

Phys 460/560 Lecture 9

I) More on the reciprocal lattice and X-Ray diffraction

- Recall the definition of the reciprocal lattice:

$$\{\vec{G}\} : e^{i\vec{G}\cdot\vec{R}} = 1 \quad \forall \vec{R} \in BL.$$

In the last lecture, we showed that electrons, photons, etc. are scattered by the lattice:

$$\hbar\vec{k} \rightarrow \hbar\vec{k} + \hbar\vec{G}$$

- In solid state physics, neutron scattering is also important. Neutrons are scattered mainly from nuclei and electronic magnetic moments. They are thus a

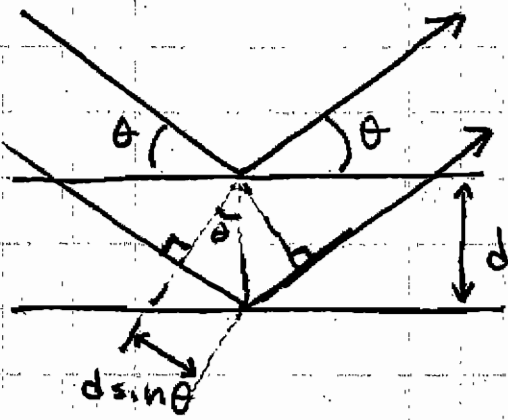
useful probe of magnetic structure.

- X-Rays have $\lambda \approx |\vec{a}_i| \approx \text{\AA} = 10^{-10} \text{ m}$ and are thus diffracted by a crystal. Why not use radiation of shorter wavelength still (e.g. γ -rays) to directly image atomic structure (geometrical optics limit)? The problem is that γ -rays have so much energy that they barely are scattered by the electrons, and mainly serve to blast apart the nuclei. Thus, one is doing nuclear physics, not solid state physics with γ -rays!

I.1 Bragg condition

Bragg gave an alternate derivation of the condition for constructive interference in X-ray scattering from a crystal. He assumed that X-rays are specularly reflected from each plane of atoms in a

crystal, and determined the condition that partial waves reflected from successive planes interfere constructively:

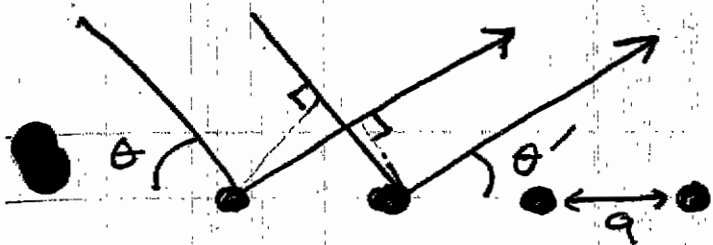


$$2d \sin \theta = n \lambda$$

At first sight, this condition seems quite different from that obtained in the last lecture,

$$2\vec{k} \cdot \vec{G} = G^2.$$

Also, the assumption of specular reflection $\theta = \theta'$ appears as an additional condition not needed in the previous derivation. However, $\theta = \theta'$ is equivalent to the condition that the partial waves scattered from each atom within a plane interfere constructively:



$$a \sin \theta - a \sin \theta' = m \lambda$$

$m=0 \Rightarrow$ dominant contribution

$$\Rightarrow \theta = \theta'$$

Furthermore, in homework problem 3, you will show that the spacing

$d(hkl)$ between parallel lattice planes that are normal to the direction $\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$

is $d(hkl) = 2\pi / |\vec{G}|$. Thus

the result $2k \cdot \vec{G} = G^2$ may be written

$$2 \left(\frac{2\pi}{\lambda} \right) \sin \theta = \frac{2\pi}{d(hkl)}$$

or $2d(hkl) \sin \theta = \lambda$. The integers hkl which define \vec{G} are not necessarily identical with the indices of a crystal plane, since they may contain a common

Indexes of Crystal Planes

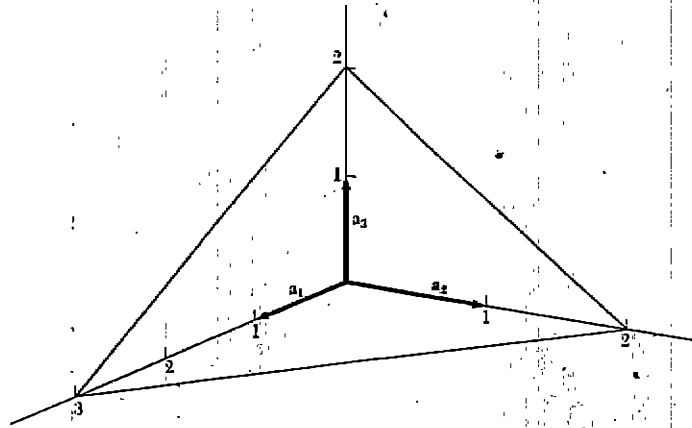


Figure 15 This plane intercepts the a_1 , a_2 , a_3 axes at $3a_1$, $2a_2$, $2a_3$. The reciprocals of these numbers are $\frac{1}{3}$, $\frac{1}{2}$, $\frac{1}{2}$. The smallest three integers having the same ratio are 2, 3, 3, and thus the indices of the plane are (233).

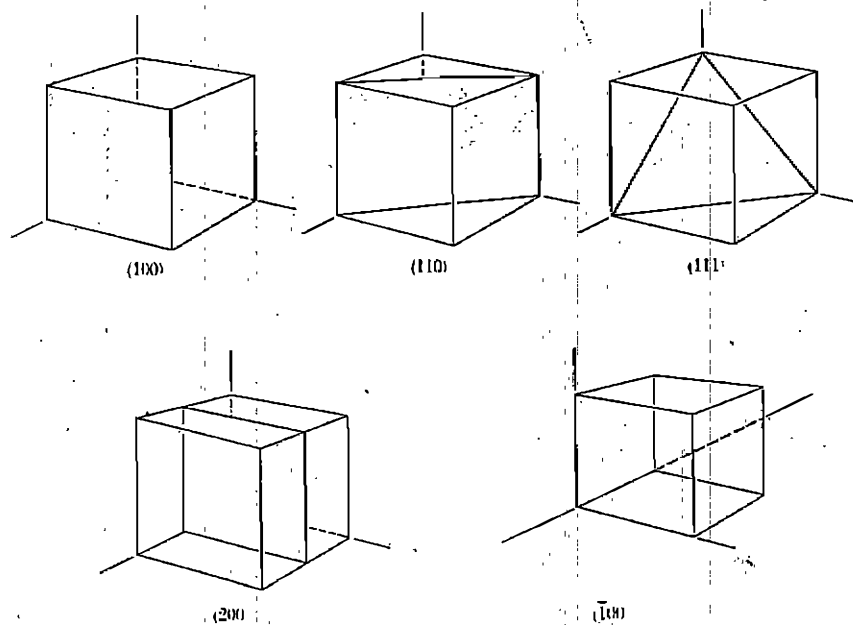


Figure 16. Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to $(\bar{1}00)$.

factor n . In that case, we have

$$d = \frac{2\pi n}{|\vec{G}|} \quad \text{and}$$

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

I.2) Structure factor \rightarrow Atomic form factor

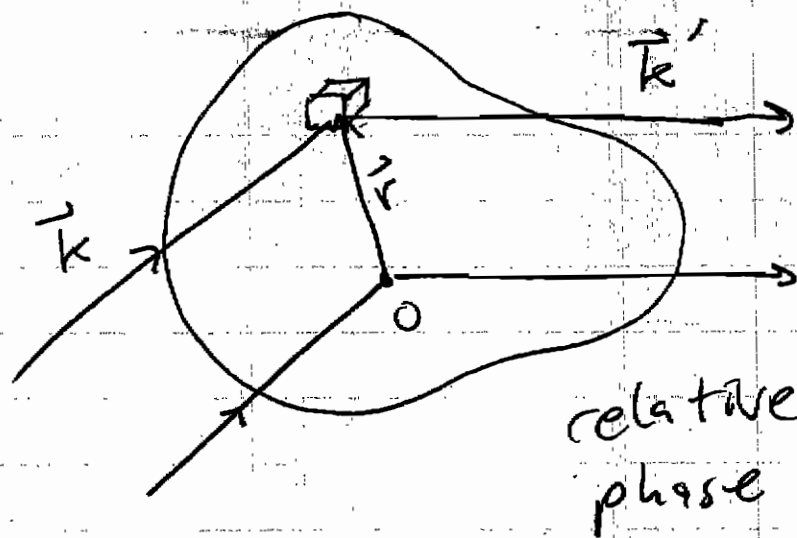
When the diffraction condition

$\Delta \vec{k} = \vec{G}$ is satisfied, the partial waves from each unit cell interfere constructively. The total scattered amplitude from a crystal with N unit cells is

$$F_{\vec{G}} = N S_{\vec{G}}$$

$S_{\vec{G}}$ is called the structure factor. The simplest approximation for $S_{\vec{G}}$ is

$$S_{\vec{G}} = \int_{\text{cell}} d^3r \rho(\vec{r}) e^{-i\vec{G} \cdot \vec{r}},$$



Let us write the charge density $\rho(\mathbf{r})$ as a sum over the S atoms per unit cell

$$\rho(\mathbf{r}) = \sum_{j=1}^S \rho_j(\mathbf{r} - \mathbf{r}_j)$$

where $\rho_j(\mathbf{r})$ is the charge density of an atom of type j located at $\mathbf{r} = 0$.

$$\begin{aligned} S_{\mathbf{G}} &= \sum_j \int d^3r \rho_j(\mathbf{r} - \mathbf{r}_j) e^{-i\mathbf{G} \cdot \mathbf{r}} \\ &= \sum_j e^{-i\mathbf{G} \cdot \mathbf{r}_j} \underbrace{\int d^3r' \rho_j(\mathbf{r}') e^{-i\mathbf{G} \cdot \mathbf{r}'}}_{f_j} \end{aligned}$$

$f_j =$ atomic form factor

Finally,

$$S_{\vec{G}} = \sum_{j=1}^s f_j e^{-i\vec{G} \cdot \vec{r}_j}$$

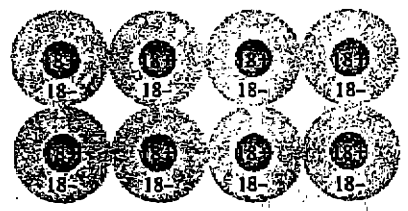
where \vec{r}_j are the locations of the s atoms per unit cell and f_j is an atomic property determined by the atomic charge density $\rho_j(\vec{r})$.

In a solid, the electrons are redistributed to form bands or extended bands. However, this typically only involves a few electrons per atom, and $\rho_j(\vec{r})$ deviates only by about 1% from the free atom value.

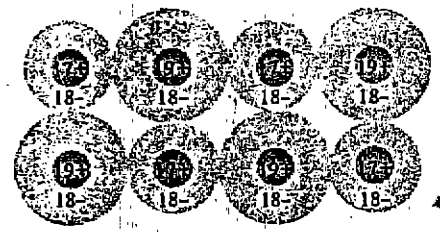
However, this small difference leads to big differences in different solids, ranging from metals to insulators to semiconductors!

Cohesion

Ar



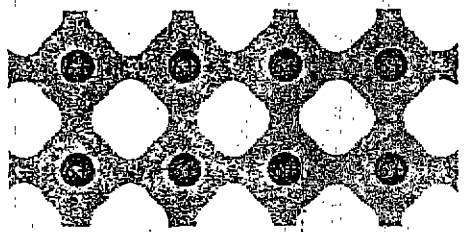
Molecular
(a)



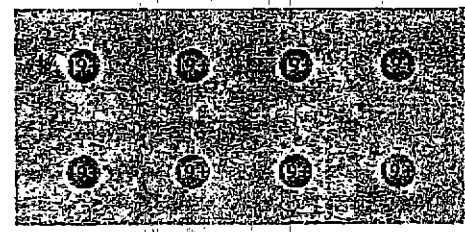
Ionic
(b)

KCl

C



Covalent
(c)



Metallic
(d)

K

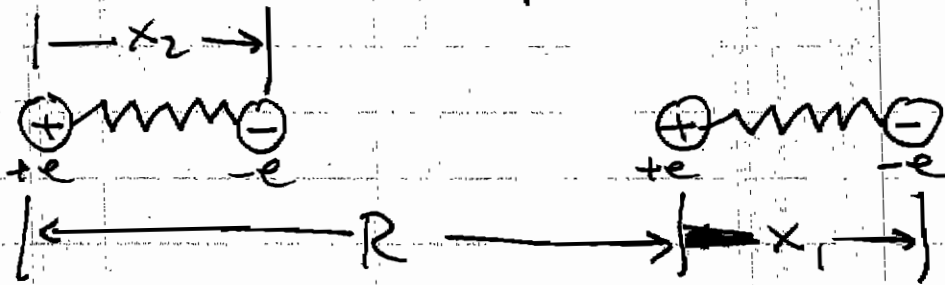
Figure 19.3
 Highly schematic two-dimensional representation of the electronic charge distribution in the basic solid types. The small circles represent the positively charged nuclei, and the shaded parts, regions in which the electronic density is appreciable (though by no means uniform). We have (a) molecular (represented by two-dimensional "argon"); (b) ionic ("potassium chloride"); (c) covalent ("carbon"); (d) metallic ("potassium").

II. 1) Inert Gas Crystals :

Van der Waals Interaction

Atoms of inert gas (eg. He, Ne, Ar, Xe) have filled electronic shells and are spherically symmetric. They do not form chemical bonds with other atoms (as a rule). Since they are spherically symmetric and electrically neutral, one might think that they would not interact at all unless brought into direct contact, when their electronic orbitals would be forced to deform, leading to a short-range repulsion. However, there is a weak long-range attraction due to correlated fluctuations of their electric dipole moments. This is a pure quantum effect known as the van der Waals interaction. It is also the source of binding in molecular crystals, i.e., crystals formed of more complex (eg. biological) molecules.

Consider a simple 1D model:



$$H_0 = \frac{p_1^2}{2m} + \frac{C}{2} x_1^2 + \frac{p_2^2}{2m} + \frac{C}{2} x_2^2$$

$\omega_0 = \sqrt{C/m}$ represents the frequency of the strongest optical transition.
 $m =$ electron mass.

$$H_1 = \frac{e^2}{R} + \frac{e^2}{R+x_1-x_2} - \frac{e^2}{R+x_1} - \frac{e^2}{R-x_2}$$

$$\approx - \frac{2e^2 x_1 x_2}{R^3}$$

$|x_1|, |x_2| \ll R$

$$\text{Let } x_s = \frac{x_1 + x_2}{\sqrt{2}} \quad x_a = \frac{x_1 - x_2}{\sqrt{2}}$$

$$\text{or } x_1 = \frac{x_s + x_a}{\sqrt{2}} \quad x_2 = \frac{x_s - x_a}{\sqrt{2}}$$

$$p_1 = \frac{p_s + p_a}{\sqrt{2}} \quad p_2 = \frac{p_s - p_a}{\sqrt{2}}$$

In terms of $x_s, x_g, p_s,$ and p_g
 $H = H_0 + H_1$, becomes:

$$H = \left[\frac{p_s^2}{2m} + \frac{1}{2} \left(C - \frac{ze^2}{R^3} \right) x_s^2 \right]$$

$$+ \left[\frac{p_g^2}{2m} + \frac{1}{2} \left(C + \frac{ze^2}{R^3} \right) x_g^2 \right]$$

$$= \hbar\omega_s \left(\hat{n}_s + \frac{1}{2} \right) + \hbar\omega_g \left(\hat{n}_g + \frac{1}{2} \right)$$

where $\omega_{s/g} = \sqrt{\frac{C \mp ze^2/R^3}{m}}$

$$\approx \omega_0 \left[1 \pm \frac{1}{2} \left(\frac{ze^2}{CR^3} \right) - \frac{1}{8} \left(\frac{ze^2}{CR^3} \right)^2 \right]$$

The ground state of the system is lowered by an amount

$$\Delta U = \hbar\frac{\omega_s}{2} + \hbar\frac{\omega_g}{2} - \hbar\omega_0$$

$$\approx -\frac{\hbar\omega_0}{8} \left(\frac{ze^2}{CR^3} \right)^2 = -\frac{A}{R^6}$$

van der Waals interaction

In addition to this long range attraction, there is a short range repulsion due to the Pauli exclusion principle. Since both atoms have filled electronic shells, they cannot overlap appreciably without promoting electrons to higher orbitals, which costs a lot of energy. This interaction depends on the detailed wavefunctions of the atoms, but can be reasonably modeled by

$$\frac{B}{r^{12}} \quad \text{or} \quad \lambda e^{-R/\rho}$$

Choosing the first form gives the Lennard-Jones potential:

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

with $A \equiv 4\epsilon\sigma^6$ and $B = 4\epsilon\sigma^{12}$.

Lattice Energy

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

where $p_{ij} R$ is the distance between atoms i and j , and R is the distance between nearest neighbors.

For the fcc lattice, one has

$$\sum_j' p_{ij}^{-12} = 12.13188,$$

$$\sum_j' p_{ij}^{-6} = 14.45392.$$

mostly due to 12 nearest neighbors

Equilibrium

$$0 = \left. \frac{dU_{\text{tot}}}{dR} \right|_{R_0} = -2Ne \left[12 (12.13) \frac{\sigma^{12}}{R_0^{13}} - 6 (14.45) \frac{\sigma^6}{R_0^7} \right]$$

$\Rightarrow R_0 = 1.09 \sigma$

$\sigma \rightarrow \epsilon$ can be determined by measurements in the gas phase [cf. van der Waals equation of state]. The observed values of R_0/σ are

	Ne	Ar	Kr	Xe
$\frac{R_0}{\sigma}$	1.14	1.11	1.10	1.09

The disagreement for the lighter atoms is due to zero point motion.

• Cohesive energy

$U_{tot}(R_0) = -2.15 (4NE)$

This overestimates the binding of Ne, Ar, Kr, and Xe by 28%, 10%, 6%, and 4%, respectively, again due to zero-pt. motion.

Ionic crystals

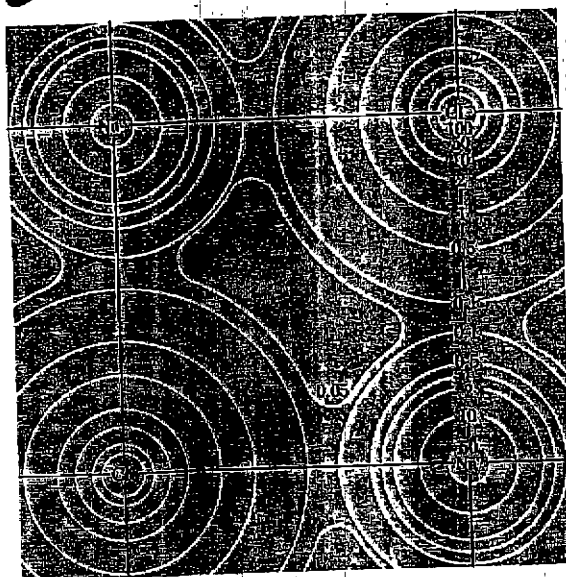


Figure 7 Electron density distribution in the base plane of NaCl, after x-ray studies by G. Schoknecht. The numbers on the contours give the relative electron concentration.

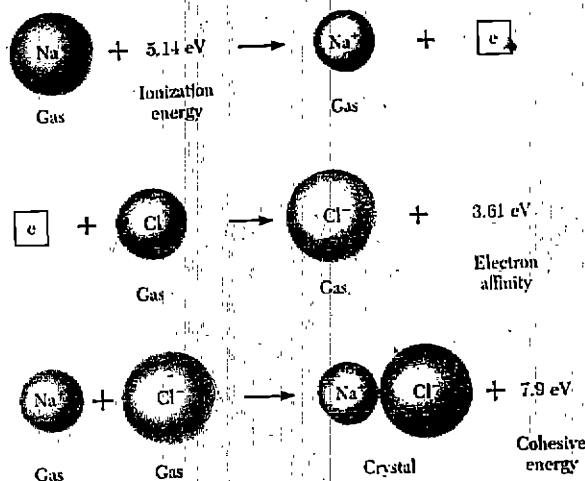


Figure 8 The energy per molecule unit of a crystal of sodium chloride is $(7.9 - 5.1 + 3.6) = 6.4 \text{ eV}$ lower than the energy of separated neutral atoms. The lattice energy with respect to separated ions is 7.9 eV per molecule unit. All values on the figure are experimental. Values of the ionization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

an ionic crystal will have approximately spherical symmetry, with some distortion near the region of contact with neighboring atoms. This picture is confirmed by x-ray studies of electron distributions (Fig. 7).

A quick estimate suggests that we are not misguided in looking to electrostatic interactions for a large part of the binding energy of an ionic crystal. The distance between a positive ion and the nearest negative ion in crystalline sodium chloride is $2.81 \times 10^{-8} \text{ cm}$, and the attractive coulomb part of the potential energy of the two ions by themselves is 5.1 eV . This value may be compared (Fig. 8) with the experimental value of 7.9 eV per molecular unit for the lattice energy of crystalline NaCl with respect to separated Na^+ and Cl^- ions. We now calculate the energy more closely.

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II. Ionic crystals

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• Electrostatic energy

$$U_i = \sum_j' U_{ij}$$

$$U_{ij} = \begin{cases} \lambda e^{-R/\rho} - \frac{q^2}{R} & (\text{n-n-}) \\ \pm \frac{q^2}{\rho_{ij} R} & (\text{otherwise}) \end{cases}$$

$\lambda e^{-R/\rho}$ represents the hard-core repulsion of the ions with inert gas structure, and $\pm q^2/\rho_{ij} R$ is the long-range Coulomb interaction.

$$U_{\text{tot}} = N U_i = N \left(z \lambda e^{-R/\rho} - \frac{z q^2}{R} \right)$$

$N = \#$ of pairs of ions

$$\alpha = \sum_j' \frac{(\pm)}{r_{ij}} = \frac{\text{Madlung constant}}{\text{(must be } \geq 0 \text{ for stability)}}$$

• Equilibrium :

$$0 = N \left. \frac{dU_i}{dr} \right|_{r_0} = - \frac{Nz\lambda}{s} e^{-r_0/s} + \frac{N\alpha q^2}{r_0^2}$$

$$r_0^2 e^{-r_0/s} = s\alpha q^2 / z\lambda$$

$$U_{tot} = - \frac{N\alpha q^2}{r_0} \left(1 - \frac{s}{r_0} \right)$$

typically $s \sim 0.1 r_0$

• Evaluation of α :

1D example: $\oplus \ominus \oplus \ominus \oplus \ominus$

$$\frac{\alpha}{r} = 2 \left[\frac{1}{r} - \frac{1}{2r} + \frac{1}{3r} - \frac{1}{4r} + \dots \right]$$

Comparing to

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$$

we find $\alpha = 2 \ln 2$.

For 3D lattices, the evaluation of α is tricky since it involves the cancellation of large positive and negative terms. One finds

Structure	α
NaCl	1.747565
CsCl	1.762675
ZnS (GaAs)	1.6381

Metals

which the valence electrons are completely separated from their ion cores and form a nearly uniform gas.

More generally, one can find aspects of covalent and molecular bonding even in metals, particularly in the noble metals in which the filled atomic *d*-shells are not very tightly bound, and as a consequence suffer considerable distortion in the metal.

It is instructive to compare the ionic radii of the metallic elements (as calculated from the structure of the ionic crystals they participate in) with the nearest-neighbor distance in the metal (Table 19.4). It is evident that the concept of ionic radius is completely irrelevant in determining the alkali metal lattice constants. This is consistent with the fact that such quantities as the alkali metal compressibilities are of the order of their electron gas values; the ions are genuinely small objects, embedded in a sea of electrons. In the noble metals, on the other hand, as noted in Chapter 15, the closed *d*-shell plays a far more important role in determining metallic properties than do the ion cores of the alkali metals. This is reflected in the fact that in Cu, Ag, and Au, the nearest-neighbor distances in the metal are not that much larger than the ionic radii in ionic crystals. In both the ionic crystals and (to only a slightly lesser degree) the metal, size is determined by the *d*-shells.

Table 19.4
IONIC RADII COMPARED WITH HALF THE NEAREST-NEIGHBOR
DISTANCES IN METALS

METAL	SINGLY IONIZED IONIC RADIUS, r_{ion} (Å)	NEAREST-NEIGHBOR HALF DISTANCE IN METAL, r_{met} (Å)	r_{met}/r_{ion}
Li	0.60	1.51	2.52
Na	0.95	1.83	1.93
K	1.33	2.26	1.70
Rb	1.48	2.42	1.64
Cs	1.69	2.62	1.55
Cu	0.96	1.28	1.33
Ag	1.26	1.45	1.15
Au	1.37	1.44	1.05

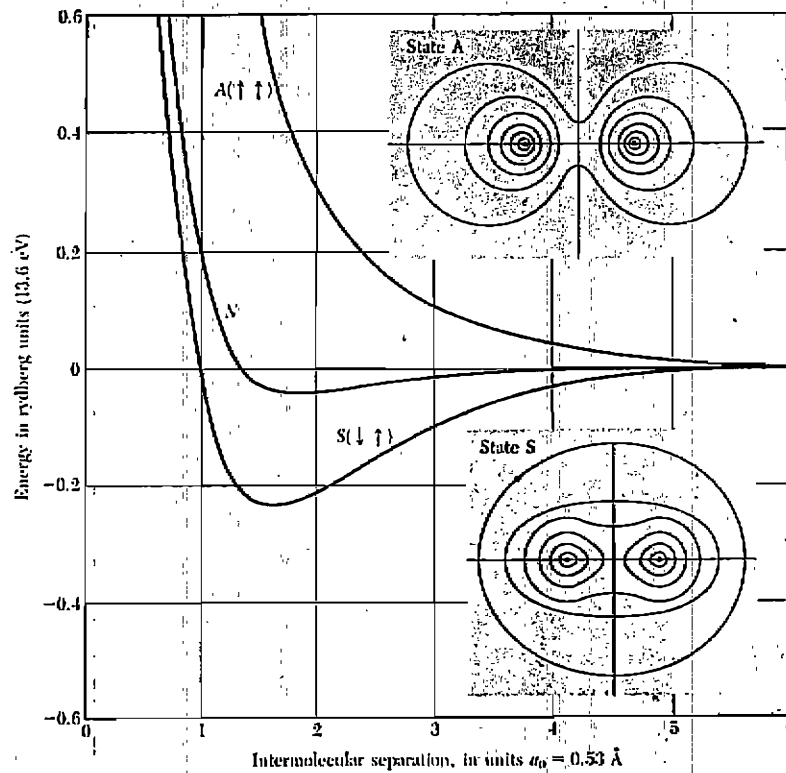
HYDROGEN-BONDED CRYSTALS

Some classifications list hydrogen-bonded crystals as a fourth category of insulator. This is in recognition of the fact that hydrogen is unique in three important ways:

1. The ion core of a hydrogen atom is a bare proton of order 10^{-13} cm in radius, a factor of 10^5 smaller than any other ion core.
2. Hydrogen is but one electron shy of the stable helium configuration, which, uniquely among stable configurations, has not eight but only two electrons in the outermost shell.
3. The first ionization potential of atomic hydrogen is unusually high (H, 13.59 eV; Li, 5.39 eV; Na, 5.14 eV; K, 4.34 eV; Rb, 4.18 eV; Cs, 3.89 eV).

As a result of these properties hydrogen can play a role unlike any other element in crystalline structures. Because of its large ionization potential, it is much more difficult to remove an electron completely from hydrogen, and it therefore does not

Covalent Bond



exchange

Figure 12 Energy of molecular hydrogen (H_2) referred to separated neutral atoms. A negative energy corresponds to binding. The curve N refers to a classical calculation with free atom charge densities; A is the result for parallel electron spins, taking the Pauli exclusion principle into account, and S (the stable state) for antiparallel spins. The density of charge is represented by contour lines for the states A and S .

Covalent Crystal

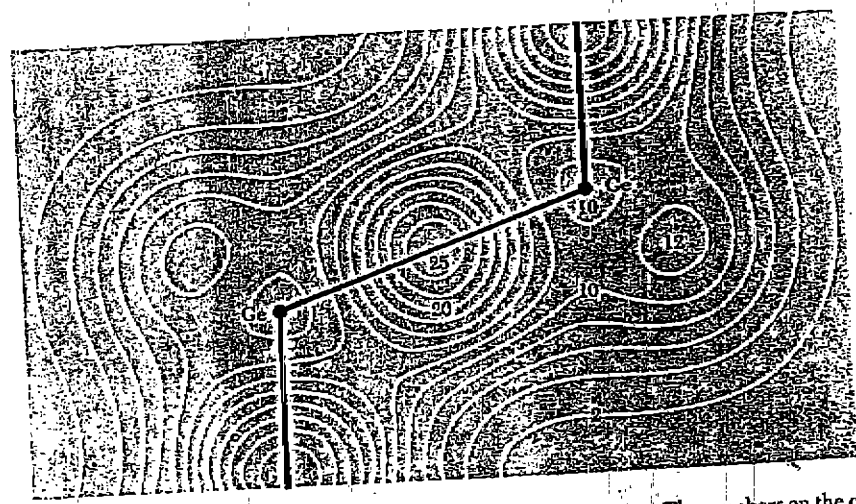


Figure 11 Calculated valence electron concentration in germanium. The numbers on the contours give the electron concentration per primitive cell, with four valence electrons per atom (eight electrons per primitive cell). Note the high concentration midway along the Ge-Ge bond, as we expect for covalent bonding. (After J. R. Chelikowsky and M. L. Cohen.)

behave as an alkali metal ion (of minute radius) in forming ionic crystals. On the other hand, it cannot behave as the atoms in typical covalent crystals, for lacking only one electron from a closed-shell configuration it can, in chemical terms, form only one covalent bond through electron sharing.²¹ Finally, because the proton has, for all practical purposes, no size at all, it can essentially sit on the surface of the large negative ions, resulting in a type of structure unattainable with any other positive ion.

One manifestation of these peculiar properties is illustrated in Figure 19.11 for the case of ice. The electron from the hydrogen atom is, like the proton, fairly well localized in the neighborhood of the oxygen ions. The positive proton resides close to a single oxygen ion, along the line joining it to one of its neighbors, thereby helping to bind the two oxygen ions together. (Note the lack of regularity in the positions of the protons. This can be observed thermodynamically in the large "residual entropy" possessed by ice at low temperatures, corresponding to the large number of ways of assigning a proton to either end of each bond, consistent with two protons being close to each oxygen atom.)

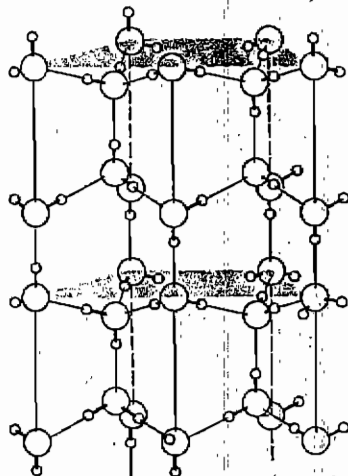


Figure 19.11

The crystal structure of one of the many phases of ice. The large circles are oxygen ions; the small circles are protons. Ice is an example in which hydrogen bonding plays a crucial role. (After L. Pauling, *The Nature of The Chemical Bond*, 3rd. ed., Cornell University Press, Ithaca, New York, 1960.)

Hydrogen Bonding

This completes our descriptive survey of some of the various solid types. We now turn to some of the elementary quantitative implications of the various structures on bulk solid properties—particularly the binding, or cohesive, energy.

PROBLEMS

1. Origin of the van der Waals Force

Consider two noble gas atoms a distance R apart, represented by fixed nuclei of charge Ze located at 0 and R , each surrounded by Z electrons. The electrons bound to the nucleus at 0 have co-

²¹ This contrasts with the four bonds that are present in tetrahedrally coordinated covalent crystals, as the result of forming two closed shells from eight electrons.