Peculiarities of Lattice Dynamics and the Melting of Alkali Metals

E.G. Maksimov, S.V. Lepeshkin, and M.V. Magnitskaya
P.N. Lebedev Physical Institute, Moscow, Russia

1. Introduction
   (*from simplicity to complexity*)

2. Melting of sodium
   (*simplicity including complexity*)

3. Melting of lithium
   (*near total complexity*)

4. Conclusions
   (*what is in the future?*)

S.V. Lepeshkin et al. JETP Lett. (2009)

At ambient conditions, the alkali elements are prototype free-electron metals:

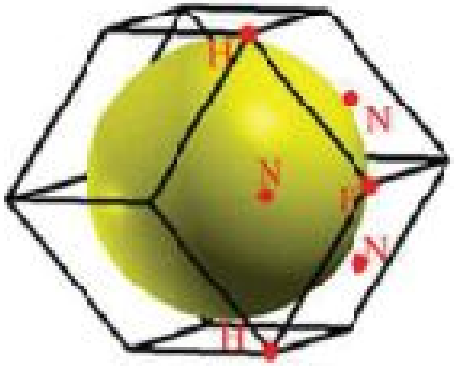
– highly symmetric crystal structure

– nearly parabolic $E(\mathbf{k})$

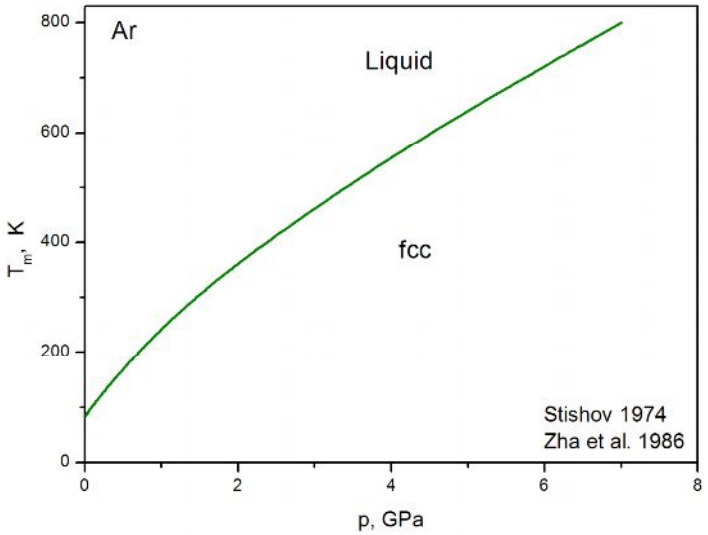
– spherical Fermi surface

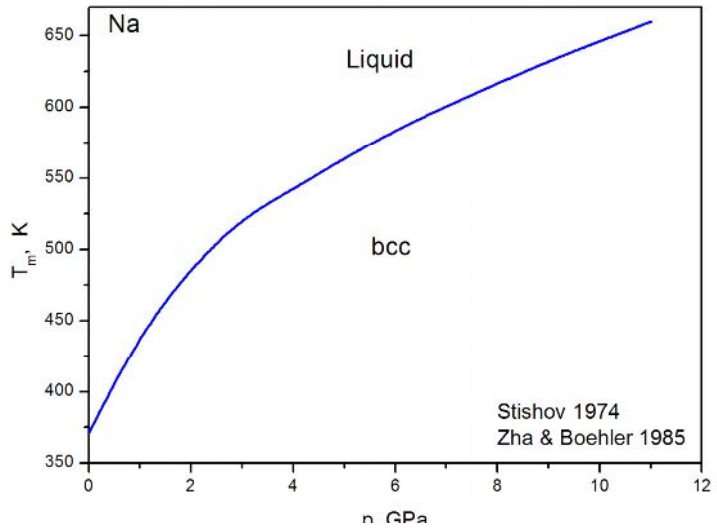
– small electron-phonon interaction → no superconductivity

– simple thermodynamic properties



Experimental melting curves of Ar, Na, and Li

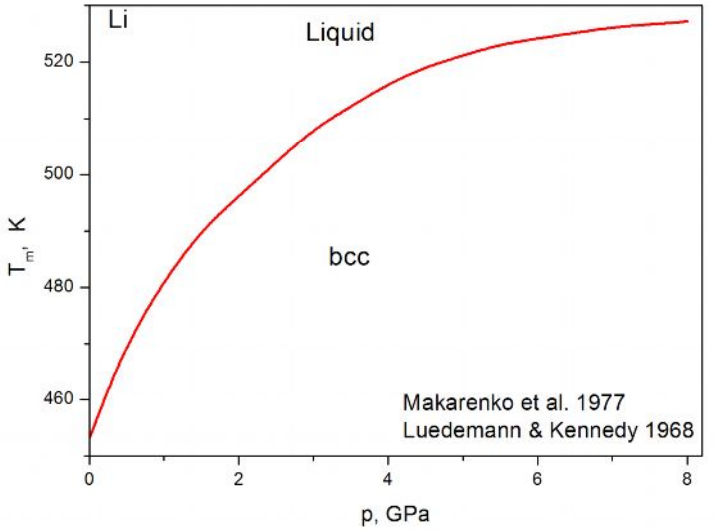




Melting in classical systems is well described by Lindemann's criterion:

$$\sqrt{\left\langle u^2(T_\mathrm{m})\right\rangle} = L d_\mathrm{NN}$$

with $L \approx$ const



Structural sequences for alkali elements at $T \sim 300$ K

Li	bcc $\xrightarrow{7.5}$ fcc $\xrightarrow{39}$ hR1 $\xrightarrow{42}$ cI16 $\xrightarrow{69}$ Li-6 $\xrightarrow{79}$ **Li-7** 9R, fcc (low T)	< 110 GPa
Na	bcc $\xrightarrow{65}$ fcc $\xrightarrow{105}$ cI16 $\xrightarrow{118}$ oP8 $\xrightarrow{125}$ host–guest $\xrightarrow{200}$ **hP4**	< 220 GPa
K	bcc $\xrightarrow{11.6}$ fcc $\xrightarrow{20}$ host–guest	< 60 GPa
Rb	bcc $\xrightarrow{7}$ fcc $\xrightarrow{13}$ oC52 $\xrightarrow{17}$ host–guest $\xrightarrow{20}$ tI4 $\xrightarrow{48}$ oC16	< 70 GPa
Cs	bcc $\xrightarrow{2.4}$ fcc $\xrightarrow{4.2}$ oC84 $\xrightarrow{4.4}$ tI4 $\xrightarrow{12}$ oC16 $\xrightarrow{72}$ dhcp	< 223 GPa

Cs becomes superconductive in the fcc phase. At $p \sim 12$ GPa $T_c \sim 1.5$ K

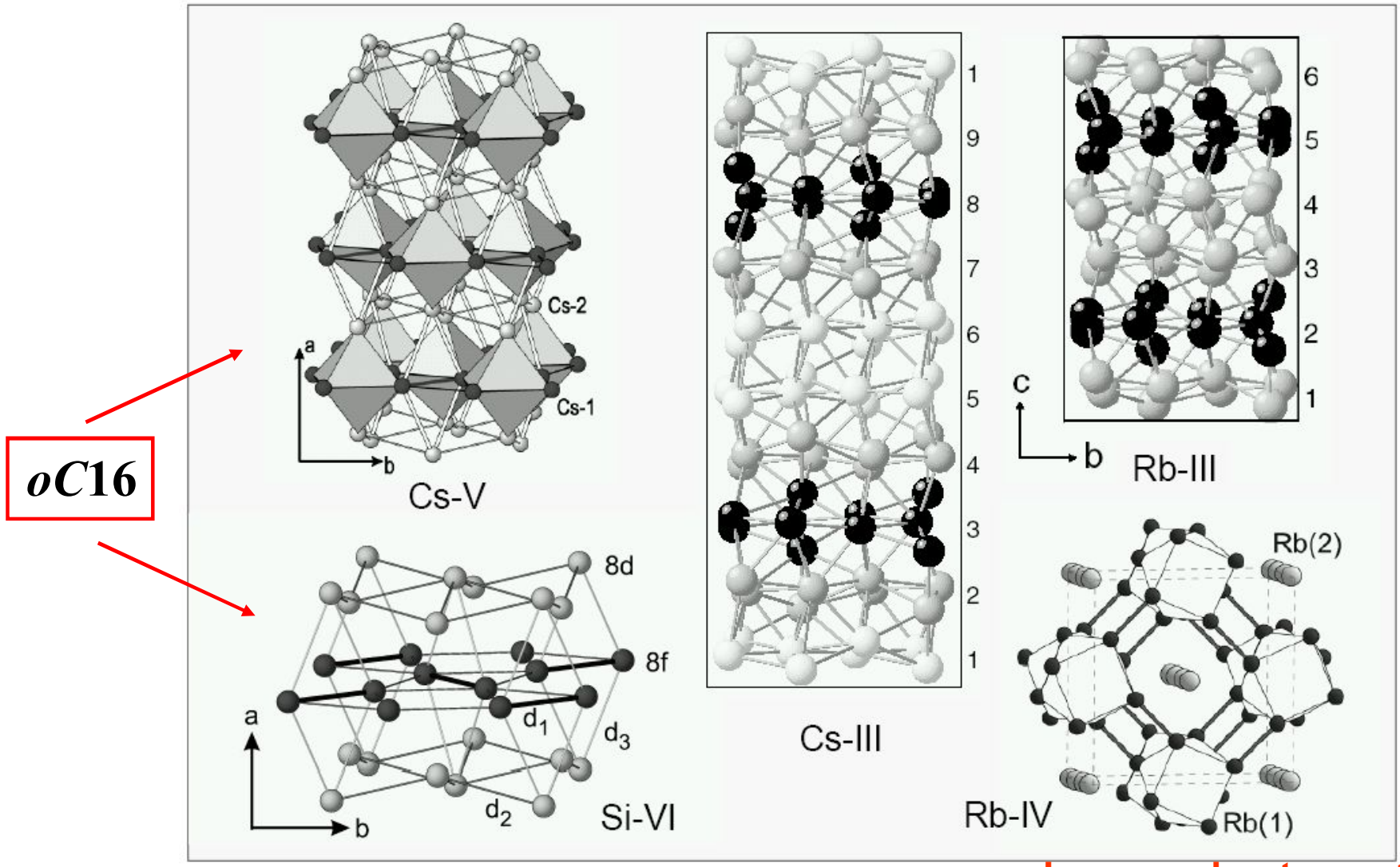
fcc Li becomes superconductive at $p > 20$ GPa. $T_c \sim 14$ K at 33 GPa

At $p \sim 80$ GPa, Li-7 becomes semiconducting with $E_g \sim 0.1$ eV

At $p \sim 200$ GPa, Na is in the semiconducting phase hP4 ($E_g \sim 2$eV)

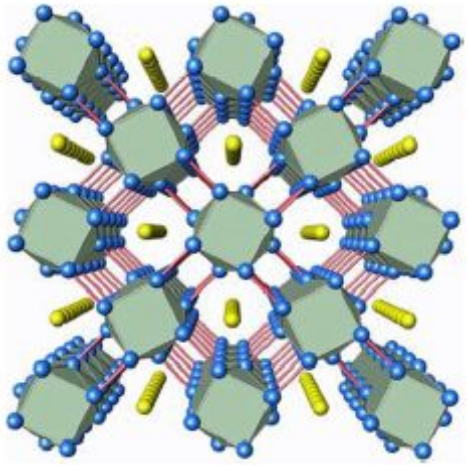
High pressure phases of alkali metals

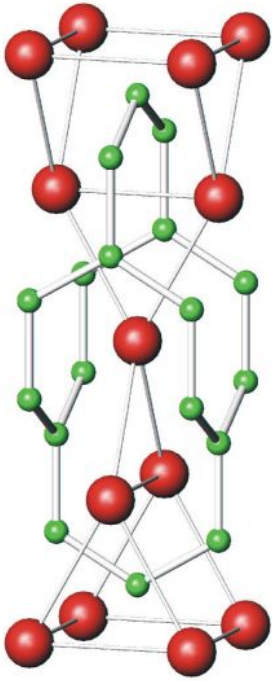
*oC*84 *oC*52



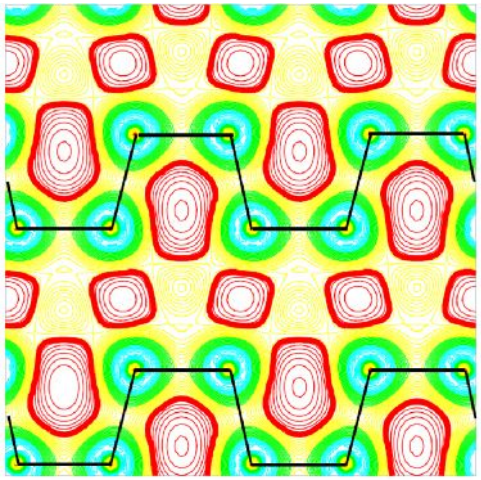
Incomm. host-guest

Incommensurate host-guest structure Rb-IV. Positions of host atoms (blue circles) correspond to the W-cation sublattice of W_5Si_3. Yellow circles are guest atoms





Cs-IV structure. Arrangement of Cs atoms (red circles) resembles the Th-cation sublattice of $ThSi_2$. **The electron clouds (green circles) 'imitate' absent Si anions**



Valence electron density in **Li-cI16**. Black lines connect the neighbor atoms. Red maxima in the interstitials **'mimic' absent As anions** in Yb_4As_3

$p - T$ phase diagrams: Quasiharmonic approach

$$E_{\text{tot}}\{n(\mathbf{r})\} = T_0\{n(\mathbf{r})\} + \frac{e^2}{2}\int \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' +$$

$T = 0$:

$$+ \int n(\mathbf{r})\, V_{\text{ext}}(\mathbf{r})\, d\mathbf{r} + E_{\text{xc}}\{n(\mathbf{r})\} + \frac{e^2}{2}\sum_{N,N'} \frac{Z_N Z_{N'}}{|\mathbf{R}_N - \mathbf{R}_{N'}|}$$

$$p(V) = -\frac{\partial E_{\text{tot}}}{\partial V} \qquad H = E_{\text{tot}} + pV$$

$0 < T < E_F$:

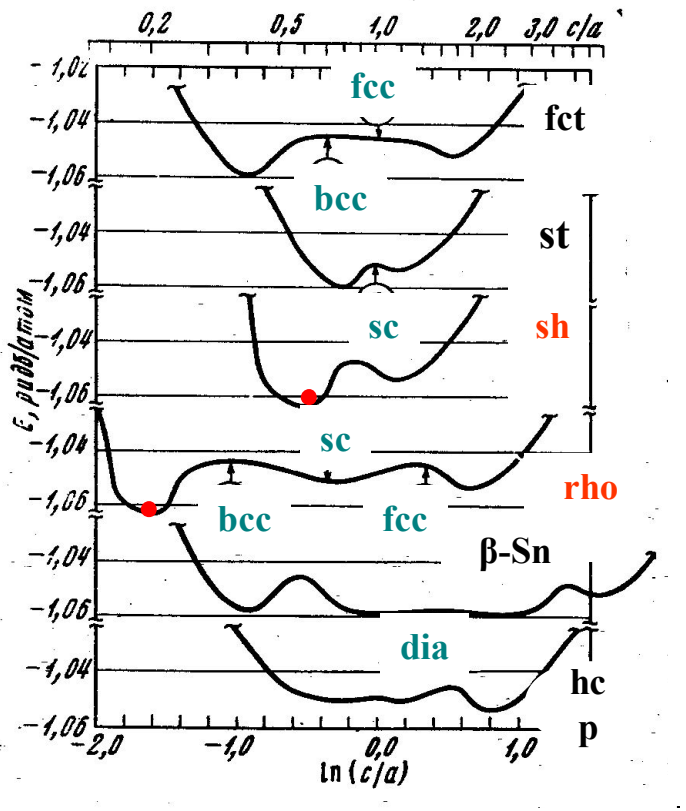
$$G = F + pV \qquad F = E_{\text{tot}}(V) + F_{\text{ph}}(V, T)$$

$$F(V,T) = E(V) + \frac{1}{2}\sum_{\mathbf{q},\lambda} \hbar\omega_{\mathbf{q}\lambda}(V) - k_B T \sum_{\mathbf{q},\lambda} \ln \frac{1}{1 - \exp(-\hbar\omega_{\mathbf{q}\lambda}(V)/k_B T)}$$

Metallic hydrogen [Brovman, Kagan & Holas *JETP* 1971]

$$E_{cr} = E_{el} + \frac{1}{2}\sum_{n,n'}\frac{e^2}{|\mathbf{R}_n - \mathbf{R}_{n'}|} + E_{ZPM} \qquad E_{ZPM} = \frac{1}{2}\sum_{\mathbf{q},\lambda}\hbar\omega_{\mathbf{q}\lambda}$$

Electron energy $E_{el} = E^{(0)} + E^{(2)} + E^{(3)} + E^{(4)} + \ldots$ is expanded as a series in the electron-proton coupling V_G/E_F, where $V_G = \dfrac{4\pi e^2}{G^2\Omega_{at}}$



sh, rho + 5 triclinic structures

– All cubic structures are not favored energetically

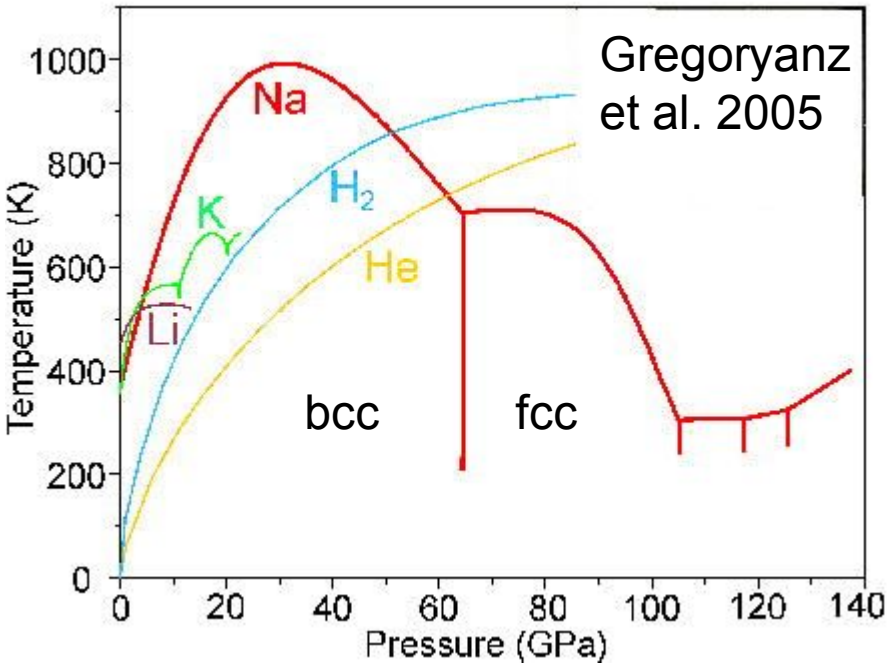
– fcc, bcc, and hcp structures are dynamically unstable up to ~ 20 Mbar ($r_s \sim 1.2$)

– Min. sh + min. rho + 5 triclinic structures form a unified family of structures

– At $1 \le r_s \le 1.65$, or 1 - 100 Mbar, highly anisotropic (chain-like and layered) structures are energetically favorable

EG Maksimov & DY Savrasov
***Solid State Commun.* 2001**
T_c = 600 K

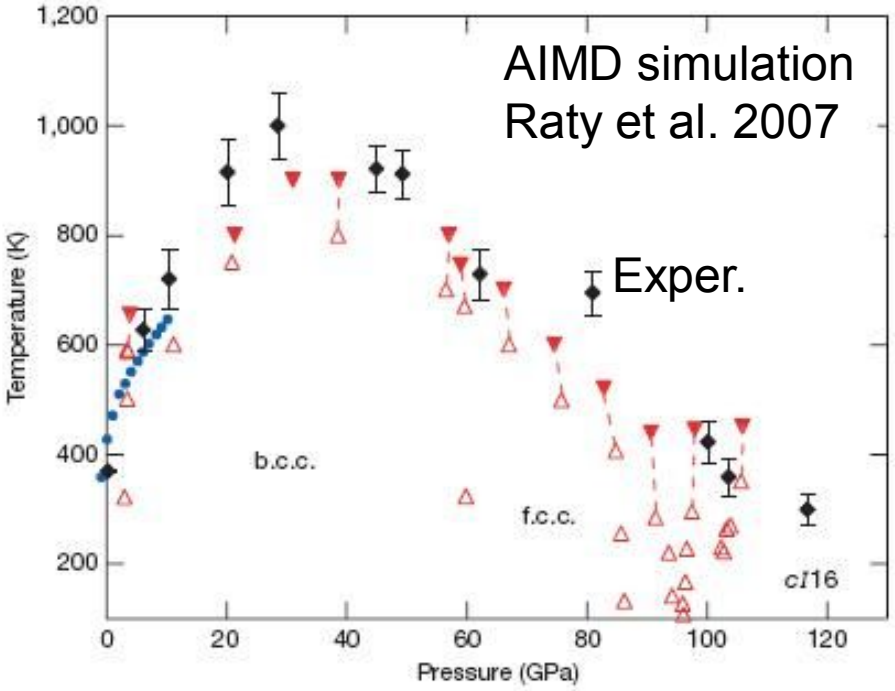
Anomalous melting of Na

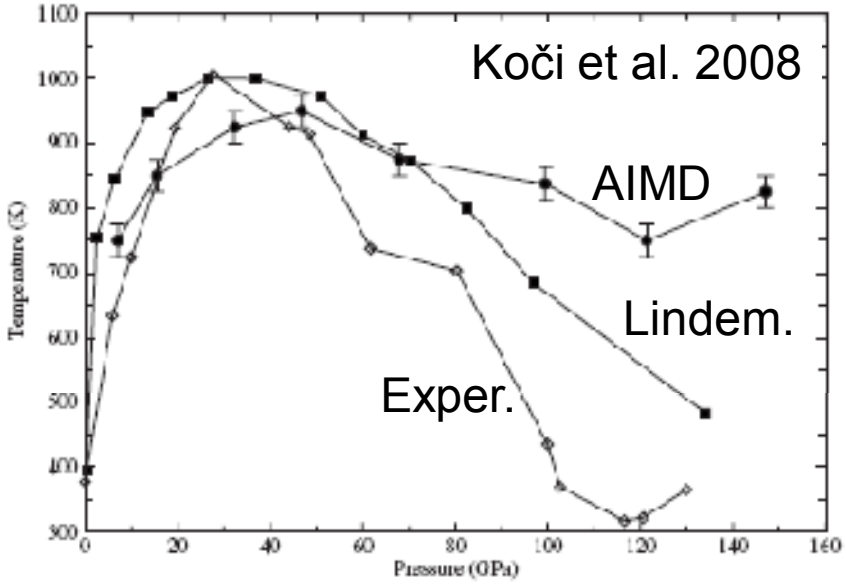


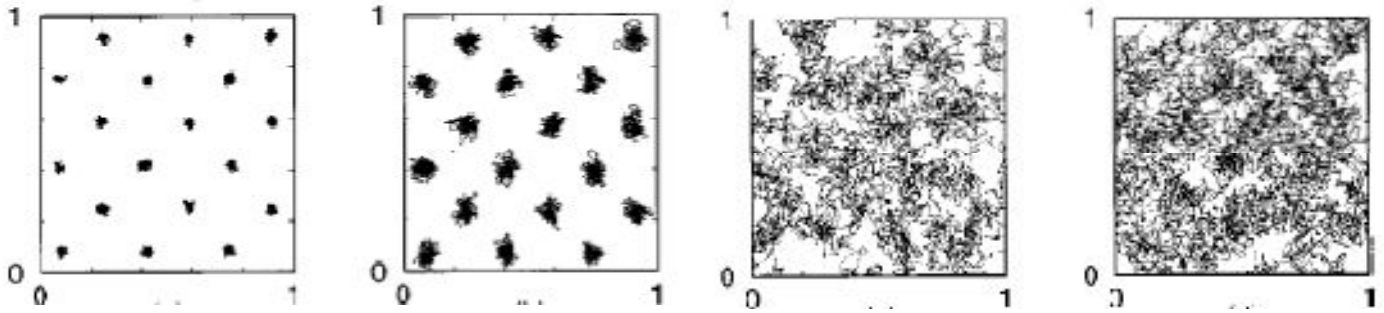
Clausius–Clapeyron equation

$$\frac{\mathrm{d}T_\mathrm{m}}{\mathrm{d}p} = \frac{\Delta V}{\Delta S}$$

Melting of Na: *ab initio* simulations





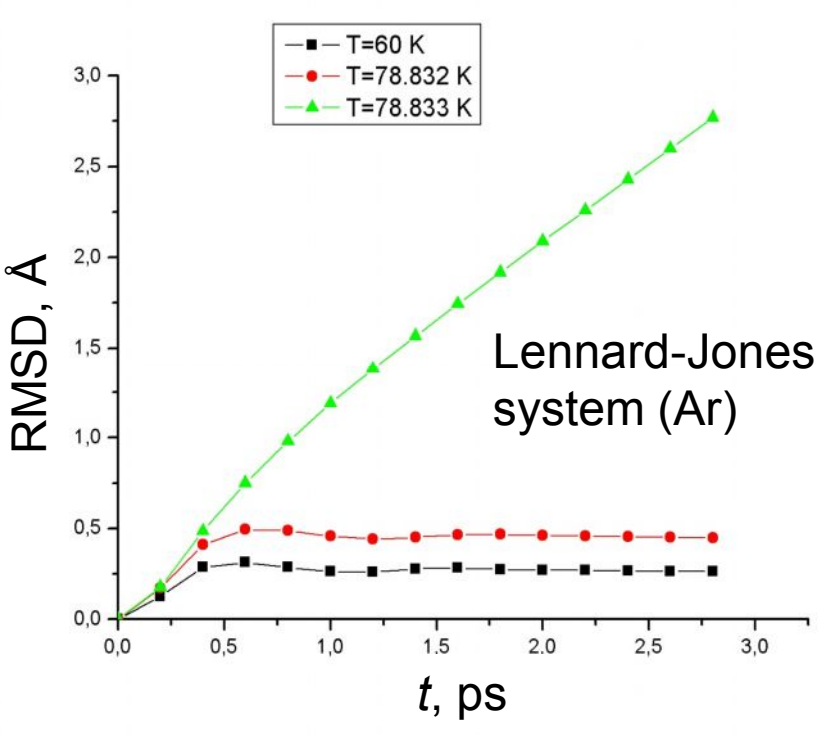


Atomic displacements as a function of temperature

Lindemann's criterion: $\sqrt{\langle u^2(T_m)\rangle} = Ld_{NN}$

where $\langle u^2(T)\rangle = \frac{\hbar}{2MN}\sum_{\mathbf{q},\lambda}\frac{\coth\left(\hbar\omega_{\mathbf{q}\lambda}/2k_BT\right)}{\omega_{\mathbf{q}\lambda}}$

$$g(\omega) = \frac{1}{N}\sum_{\mathbf{q},\lambda}\delta\left(\omega-\omega_{\mathbf{q}\lambda}\right) \qquad \langle u^2(T)\rangle = \frac{\hbar}{2M}\int_0^\infty \frac{d\omega}{\omega}g(\omega)\coth\frac{\hbar\omega}{2k_BT}$$



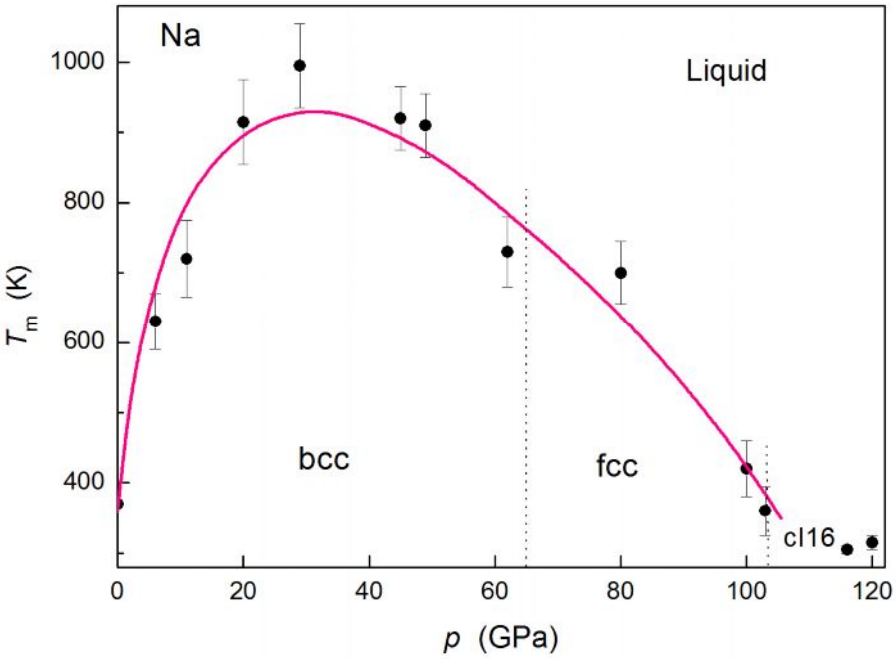
at high T

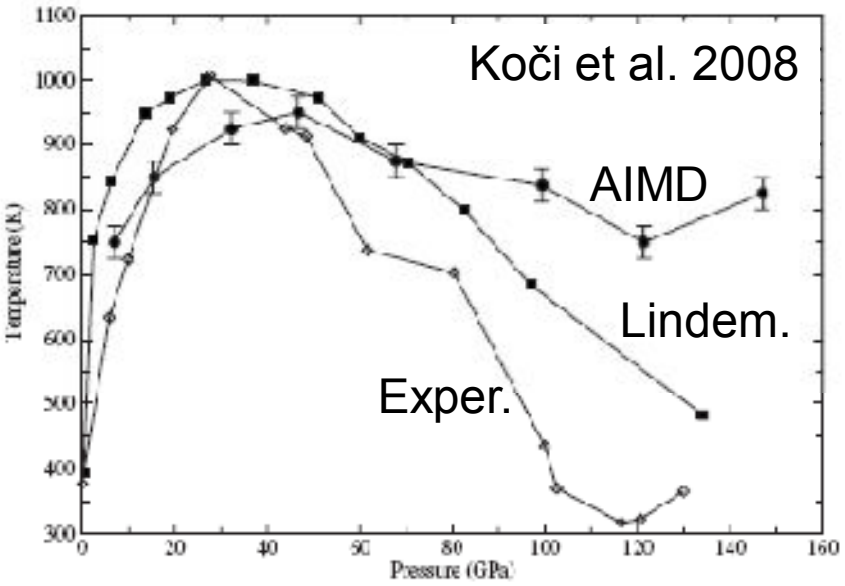
$$T_m = \frac{\left(Ld_{NN}\right)^2}{k_B}\frac{M}{\langle\omega^{-2}\rangle}$$

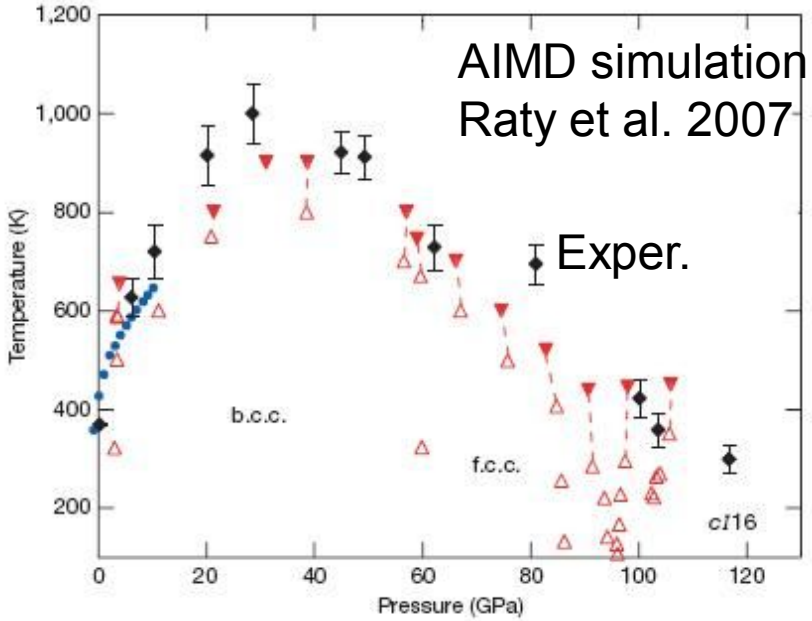
$$\langle\omega^{-2}\rangle = \int_0^\infty \frac{g(\omega)d\omega}{\omega^2}$$

Melting curve of Na

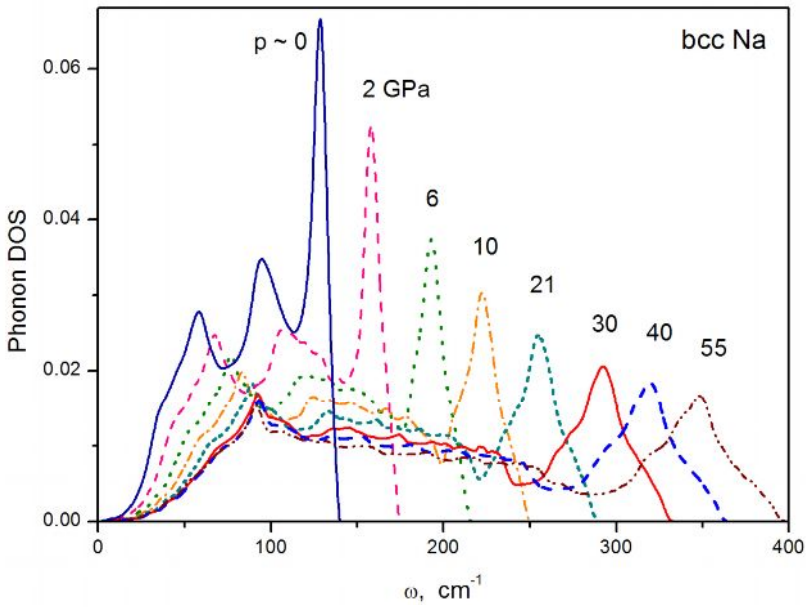
Lepeshkin et al. JETP Lett. 2009

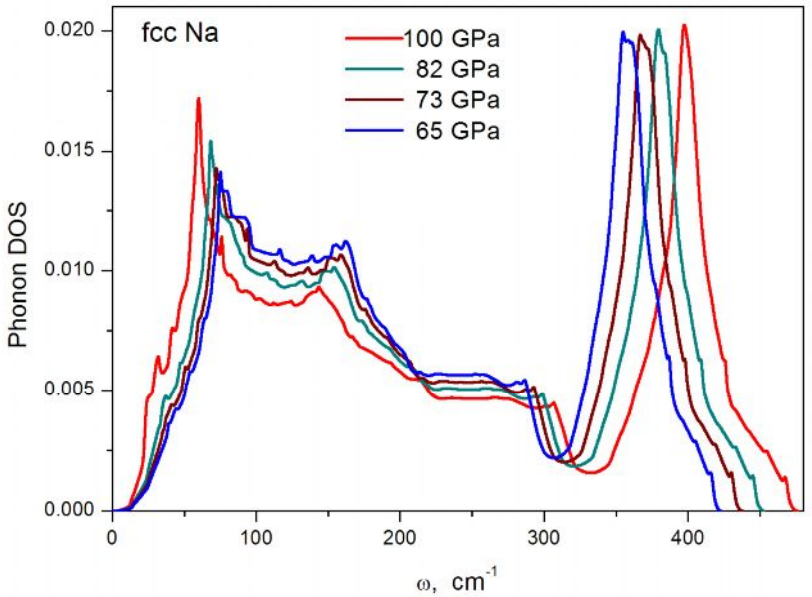


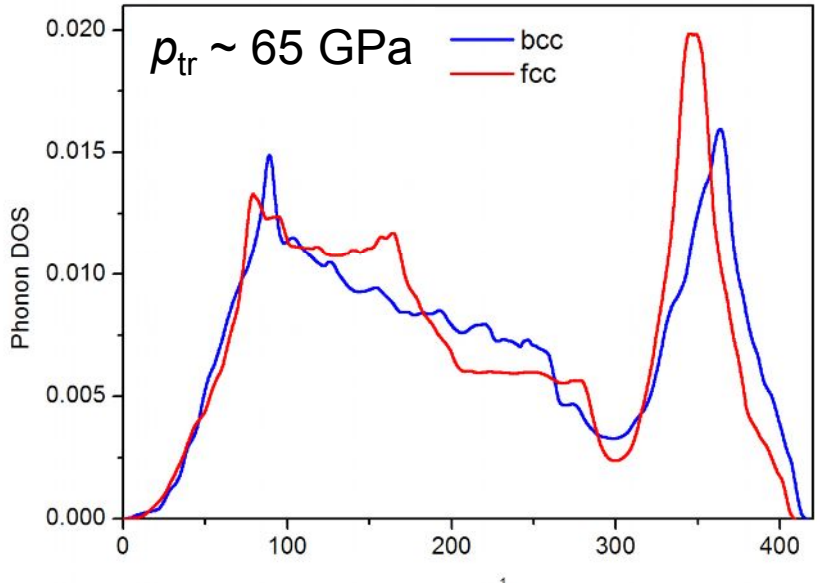


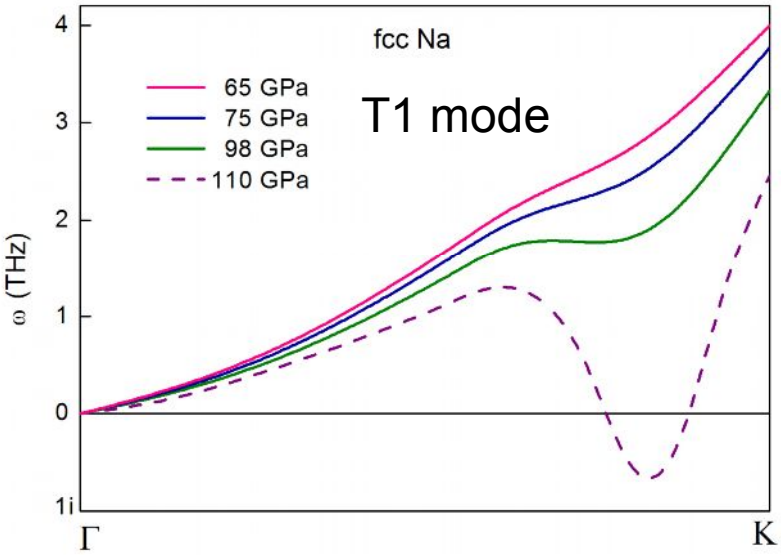


Na: phonon spectra at various pressures



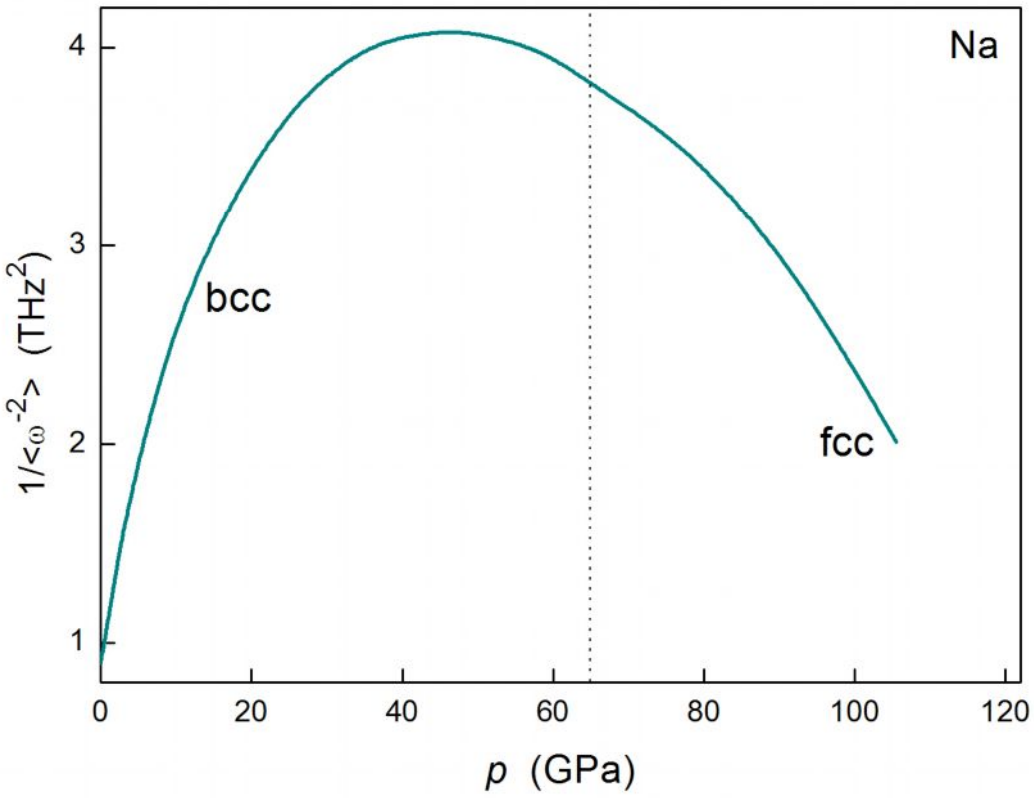






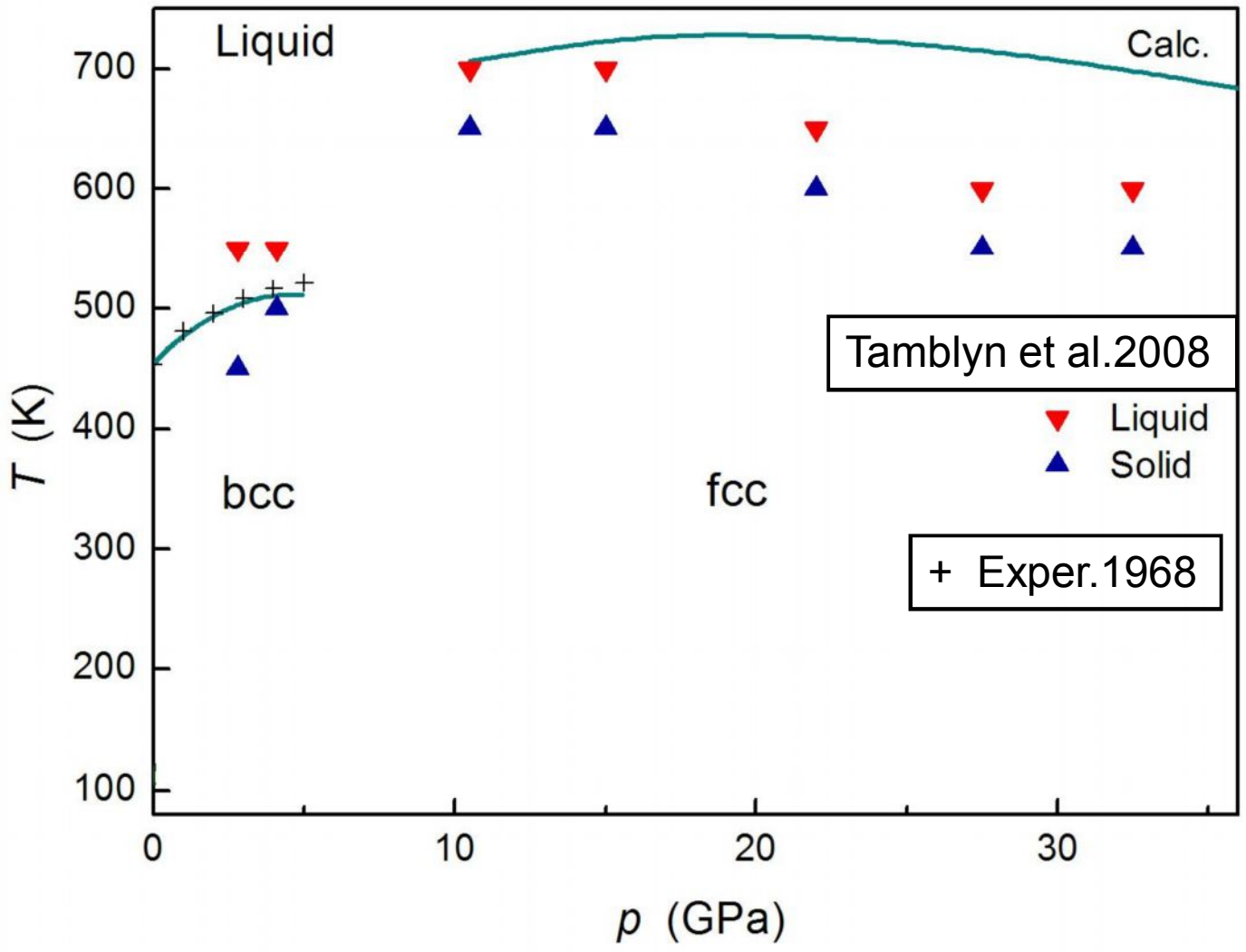
Characteristic frequency of Na

$$T_m \approx \frac{(L d_{\mathrm{NN}})^2}{k_{\mathrm{B}}} \frac{M}{\langle \omega^{-2} \rangle} \qquad \langle \omega^{-2} \rangle = \int_0^\infty \frac{g(\omega) d\omega}{\omega^2}$$

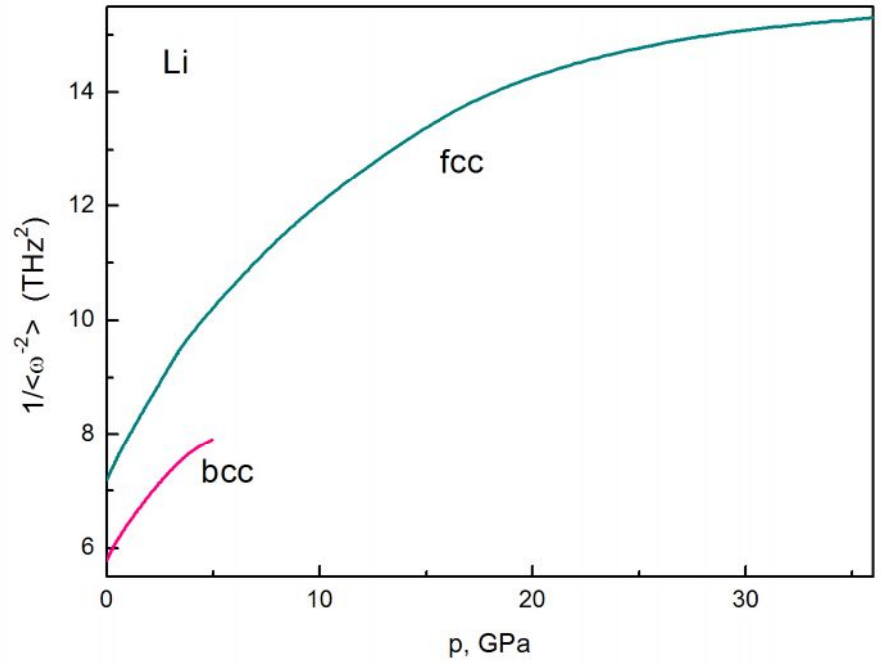


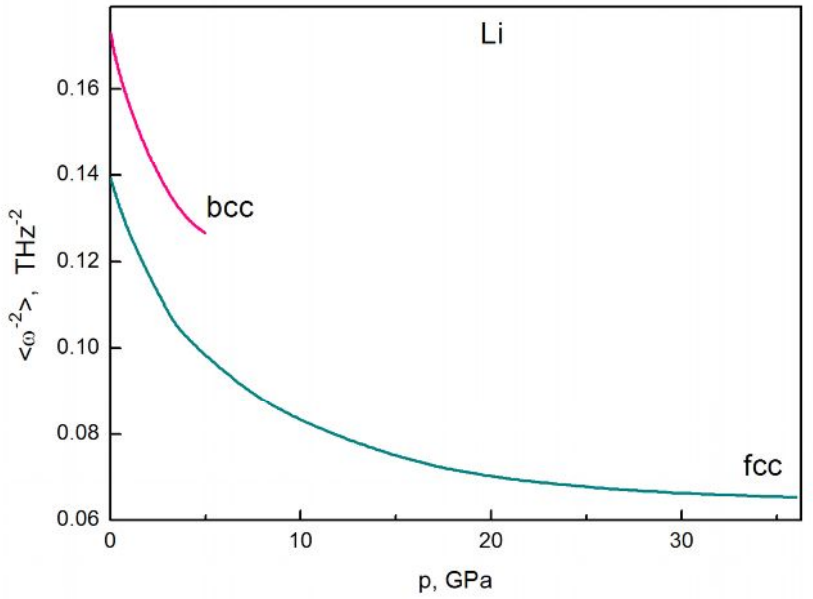
At p_{tr} = 65 GPa, $\langle \omega^{-2} \rangle_{bcc} = \langle \omega^{-2} \rangle_{fcc}$

Melting curve of Li [*Lepeshkin et al. JETP Lett. 2009*]



Lithium: Characteristic frequency $\langle\omega^{-2}\rangle$

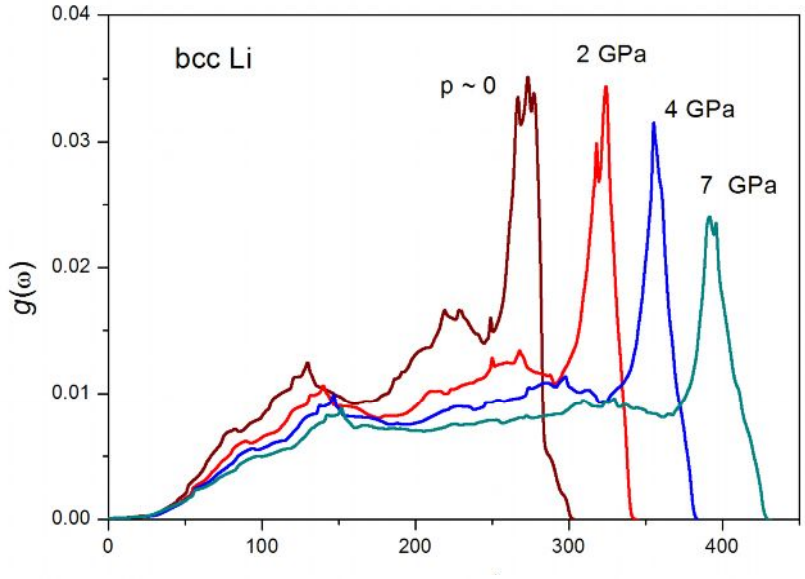


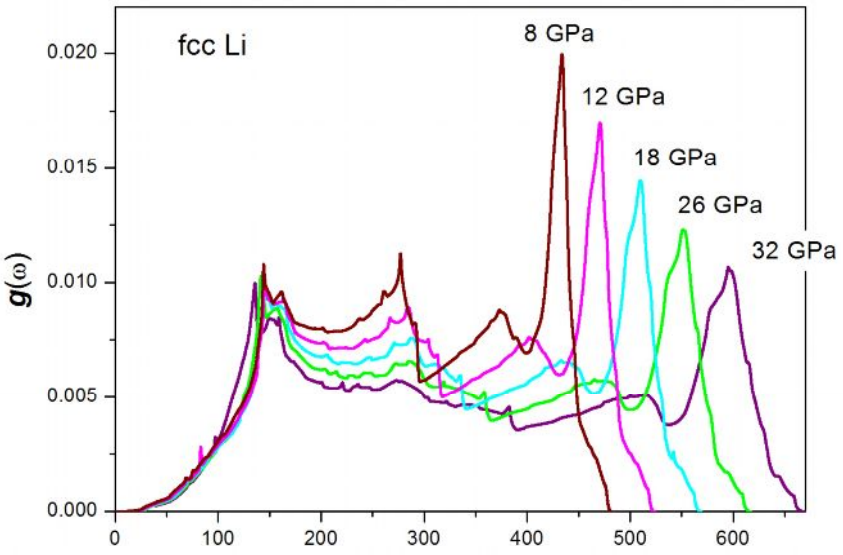


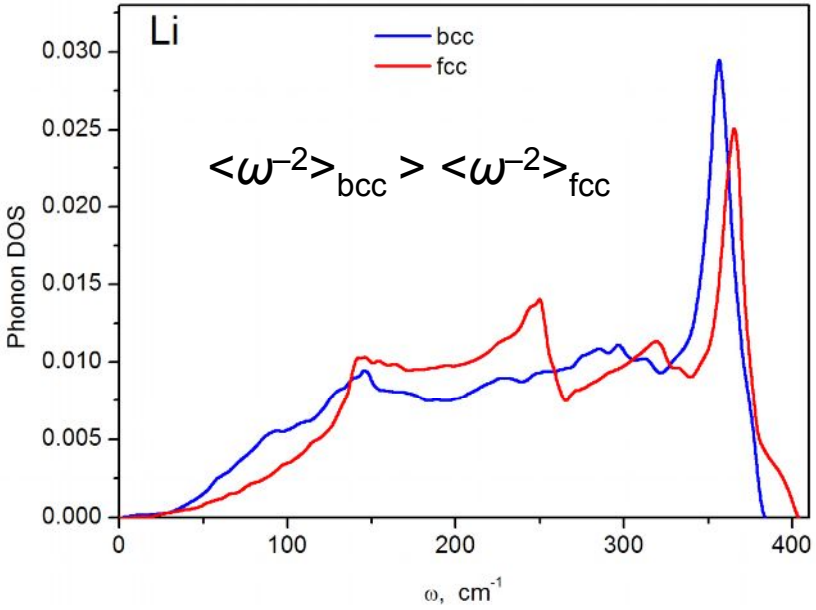
At any pressure, there is a jump in the characteristic frequency:

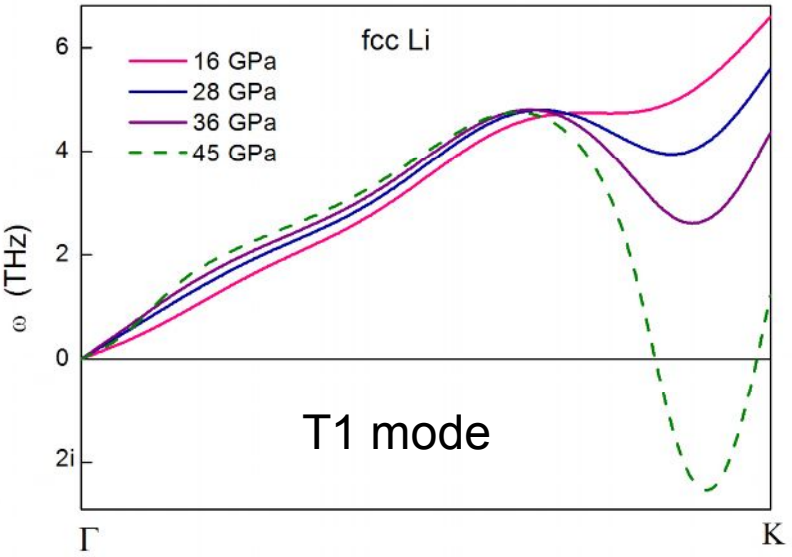
$$\frac{1}{\left\langle \omega^{-2} \right\rangle_{\text{bcc}}} < \frac{1}{\left\langle \omega^{-2} \right\rangle_{\text{fcc}}}$$

Phonon spectra of Li at various *p*

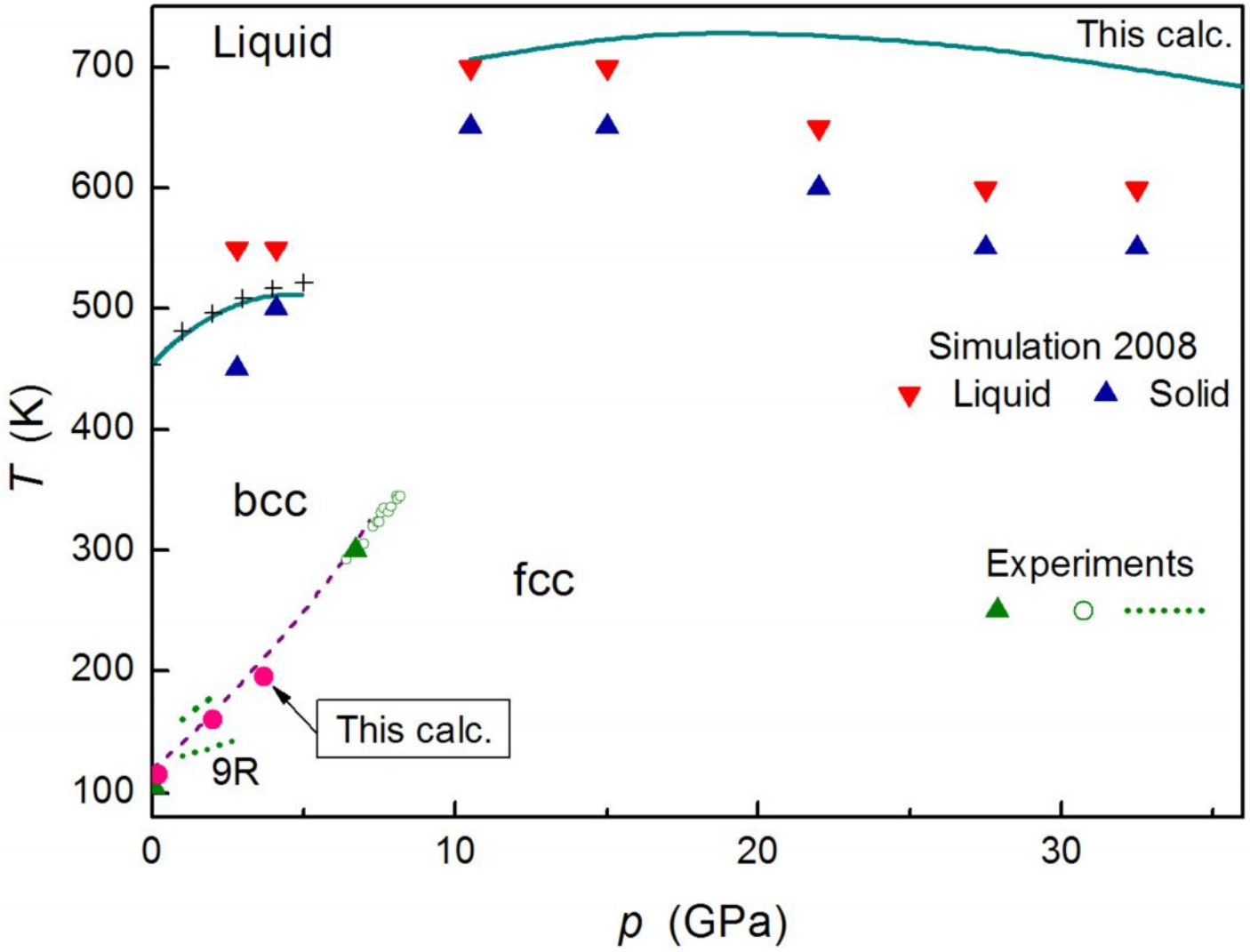




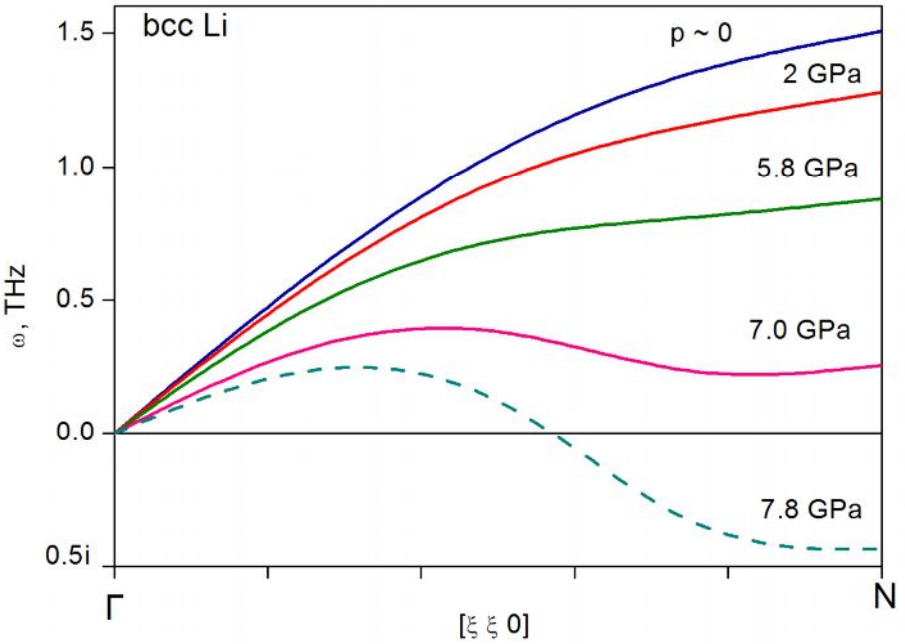


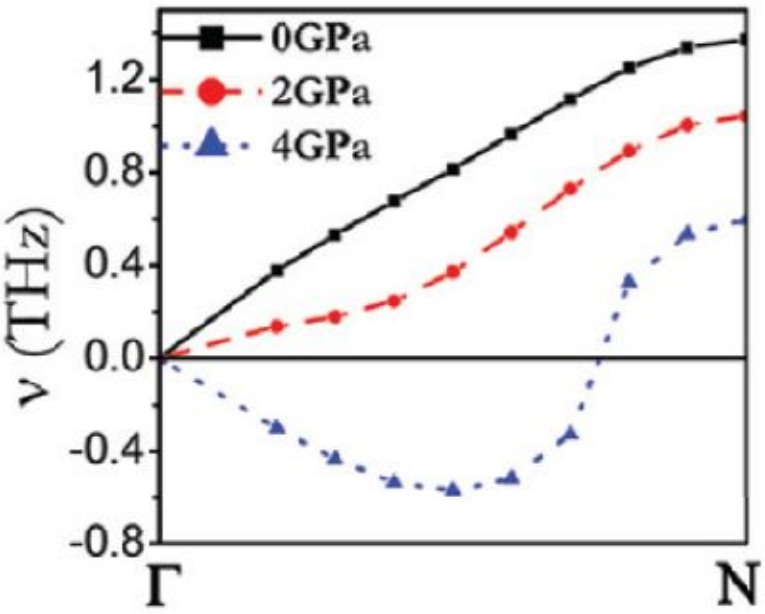


Phase diagram of Li



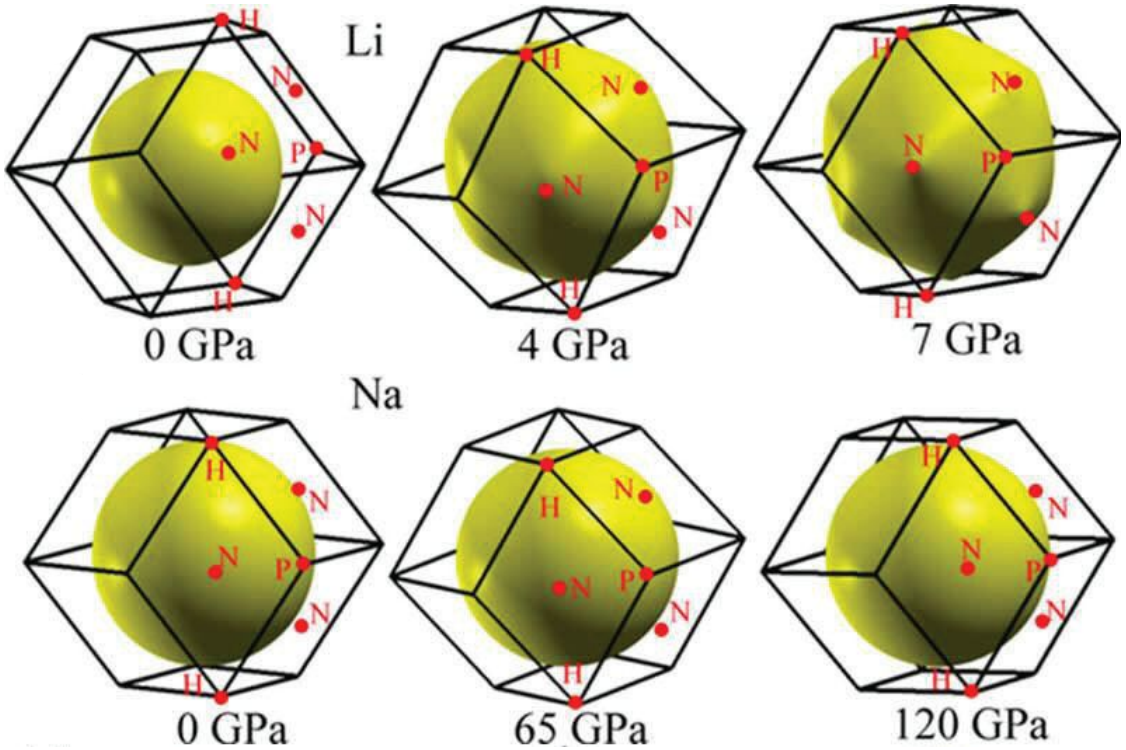
Phonon dispersions of bcc Li (transversal T1 mode)





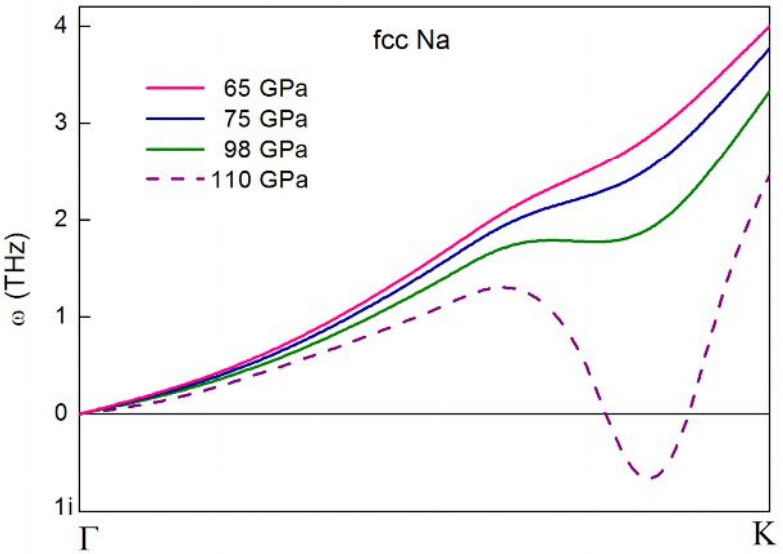
Xie et al. 2008

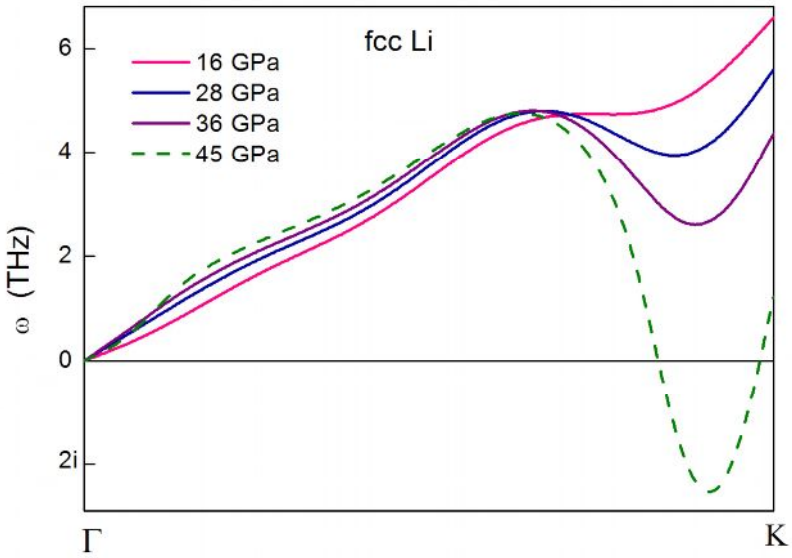
Fermi surfaces of bcc Li and Na at various pressures



Y. Xie et al. 2008

fcc Na and Li: dispersions of T1 mode at various *p*

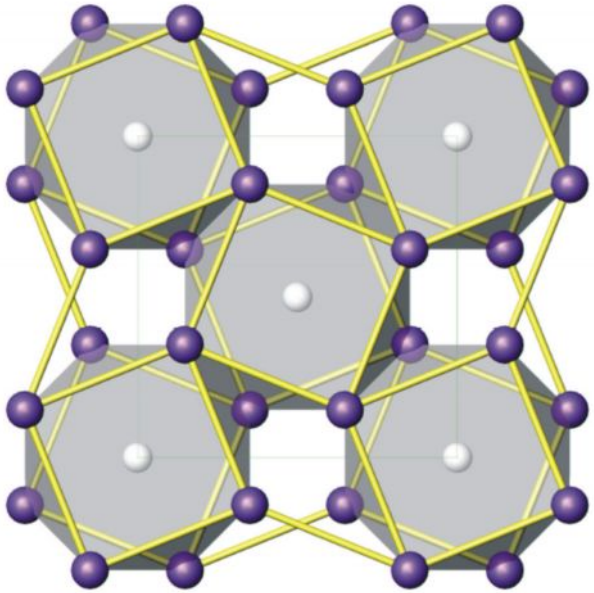




Phonon instabilities of different types

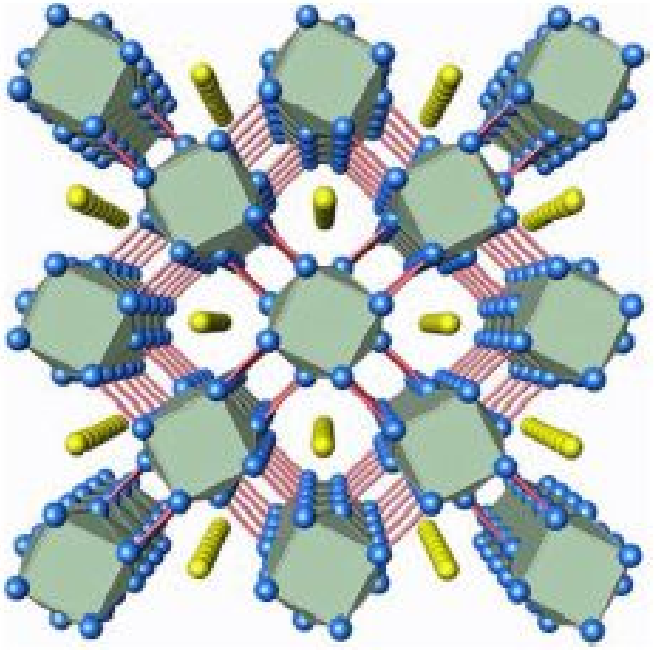
Conclusions

Composite (host-guest) structures

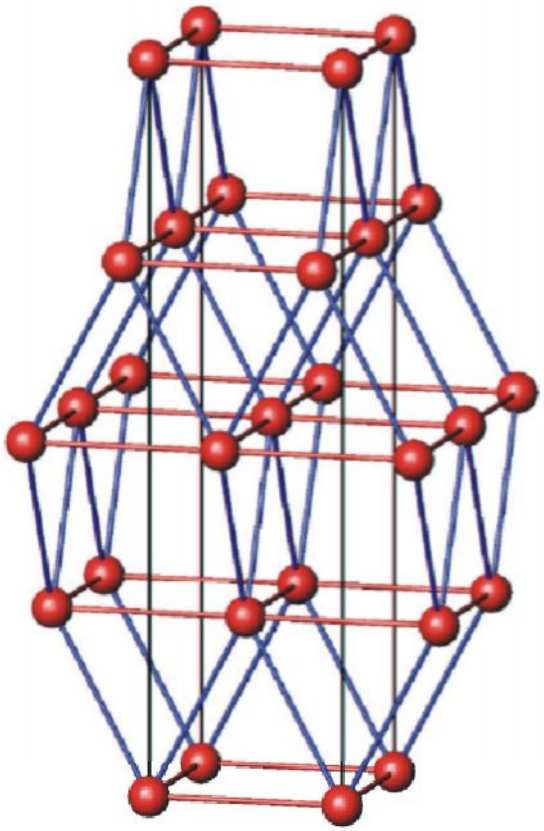


Incommensurate crystal structure of the Rb-IV phase. The arrangement of guest atoms is similar to the cation sublattice of W_5Si_3 structure. A similar structure was also found for K-III high-pressure phase. [*U. Schwarz et al. PRL 1999*]

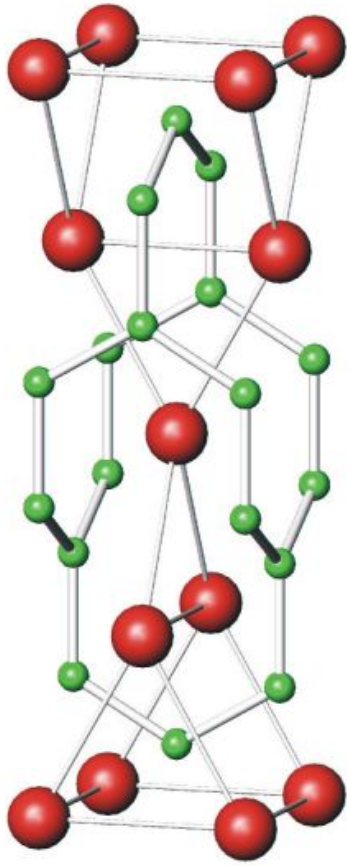
Crystal structure of the Ba-IV phase along the tetragonal *c*-axis. One set of Ba atoms forms a framework (*Z*=8) which is filled with ***incommensurate*** chains of a second set of Ba atoms. This type of structure was later found for Sr and group-V elements (As, Sb, Bi) [*R. Nelmes et al. PRL 1999*]



Cs-IV structure



The $ThSi_2$ structure. The cation (Th) sublattice resembles the arrangement of Cs atoms in the Cs-IV structure. The electrons in Cs-IV 'imitate' absent anions in the Si sites



The bct crystal structure of Cs-IV ($Z = 4$). The structure is made up of layers of collinear face-sharing trigonal prisms, the layers being stacked along the vertical *c*-axis.The prism orientation changes by 90° in subsequent layers
[*K. Takemura et al. PRL 1982*]