_c$

• Evolution of electronic structure under pressure

• Calculation of phonons, el.-ph. matrix elements and spectral function; determination of lattice instability and $T_c$

• Analysis of the results in terms of Fermi surface geometry, nesting function

• Summarizing Comments
“Superconductivity in Compressed Lithium at 20 K”

The initial report of superconductivity at elevated temperature in lithium

\( T_c \) vs. Pressure


Appearance of superconductivity above 30 GPa; 20 K at 50 GPa.
Quick Confirmation: Geophysical Lab

\[ T_c \text{ vs. Pressure} \]

- Struzhkin, Eremits, Gan, Mao, Hemley,
  - *Science 298, 1213 (2002).*

- Superconductivity and identification of phases.
- \( T_c = 16\text{K} \) in fcc phase around 40 GPa.
Further elucidation: Washington Univ.

- Deemyad and Schilling,
  - *PRL 91, 167001 (2003).*

- Superconductivity peak at 30 GPa in fcc phase
- Near-hydrostatic conditions
- Rise in $T_c$ beyond 40 GPa.
Computational Methods

• LAPW, FPLO codes for
  – study of change of electronic structure under pressure

Savrasov’s full potential LMTO code for calculation of:
• phonon dispersion curves
• el-ph matrix elements
• spectral function

Savrasov, PR B 54, 16470 (1996)
Savrasov & Savrasov, ibid. 16487 (1996)
Some Basic Orientation

- Fermi surface of Li in fcc structure at 35 GPa
  - \(V/V_0 = 0.51\)

- Necks appear along <111> directions
  - (a la Cu) at 20 PGa

- Velocities: 0.3 on necks, 0.7 on bellies \((10^8 \text{ cm/s})\)
Formalism: Electron-Phonon Coupling

Phonon scattering electron: from Fermi surface to Fermi surface

The electron-phonon coupling strength for phonon \((\vec{Q}, \nu)\) is given by\([1]\)

\[
\lambda_{Q,\nu} = \frac{2}{\omega_{Q,\nu}} \sum_k |M_{k,k+Q}|^2 \delta(\varepsilon_k) \delta(\varepsilon_{k+Q}) = \frac{2V_c}{\omega_{Q,\nu}} |M|^2 \int_L \frac{dL(k, Q)}{|\vec{v}_k \times \vec{v}_{k+Q}|}
\]

\[
\xi_{Q} = \sum_k \delta(\varepsilon_k) \delta(\varepsilon_{k+Q}) = V_c \int_L \frac{dL(k, Q)}{|\vec{v}_k \times \vec{v}_{k+Q}|}
\]

\(L\) is the line of intersection between the Fermi surface, and its \(\vec{q}\)-displaced image.

Phonon softening: electron-hole pair emission/reabsorption

The phonon frequency is renormalized downward by the strong coupling, which is expressed in terms of the associated phonon self-energy \(\Pi(Q, \omega)\):

\[
\omega^2_{Q,\nu} = \Omega^2_{Q,\nu} + 2\Omega^2_{Q,\nu} \Pi(Q, \omega_{Q,\nu})
\]

\[
\Pi(Q, \omega) = -2 \sum_k |M_{k,k+Q}|^2 \frac{f_k - f_{k+Q}}{\varepsilon_{k+Q} - \varepsilon_k - \omega - i\delta'}
\]
Strong coupling superconductivity

BCS weak-coupling:

\[ T_c = 1.14 \langle \omega \rangle \exp \left( \frac{-1}{N(0)V} \right) \]

Strong coupling (McMillan):

\[ T_c = \omega_0 \exp \left( \frac{-(1 + \lambda)}{\lambda - \mu^* - \langle \omega \rangle/\omega_0 \lambda \mu^*} \right) \]

Allen-Dynes corrections:

\[ T_c \sim \langle \langle \omega^2 \rangle \lambda \rangle^{1/2} \]

el-ph coupling strength

\[ \lambda = 2 \int d\omega \frac{\alpha^2 F(\omega)}{\omega} \]

el-ph spectral function

\[ \alpha^2 F(\omega) = \frac{1}{N(0)} \sum_{k,k'} |M_{kk'}|^2 \delta(\omega - \Omega_{k-k'}) \delta(\epsilon_k) \delta(\epsilon_{k'}) \]

In strong coupling VN(0) -> \lambda-\mu^*
Evolution of Bands under Pressure

Changes are:
- neck along (111)
- increase in p character
- little change in bandwidth
Under pressure, the $T_1$ transverse phonon branch becomes unstable near the BZ boundary (already around 25 GPa)

Phonons are stable in other directions
Under pressure the $T_1$ transverse phonon branch becomes unstable near the BZ boundary (already around 25 GPa).

Phonons are stable in other directions.
Electron-Phonon Spectral Function

Evolution of el-ph coupling weight with pressure

P=0: weak, evenly spread

P=10: LA mode hardens, weight grows at 30 meV

P=20: LA mode is harder, large weight at 15 meV

P=35: instability (see low frequency region)

El-ph weight grows at low energy (not high as in MgB2)
Material Constants from the Spectral Function

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>(a (a_B))</th>
<th>(V/V_0)</th>
<th>(N(E_F)) (states/Ry/spin/atom)</th>
<th>(&lt;\omega&gt;) (meV)</th>
<th>(&lt;\omega^2&gt;^{1/2}) (K)</th>
<th>(\omega_m) (K)</th>
<th>(\lambda)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.0069</td>
<td>1.00</td>
<td>3.537</td>
<td>21</td>
<td>278</td>
<td>209</td>
<td>0.42</td>
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<tr>
<td>10</td>
<td>7.2298</td>
<td>0.74</td>
<td>3.031</td>
<td>22</td>
<td>229</td>
<td>225</td>
<td>0.65</td>
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<tr>
<td>20</td>
<td>6.8003</td>
<td>0.61</td>
<td>2.789</td>
<td>10</td>
<td>170</td>
<td>84</td>
<td>3.15</td>
</tr>
<tr>
<td>35</td>
<td>6.4085</td>
<td>0.51</td>
<td>2.573</td>
<td>10</td>
<td>220</td>
<td>130</td>
<td>2.77</td>
</tr>
</tbody>
</table>

Calculating \(T_c\) supposing that \(\mu^*=0.15\), one obtains using Allen-Dynes equation:

- \(P=0\) GPa: \(T_c = 0.4\) K
- \(P=10\) GPa: \(T_c = 5\) K
- \(P=20\) GPa: \(T_c = 20\) K

Clearly these numbers are not really accurate. Anharmonic corrections will become large, when phonons begin to become soft/unstable.
Fermi Surface Nesting Function for Li (35 GPa)

\[ \xi_Q = \sum_k \delta(\varepsilon_k) \delta(\varepsilon_{k+Q}) = V_c \int_L \frac{d\mathcal{L}(k, Q)}{|\mathbf{v}_k \times \mathbf{v}_{k+Q}|} \]

Hot spots (yellow) arising from the intersection shown above \([Q=0.71(1,1,0)]\)

Nesting function in three planes

(red is high intensity)
Analytic Properties of Nesting Function

\[ \xi_Q = \sum_k \delta(\varepsilon_k) \delta(\varepsilon_{k+Q}) = V_c \int_L \frac{dL(k, Q)}{|\vec{v}_k \times \vec{v}_{k+Q}|} \]

<table>
<thead>
<tr>
<th></th>
<th>nesting function</th>
<th>Susceptibility</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>elliptic</td>
<td>discontinuity</td>
</tr>
<tr>
<td></td>
<td>hyperbolic</td>
<td>Logarithmic divergence</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Infinite slope</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Kink (local maximum)</td>
</tr>
</tbody>
</table>

Orientation of normals is important for susceptibility!

Singularities are not isolated -> singular surfaces in q-space
Analytic Properties of Nesting Function

\[ \xi_Q = \sum_k \delta(\varepsilon_k) \delta(\varepsilon_{k+Q}) = V_c \int_L \frac{d\mathcal{L}(k, Q)}{|\vec{v}_k \times \vec{v}_{k+Q}|} \]

<table>
<thead>
<tr>
<th>Type</th>
<th>Expression</th>
</tr>
</thead>
</table>
| elliptic        | \[ \xi(Q+q) = \pi V_c/(2|v_k v_{k+Q}||\Gamma^{1/2} \theta(q) \]
| hyperbolic      | \[ \xi(Q+q) \sim - \pi V_c/(|v_k v_{k+Q}||\Gamma^{1/2}) \ln(|q|) \]

\( \Gamma \) - Gaussian curvature of the difference surface
The Nesting Function in fcc Li
The Nesting Function in fcc Li
The Nesting Function in fcc Li
Phonon polarization: $Q = (2/3, 2/3, 0)$

$Q \sim X: L \rightarrow L$

$(0,0,-1) \rightarrow (-1/2,1/2,1/2) \rightarrow (-1/2,1/2,-1/2)$

- $dV/dR \sim p$-like distribution
- $\psi^*_k(r)\psi_{k+Q}(r)$
Phonon polarization: $Q=(2/3,2/3,0)$

$Q \sim X: \quad L \rightarrow L$

$(0,0,-1) \rightarrow (-1/2,1/2,1/2) \rightarrow (-1/2,1/2,-1/2)$

- $dV/dR \sim \text{p-like distribution}$
- $\psi^*_k(r)\psi_{k+Q}(r)$
Band structure evolves strongly under pressure: change from s metal to sp metal.

Fermi surface in fcc structure develops necks along the (111) directions.

On-Fermi-surface scattering processes become focused onto certain hot spots due to necks (hyperbolic singularities).

Hot spots + large matrix elements → instability!
Summarizing Comments [2]

- Large matrix elements occur only for T1 branch
- Since fcc phase persists to 40 GPa, it must be anharmonically stabilized (it is harmonically unstable)
- The simple metal Li becomes a complex metal and a super superconductor at high pressure!