PHY 752 Solid State Physics
11-11:50 AM MWF Olin 103

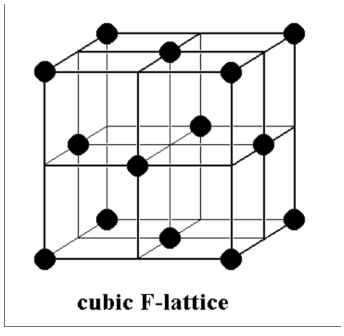
Plan for Lecture 17:

Reading: Chapter 6 in GGGPP
Electronic properties of selected materials

1. **Rare-gas solids**
2. **Ionic crystals**

4	Wed, 9/02/2015	Chap. 1.6, 2.1	Crystal structures	#4
5	Fri, 9/04/2015	Chap. 2	Group theory	#5
6	Mon, 9/07/2015	Chap. 2	Group theory	#6
7	Wed, 9/09/2015	Chap. 2	Group theory	#7
8	Fri, 9/11/2015	Chap. 2	Group theory	#7
9	Mon, 9/14/2015	Chap. 2.4-2.7	Densities of states	#8
10	Wed, 9/16/2015	Chap. 3	Free electron model	#9
11	Fri, 9/18/2015	Chap. 4	One electron approximations to the many electron problem	#10
12	Mon, 9/21/2015	Chap. 4	One electron approximations to the many electron problem	#11
13	Wed, 9/23/2015	Chap. 4	Density functional theory	#12
14	Fri, 9/25/2015	Chap. 5	Implementation of density functional theory	#13
15	Mon, 9/28/2015	Chap. 5	Implementation of density functional theory	#14
16	Wed, 9/30/2015	Chap. 5	First principles pseudopotential methods	#15
17	Fri, 10/02/2015	Chap. 6	Example electronic structures	#16
18	Mon, 10/05/2015			
19	Wed, 10/07/2015			
20	Fri, 10/09/2015			
	Mon, 10/12/2015		No class	Take-home exam
	Wed, 10/14/2015		No class	Take-home exam due
	Fri, 10/16/2015		Fall break -- no class	

Electronic structures of rare gas solids -- fcc structure



cubic F-lattice

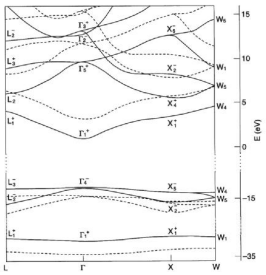


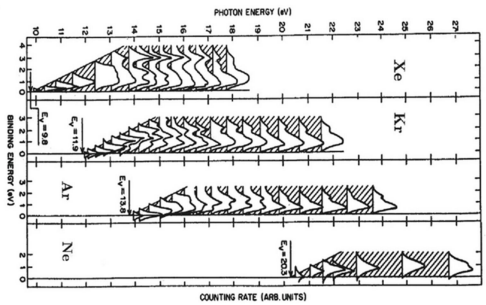
Figure 6.1 Energy bands of solid argon with inclusion of correlation effects (solid line). For comparison the energy bands in the Hartree-Fock approximation are also reported (dashed lines); correlation effects shift (almost rigidly) the Hartree-Fock conduction bands to lower energies, and the Hartree-Fock valence bands to higher energies [With permission from Fig. 1, Phys. Rev. B 29, 2891 (1984)].

Summary of band gaps and widths

Table 6.1 Relevant parameters of the band structure of rare-gas solids as obtained from experiments. The energies are in eV [With permission from Table I, Phys. Rev. Lett. *34*, 528 (1975)].

	Ne	Ar	Kr	Xe
Band-gap energy E_G	21.7	14.2	11.6	9.3
Top valence band $E(\Gamma_4^-)$	−20.3	−13.8	−11.9	−9.8
Bottom conduction band $E(\Gamma_1^+)$	1.4	0.4	−0.3	−0.5
Valence band width	1.3	1.7	2.3	3.0
$\Delta_{SO}^{(gas)}$	0.14	0.22	0.67	1.31
$\Delta_{SO}^{(solid)}$	≈0.1	0.2	0.64	1.3

Photo emission spectrum



Simple model of cohesive energy of rare-gas solids

Lennard-Jones model between each pair of atoms

$$U(R) = \varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - 2\left(\frac{\sigma}{R}\right)^{6}\right]$$

Cohesive energy of the solid

$$U_S(R) = \frac{1}{2}N\varepsilon\left[\sum_{j(\neq i)}\left(\frac{\sigma}{R_{ij}}\right)^{12} - 2\sum_{j(\neq i)}\left(\frac{\sigma}{R_{ij}}\right)^{6}\right].$$

For fcc lattice:

$$A_{12} = \sum_{j(\neq i)}\left(\frac{1}{p_{ij}}\right)^{12} = 12 + \frac{6}{\sqrt{2}^{12}} + \frac{24}{\sqrt{3}^{12}} + \cdots = 12.132\,,$$

$$A_6 = \sum_{j(\neq i)}\left(\frac{1}{p_{ij}}\right)^{6} = 12 + \frac{6}{\sqrt{2}^{6}} + \frac{24}{\sqrt{3}^{6}} + \cdots = 14.454\,.$$

Table 6.2 Parameters of the Lennard-Jones potential $U(R) = \varepsilon[(\sigma/R)^{12} - 2(\sigma/R)^6]$ for a pair of rare-gas atoms, as provided by S. Gonçalves and H. Bonadeo, Phys. Rev. B *46*, 10738 (1992). In the table, we also report the static properties of rare-gas solids (nearest neighbor distance, cohesive energy, and bulk modulus) calculated from the given set of parameters ε and σ. The experimental values of the nearest neighbor distance are taken from R. W. G. Wyckoff "Crystal Structures" (Interscience, New York, 1963). The experimental binding energies are quoted by E. R. Dobbs and G. O. Jones, Rep. Progr. Phys. *20*, 516 (1957). The experimental values of the bulk modulus are quoted by P. Korpium and E. Lüscher in "Rare Gas Solids" (edited by M. L. Klein and J. A. Venables) vol. II, p. 729 (Academic Press, London, 1977).

Pair of rare-gas atoms			**Rare-gas solids**					
			Nearest neighbor distance (Å)		***Binding energy*** (eV/atom)		***Bulk modulus*** (kbar)	
	σ(Å)	ε(eV)	***Calc.*** ***Eq. (6.6)***	***Exp.***	***Calc.*** ***Eq. (6.7)***	***Exp.***	***Calc.*** ***Eq. (6.10)***	***Exp.***
Ne	3.25	0.0024	3.16	3.13	0.021	0.020	11.9	11.1
Ar	3.87	0.0098	3.76	3.72	0.084	0.080	28.8	28.6
Kr	4.11	0.0135	3.99	4.05	0.116	0.112	33.1	34.1
Xe	4.46	0.0185	4.33	4.38	0.159	0.166	35.5	37.9

Some details

$$U_S(R) = \frac{1}{2}N\varepsilon\left[A_{12}\left(\frac{\sigma}{R}\right)^{12} - 2A_6\left(\frac{\sigma}{R}\right)^{6}\right].$$

$$R_0 = \left(\frac{A_{12}}{A_6}\right)^{1/6}\cdot\sigma = 0.971\,\sigma\,.$$

$$U_S(R_0) = -\frac{1}{2}N\varepsilon\frac{A_6^2}{A_{12}} = -8.61\,N\varepsilon\,.$$

Plot of Lennard-Jones potential

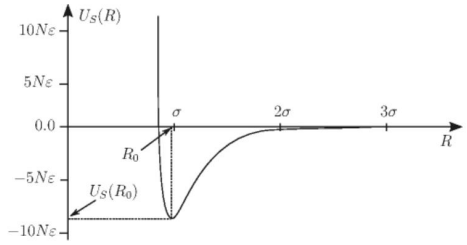


Figure 6.3 Behavior of the crystal energy $U_S(R)$ for a rare-gas solid as a function of the nearest neighbor distance R. The minimum of the curve provides the cohesive energy $U_S(R_0)$ and the equilibrium position R_0. The slope is related to the applied pressure, and the curvature near R_0 is related to the bulk modulus.

Bulk modulus

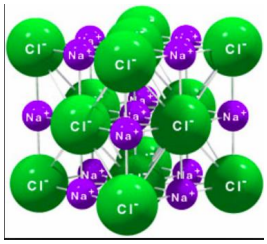
$$B_0 = \left(-V\frac{dp}{dV}\right)_{V=V_0} = \left(V\frac{d^2U_S}{dV^2}\right)_{V=V_0}.$$

For this case:

$$B_0 = V_0\left(\frac{dR}{dV}\right)^2_{V=V_0}\left(\frac{d^2U_S}{dR^2}\right)_{R=R_0}.$$

$$\boxed{B_0 = 4\sqrt{2}\frac{\varepsilon}{\sigma^3}\left(\frac{A_6}{A_{12}}\right)^{3/2}\cdot A_6 = 106.3\,\frac{\varepsilon}{\sigma^3}}.$$

Ionic solids



Ewald summation methods -- motivation

Consider a collection of point charges $\{q_i\}$ located at points $\{\mathbf{r}_i\}$. The energy to separate these charges to infinity($\mathbf{r}_i \to \infty$) is

$$W = \frac{1}{4\pi\epsilon_0} \sum_{(i,j;i>j)} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

Here the summation is over all pairs of (i, j), excluding $i = j$. It is convenient to sum over all particles and divide by 2 to compensate for the double counting:

$$W = \frac{1}{8\pi\epsilon_0} \sum_{i,j;i\neq j} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

Here the summation is over all pairs of i, j, excluding $i = j$. The energy W scales as the number of particles N. As N $\to \infty$, the ratio W / N remains well-defined in principle, but difficult to calculate in practice.

Ewald summation methods – exact results for periodic systems

$$\frac{W}{N} = \sum_{\alpha\beta} \frac{q_\alpha q_\beta}{8\pi\varepsilon_0} \left(\frac{4\pi}{\Omega} \sum_{\mathbf{G}\neq\mathbf{0}} \frac{e^{-i\mathbf{G}\cdot\boldsymbol{\tau}_{\alpha\beta}}\, e^{-G^2/\eta}}{G^2} - \sqrt{\frac{\eta}{\pi}}\delta_{\alpha\beta} + \sum_{\mathbf{T}}{}' \frac{\mathrm{erfc}(\frac{1}{2}\sqrt{\eta}\,|\boldsymbol{\tau}_{\alpha\beta} + \mathbf{T}|)}{|\boldsymbol{\tau}_{\alpha\beta} + \mathbf{T}|} \right) - \frac{4\pi Q^2}{8\pi\varepsilon_0 \Omega \eta}.$$

See lecture notes for details.