PHY 3205
Solid State Physics I

Crystal Bindings

Dr. Mohammad Abdur Rashid

Bragg's Diffraction

$$2d \sin \theta = n\lambda$$

X-ray diffraction pattern

X-ray diffraction pattern of the single crystal cubic SiC at 75 GPa. Diffraction peaks positions are marked by the open black squares. Peak indices are written near each box. Broad intense peaks are from diamond, intermittent circles are from the gasket, and Ne pressure medium. Please note that some reflections appear as small arcs due to a small crystal bent under pressure. This does not affect the accuracy of the sample volume determination, but it produces a small uncertainty in the angular orientation of the sample. The diffraction peaks look like dots at lower pressures.

X-ray diffraction pattern

X-ray diffraction pattern of the TaNbHfZrTi alloy. The indexed peaks belong to a BCC crystal lattice with the lattice parameter a = 340.4 pm.

X-ray diffraction pattern

Figure 16 Explanation of the absence of a (100) reflection from a body-centered cubic lattice. The phase difference between successive planes is π, so that the reflected amplitude from two adjacent planes is $1 + e^{-i\pi} = 1 - 1 = 0$.

Figure 17 Comparison of x-ray reflections from KCl and KBr powders. In KCl the numbers of electrons of K^+ and Cl^- ions are equal. The scattering amplitudes $f(K^+)$ and $f(Cl^-)$ are almost exactly equal, so that the crystal looks to x-rays as if it were a monatomic simple cubic lattice of lattice constant $a/2$. Only even integers occur in the reflection indices when these are based on a cubic lattice of lattice constant a. In KBr the form factor of Br^- is quite different to that of K^+, and all reflections of the fcc lattice are present. (Courtesy of R. van Nordstrand.)

Crystal Bindings

Crystals of Inert Gas; Ionic Crystals; Binding Energy and Bulk Modulus; Covalent; Metallic and Hydrogen Bonded Crystals.

Introduction to Solid State Physics – Charles Kittel

Chapter 3

What keeps the crystal intact?

The principal types of crystalline binding. In (a) neutral atoms with closed electron shells are bound together weakly by the van der Waals forces associated with fluctuations in the charge distributions. In (b) electrons are transferred from the alkali atoms to the halogen atoms, and the resulting ions are held together by attractive electrostatic forces between the positive and negative ions. In (c) the valence electrons are taken away from each alkali atom to form a communal electron sea in which the positive ions are dispersed. In (d) the neutral atoms are bound together by the overlapping parts of their electron distributions.

What keeps the crystal intact?

The attractive electrostatic interaction between the negative charges of the electrons and the positive charges of the nuclei is entirely responsible for the cohesion of solids. Magnetic forces have only a weak effect on cohesion, and gravitational forces are negligible. Specialized terms categorize distinctive situations: exchange energy, van der Waals forces, and covalent bonds.

The cohesive energy of a crystal is defined as the energy that must be added to the crystal to separate its components into neutral free atoms at rest, at infinite separation, with the same electronic configuration. The term lattice energy is used in the discussion of ionic crystals and is defined as the energy that must be added to the crystal to separate its component ions into free ions at rest at infinite separation.

Table 1 Cohesive energies

Energy required to form separated neutral atoms in their ground electronic state from the solid at 0 K at 1 atm. The data were supplied by Prof. Leo Brewer.

Li	Be											B	C	N	O	F	Ne
158.	320.											561	711.	474.	251.	81.0	1.92
1.63	3.32											5.81	7.37	4.92	2.60	0.84	0.020
37.7	76.5											134	170.	113.4	60.03	19.37	0.46
Na	Mg											Al	Si	P	S	Cl	Ar
107.	145.											327.	446.	331.	275.	135.	7.74
1.113	1.51											3.39	4.63	3.43	2.85	1.40	0.080
25.67	34.7											78.1	106.7	79.16	65.75	32.2	1.85
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
90.1	178.	376	468.	512.	395.	282.	413.	424.	428.	336.	130	271.	372.	285.3	237	118.	11.2
0.934	1.84	3.90	4.85	5.31	4.10	2.92	4.28	4.39	4.44	3.49	1.35	2.81	3.85	2.96	2.46	1.22	0.116
21.54	42.5	89.9	111.8	122.4	94.5	67.4	98.7	101.3	102.4	80.4	31.04	64.8	88.8	68.2	56.7	28.18	2.68
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
82.2	166.	422.	603.	730.	658	661.	650.	554.	376.	284.	112.	243.	303.	265.	211	107.	15.9
0.852	1.72	4.37	6.25	7.57	6.82	6.85	6.74	5.75	3.89	2.95	1.16	2.52	3.14	2.75	2.19	1.11	0.16
19.64	39.7	100.8	144.2	174.5	157.2	158.	155.4	132.5	89.8	68.0	26.73	58.1	72.4	63.4	50.34	25.62	3.80
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
77.6	183.	431.	621.	782.	859.	775.	788.	670.	564.	368.	65.	182.	196.	210.	144.		19.5
0.804	1.90	4.47	6.44	8.10	8.90	8.03	8.17	6.94	5.84	3.81	0.67	1.88	2.03	2.18	1.50		0.202
18.54	43.7	103.1	148.4	186.9	205.2	185.2	188.4	160.1	134.7	87.96	15.5	43.4	46.78	50.2	34.5		4.66
Fr	Ra	Ac															
	160.	410.															
	1.66	4.25															
	38.2	98.															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			417.	357.	328.		206.	179.	400.	391.	294.	302.	317.	233.	154.	428.	
			4.32	3.70	3.40		2.14	1.86	4.14	4.05	3.04	3.14	3.29	2.42	1.60	4.43	
			99.7	85.3	78.5		49.3	42.8	95.5	93.4	70.2	72.3	75.8	55.8	37.1	102.2	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	
			598.		536.	456	347.	264.	385								
			6.20		5.55	4.73	3.60	2.73	3.99								
			142.9		128.	109.	83.0	63.	92.1								

kJ/mol ⟷ eV/atom ⟷ kcal/mol

Crystals of inert gas

Cubic close-packed (fcc) crystal structure of the inert gases Ne, Ar, Kr, and Xe. The lattice parameters of the cubic cells are 4.46, 5.31, 5.64, and 6.13 Å, respectively, at 4 K.

Crystals of inert gas

The inert gases form the simplest crystals. The electron distribution is very close to that of the free atoms. The crystals are transparent insulators, weakly bound, with low melting temperatures. The atoms have very high ionization energies. The outermost electron shells of the atoms are completely filled, and the distribution of electron charge in the free atom is spherically symmetric. In the crystal the inert gas atoms pack together as closely as possible: the crystal structures are all cubic close-packed (fcc), except He^3 and He^4.

What holds an inert gas crystal together? The electron distribution in the crystal is not significantly distorted from the electron distribution around the free atoms because not much energy is available to distort the free atom charge distributions. The cohesive energy of an atom in the crystal is only 1 percent or less of the ionization energy of an atomic electron. Part of this distortion gives the van der Waals interaction.

Crystals of inert gas

Table 4 Properties of inert gas crystals

(Extrapolated to 0 K and zero pressure)

	Nearest-neighbor distance, in Å	Experimental cohesive energy		Melting point, K	Ionization potential of free atom, eV	Parameters in Lennard-Jones potential, Eq. 10	
		kJ/mol	eV/atom			ϵ, in 10^{-16} erg	σ, in Å
He	(liquid at zero pressure)				24.58	14	2.56
Ne	3.13	1.88	0.02	24.56	21.56	50	2.74
Ar	3.76	7.74	0.080	83.81	15.76	167	3.40
Kr	4.01	11.2	0.116	115.8	14.00	225	3.65
Xe	4.35	16.0	0.17	161.4	12.13	320	3.98

Van der Waals-London Interaction

Consider two identical inert gas atoms at a separation R large in comparison with the radii of the atoms. If the charge distributions on the atoms were rigid, the interaction between atoms would be zero, because the electrostatic potential of a spherical distribution of electronic charge is canceled outside a neutral atom by the electrostatic potential of the charge on the nucleus. Then the inert gas atoms could show no cohesion and could not condense. But the atoms induce dipole moments in each other, and the induced moments cause an attractive interaction between the atoms.

Van der Waals-London Interaction

As a model, we consider two identical linear harmonic oscillators 1 and 2 separated by R. Each oscillator bears charges $\pm e$ with separations x_1 and x_2, as in Fig. 3. The particles oscillate along the x axis. Let p_1 and p_2 denote the momenta. The force constant is C. Then the hamiltonian of the unperturbed system is

$$\mathcal{H}_0 = \frac{1}{2m} p_1^2 + \tfrac{1}{2} C x_1^2 + \frac{1}{2m} p_2^2 + \tfrac{1}{2} C x_2^2 \quad . \tag{1}$$

Each uncoupled oscillator is assumed to have the frequency ω_0 of the strongest optical absorption line of the atom. Thus $C = m\omega_0^2$.

Let $\mathcal{H}_1$ be the coulomb interaction energy of the two oscillators. The geometry is shown in the figure. The internuclear coordinate is R. Then

$$\text{(CGS)} \qquad \mathcal{H}_1 = \frac{e^2}{R} + \frac{e^2}{R + x_1 - x_2} - \frac{e^2}{R + x_1} - \frac{e^2}{R - x_2} \ ; \tag{2}$$

in the approximation $|x_1|, |x_2| \ll R$ we expand (2) to obtain in lowest order:

$$\mathcal{H}_1 \cong -\frac{2e^2 x_1 x_2}{R^3} \ . \tag{3}$$

The total hamiltonian with the approximate form (3) for $\mathcal{H}_1$ can be diagonalized by the normal mode transformation

$$x_s \equiv \frac{1}{\sqrt{2}}(x_1 + x_2) \ ; \qquad x_a \equiv \frac{1}{\sqrt{2}}(x_1 - x_2) \ , \tag{4}$$

or, on solving for x_1 and x_2,

$$x_1 = \frac{1}{\sqrt{2}}(x_s + x_a) \ ; \qquad x_2 = \frac{1}{\sqrt{2}}(x_s - x_a) \ . \tag{5}$$

The subscripts s and a denote symmetric and antisymmetric modes of motion. Further, we have the momenta p_s, p_a associated with the two modes:

$$p_1 \equiv \frac{1}{\sqrt{2}}(p_s + p_a) \ ; \qquad p_2 \equiv \frac{1}{\sqrt{2}}(p_s - p_a) \ . \tag{6}$$

The total hamiltonian $\mathcal{H}_0 + \mathcal{H}_1$ after the transformations (5) and (6) is

$$\mathcal{H} = \left[\frac{1}{2m}p_s^2 + \frac{1}{2}\left(C - \frac{2e^2}{R^3}\right)x_s^2\right] + \left[\frac{1}{2m}p_a^2 + \frac{1}{2}\left(C + \frac{2e^2}{R^3}\right)x_a^2\right] \ . \tag{7}$$

The two frequencies of the coupled oscillators are found by inspection of (7) to be

$$\omega = \left[\left(C \pm \frac{2e^2}{R^3}\right) \Big/ m\right]^{1/2} = \omega_0 \left[1 \pm \frac{1}{2}\left(\frac{2e^2}{CR^3}\right) - \frac{1}{8}\left(\frac{2e^2}{CR^3}\right)^2 + \cdots\right] , \qquad (8)$$

with ω_0 given by $(C/m)^{1/2}$. In (8) we have expanded the square root.

The zero point energy of the system is $\frac{1}{2}\hbar(\omega_s + \omega_a)$; because of the interaction the sum is lowered from the uncoupled value $2 \cdot \frac{1}{2}\hbar\omega_0$ by

$$\Delta U = \tfrac{1}{2}\hbar(\Delta\omega_s + \Delta\omega_a) = -\hbar\omega_0 \cdot \frac{1}{8}\left(\frac{2e^2}{CR^3}\right)^2 = -\frac{A}{R^6} \ . \qquad (9)$$

This attractive interaction varies as the minus sixth power of the separation of the two oscillators.

This is called the van der Waals interaction, known also as the London interaction or the induced dipole-dipole interaction.

Repulsive Interaction

As the two atoms are brought together, their charge distributions gradually overlap, thereby changing the electrostatic energy of the system. At sufficiently close separations the overlap energy is repulsive, in large part because of the **Pauli exclusion principle**. The elementary statement of the principle is that two electrons cannot have all their quantum numbers equal. When the charge distributions of two atoms overlap, there is a tendency for electrons from atom *B* to occupy in part states of atom *A* already occupied by electrons of atom *A*, and vice versa.

Repulsive Interaction: Pauli exclusion principle

Electronic charge distributions overlap as atoms approach.
The solid circles denote the nuclei.

Repulsive Interaction: Pauli exclusion principle

Repulsive Interaction

We make no attempt here to evaluate the repulsive interaction from first principles. Experimental data on the inert gases can be fitted well by an empirical repulsive potential of the form B/R^{12}, where B is a positive constant, when used together with a long-range attractive potential. The constants A and B are empirical parameters determined from independent measurements made in the gas phase; the data used include the virial coefficients and the viscosity. It is usual to write the total potential energy of two atoms at separation R as

$$U(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right], \qquad (10)$$

Repulsive Interaction

$$U(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right],$$

where ϵ and σ are the new parameters, with $4\epsilon\sigma^6 = A$ and $4\epsilon\sigma^{12} = B$. The potential (10) is known as the Lennard-Jones potential, Fig. 6. The force between the two atoms is given by $-dU/dR$. Values of ϵ and σ given in Table 4 can be obtained from gas-phase data, so that calculations on properties of the solid do not involve disposable parameters.

Other empirical forms for the repulsive interaction are widely used, in particular the exponential form $\lambda \exp(-R/\rho)$, where ρ is a measure of the range of the interaction. This is generally as easy to handle analytically as the inverse power law form.

Lennard-Jones potential

$$U(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

Equilibrium Lattice Constants

If we neglect the kinetic energy of the inert gas atoms, the cohesive energy of an inert gas crystal is given by summing the Lennard-Jones potential (10) over all pairs of atoms in the crystal. If there are N atoms in the crystal, the total potential energy is

$$U_{\text{tot}} = \tfrac{1}{2}N(4\epsilon)\left[\sum_j{}' \left(\frac{\sigma}{p_{ij}R}\right)^{12} - \sum_j{}' \left(\frac{\sigma}{p_{ij}R}\right)^{6}\right], \tag{11}$$

where $p_{ij}R$ is the distance between reference atom i and any other atom j, expressed in terms of the nearest-neighbor distance R. The factor $\frac{1}{2}$ occurs with the N to compensate for counting twice each pair of atoms.

Equilibrium Lattice Constants

$$U_{\text{tot}} = \tfrac{1}{2}N(4\epsilon)\left[\sum_j{}' \left(\frac{\sigma}{p_{ij}R}\right)^{12} - \sum_j{}' \left(\frac{\sigma}{p_{ij}R}\right)^{6}\right]$$

The summations in (11) have been evaluated, and for the fcc structure

$$\sum_j{}' p_{ij}^{-12} = 12.13188 \ ; \qquad \sum_j{}' p_{ij}^{-6} = 14.45392 \ . \tag{12}$$

There are 12 nearest-neighbor sites in the fcc structure; we see that the series are rapidly converging and have values not far from 12. The nearest neighbors contribute most of the interaction energy of inert gas crystals. The corresponding sums for the hcp structure are 12.13229 and 14.45489.

Equilibrium Lattice Constants

If we take U_{tot} in (11) as the total energy of the crystal, the equilibrium value R_0 is given by requiring that U_{tot} be a minimum with respect to variations in the nearest-neighbor distance R:

$$\frac{dU_{tot}}{dR} = 0 = -2N\epsilon\left[(12)(12.13)\frac{\sigma^{12}}{R^{13}} - (6)(14.45)\frac{\sigma^{6}}{R^{7}}\right] , \qquad (13)$$

whence

$$R_0/\sigma = 1.09 , \qquad (14)$$

the same for all elements with an fcc structure. The observed values of R_0/σ, using the independently determined values of σ given in Table 4, are:

	Ne	Ar	Kr	Xe
R_0/σ	1.14	1.11	1.10	1.09 .

Cohesive Energy

The cohesive energy of inert gas crystals at absolute zero and at zero pressure is obtained by substituting (12) and (14) in (11):

$$U_{\text{tot}}(R) = 2N\epsilon\left[(12.13)\left(\frac{\sigma}{R}\right)^{12} - (14.45)\left(\frac{\sigma}{R}\right)^{6}\right] , \tag{15}$$

and, at $R = R_0$,

$$U_{\text{tot}}(R_0) = -(2.15)(4N\epsilon) , \tag{16}$$

the same for all inert gases. This is the calculated cohesive energy when the atoms are at rest. Quantum-mechanical corrections act to reduce the binding by 28, 10, 6, and 4 percent of Eq. (16) for Ne, Ar, Kr, and Xe, respectively.

The heavier the atom, the smaller the quantum correction. We can understand the origin of the quantum correction by consideration of a simple model in which an atom is confined by fixed boundaries. If the particle has the quantum wavelength λ, where λ is determined by the boundaries, then the particle has kinetic energy $p^2/2M = (h/\lambda)^2/2M$ with the de Broglie relation $p = h/\lambda$ for the connection between the momentum and the wavelength of a particle. On this model the quantum zero-point correction to the energy is inversely proportional to the mass. The final calculated cohesive energies agree with the experimental values of Table 4 within 1 to 7 percent.

One consequence of the quantum kinetic energy is that a crystal of the isotope Ne^{20} is observed to have a larger lattice constant than a crystal of Ne^{22}. The higher quantum kinetic energy of the lighter isotope expands the lattice because the kinetic energy is reduced by expansion. The observed lattice constants (extrapolated to absolute zero from 2.5 K) are Ne^{20}, 4.4644 Å; Ne^{22}, 4.4559 Å.

Ionic Crystals

The electronic configurations of all ions of a simple ionic crystal correspond to closed electronic shells, as in the inert gas atoms. In lithium fluoride the configuration of the neutral atoms are, according to the periodic table in the front endpapers of this book, Li: $1s^2 2s$, F: $1s^2 2s^2 2p^5$. The singly charged ions have the configurations Li^+:$1s^2$, F^-: $1s^2 2s^2 2p^6$, as for helium and neon, respectively. Inert gas atoms have closed shells, and the charge distributions are spherically symmetric. We expect that the charge distributions on each ion in an ionic crystal will have approximately spherical symmetry, with some distortion near the region of contact with neighboring atoms.

Figure 7 Electron density distribution in the base plane of NaCl, after x-ray studies by G. Schoknecht. The numbers on the contours give the relative electron concentration.

Figure 8 The energy per molecule unit of a crystal of sodium chloride is $(7.9 - 5.1 + 3.6) = 6.4$ eV lower than the energy of separated neutral atoms. The lattice energy with respect to separated ions is 7.9 eV per molecule unit. All values on the figure are experimental. Values of the ionization energy are given in Table 5, and values of the electron affinity are given in Table 6.

Table 6 Electron affinities of negative ions

The electron affinity is positive for a stable negative ion.

Atom	Electron affinity energy eV	Atom	Electron affinity energy eV
H	0.7542	Si	1.39
Li	0.62	P	0.74
C	1.27	S	2.08
O	1.46	Cl	3.61
F	3.40	Br	3.36
Na	0.55	I	3.06
Al	0.46	K	0.50

Source: H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data 4, 539 (1975).

Electrostatic or Madelung Energy

The long-range interaction between ions with charge $\pm q$ is the electrostatic interaction $\pm q^2/r$, attractive between ions of opposite charge and repulsive between ions of the same charge. The ions arrange themselves in whatever crystal structure gives the strongest attractive interaction compatible with the repulsive interaction at short distances between ion cores. The repulsive interactions between ions with inert gas configurations are similar to those between inert gas atoms. The van der Waals part of the attractive interaction in ionic crystals makes a relatively small contribution to the cohesive energy in ionic crystals, of the order of 1 or 2 percent. The main contribution to the binding energy of ionic crystals is electrostatic and is called the **Madelung energy**.

Electrostatic or Madelung Energy

Electrostatic or Madelung Energy

ANY
QUESTIONS?