The Abdus Salam
International Centre for Theoretical Physics

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International Atomic
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**13th International Workshop on
Computational Physics and Materials Science:
Total Energy and Force Methods**

11 - 13 January 2007

Pressure Induced Complexity in Light Alkalies

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SPAIN

Pressure Induced Complexity in Light Alkalies

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and
Donostia International Physics Center (DIPC)

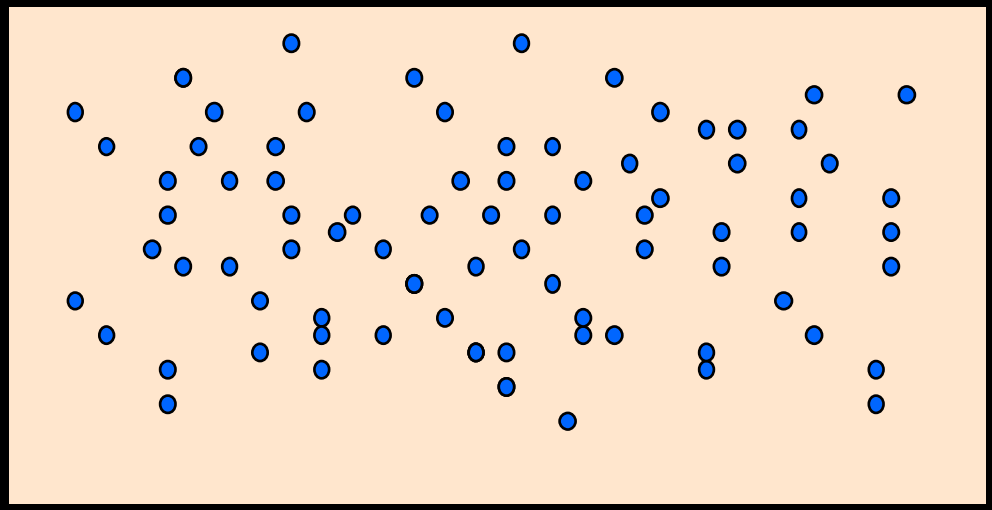
13th International Workshop on
Computational Physics and Materials Science:
Total Energy and Force Methods

Trieste, January 11

Outline

1. Introduction.
2. Fermi Surface Deformation in Lithium under Pressure:
    - bcc to fcc structural transition: Hume-Rothery mechanism.
    - fcc to *cI16* transition: Peierls-like mechanism.
3. Dynamic Screening and Optical Properties.
4. Anomalous Melting curve of Lithium?
5. Conclusions.

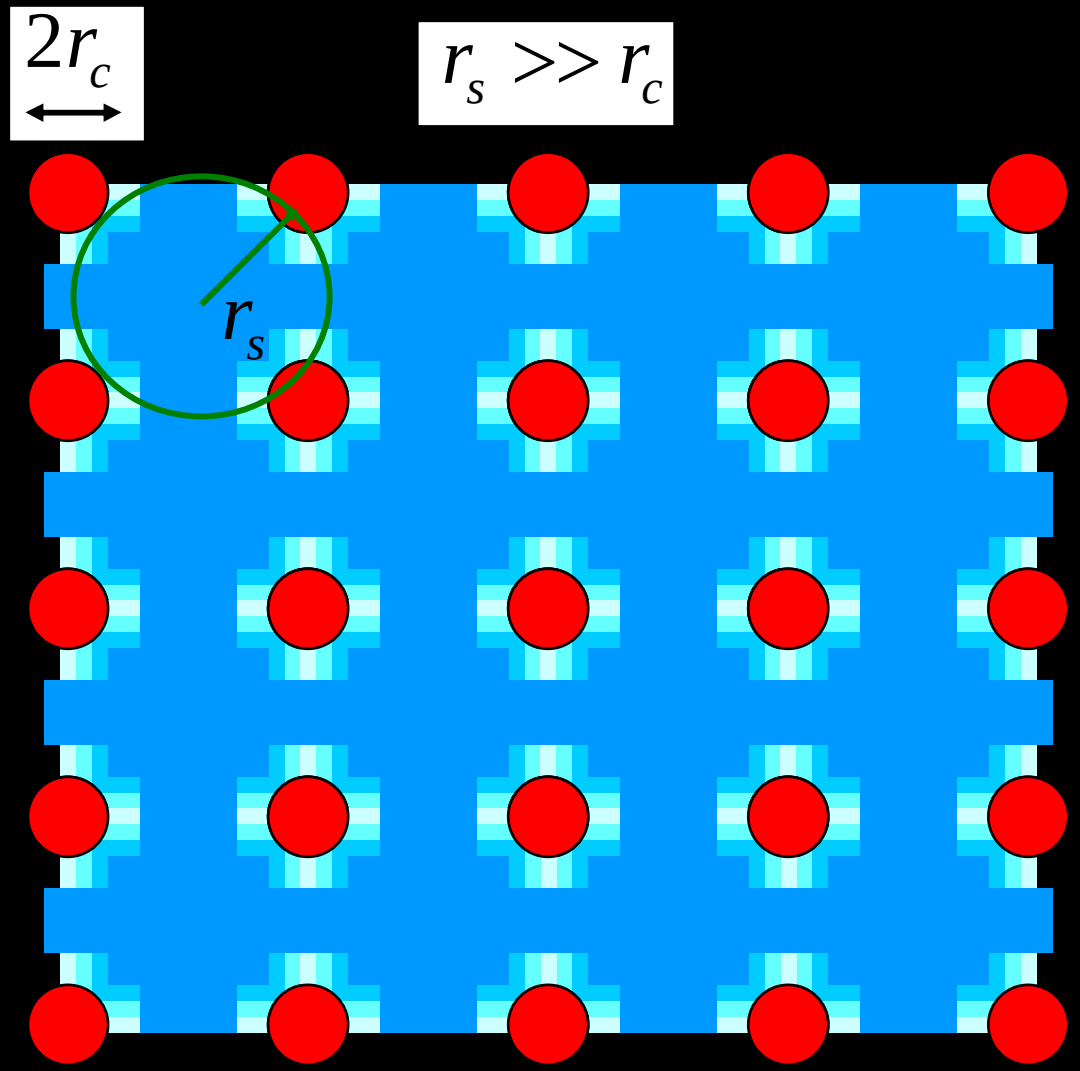
Elementary Energetics: The Electron Gas



$$\frac{E}{N} = \left\{ \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + E_{\mathrm{cor}} \right\} \ \mathrm{Ryd}$$

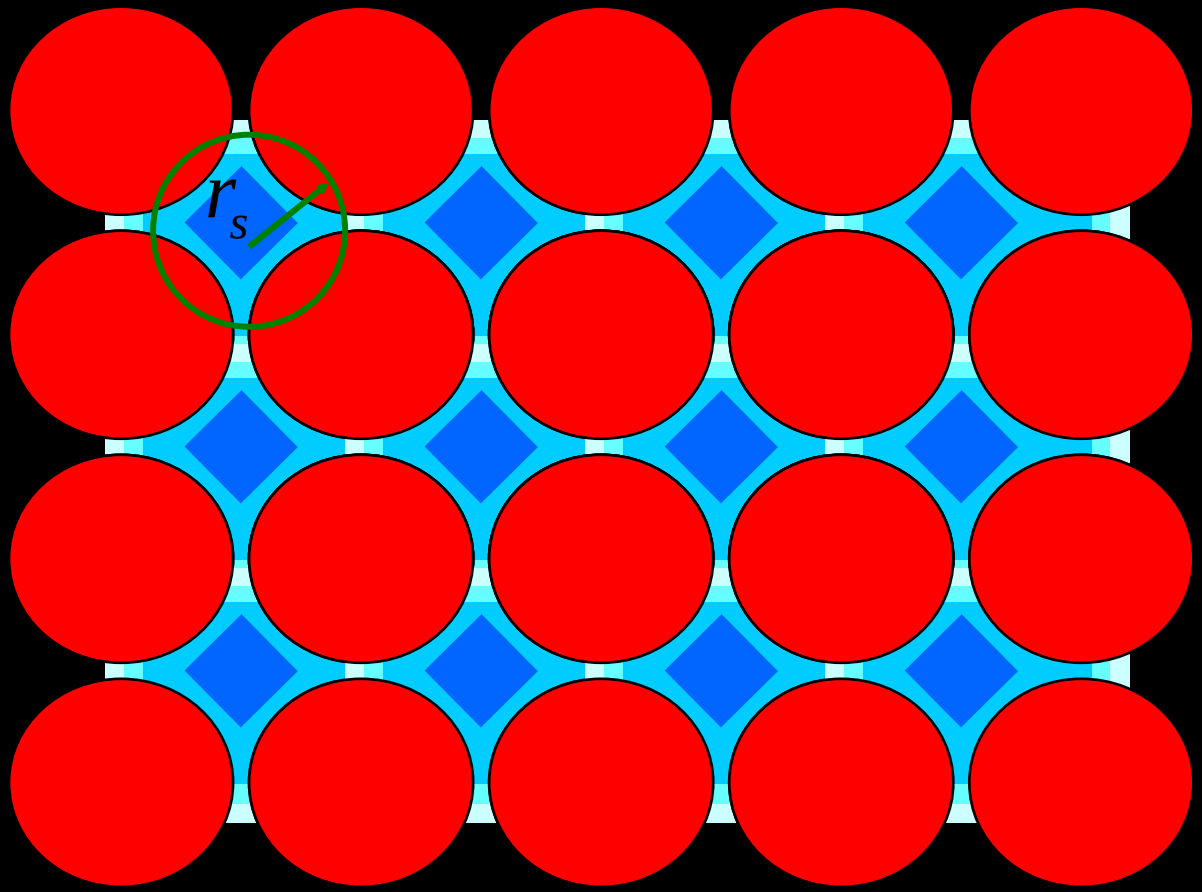
Weak dependence at high density

Corrections from Ion Cores: Interfering Length Scales



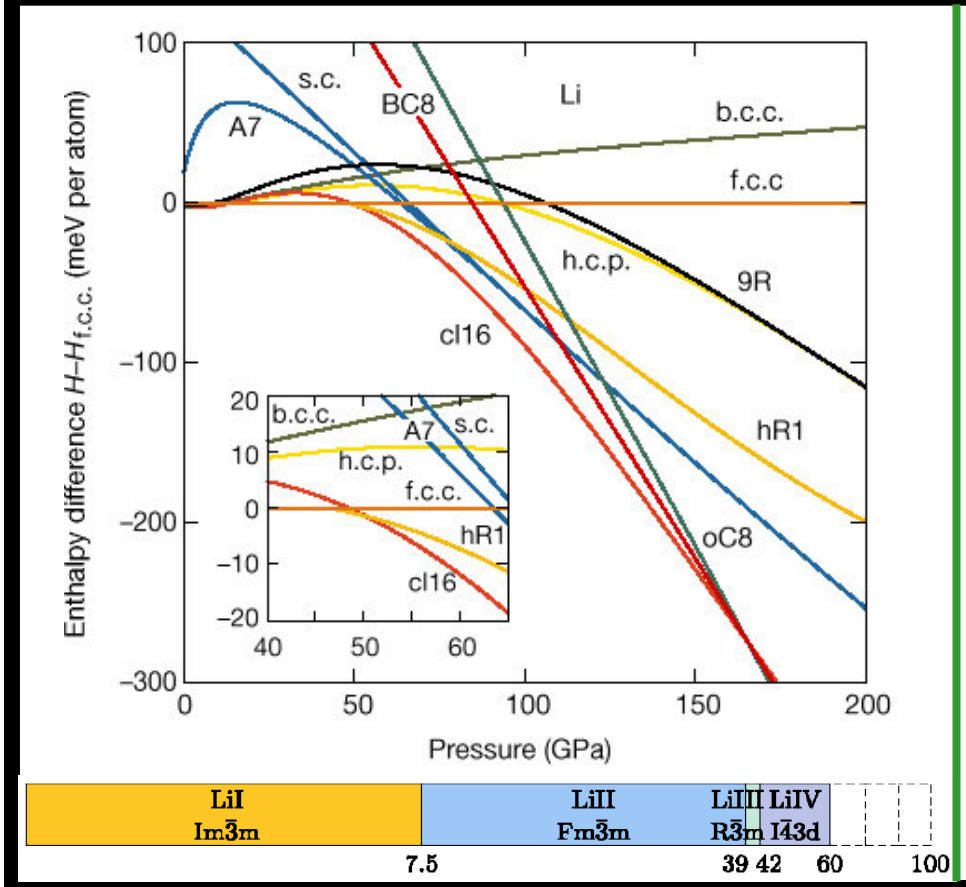
But suppose we force r_c to be similar or larger than r_s

$$r_c \cong r_s$$



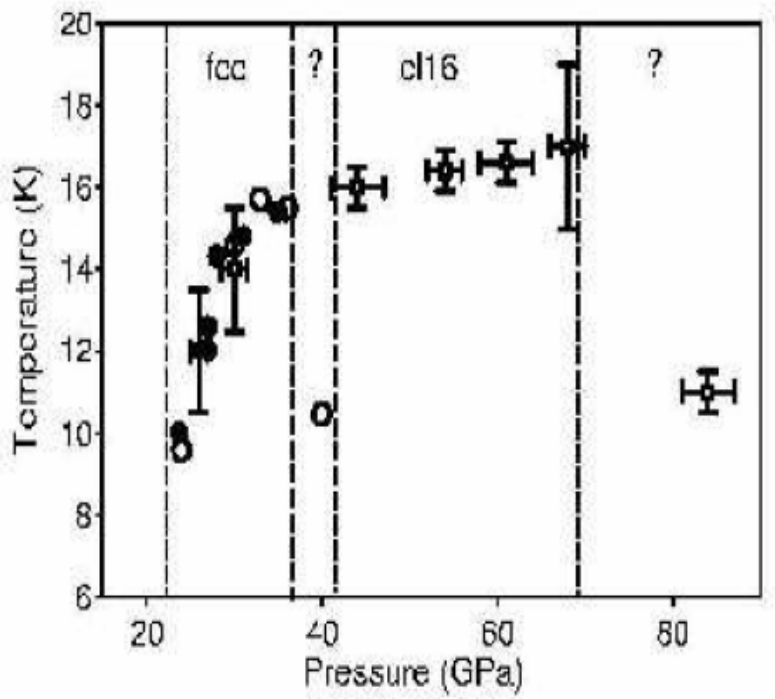
Electronic Localization at Interstitials!

Complex Structures in Lithium under Pressure



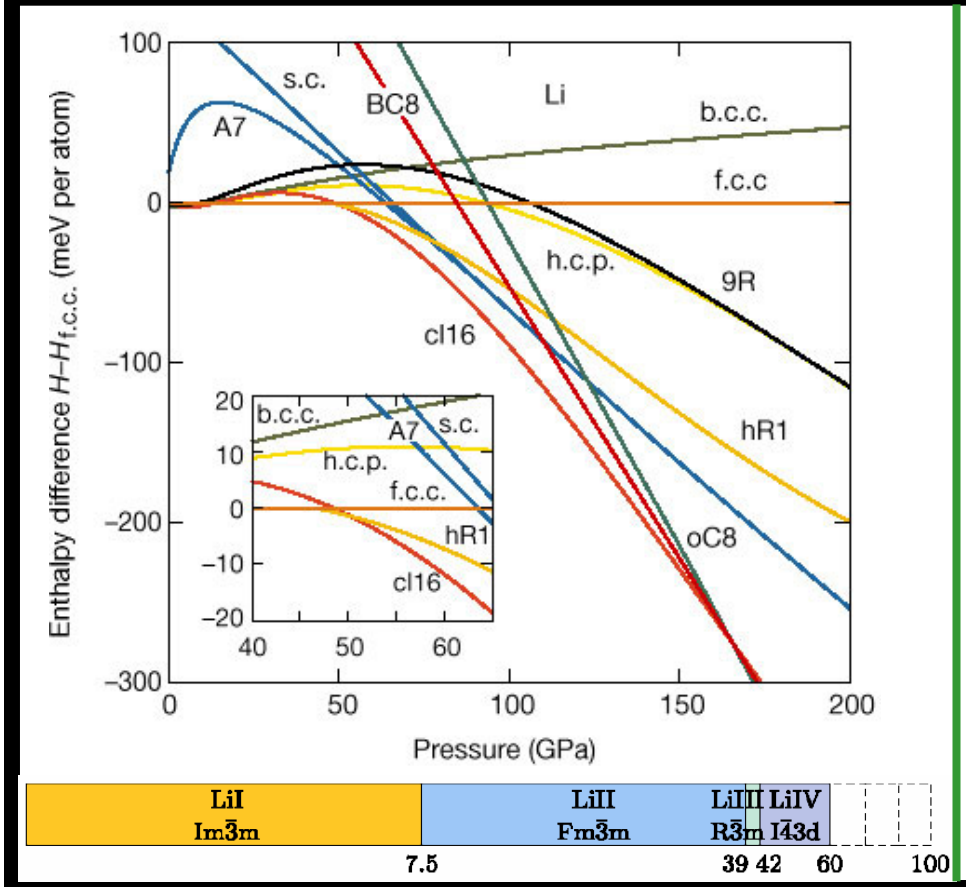
J.B. Neaton and N.W. Ashcroft , Nature, **400**, 141 (1999);
M. Hanfland, K. Syassen, *et al* , Nature, **408**, 174 (2000)

Lithium Superconducts at 17 K



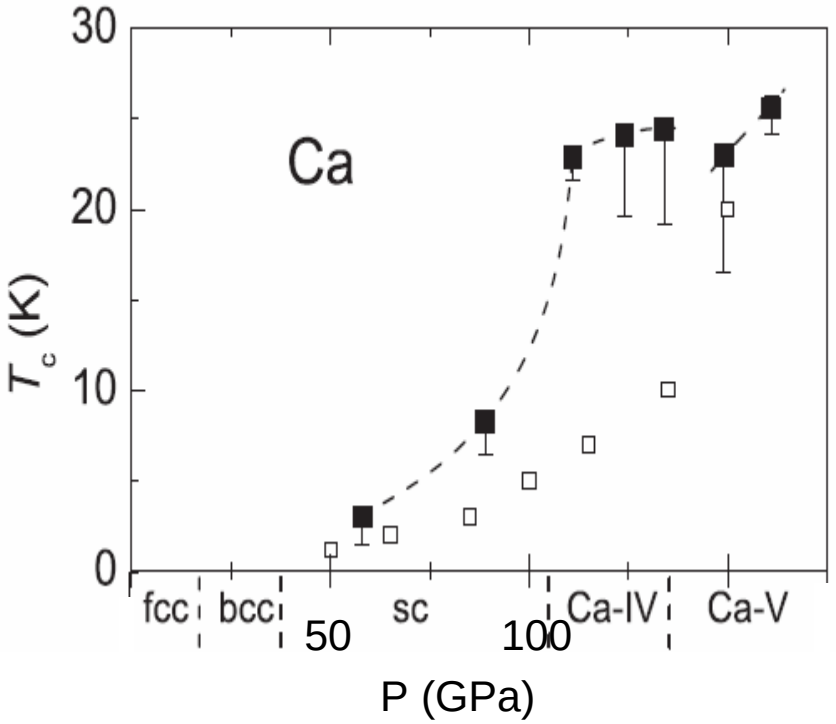
V.V. Struzhkin, M.L. Eremets, *et al*, Science, **298**, 1213 (2002);
K. Shimizu, H. Ishikawa, *et al*, Nature, **419**, 597 (2002) ;
S. Deemyad, *et al*, Phys. Rev. Lett., **91**, 167001 (2003).

Complex Structures in Lithium under Pressure



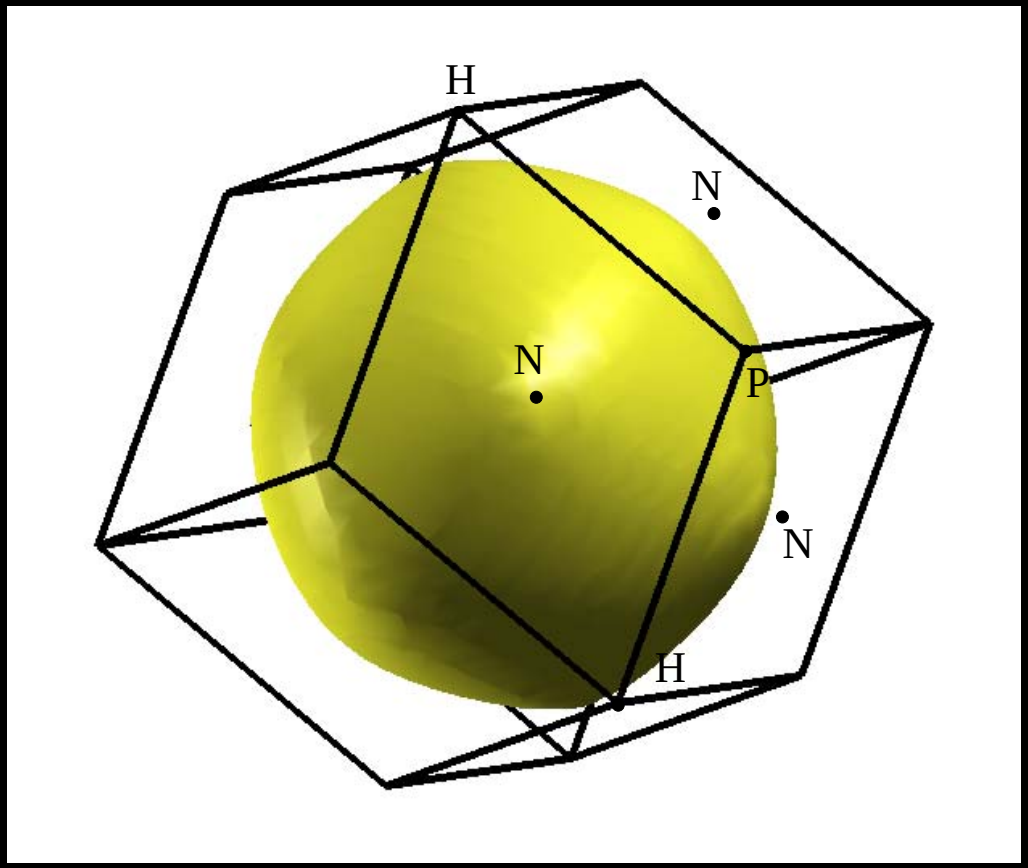
J.B. Neaton and N.W. Ashcroft , Nature, **400**, 141 (1999);
M. Hanfland, K. Syassen, *et al* , Nature, **408**, 174 (2000)

Calcium Superconducts at 25 K



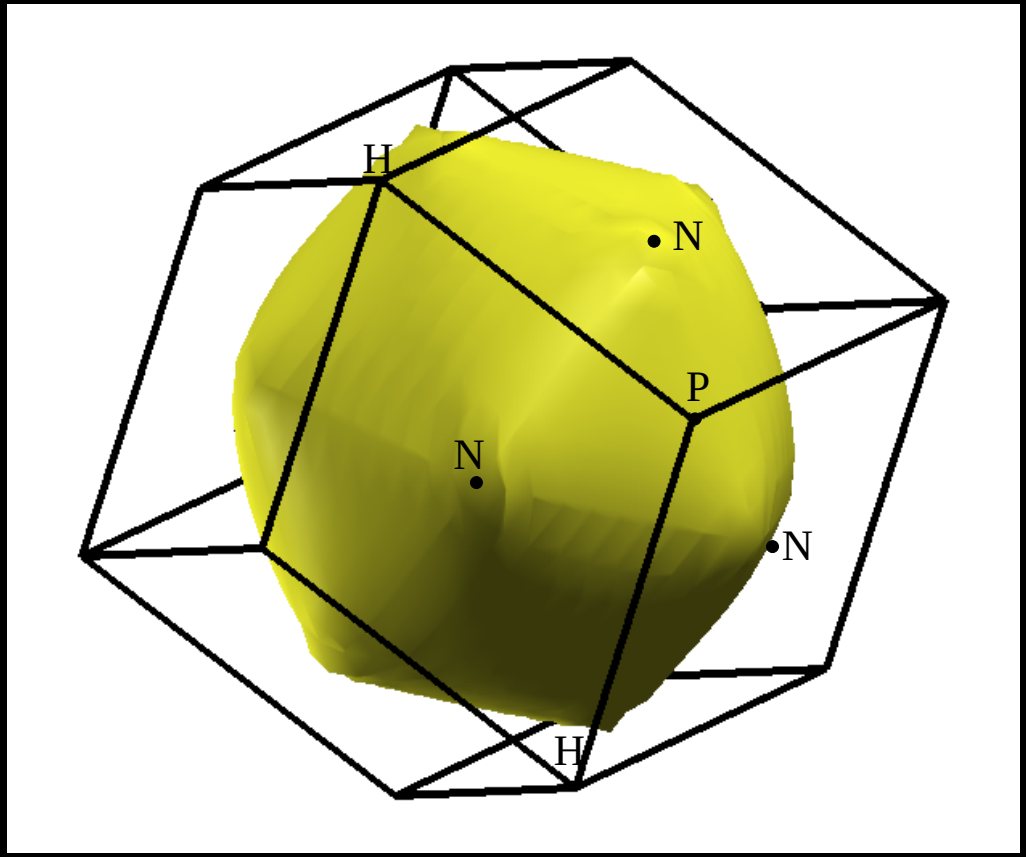
T. Yabuuchi, T. Matsuoka, Y. Nakamoto, and K. Shimizu,
J. Phys. Soc. Jpn. **75**, 083703 (2006).

Fermi Surface of *bcc* Lithium at P=0 GPa

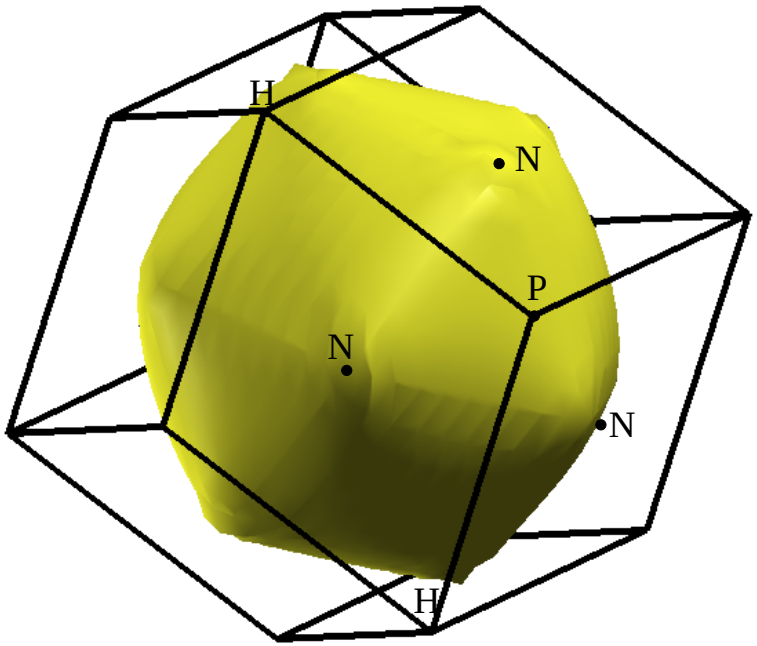


Fermi Surface of *bcc* Lithium at P=8 GPa

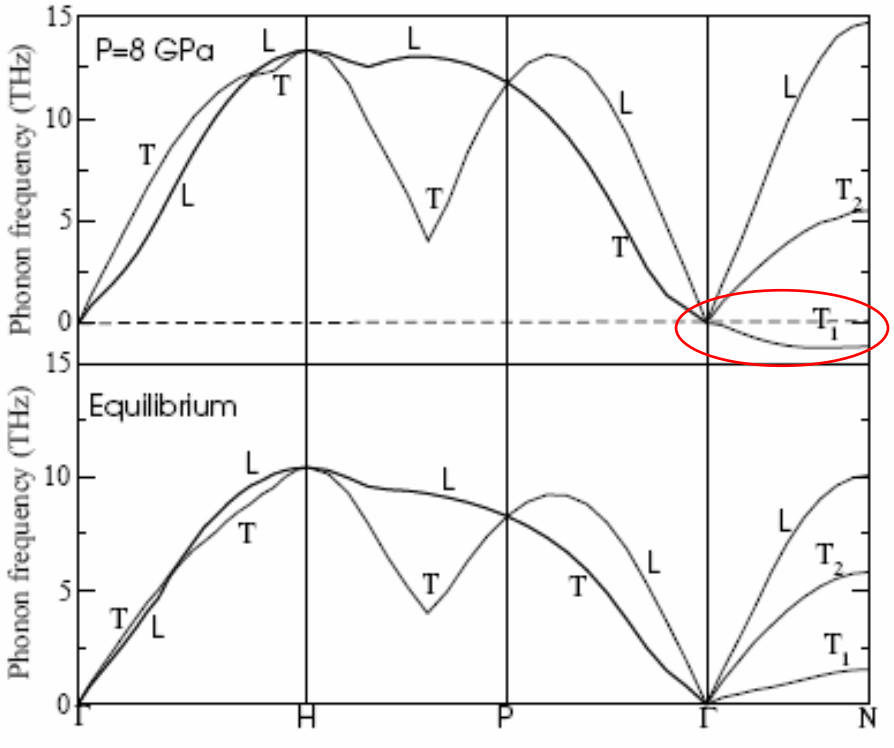
A. Rodriguez-Prieto, A. Bergara, V.M. Silkin, and P.M.Echenique,
Phys. Rev. B **74**, 172104 (2006)



Fermi Surface of *bcc* Lithium at P=8 GPa



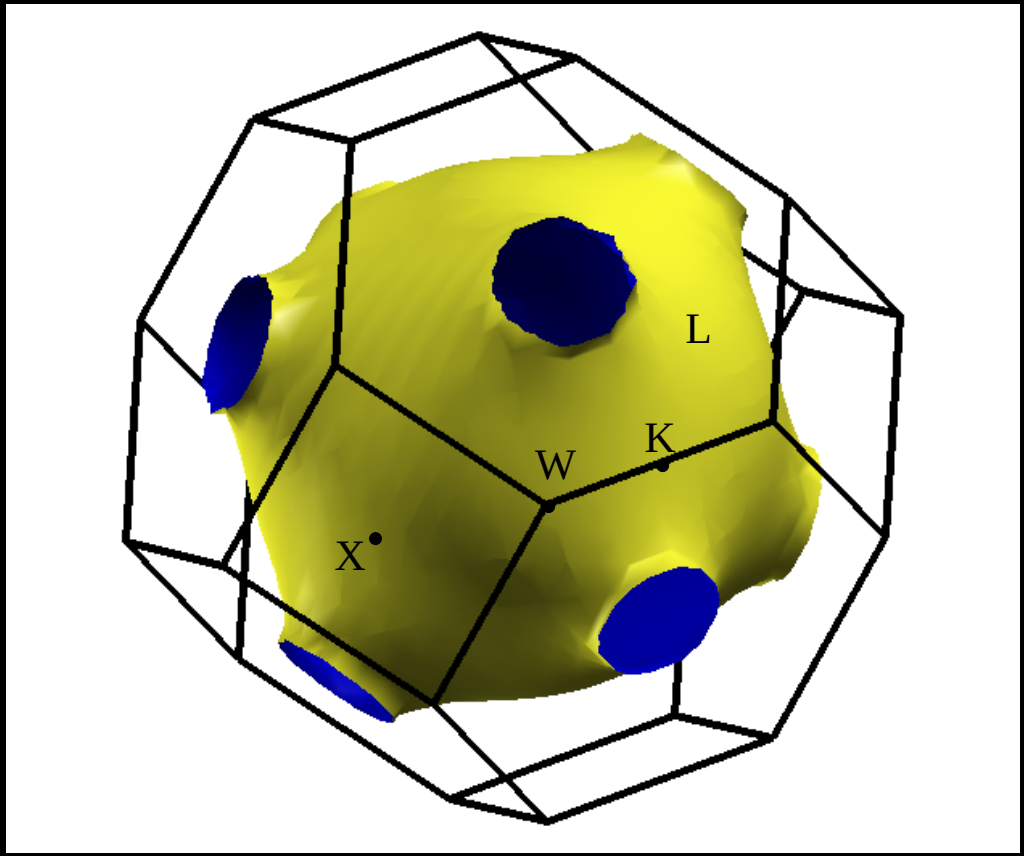
Phonon Frequencies



At 5 GPa the Fermi surface starts touching the BZ at the N point,corresponding to the experimetal *bcc* to *fcc* transition via a Hume-Rothery mechanism.

Fermi Surface of *fcc* Lithium at P=30 GPa

A. Rodriguez-Prieto, A. Bergara, V.M. Silkin, and P.M.Echenique,
Phys. Rev. B **74**, 172104 (2006)

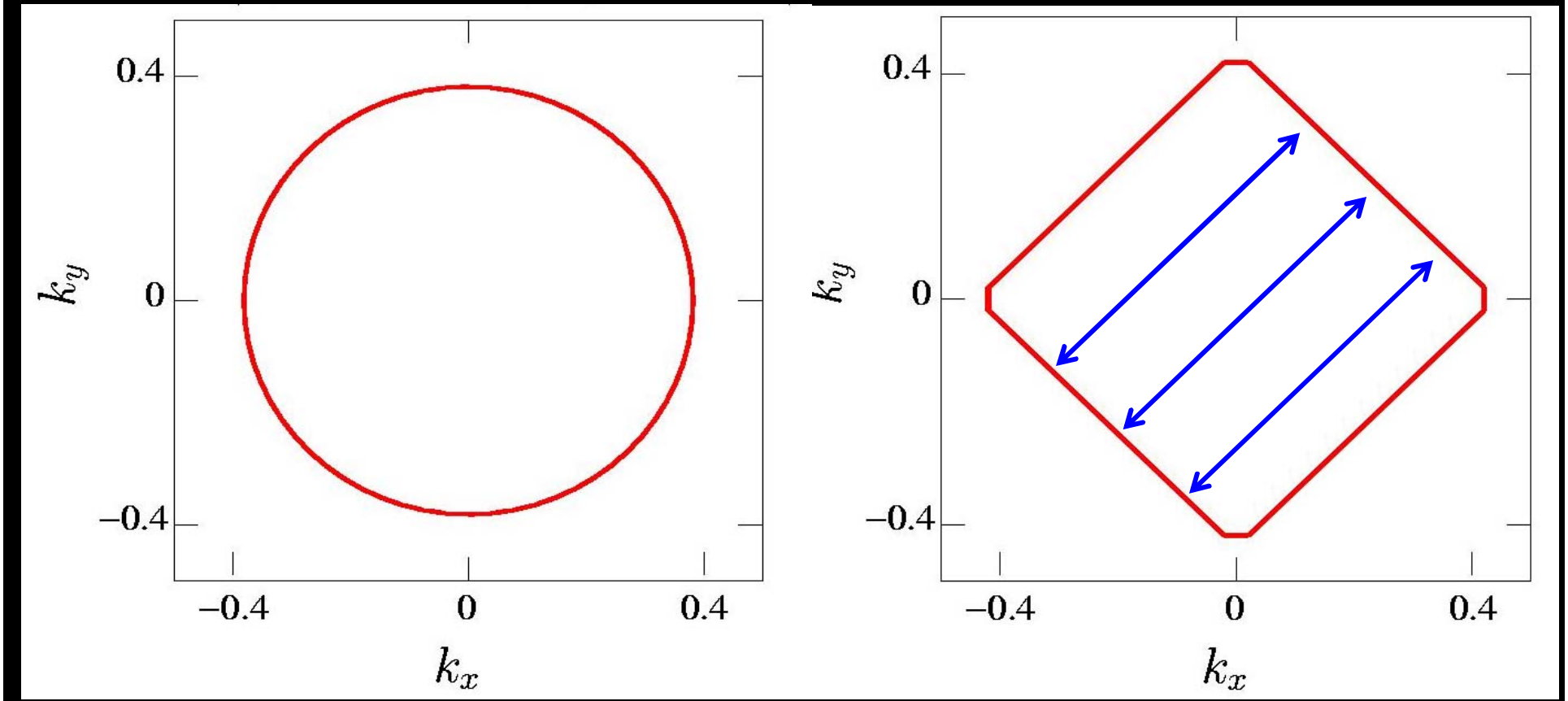


Lithium Monolayer

A. Rodriguez-Prieto and A. Bergara, Phys. Rev. B **72**, 125406 (2005)

Fermi *line* (Equilibrium)

Fermi *line* (sq, r_s=2.1 a.u.)



From Itinerant to **Hubbard** Description for Electrons ! !

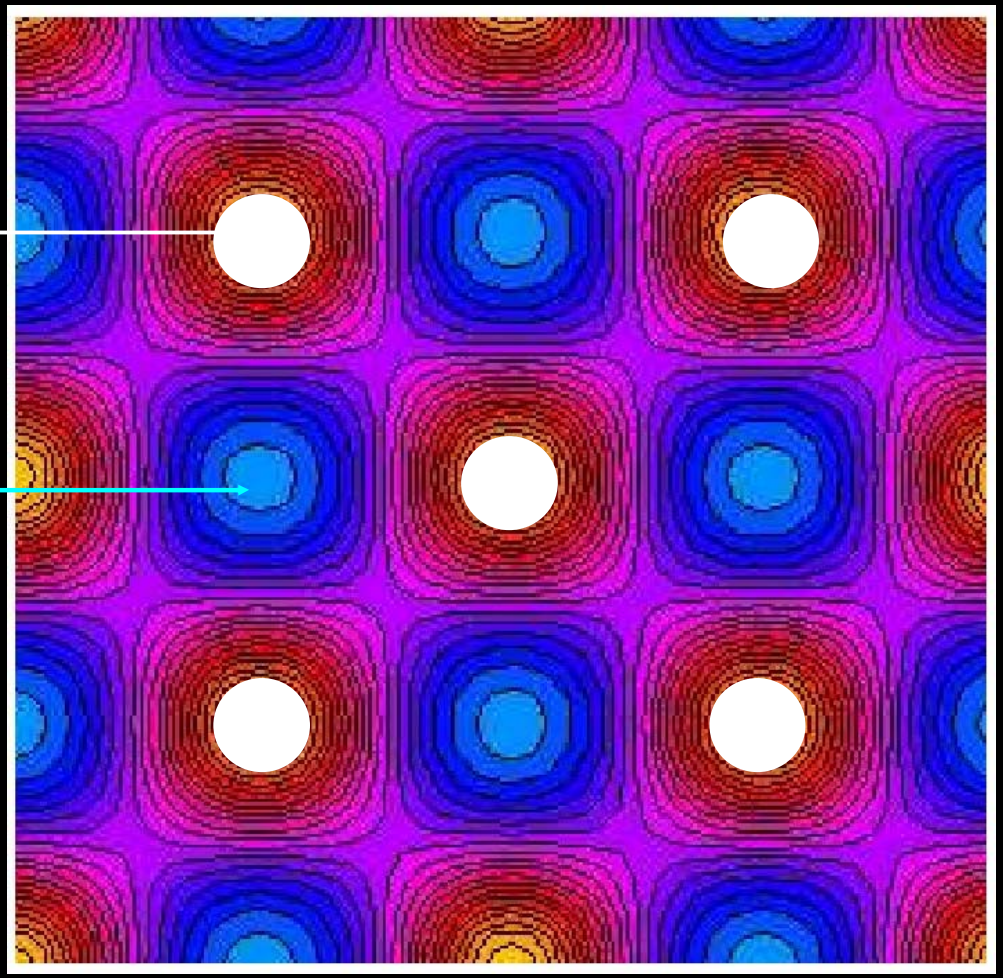
Lithium Monolayer

A. Rodriguez-Prieto and A. Bergara, Phys. Rev. B **72**, 125406 (2005)

Electronic Charge Density (sq, r_s=2.1 a.u.)

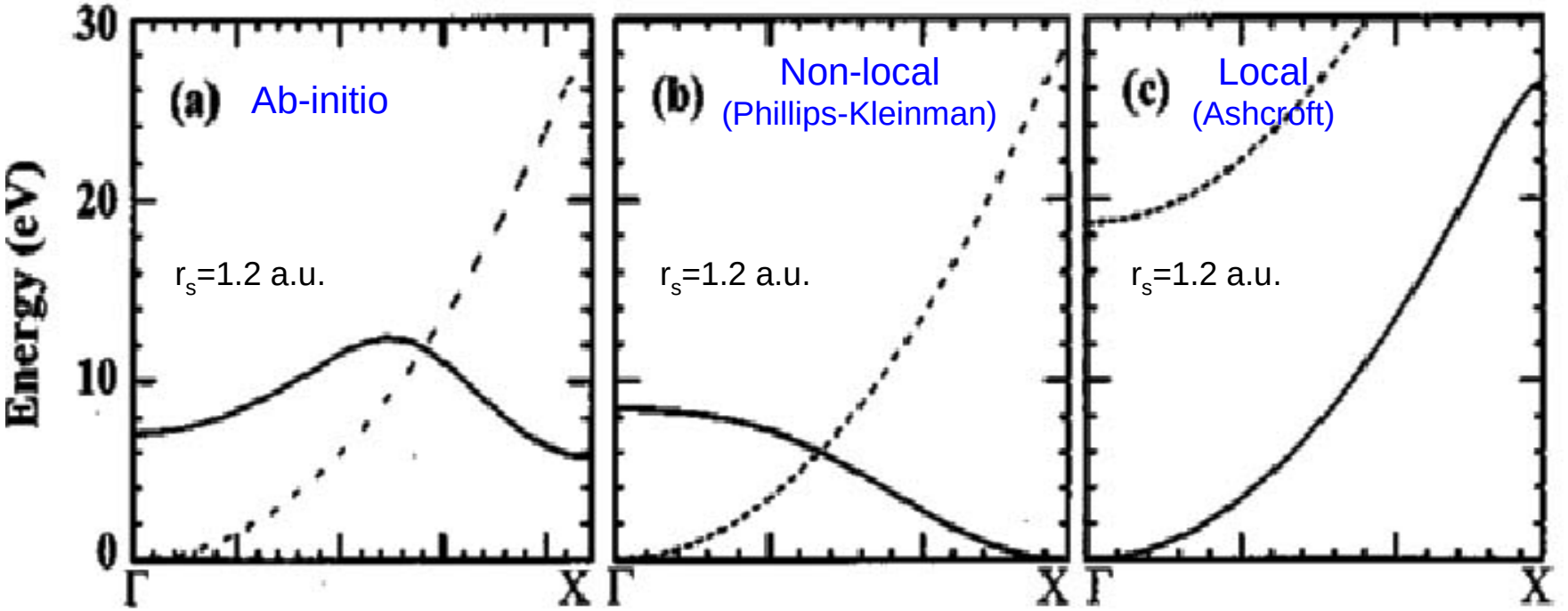
Li ions

Electronic localization



Increasing Non-locality with Pressure

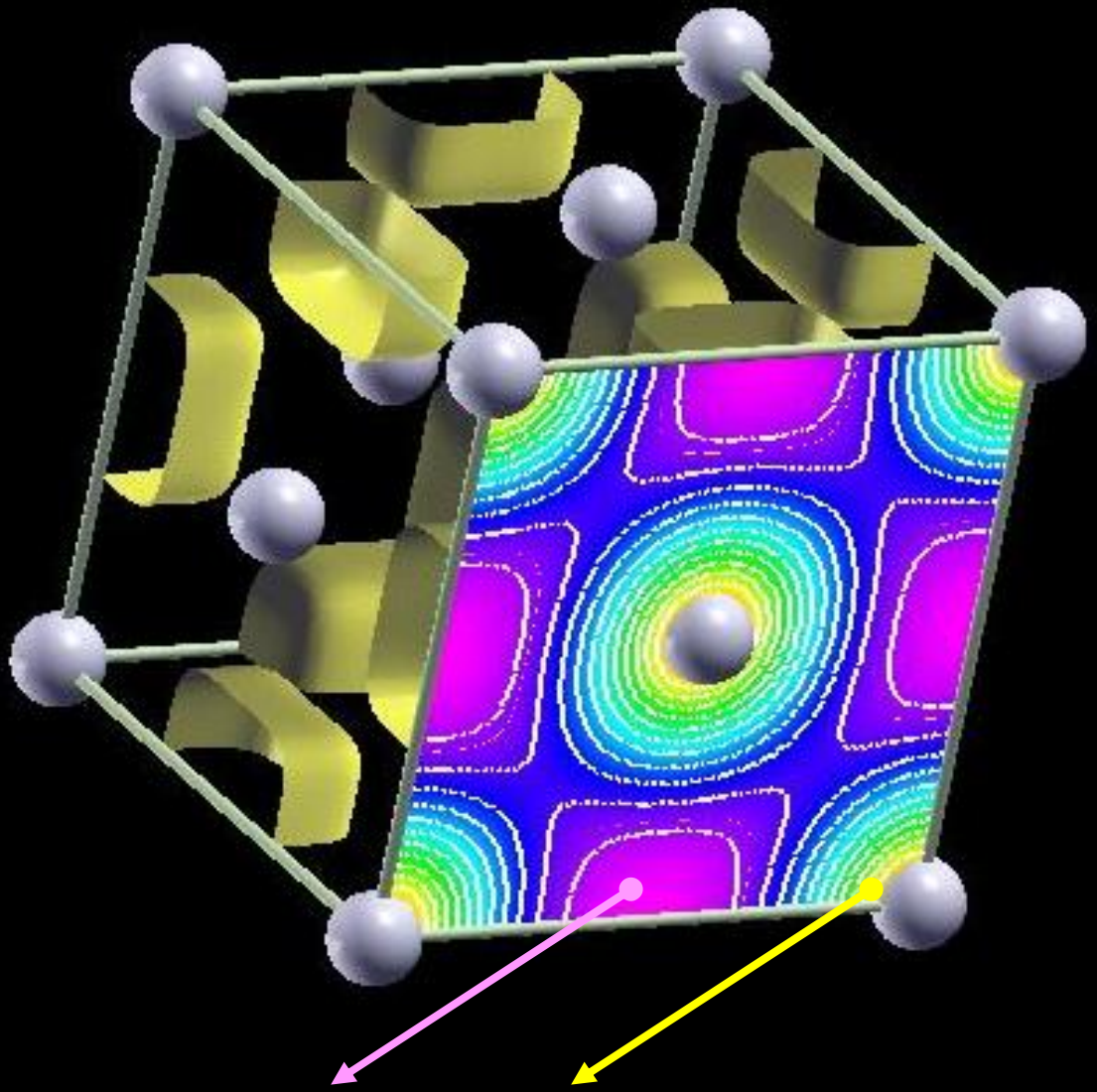
A. Bergara, J.B. Neaton, and N.W. Ashcroft, PRB **62,** 8495 (2000)



(b) Phillips-Kleinman Non-local Pseudopotential: $V = V_{\text{loc}}(r) + \sum_{c,\mathbf{R}} (\varepsilon - E_c) \left| \psi_{c,\mathbf{R}} \right\rangle \left\langle \psi_{c,\mathbf{R}} \right|$

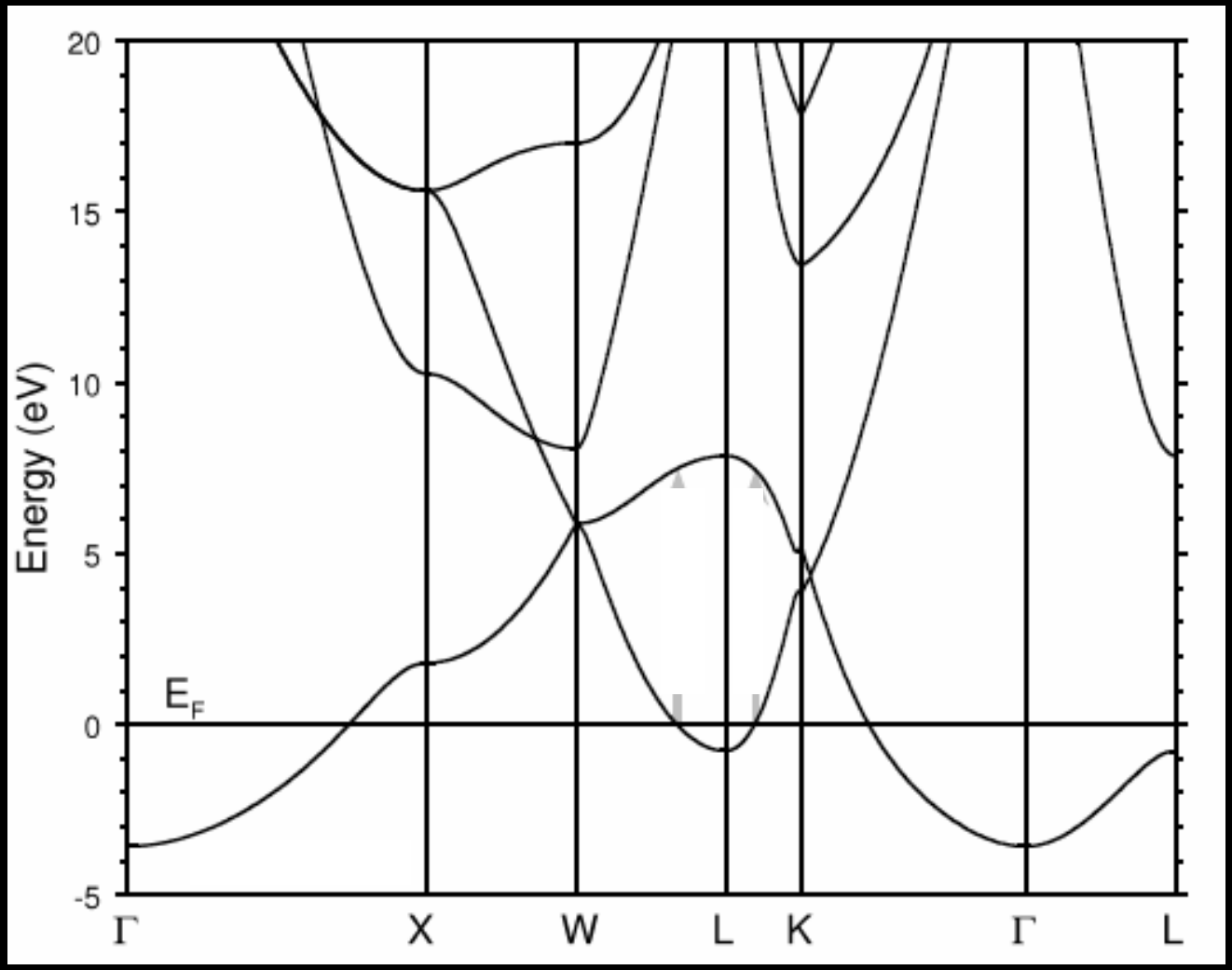
(c) Ashcroft Empty-core Local Pseudopotential: $V(\mathbf{G}) = \dfrac{-4\pi Z}{\mathbf{G}^2 \Omega} \cos G R_c$

Charge Density of *fcc* Lithium at P=30 GPa



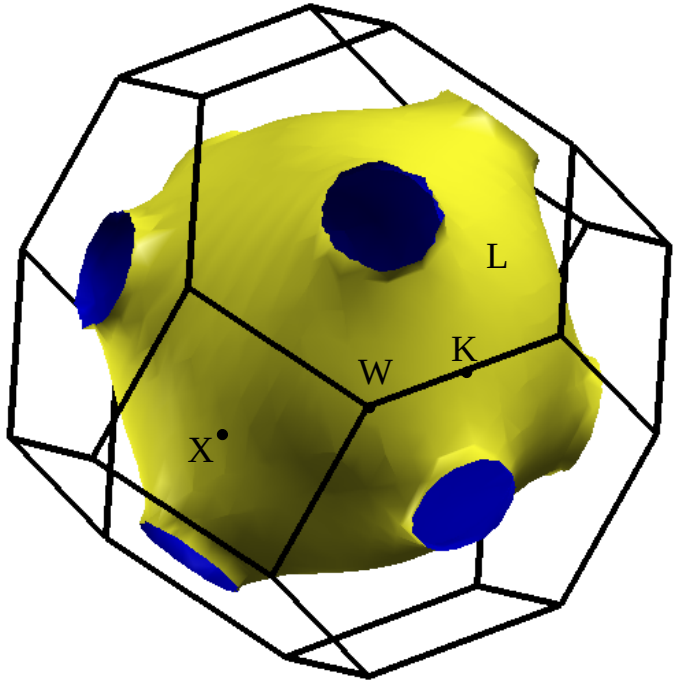
Maximum and minimun electronic charge

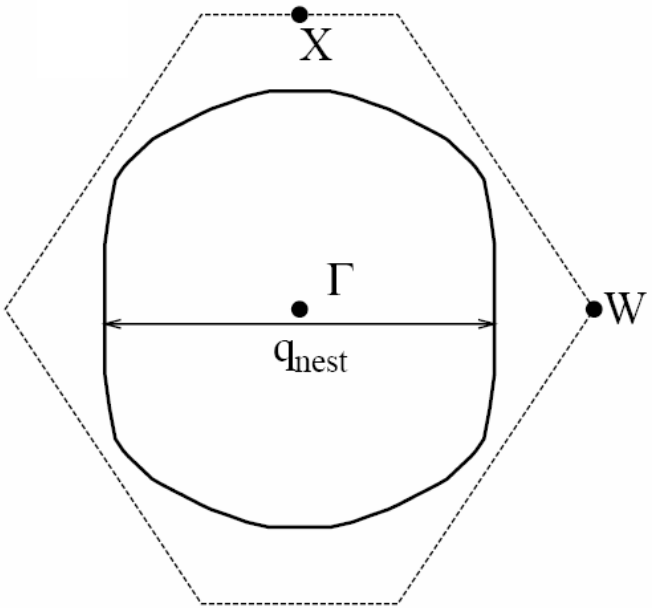
Band structure (fcc, P=30 GPa)



Fermi Surface of *fcc* Lithium at 30 GPa

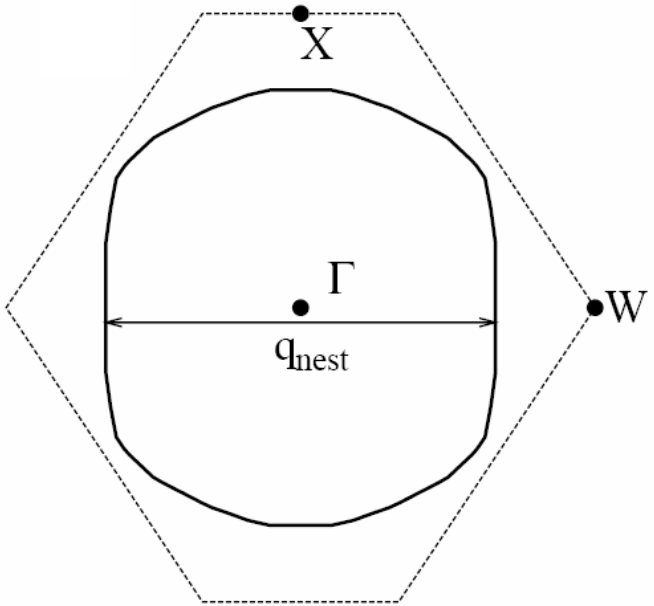
Cross section along ΓXW





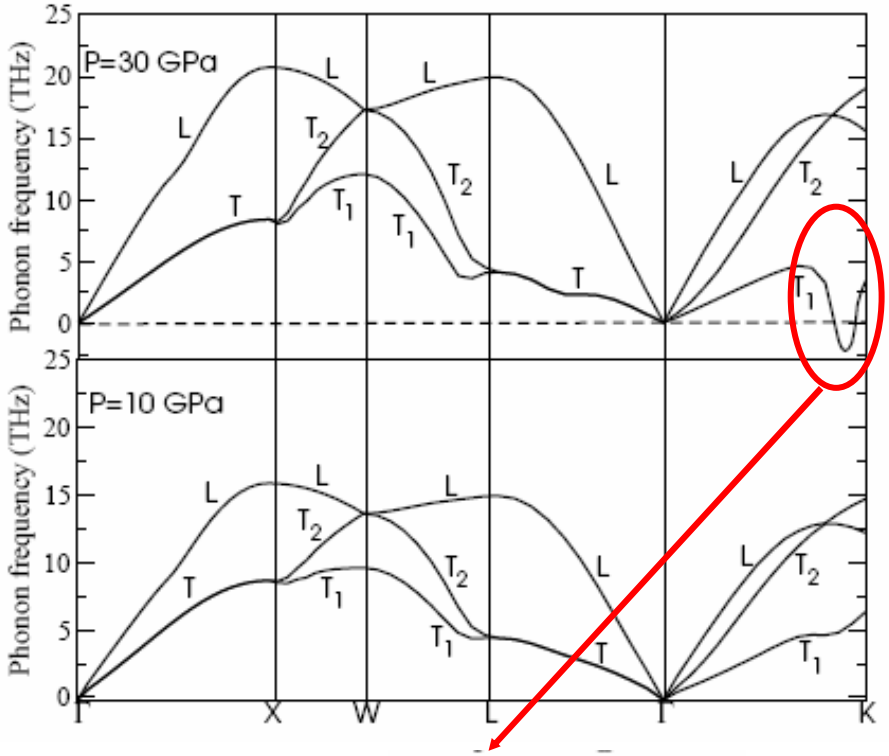
A. Rodriguez-Prieto, A. Bergara, V.M. Silkin, and P.M.Echenique,
Phys. Rev. B **74**, 172104 (2006)

Fermi Surface section along *ΓXW* at 30 GPa



$$\mathbf{q}_{\mathrm{nest}} = 2\pi/a(4/3, 2/3, 0) \ (\approx 2k_{\mathrm{F}})$$

Phonon Frequencies

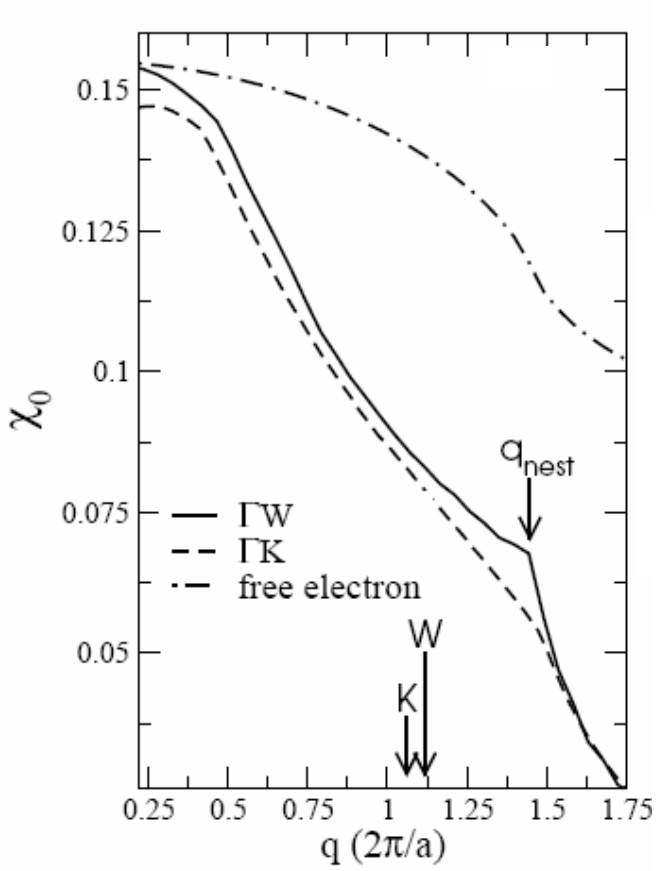


$$\mathbf{q}_{\mathrm{inst}} = 2\pi/a(-2/3, 2/3, 0)$$

$$\mathbf{q}_{\mathrm{inst}} = \mathbf{q}_{\mathrm{nest}} + \mathbf{G} \text{ with } \mathbf{G} = 2\pi/a(-2, 0, 0)$$

Ab initio Electronic Susceptibility

A. Rodriguez-Prieto, A. Bergara, V.M. Silkin, and P.M.Echenique,
Phys. Rev. B **74**, 172104 (2006)



$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \frac{1}{\Omega}\sum_{\mathbf{k}}^{BZ}\sum_{n,n'}\frac{f_{n\mathbf{k}} - f_{n'\mathbf{k}+\mathbf{q}}}{\varepsilon_{n\mathbf{k}} - \varepsilon_{n'\mathbf{k}+\mathbf{q}} + (\omega + \mathrm{i}\eta)} \times \langle\psi_{n\mathbf{k}}|e^{-\mathrm{i}(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\psi_{n'\mathbf{k}+\mathbf{q}}\rangle \times \langle\psi_{n'\mathbf{k}+\mathbf{q}}|e^{\mathrm{i}(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|\psi_{n\mathbf{k}}\rangle$$

Ab initio Electronic Susceptibility

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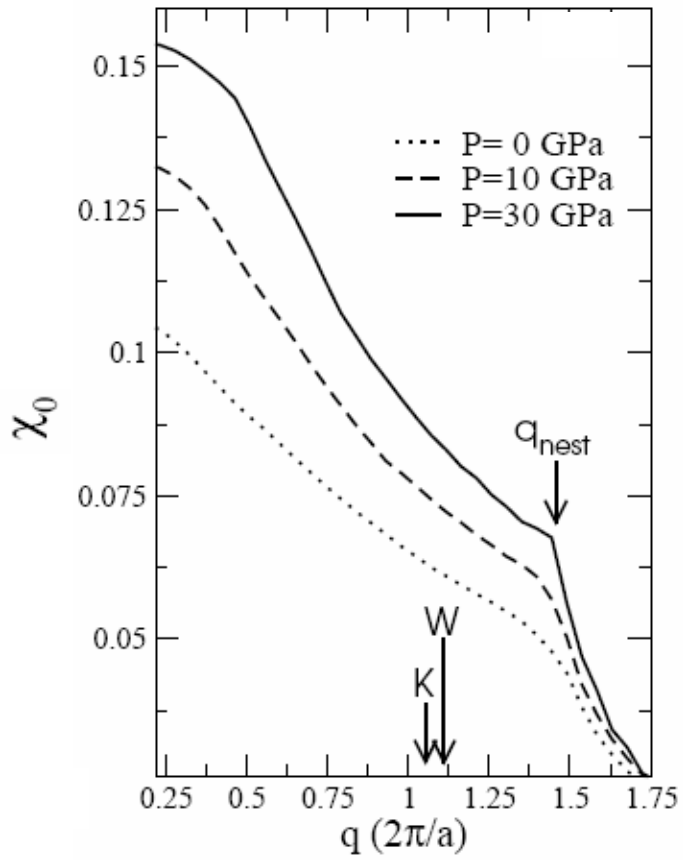
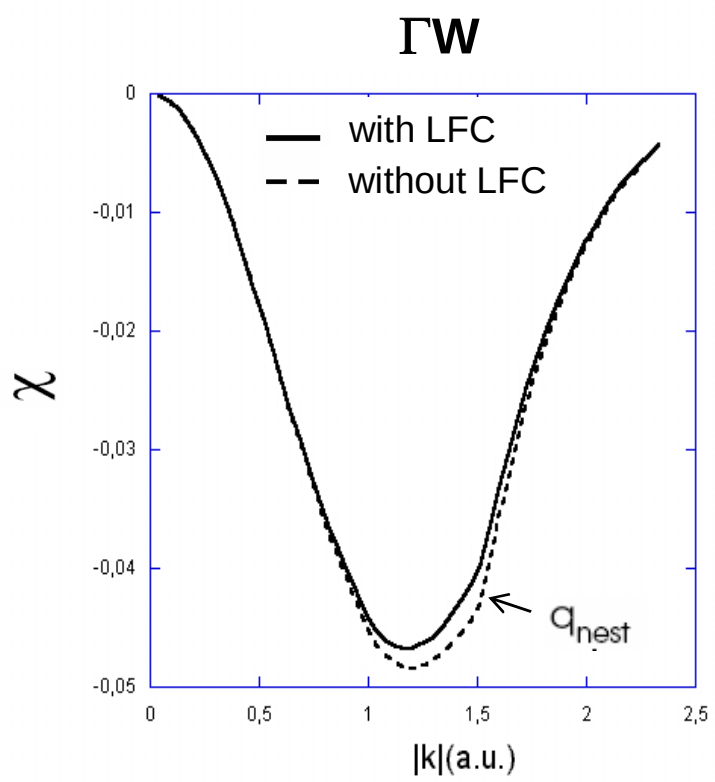


$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \frac{1}{\Omega}\sum_{\mathbf{k}}^{BZ}\sum_{n,n'}\frac{f_{n\mathbf{k}} - f_{n'\mathbf{k}+\mathbf{q}}}{\varepsilon_{n\mathbf{k}} - \varepsilon_{n'\mathbf{k}+\mathbf{q}} + (\omega + \mathrm{i}\eta)} \times \langle\psi_{n\mathbf{k}}|e^{-\mathrm{i}(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\psi_{n'\mathbf{k}+\mathbf{q}}\rangle \times \langle\psi_{n'\mathbf{k}+\mathbf{q}}|e^{\mathrm{i}(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|\psi_{n\mathbf{k}}\rangle$$

Ab initio Electronic Susceptibility

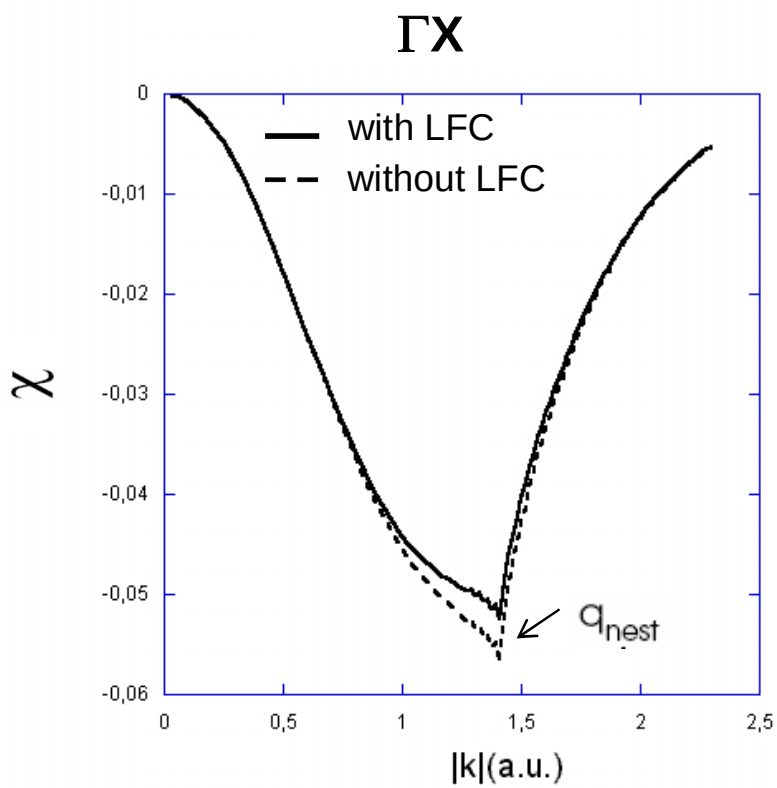


0 (RPA)

$$\chi = \chi^0 + \chi^0 (V + K^{xc}) \chi$$

$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \frac{1}{\Omega} \sum_{\mathbf{k}}^{BZ} \sum_{n,n'} \frac{f_{n\mathbf{k}} - f_{n'\mathbf{k}+\mathbf{q}}}{\varepsilon_{n\mathbf{k}} - \varepsilon_{n'\mathbf{k}+\mathbf{q}} + (\omega + \mathrm{i}\eta)} \times \langle \psi_{n\mathbf{k}} | e^{-\mathrm{i}(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{n'\mathbf{k}+\mathbf{q}} \rangle \times \langle \psi_{n'\mathbf{k}+\mathbf{q}} | e^{\mathrm{i}(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} | \psi_{n\mathbf{k}} \rangle$$

Ab initio Electronic Susceptibility

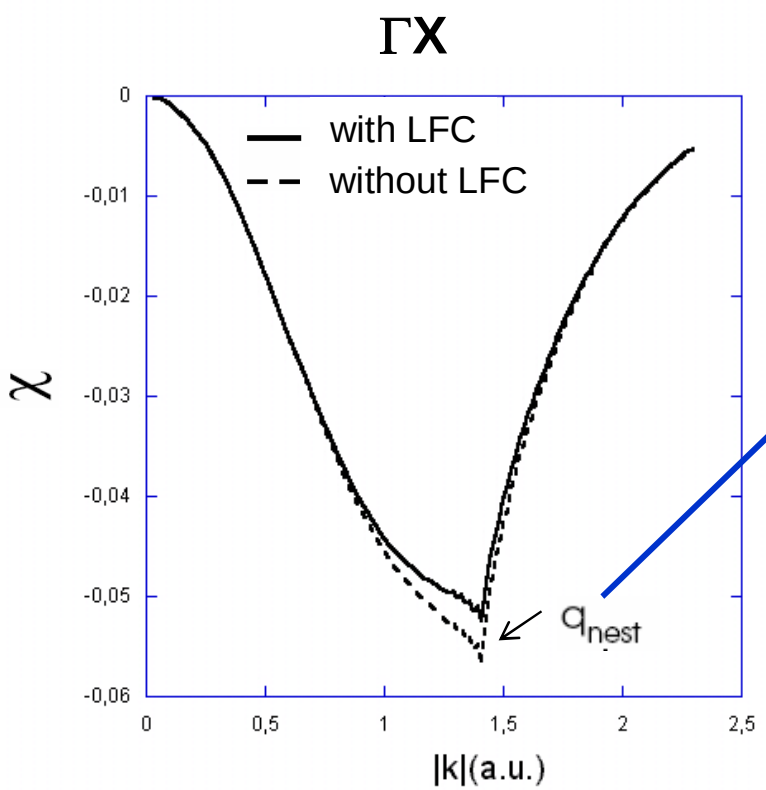


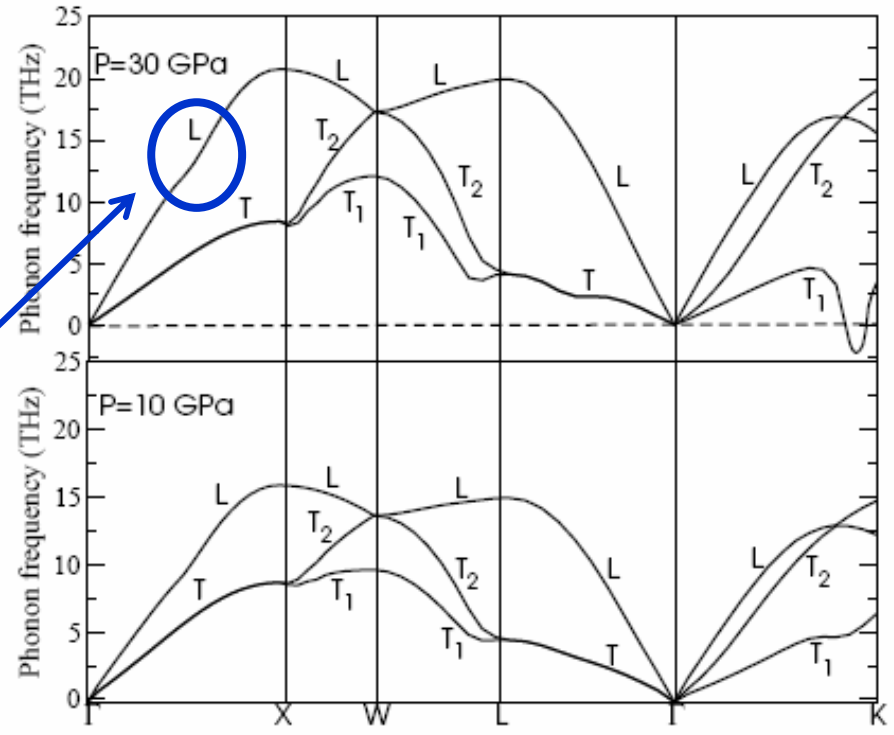
0 (RPA)

$$\chi = \chi^0 + \chi^0 (V + K^{xc}) \chi$$

$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \frac{1}{\Omega} \sum_{\mathbf{k}}^{BZ} \sum_{n,n'} \frac{f_{n\mathbf{k}} - f_{n'\mathbf{k}+\mathbf{q}}}{\varepsilon_{n\mathbf{k}} - \varepsilon_{n'\mathbf{k}+\mathbf{q}} + (\omega + \mathrm{i}\eta)} \times \langle \psi_{n\mathbf{k}} | e^{-\mathrm{i}(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{n'\mathbf{k}+\mathbf{q}} \rangle \times \langle \psi_{n'\mathbf{k}+\mathbf{q}} | e^{\mathrm{i}(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} | \psi_{n\mathbf{k}} \rangle$$

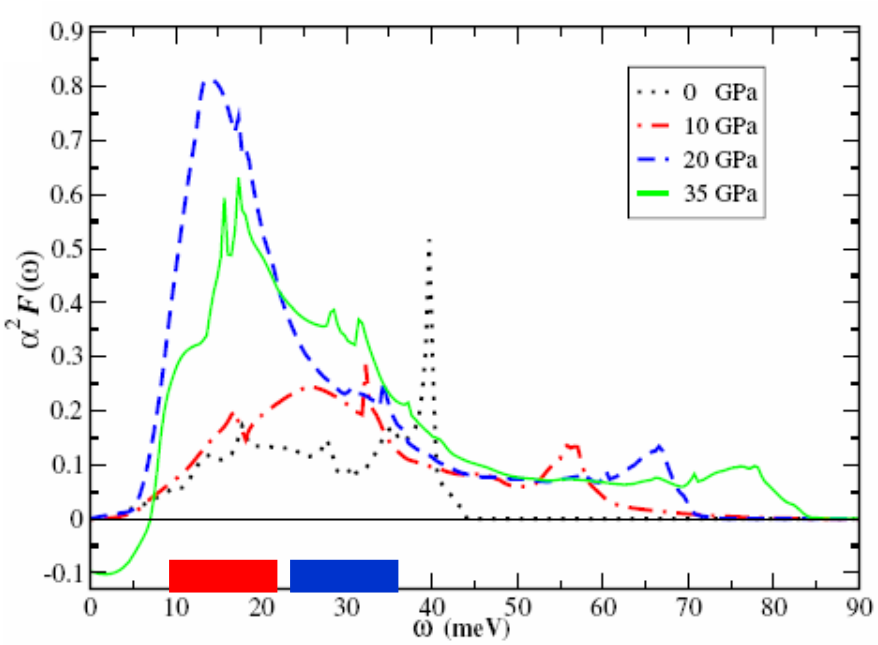
Ab initio Electronic Susceptibility

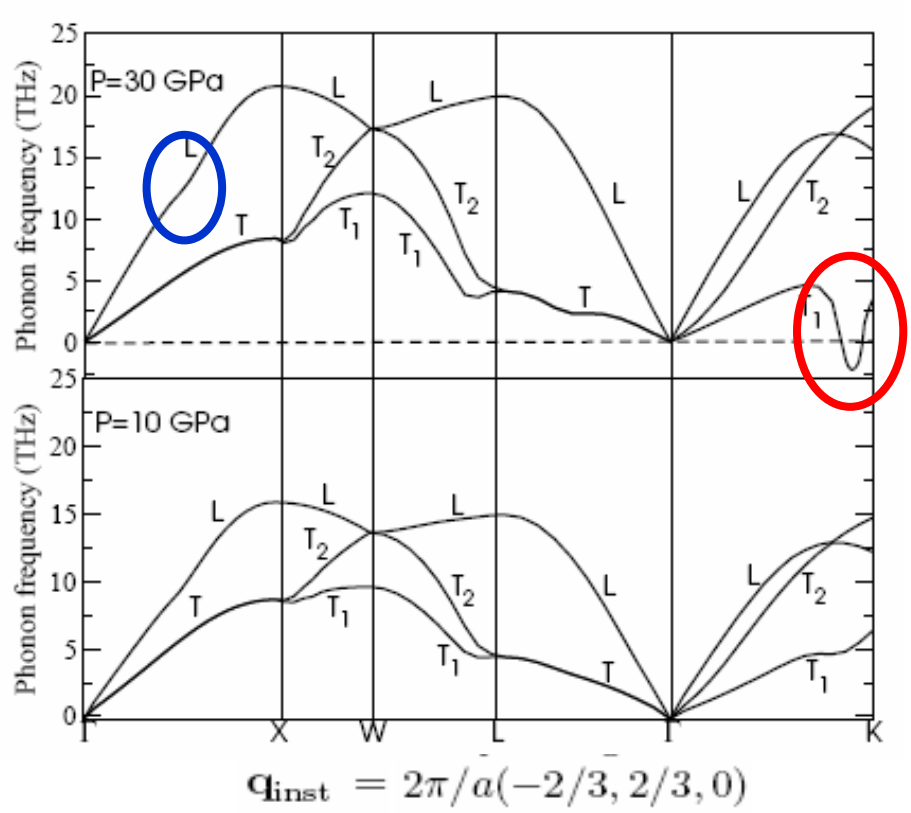




Electron-phonon Coupling for high Tc Superconductivity

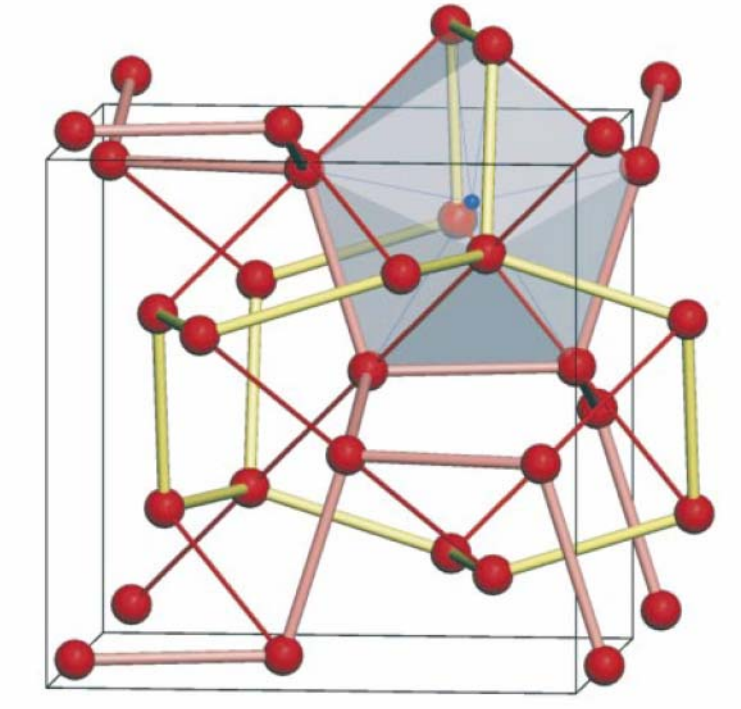
Phonon Frequencies

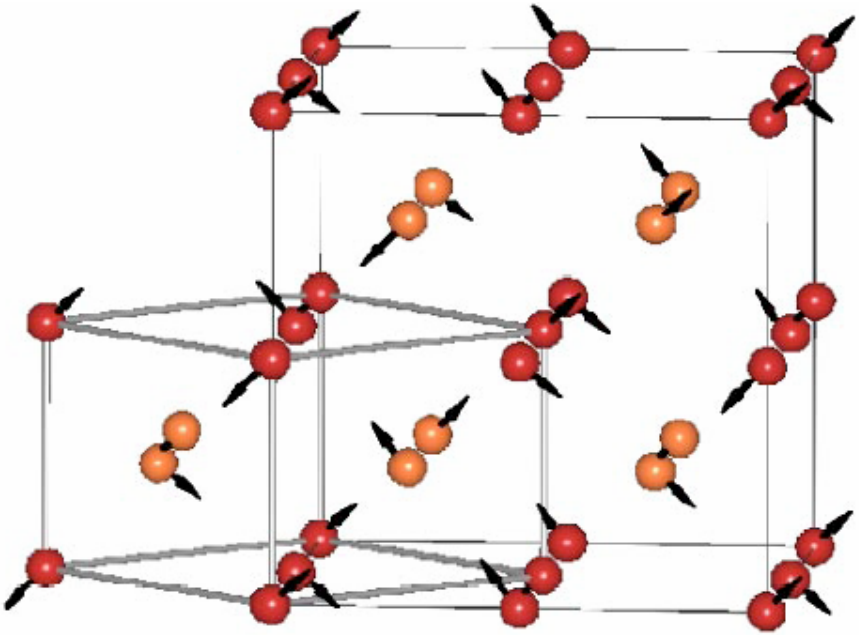




J.S. Tse,*et al* J. Phys.: Condens. Matter **17**, S911 (2005);
D. Kasinathan, et al, Phys. Rev. Lett. **96**, 047004 (2006);
G. Profeta *et al*, Phys. Rev. Lett. **96**, 047007 (2006).

cI16 Structure

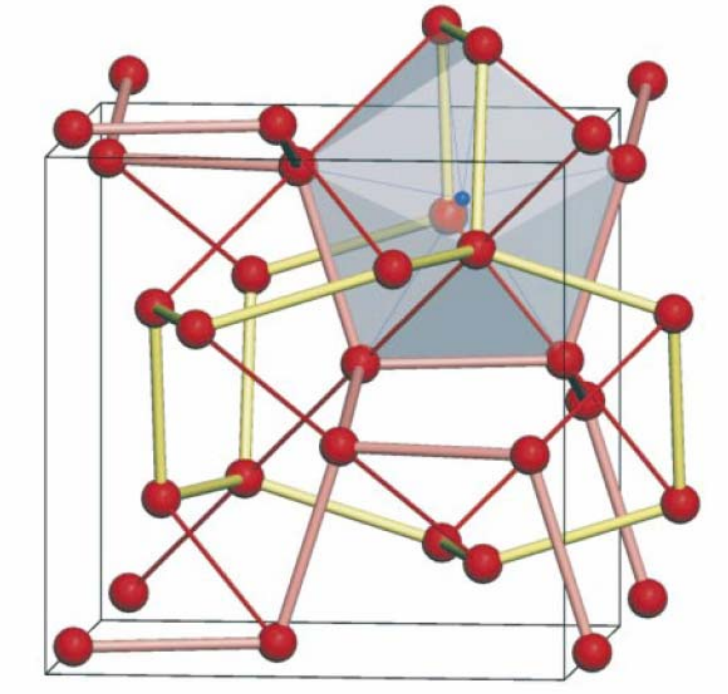




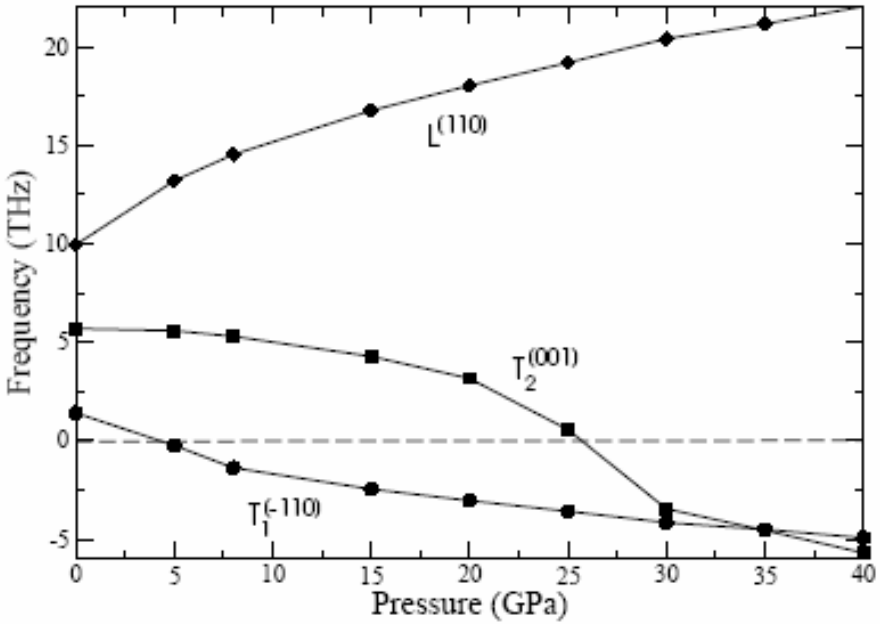
M. Hanfland, K. Syassen, N. E. Christensen, and D. L. Novikov, Nature **408**, 174 (2000)

H. Katzke and P. Toledano, Phys. Rev. B**71**, 184101 (2005)

cI16 Structure

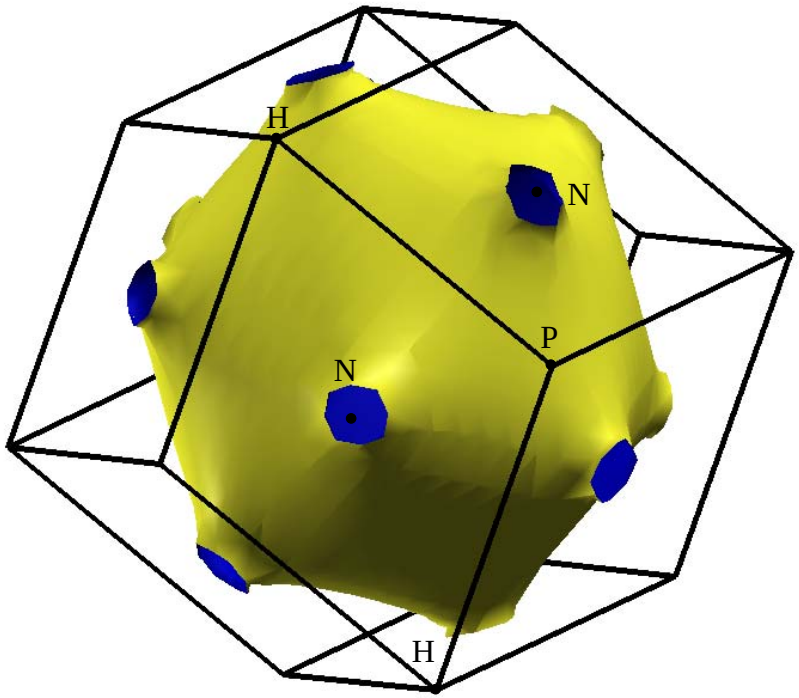


Phonon Frequencies of *bcc* Lithium at *N*

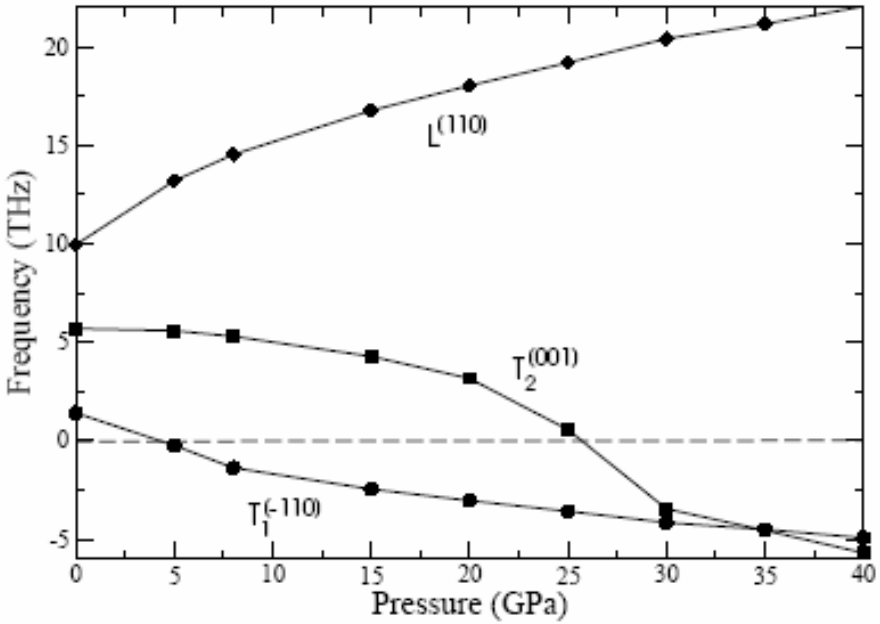


A. Rodriguez-Prieto, A. Bergara, and V.M. Silkin,
to be published in J. Phys. Soc. Jpn. (2007)

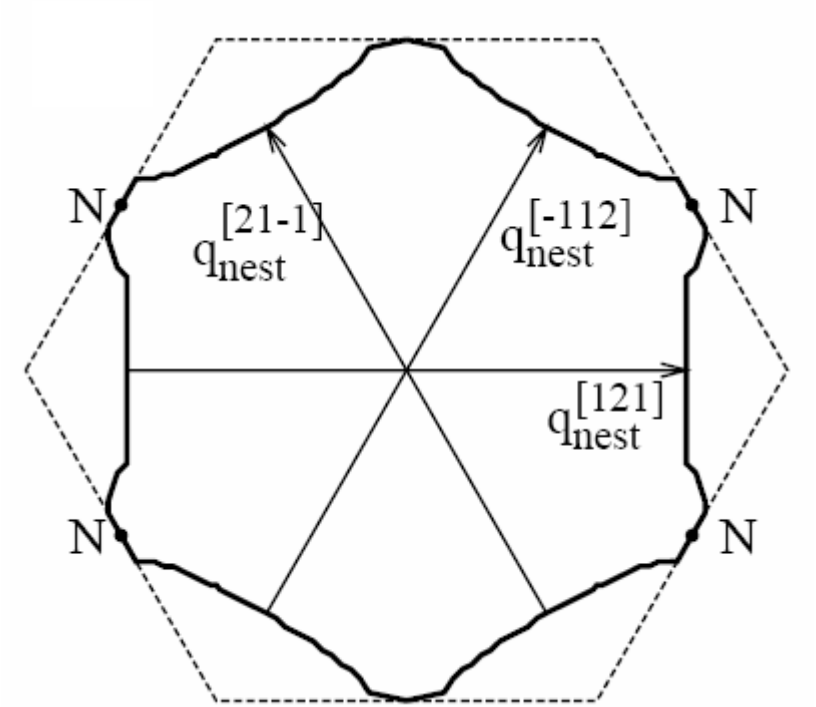
Fermi Surface of *bcc* Lithium at 40 GPa



Phonon Frequencies of *bcc* Lithium at *N*

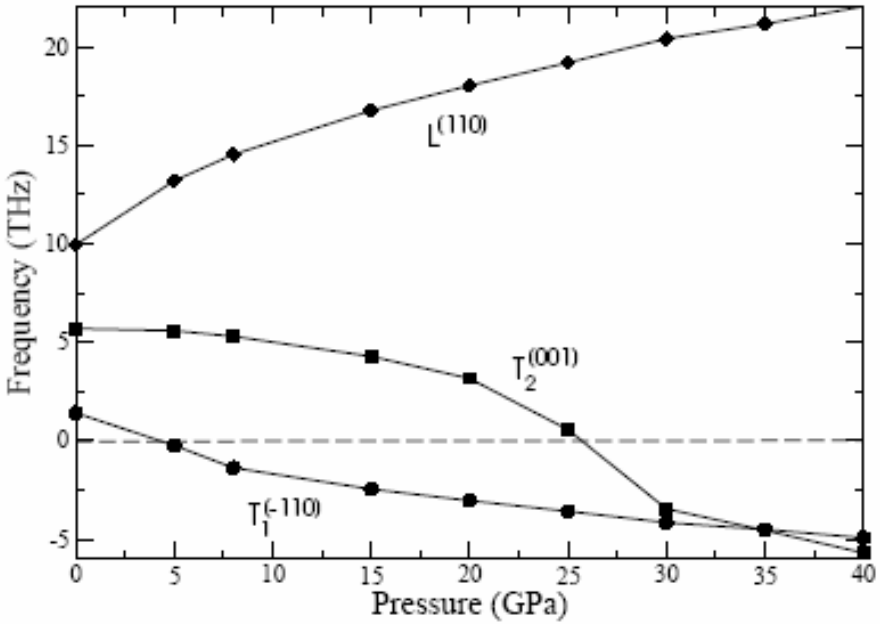


Fermi Surface Cross Section of *bcc* Lithium at 40 GPa



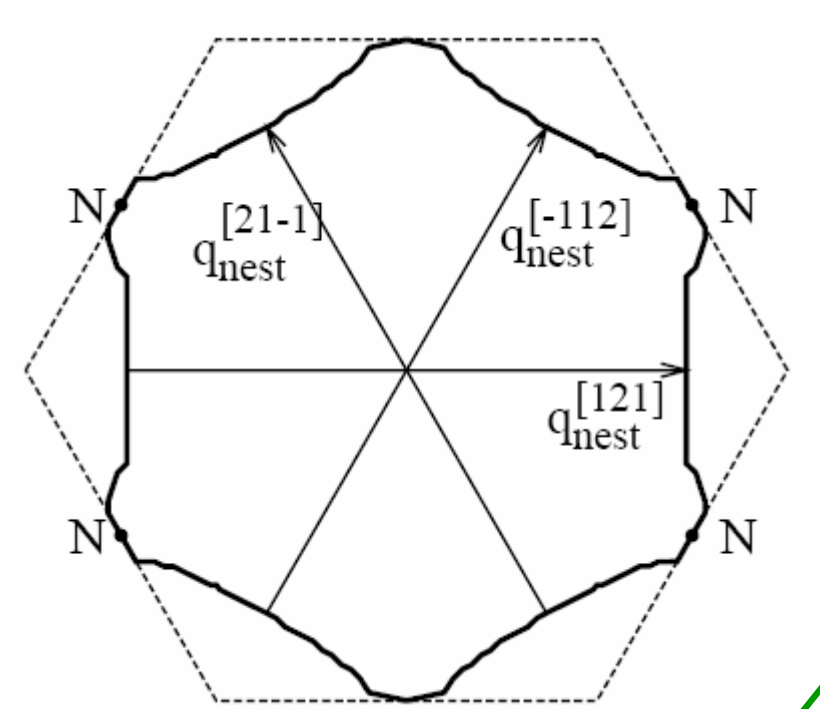
$$\mathbf{q}_{\mathrm{nest}}^{[121]} = \pi/a(1,2,1) = 2k_{\mathrm{F}}$$

Phonon Frequencies of *bcc* Lithium at *N*



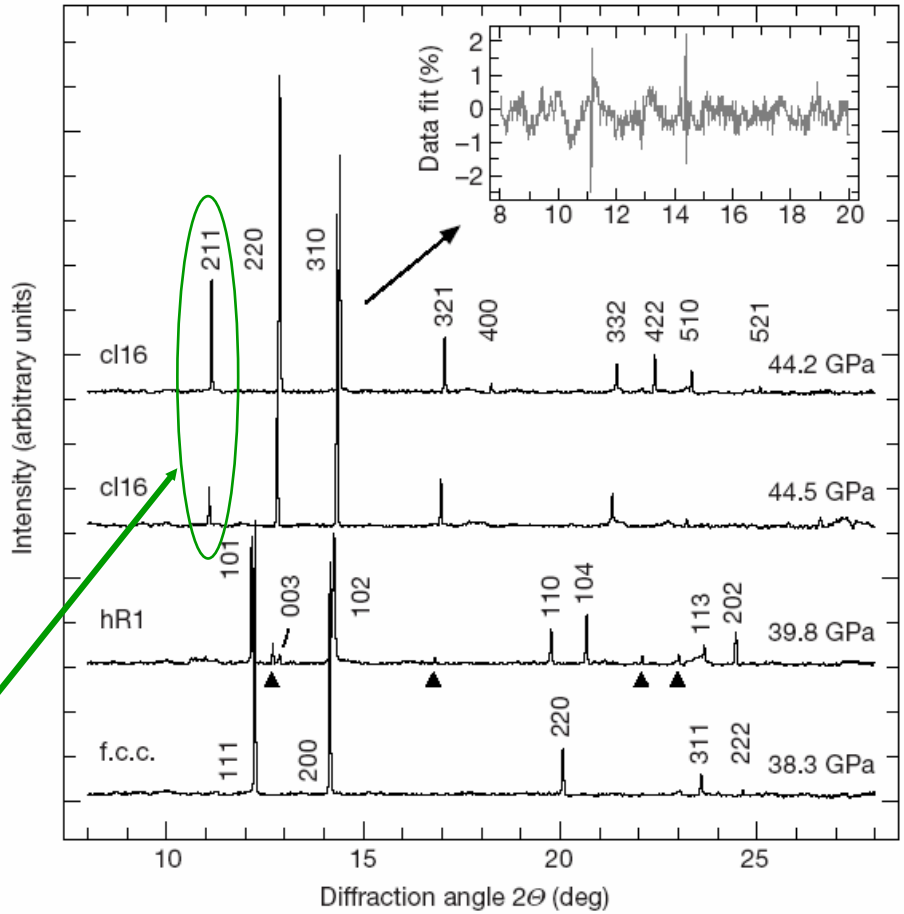
$$\mathbf{q}_{\mathrm{nest}}^{[121]} + \mathbf{G} = \pi/a\,(1,0,1) = \Gamma N \quad \text{with} \quad \mathbf{G} = \pi/a\,(0,-2,0)$$

Fermi Surface Cross Section of *bcc* Lithium at 40 GPa



$$\mathbf{q}_{\mathrm{nest}}^{[121]} = \pi/a(1,2,1) = 2k_{\mathrm{F}}$$

X-ray diffraction diagram of Lithium



M. Hanfland, K. Syassen, N. E. Christensen, and D. L. Novikov, Nature **408**, 174 (2000)

Dynamic Response Function of Lithium under Pressure

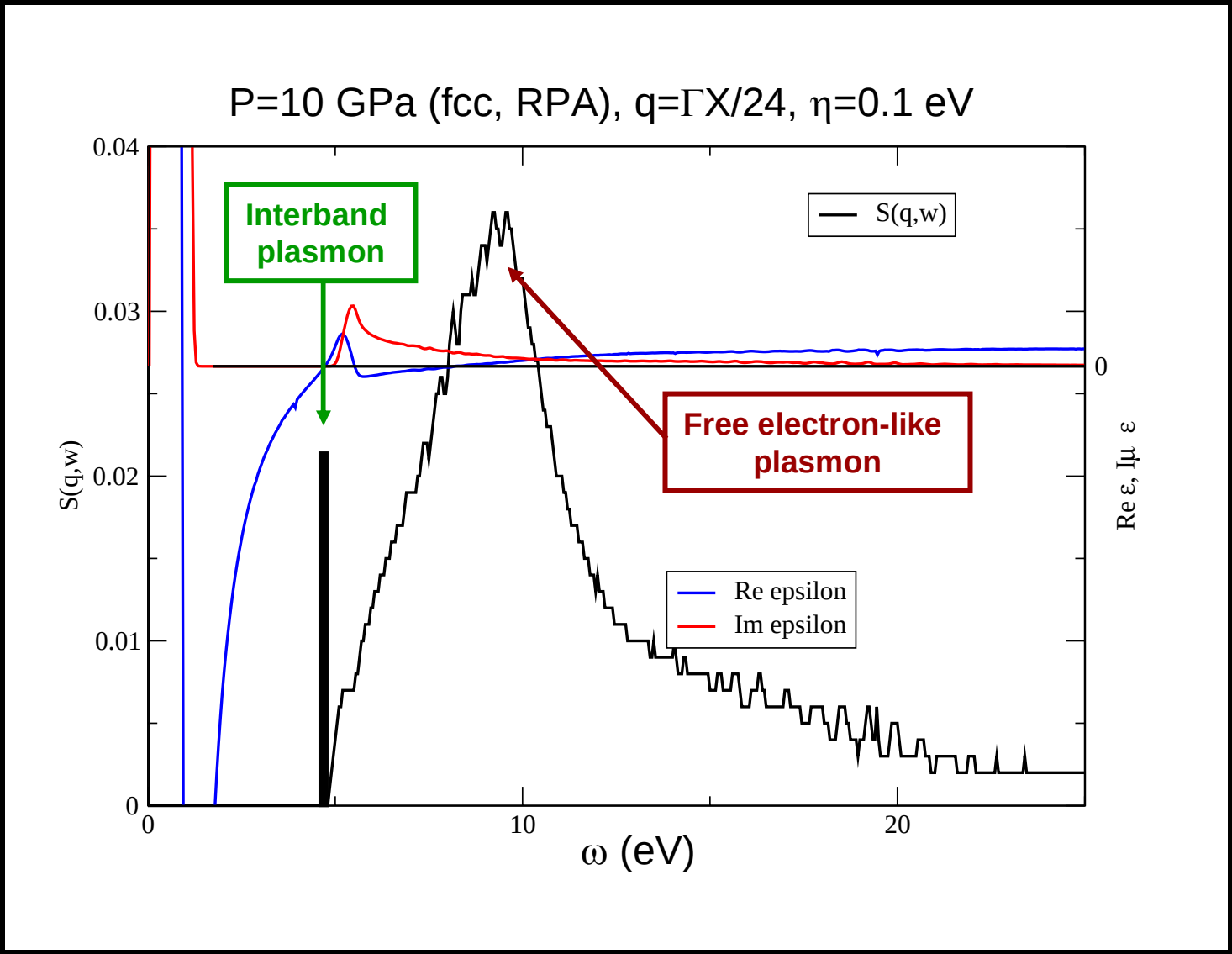
$$\epsilon^{-1} = 1 + V\chi$$

$$\chi = \chi^0 + \chi^0(V + K^{xc})\chi$$

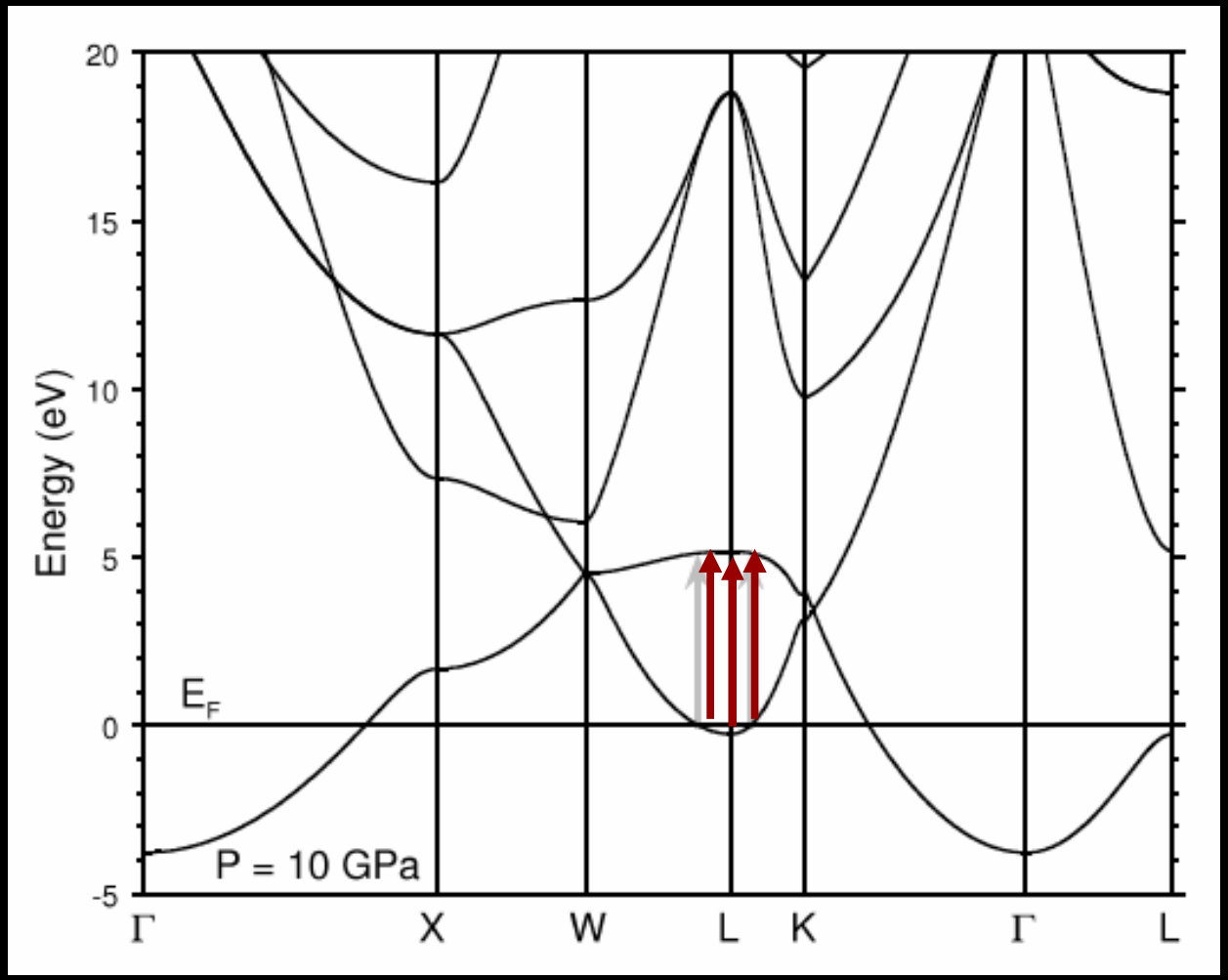
=0 (RPA)

$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \frac{1}{\Omega}\sum_{\mathbf{k}}^{BZ}\sum_{n,n'}\frac{f_{n\mathbf{k}} - f_{n'\mathbf{k}+\mathbf{q}}}{\varepsilon_{n\mathbf{k}} - \varepsilon_{n'\mathbf{k}+\mathbf{q}} + (\omega + \mathrm{i}\eta)} \times \langle\psi_{n\mathbf{k}}|e^{-\mathrm{i}(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\psi_{n'\mathbf{k}+\mathbf{q}}\rangle \times \langle\psi_{n'\mathbf{k}+\mathbf{q}}|e^{\mathrm{i}(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|\psi_{n\mathbf{k}}\rangle$$

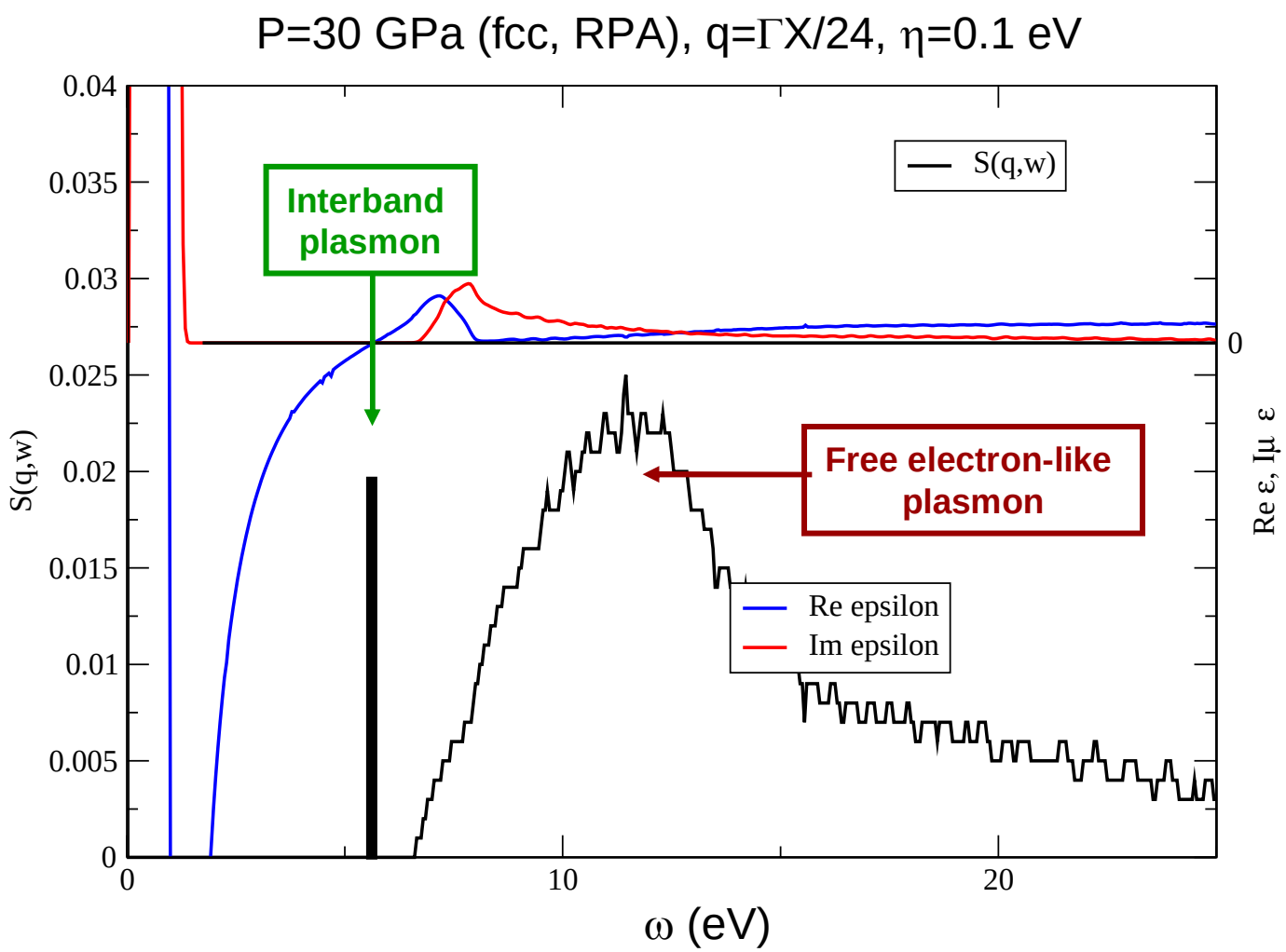
New Undamped Plasmon in Lithium under Pressure



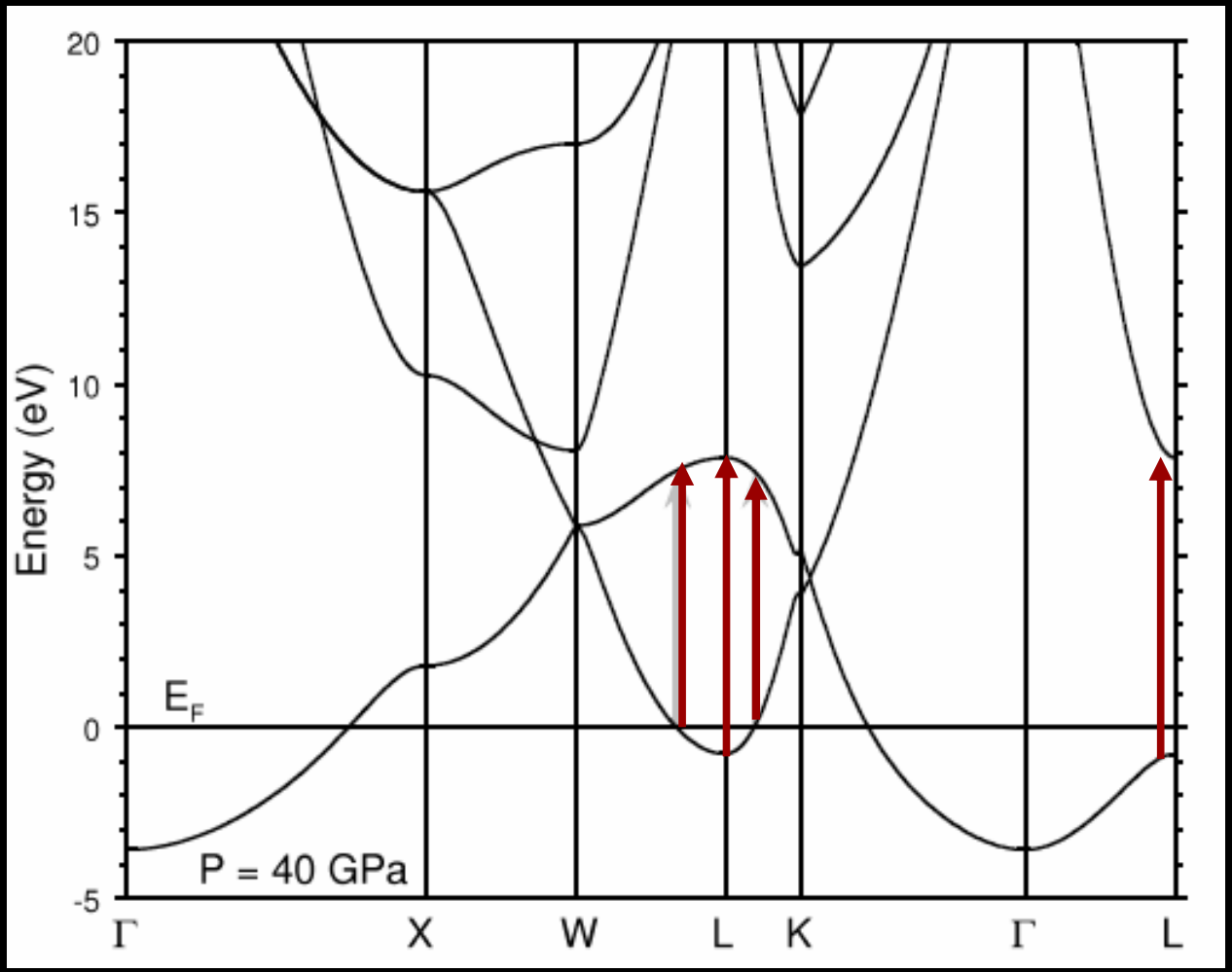
Band structure (fcc, P=10 GPa)



New Undamped Plasmon in Lithium under Pressure



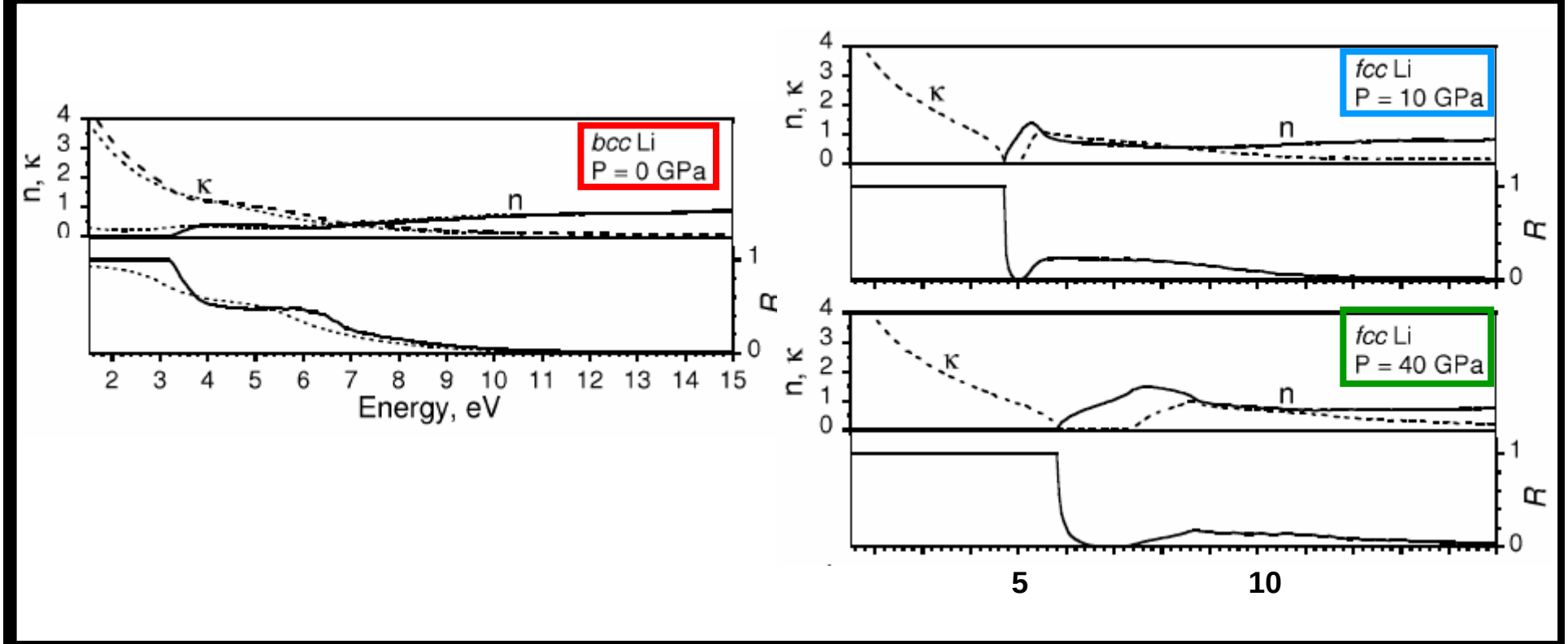
Band structure (fcc, P=30 GPa)



Plasmon energies and line-widths

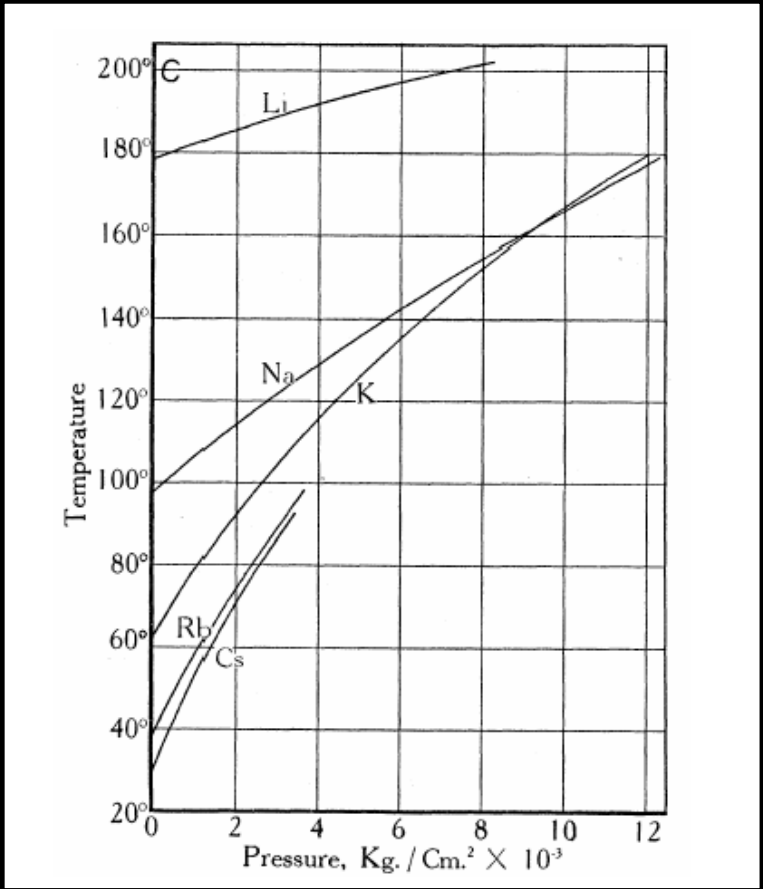
Pressure	E_p^A	Δ_p^A	E_p^B	E_o
		fcc		
P=0	7.6	2.3	–	3.3
P=10	9.2	4.8	4.7	5.1
P=20	10.4	5.2	5.25	6.2
P=30	11.5	5.4	5.6	7.0
P=40	12.4	5.5	5.8	7.5
		bcc		
P=0	7.28	2.6		

Optical Properties



Unexplored Properties

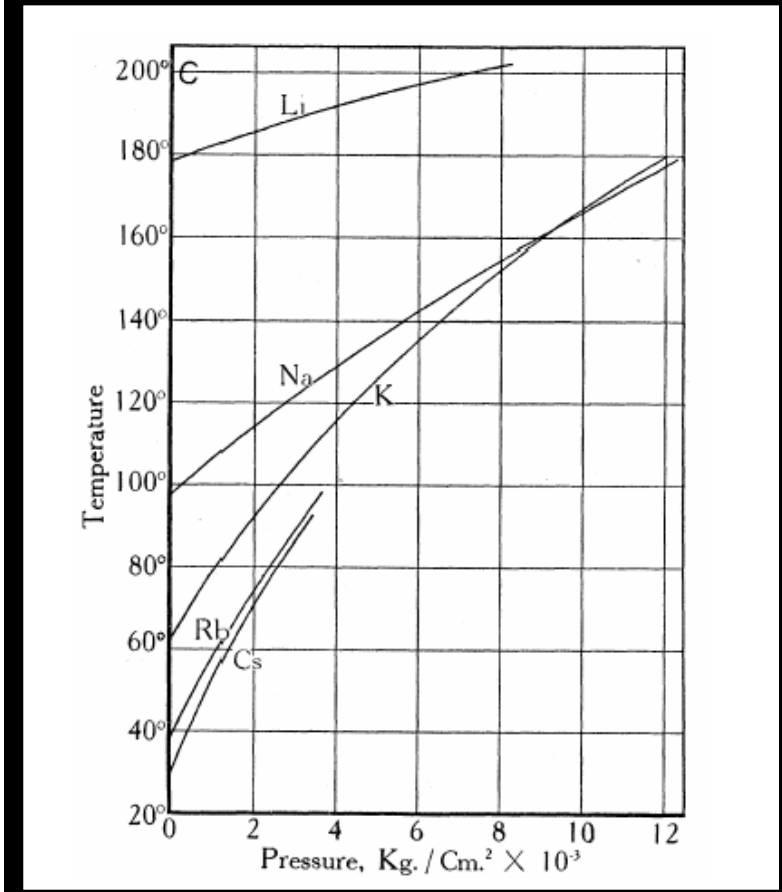
Melting Curve of the Alkalies



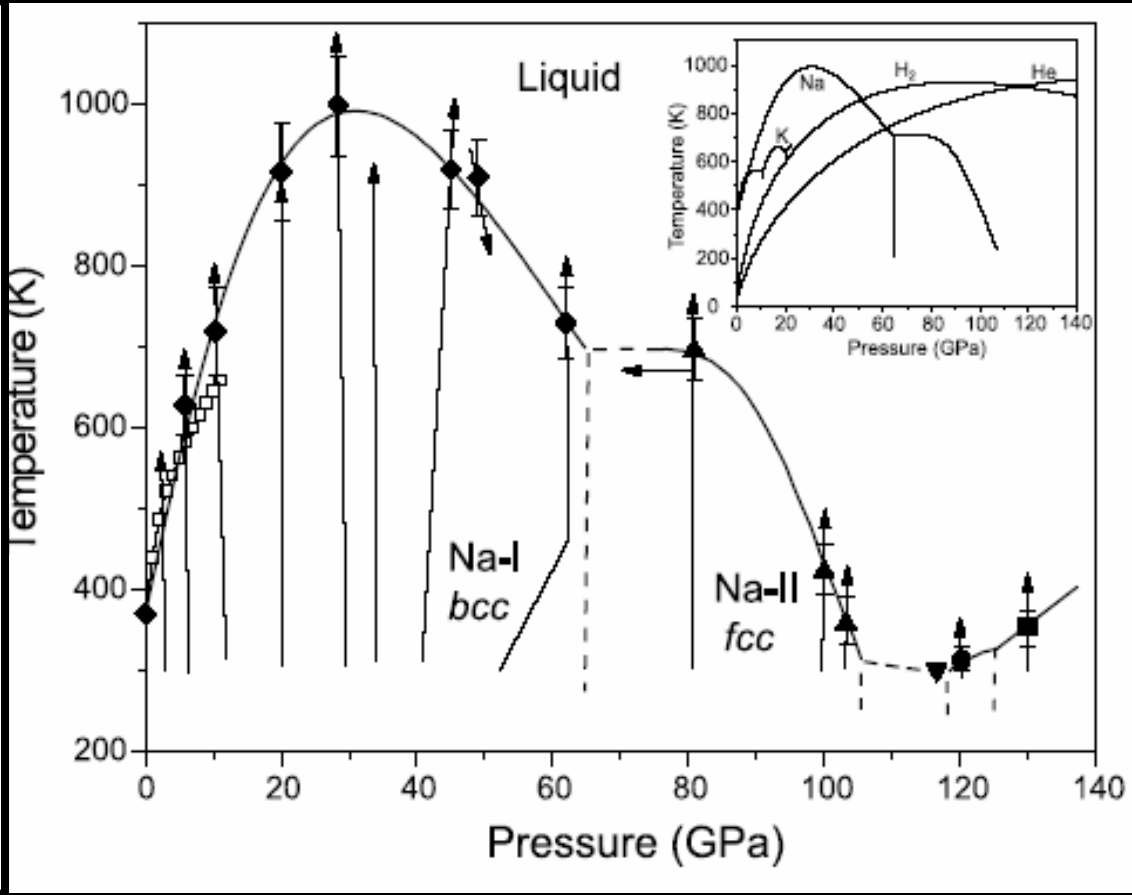
P.W. Bridgman,
Phys. Rev. **27**, 68 (1926)

Unexplored Properties

Melting Curve of the Sodium



P.W. Bridgman,
Phys. Rev. **27**, 68 (1926)



E. Gregoryanz, O. Degtyareva, M. Somayazulu, R.J. Hemley, and H-k. Mao,
Phys. Rev. Letts. **94**, 185502 (2006).

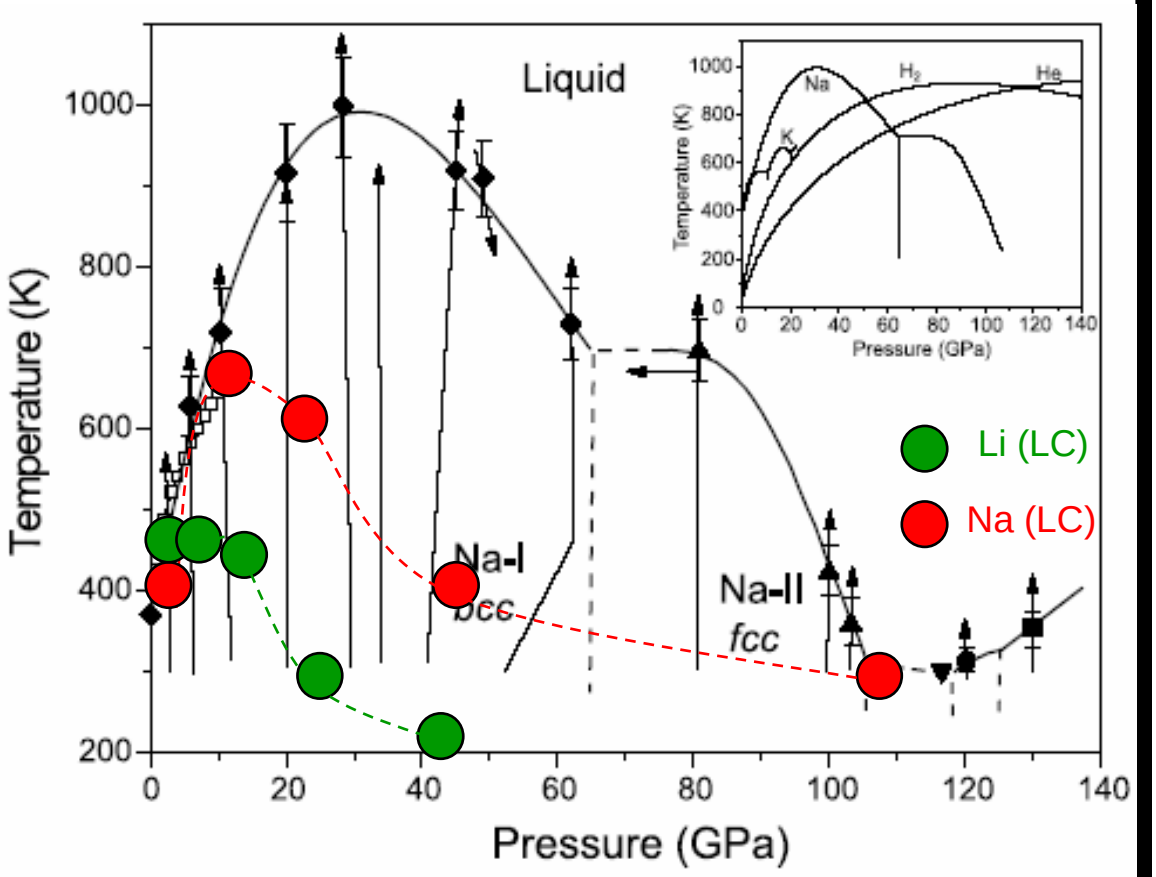
Anomalous Melting-curve of Lithium?

Lindemann Melting Criterion

$$T_m = CMv^{2/3}\Theta_D^2$$

$$\Theta_D = 1.4\frac{\hbar}{k_B}\sqrt{\langle\omega^2\rangle}$$

$$\langle\omega^2\rangle = \frac{2}{\lambda}\int_0^\infty d\omega\omega\alpha^2 F(\omega)$$



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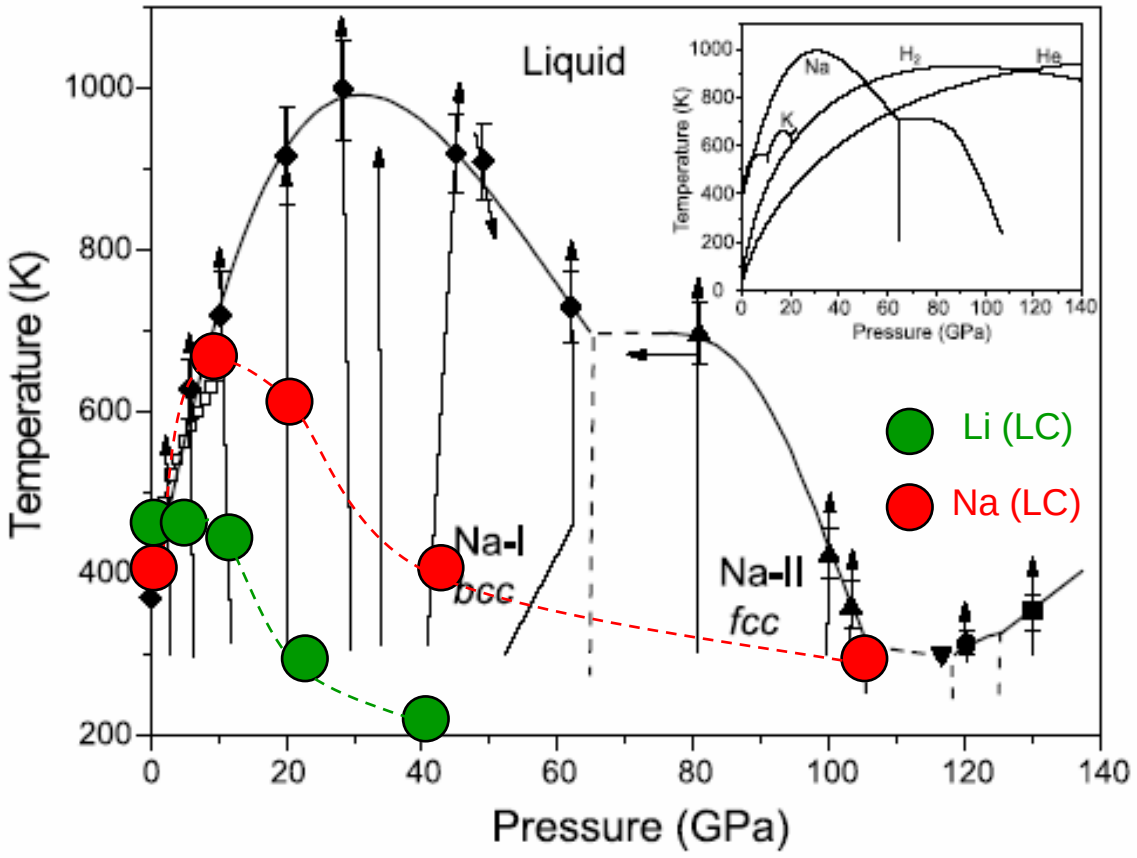
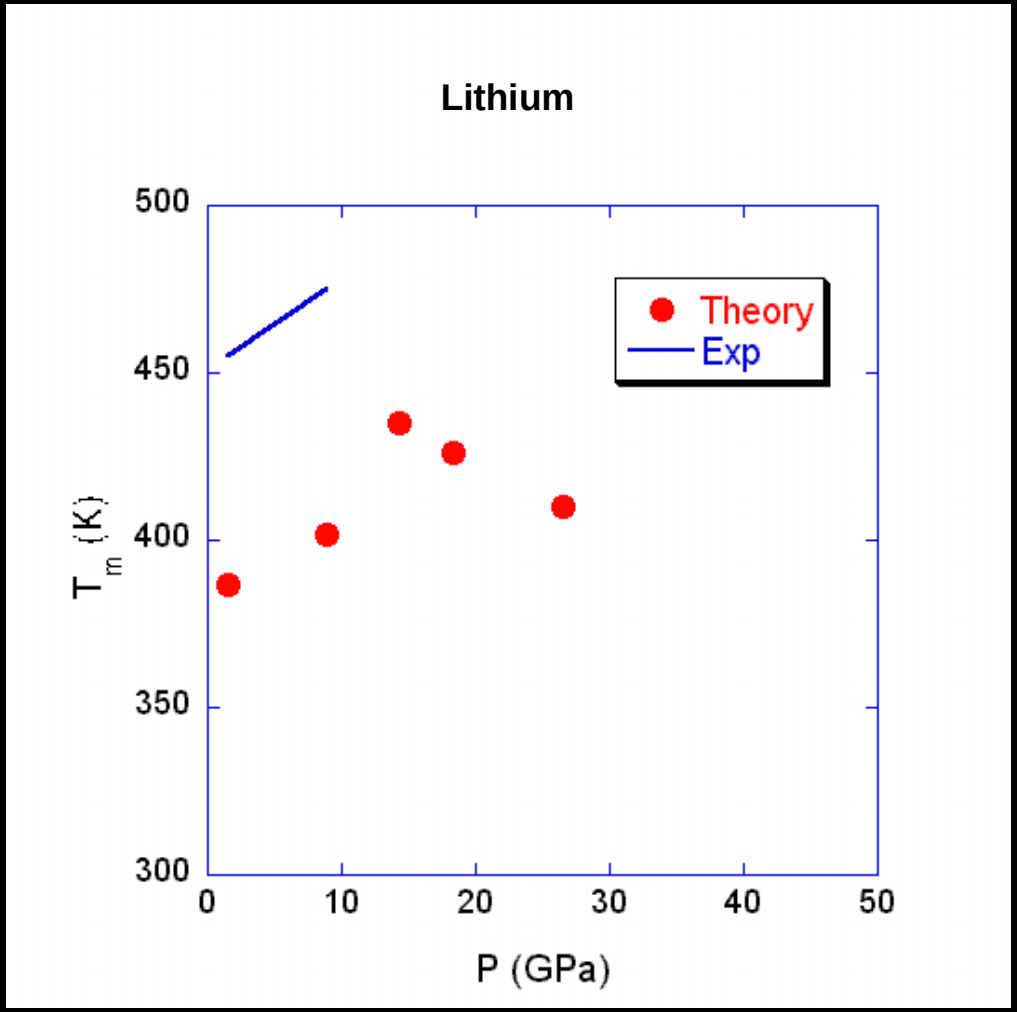


$$\lambda_B = \frac{h}{p_{20meV}} \cong 0.8\ \text{Å} \cong \frac{d_{li-li}^{40GPa}}{4}$$

Anomalous Melting-curve of Lithium?

A. Rodriguez-Prieto, D. Alfè, and A. Bergara;
to be published.



Conclusions

- **Fermi surface deformation, nesting and increasing crystal local-field effects originates the observed comlexity:**
  - **Soft-modes and strutural transition to complex phases.**
  - **Enhanced Tc Superconductivity.**
  - **New Undamped Plasmon.**
  - **Possible Anomalous Melting Curve.**
- **Not unique of Lithium nor the alcalies.**

In collaboration with:

- D. Alfè (*University College London*)
- N.W. Ashcroft (*Cornell University*)
- P.M. Echenique (*Univ. of the Basque Country and DIPC*)
- J.B. Neaton (*Molecular Foundry, LBNL*)
- A. Rodriguez-Prieto (*Univ. of the Basque Country and DIPC*)
- V.M. Silkin (*Donostia International Physics Center*)