Physical features of multicomponent Coulomb crystals

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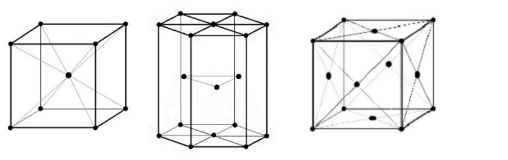
One component crystal: Z, M, with uniform electron background.

In their lowest energy state the nuclei form a body centred cubic lattice[7,8]

Ruderman M. (1968) "Crystallization and Torsional Oscillations of Superdense Stars"

but only three lattices was concerned:
BCC (body-centered cubic),
FCC (face-centered cubic),
HCP (hexagonal close packing)

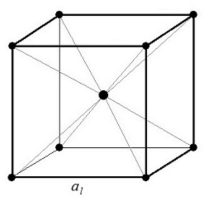


ζ — Madelung constant

$$U_{\rm M} = \sum_{i=1}^{N}\sum_{j=1}^{i-1}\frac{Z_iZ_je^2}{|\mathbf{R}_i-\mathbf{R}_j|} - n_e\sum_{i=1}^{N}Z_ie^2\int_V\frac{d\mathbf{r}}{|\mathbf{R}_i-\mathbf{r}|}+\frac{n_e^2}{2}\int_V\int_V\frac{e^2d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}$$

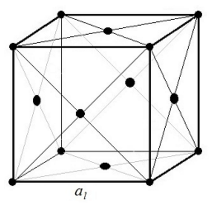
$$U_{\rm M} = N\frac{Z^2e^2}{a}\zeta, \qquad a \text{ is ion sphere radius}$$

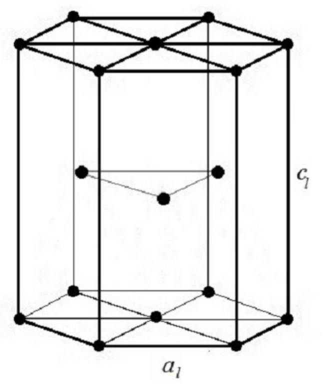
$$\zeta = \frac{a}{2N_{\rm cell}}\sum_{lpp'}(1-\delta_{pp'}\delta_{\mathbf{R}_l0})\frac{{\rm erfc}\,(AY_{lpp'})}{Y_{lpp'}} - \frac{Aa}{\sqrt{\pi}} - \frac{3}{8A^2a^2} + \frac{3}{2N_{\rm cell}^2a^2}\sum_{mpp'}(1-\delta_{\mathbf{G}_m0})\frac{1}{G_m^2}\exp\left[-\frac{G_m^2}{4A^2}+i\mathbf{G}_m(\boldsymbol{\chi}_p-\boldsymbol{\chi}_{p'})\right].$$



BCC lattice $\quad \zeta = -0.895929255682$

FCC lattice $\quad \zeta = -0.895873615195$





HCP lattice $\quad \zeta = -0.895838120459$

in the HCP lattice $h \equiv c_l/a_l = \sqrt{8/3} \approx 1.6329932$
but it comes from the "sphere packing problem" and
it is not absolutely appropriate for Coulomb crystals and
for terrestrial crystals (in Cd $h \approx 1.886$; in Be $h \approx 1.568$)
$\Rightarrow$ in the HCP lattice ζ is minimal if $h \approx 1.6356394$
$\zeta(h_{\rm min}) = -0.895838451203$

Orthogonal lattices

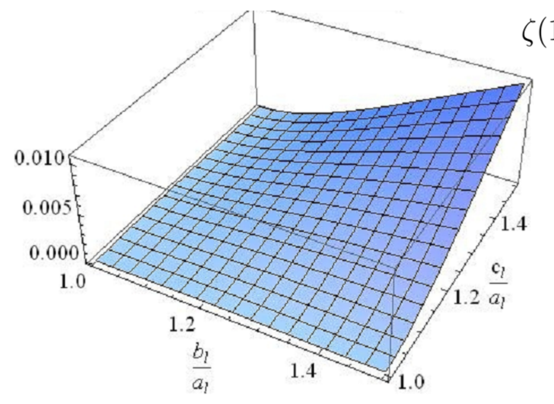
$\zeta \Rightarrow \zeta(b_l/a_l; c_l/a_l)$

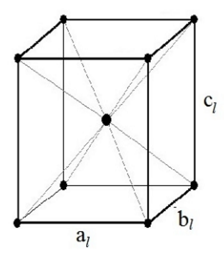
BCO (body-centered orthogonal)

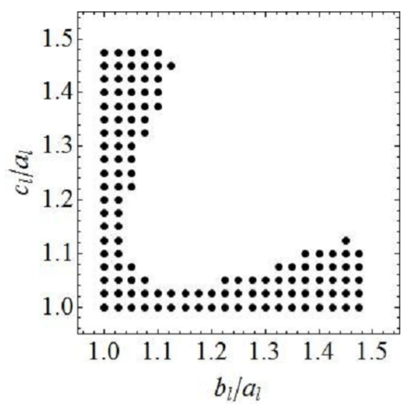
$\Delta\zeta = \zeta(b_l/a_l, c_l/a_l) - \zeta(1,1)$

$\zeta(1,1) = -0.895929255682$

$\zeta(1,\sqrt{2}) = \zeta(\sqrt{2},1) = \zeta_{\rm FCC}$

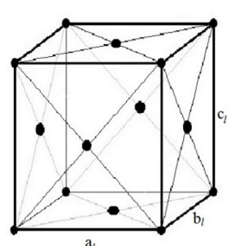






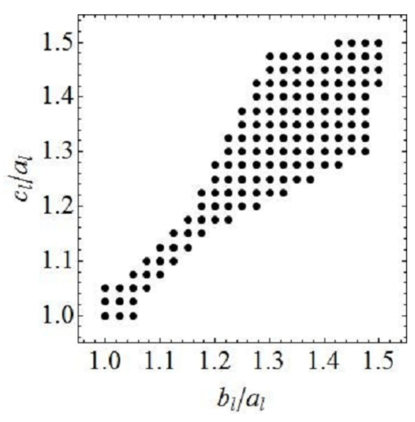
lattice should be stable $\Rightarrow \omega_i(\mathbf{k}) > 0 \Rightarrow$
set of values b_l/a_l and c_l/a_l
for which the BCO lattice is stable

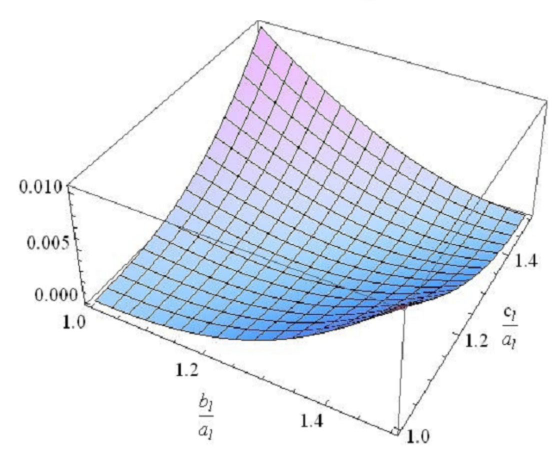
FCO (face-centered orthogonal)



$\zeta(1,1) = -0.895873615195 \qquad \zeta(\sqrt{2},\sqrt{2}) = \zeta_{\rm BCC}$

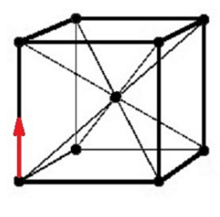
stability zone for the FCO lattice





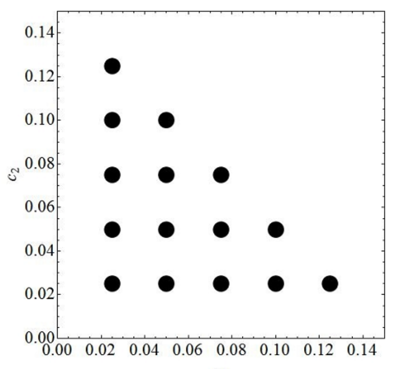
for any b_l/a_l and c_l/a_l
the Madelung constant of the BCC lattice is smaller
than the Madelung constant of BCO and FCO lattices

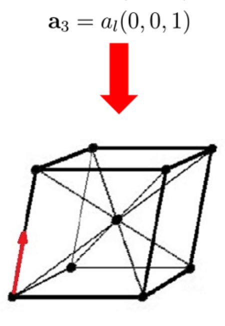
Tilted BCC lattice



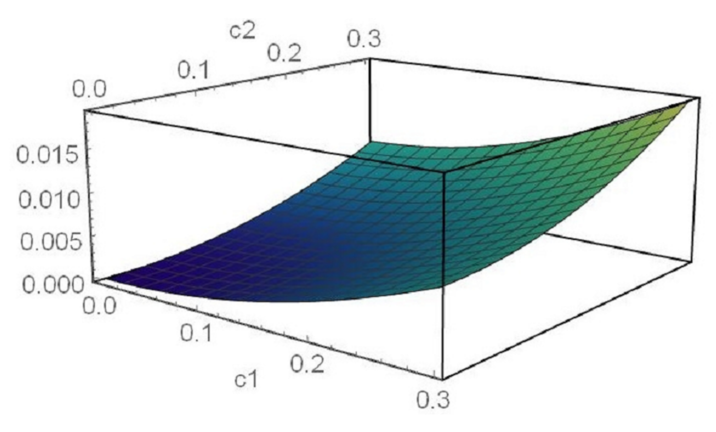
$\mathbf{a}_1 = a_l(1,0,0)$
$\mathbf{a}_2 = a_l(0,1,0)$
$\mathbf{a}_3 = a_l(0,0,1)$

$\zeta \Rightarrow \zeta(c_1,c_2)$
$\zeta(c_1,c_2) > \zeta(1,1) \quad \forall c_1, c_2$



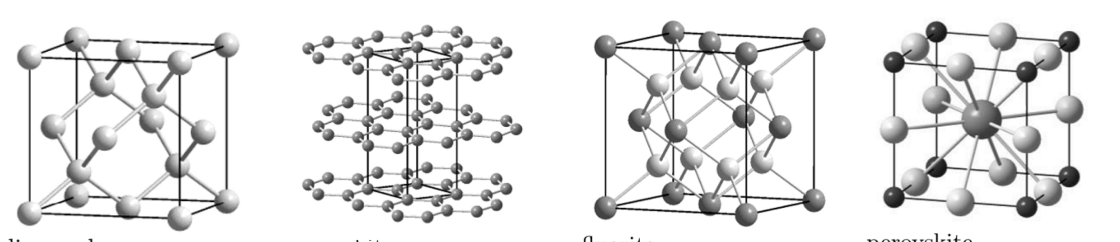


$\mathbf{a}_1 = a_l(1,0,0)$
$\mathbf{a}_2 = a_l(0,1,0)$
$\mathbf{a}_3 = a_l(c_1,c_2,c_3)$
$c_3 = \sqrt{1-c_1^2-c_2^2}$



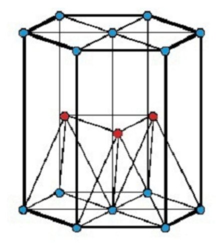
Other one component lattices

simple cubic lattice or SC (not stable) $\zeta = -0.88005944211$
hexagonal lattice or H (not stable): $\zeta(h)$, h the same as in the HCP lattice
$\zeta(0.928) = -0.887321284742$ — minimum and $\zeta(\sqrt{8/3}) = -0.77943336427$



diamond $\zeta = -0.83542570276483$; graphite $\zeta = -0.840878927$; fluorite $\zeta = -0.86445318436682$; perovskite $\zeta = -0.8473240413727$

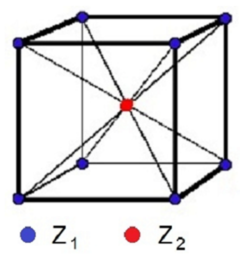
Multi component crystal: Z_i, M_i, with uniform electron background.



$$U_{\rm M} = N\frac{e^2}{a}\tilde\zeta,$$
$$\tilde\zeta = \frac{a}{2N_{\rm cell}}\sum_{lpp'}Z_pZ_{p'}(1-\delta_{pp'}\delta_{\mathbf{R}_l0})\frac{{\rm erfc}\,(AY_l)}{Y_l} - \frac{Aa}{N_{\rm cell}\sqrt{\pi}}\sum_p Z_p^2 - \frac{3}{8N_{\rm cell}^2A^2a^2}\sum_{pp'}Z_pZ_{p'} + \frac{3}{2N_{\rm cell}^2a^2}\sum_{mpp'}Z_pZ_{p'}(1-\delta_{\mathbf{G}_m0})\frac{1}{G_m^2}\exp\left[-\frac{G_m^2}{4A^2}+i\mathbf{G}_m(\boldsymbol{\chi}_p-\boldsymbol{\chi}_{p'})\right].$$

$N_1 = N_2$ concentrations of different types of ions are equal

Binary BCC and HCP (with $h = \sqrt{8/3}$) lattices



$$U_{\rm M} = N\frac{Z_1^2e^2}{a}\left[\frac{1+\alpha^2}{2^{4/3}}\zeta_1 + \alpha\left(\zeta_2 - \frac{\zeta_1}{2^{1/3}}\right)\right], \qquad \alpha \equiv Z_2/Z_1$$

ζ_1 — Madelung constant of one component crystal (BCC or HCP)
ζ_2 — Madelung constant of crystal with $Z_2 = 0$ (SC or H)

Binary BCC lattice is stable if $1/3.6 \le \alpha \le 3.6$
Binary HCP lattice is stable if $0.8 \le \alpha \le 1.25$

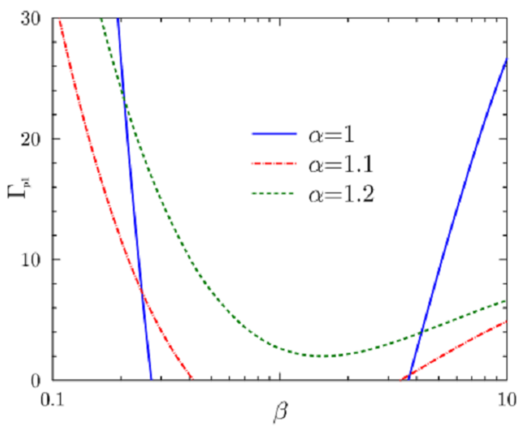
Zero-point ion vibrations $u_1(\alpha,\beta)$

BCC and HCP lattices (with Z_1, M_1 and Z_2, M_2)

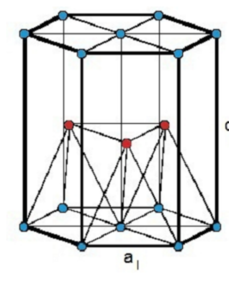
$$\frac{F_0}{NT_{\rm p1}} = \Gamma_{\rm p1}\left(\frac{2}{1+\beta}\right)^{1/3}\zeta(\alpha) + 1.5\sqrt{\frac{(1+\alpha)(\alpha+\beta)}{2\beta(1+\beta)}}u_1(\alpha,\beta)$$

$\beta \equiv M_2/M_1$ $\Gamma_{\rm p1} \equiv Z_1^2e^2/(a_1T_{\rm p1})$, $T_{\rm p1} \equiv \hbar\omega_{\rm p1}$,
$a_1 \equiv (4\pi n_1/3)^{-1/3}$, $\omega_{\rm p1} = \sqrt{4\pi n_1Z_1^2e^2/M_1}$ and $n_1 = \rho/M_1$

Difference between BCC and HCP lattices depends on $\Gamma_{\rm p1}$, α and β. For parameters lying above lines F_0 of the BCC lattice is smaller than F_0 of the HCP lattice, for parameters lying below — bigger.



Binary HCP lattice with arbitrary $h \equiv c_l/a_l \in (1.1; 1.8)$



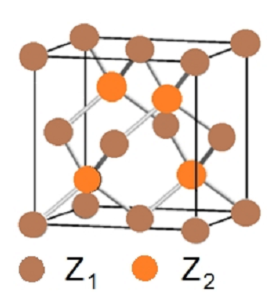
$$U_{\rm M} = \zeta\frac{Z_1^2e^2}{a} = \left[K_1(h)(Z_1^2+Z_2^2) + K_2(h)Z_1Z_2\right]\frac{e^2}{a}$$

$K_1(h) = -0.16189364 - 0.55794127h + 0.59395608h^2 - 0.30110564h^3 + 0.08557277h^4 - 0.01011867h^5$
$K_2(h) = -0.51157571 + 1.07142579h - 1.17187583h^2 + 0.56326835h^3 - 0.14312075h^4 + 0.0150406h^5$

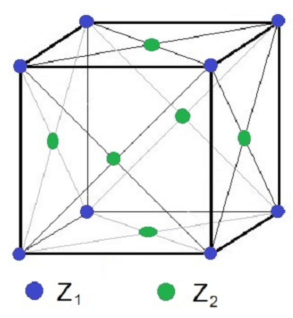
At $\alpha = 1.2$ Madelung energy is minimal if $h_{\rm min} \approx 1.6$ and it is equal -1.08744

Binary diamond

$$U_{\rm M} = -\left[0.3555276797978(Z_1^2+Z_2^2) + 0.124370343169Z_1Z_2\right]\frac{e^2}{a}$$

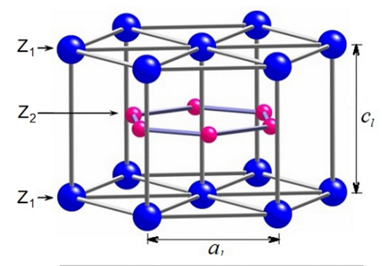


Binary FCC lattice; $N_2 = 3N_1$



$$U_{\rm M} = \zeta\frac{Z_1^2e^2}{a}(0.138600677 + 0.1707354535\alpha + 0.5865374846\alpha^2)$$

Binary FCC lattice is stable at $0.66 \le \alpha \le 1.38$



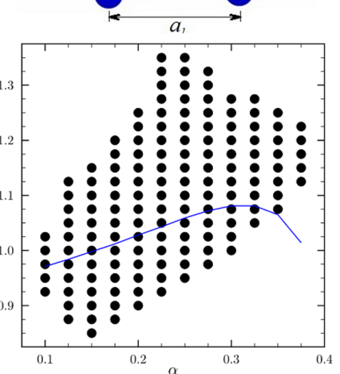
Binary MgB_2 lattice

with arbitrary $h \equiv c_l/a_l \in (0.5; 1.85)$; $N_2 = 2N_1$

$$U_{\rm M} = \frac{Z_1^2e^2}{a}\zeta(h,\alpha) = \frac{Z_1^2e^2}{a}\left(C_1(h) + C_2(h)\alpha + C_3(h)\alpha^2\right)$$

$C_1(h) \approx 0.383321 - 3.09006h + 7.21763h^2 - 9.63175h^3 + 7.80169h^4 - 3.7803h^5 + 1.00879h^6 - 0.114044h^7$
$C_2(h) \approx -0.6779 + 1.87234h - 3.26584h^2 + 3.70539h^3 - 2.97767h^4 + 1.5165h^5 - 0.430256h^6 + 0.0514738h^7$
$C_3(h) \approx 0.381939 - 4.85327h + 11.5234h^2 - 15.4381h^3 + 12.646h^4 - 6.19333h^5 + 1.66776h^6 - 0.189958h^7$

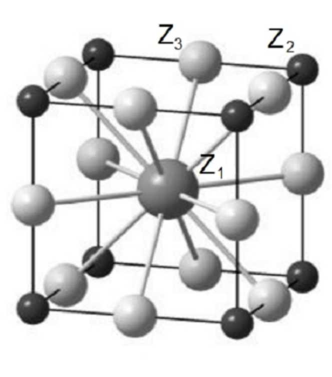
stability region of the MgB_2 lattice and dependence $h(\alpha)$ at which $U_{\rm M}$ is minimal $\Longrightarrow$



Three component perovskite lattice

$$N_3 = 3N_2 = 3N_1$$

$$U_{\rm M} = e^2(-0.102932376777(Z_1^2+Z_2^2) - 0.058185774325Z_1Z_2 - 0.126797403936Z_1Z_3 - 0.020881575292Z_2Z_3 - 0.435594534266Z_3^2)/a$$



If $5/18 \le \alpha \le 3.6$ binary BCC lattice has minimal $U_{\rm M}$
If $0.1 \le \alpha \le 5/18$ ions could form binary MgB_2 lattice

One component crystal: Z, M, with polarized electron background

BCC, FCC and HCP lattices

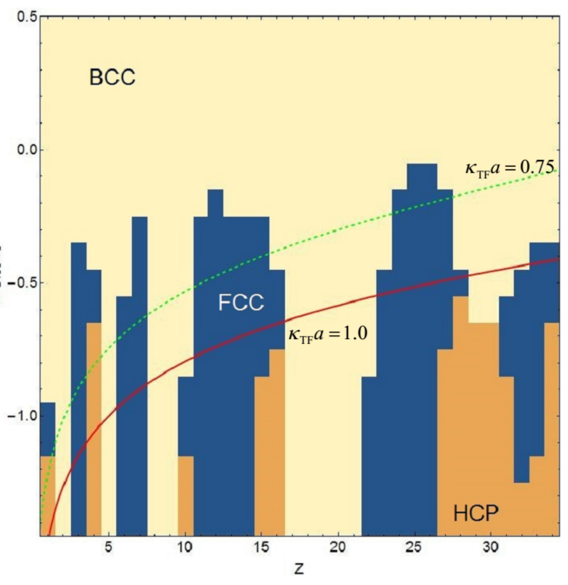
Jancovici approach $\Rightarrow$ linear response $\kappa_{\rm TF}a < 1$

$$\zeta \quad\Rightarrow\quad \zeta + \eta_J(\kappa_{\rm TF}a)^2$$

$\kappa_{\rm TF} \equiv (4\pi e^2\partial n_e/\partial\mu_e)^{1/2}$
η_J depends on $x_r \equiv p_{\rm F}/(m_ec)$ and $\kappa_{\rm TF}a$

At $x_{\rm r} > 1$ electrostatic energy of the BCC lattice is smaller than electrostatic energy of other lattices. At smaller $x_{\rm r}$ variants are possible.

The diagram shows which lattice (BCC, FCC or HCP) has the lowest electrostatic energy at fixed $\lg x_r$ and Z.

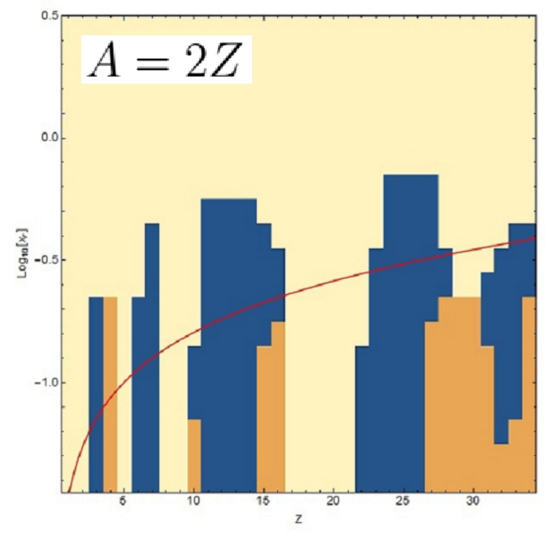


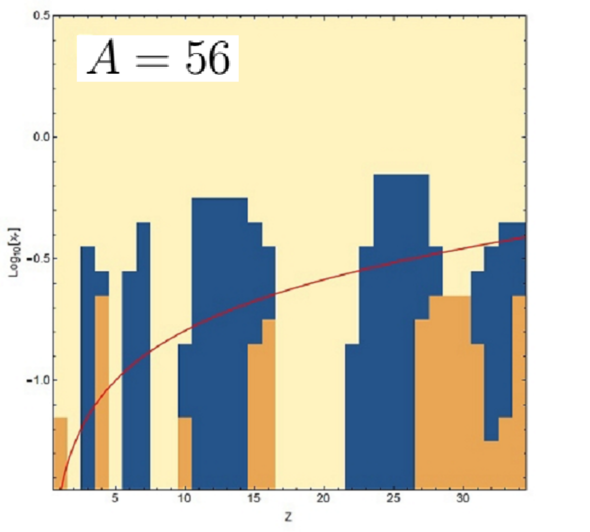
Zero-point ion vibrations $u_1(\kappa_{\rm TF}a)$

Tomac-Fermi approach $\epsilon(q) = 1 + \kappa_{\rm TF}^2/q^2$

$$\frac{F_0}{NT_{\rm p}} = \Gamma_{\rm p}\left(\zeta + \eta_J(\kappa_{\rm TF}a)^2\right) + 1.5u_1$$

$\Gamma_{\rm p} \equiv Z^2e^2/(aT_{\rm p})$, $T_{\rm p} \equiv \hbar\omega_{\rm p}$, $\omega_{\rm p} = \sqrt{4\pi nZ^2e^2/M}$

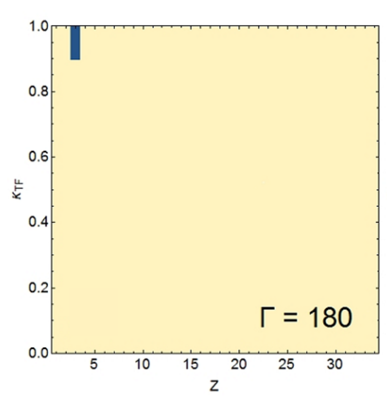


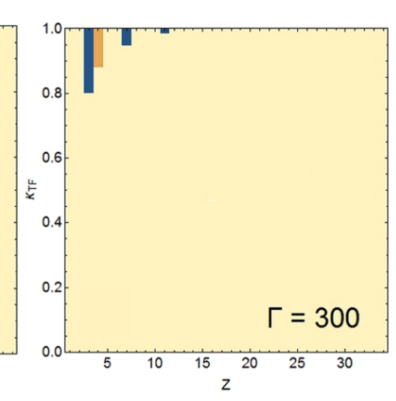


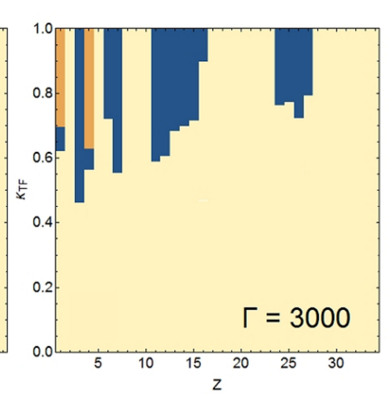
At high temperatures

$$\frac{F^{\rm tot}}{NT} = \Gamma\left(\zeta + \eta_J(\kappa_{\rm TF}a)^2\right) + 3\left[u_{\rm ln} - \ln t\right]$$

$\Gamma \equiv Z^2e^2/(aT)$, $t \equiv T/T_{\rm p}$, $T_{\rm p} \equiv \hbar\omega_{\rm p}$, $\omega_{\rm p} = \sqrt{4\pi nZ^2e^2/M}$, $u_{\rm ln} = \langle\ln(\omega/\omega_{\rm p})\rangle$

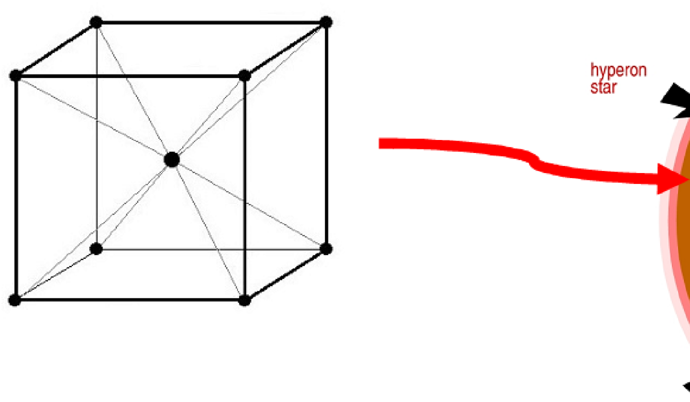


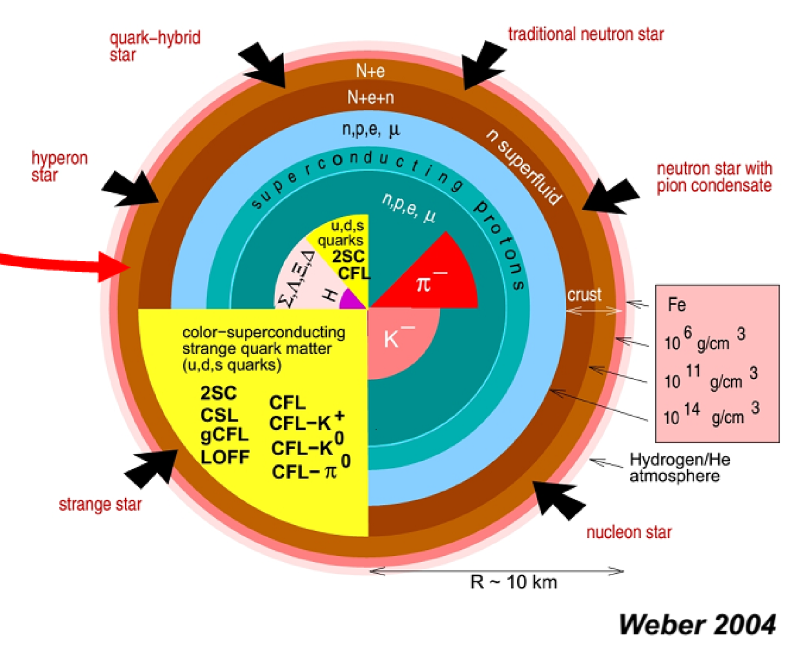




At $\Gamma = 180$ the total free energy of the BCC lattice is smaller than the total free energy of other lattices at any Z and any $\kappa_{\rm TF}a > 1$ except case $Z = 3$ and $k_{\rm TF}a > 0.9$

Resume:
— BCC lattice has the smallest electrostatic energy among all one component Coulomb crystals with uniform electron background but it is not a valid proposition for crystals with polarized electron background;
— binary BCC lattice is stable if $5/18 \le \alpha \le 3.6$;
— binary MgB_2 lattice is stable if $0.1 \le \alpha \le 0.375$;
— total free energy of binary BCC lattice at $T = 0$ could be both larger and smaller than the total free energy of binary HCP lattice.
It depends on density and chemical composition;





Weber 2004

The ground state of the OCP of ions corresponds to the body-centered cubic (bcc) lattice.

Haensel, Potekhin, Yakovlev 2007