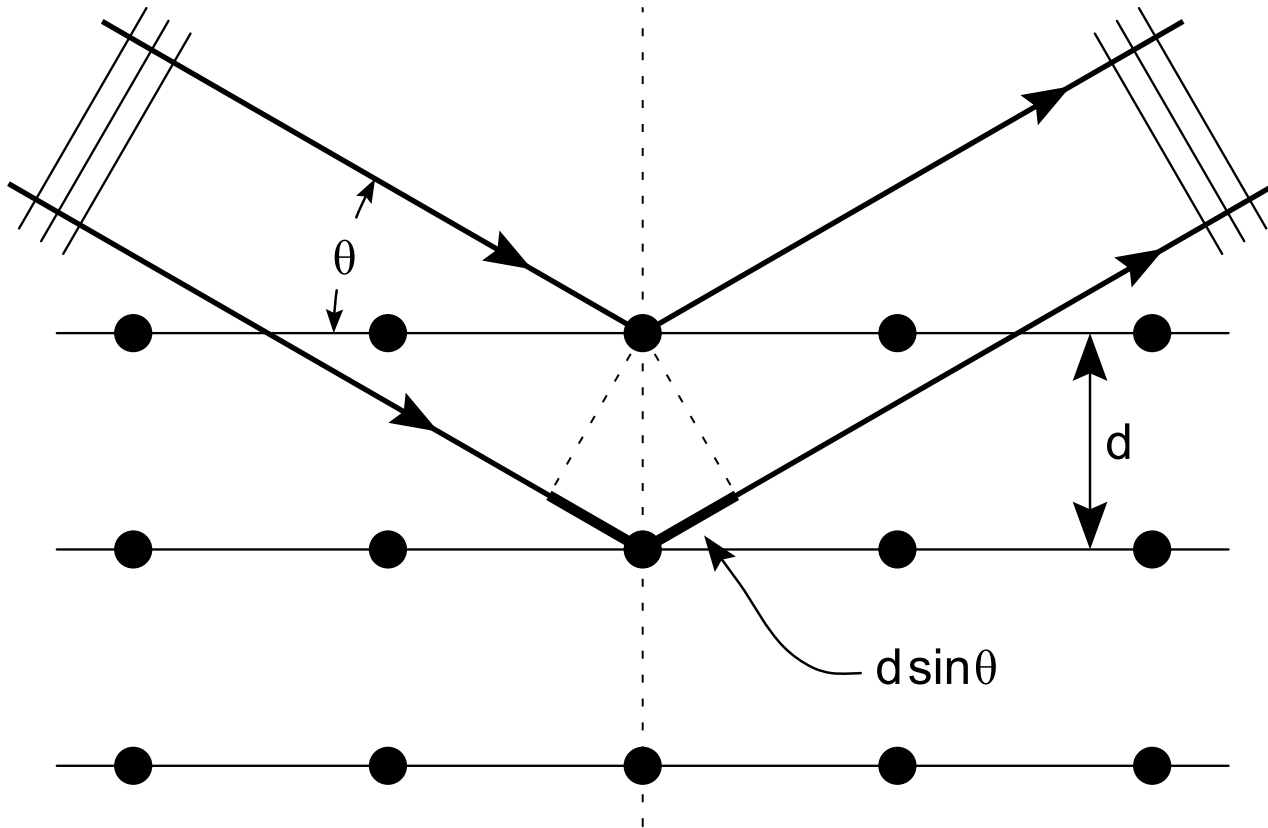# PHY 3205
Solid State Physics I

Crystal Bindings

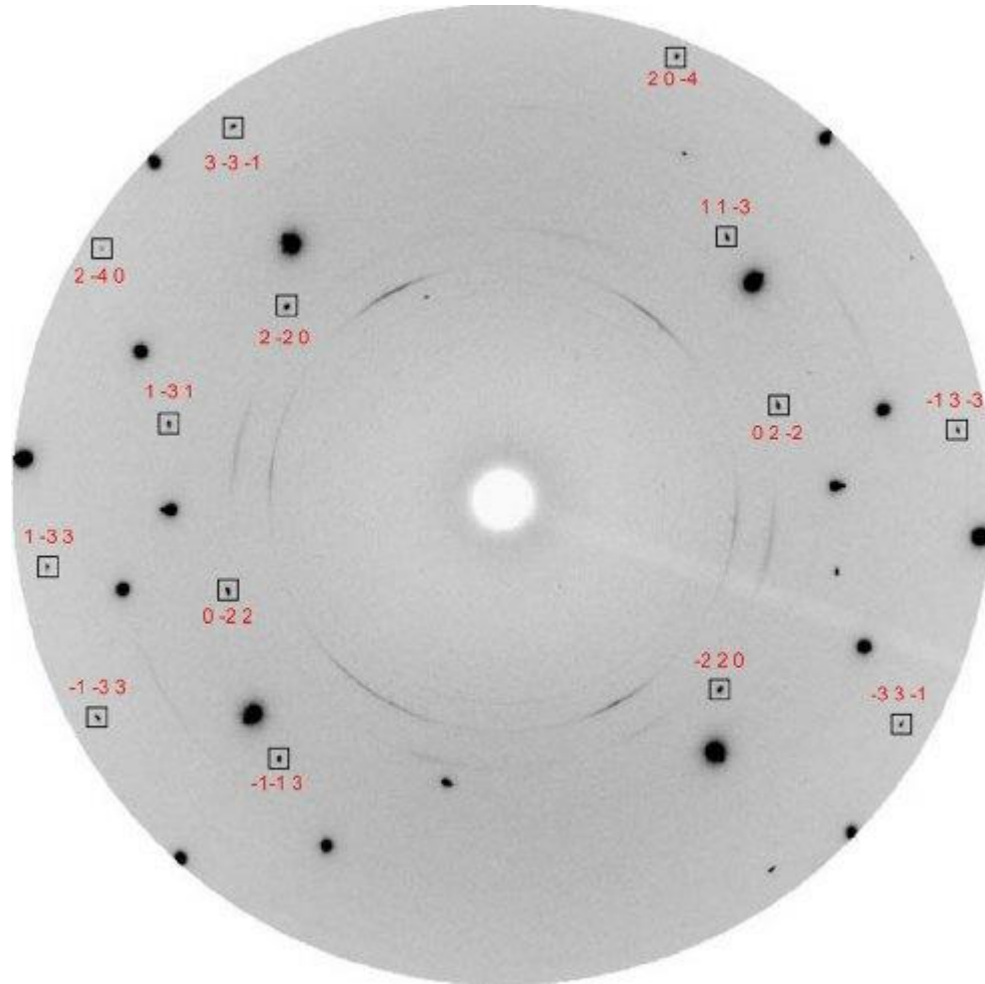### Dr. Mohammad Abdur Rashid

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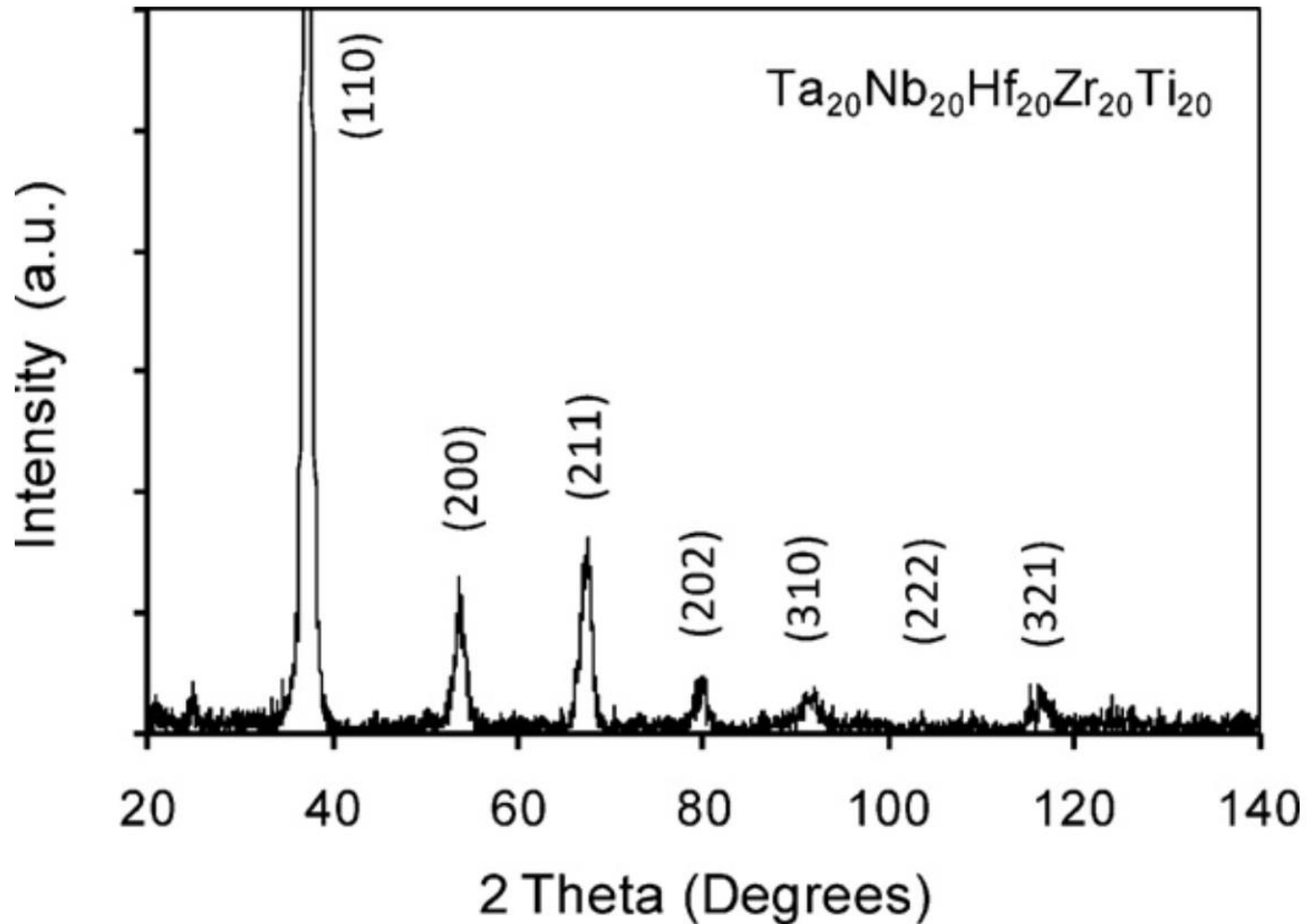
X-ray diffraction pattern of the TaNbHfZrTi alloy. The indexed peaks belong to a BCC crystal lattice with the lattice parameter $a = 340.4$ pm.

X-ray diffraction pattern
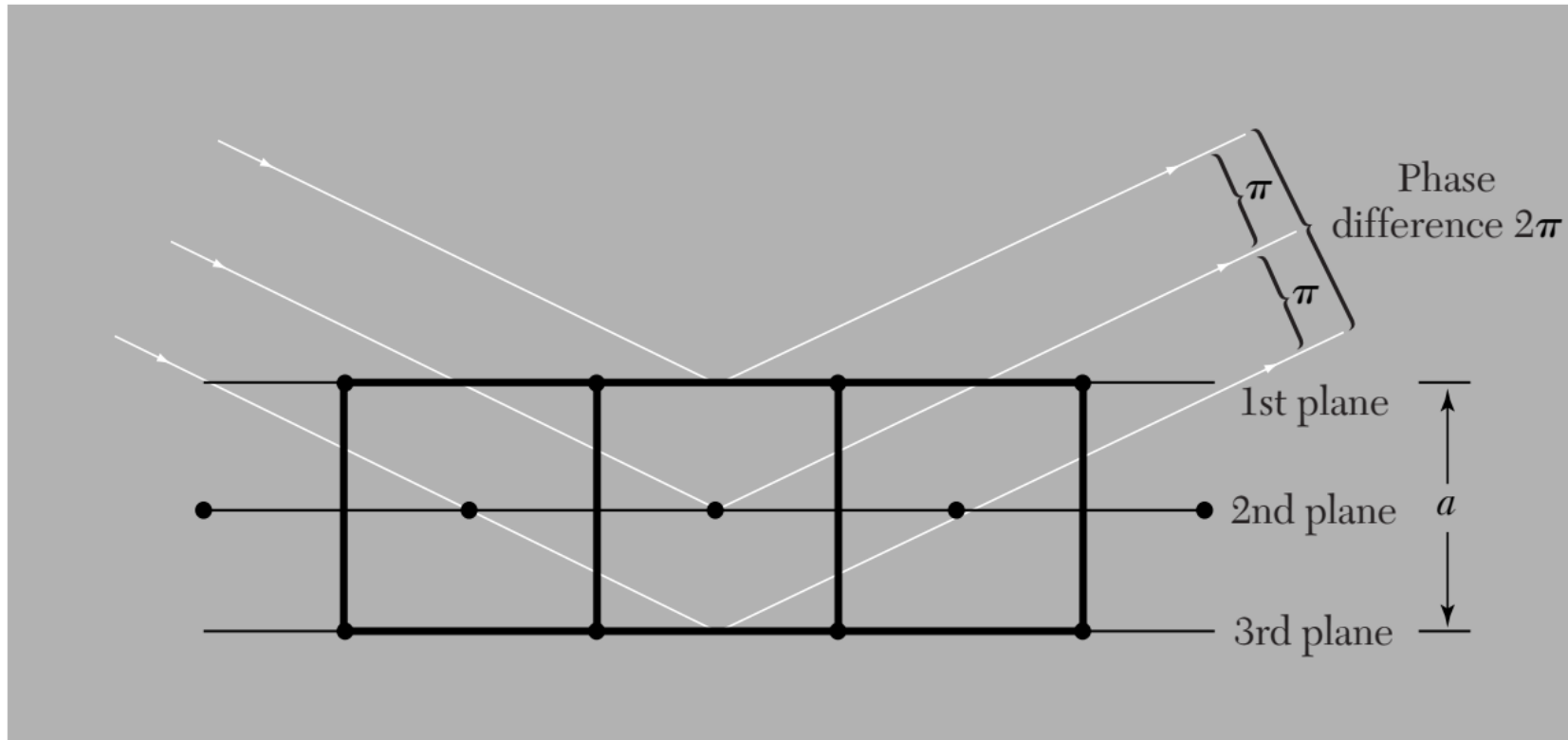

Figure 16 Explanation of the absence of a (100) reflection from a body-centered cubic lattice. The phase difference between successive planes is π, so that the reflected amplitude from two adjacent planes is $1 + e^{-i\pi} = 1 - 1 = 0$.

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.)
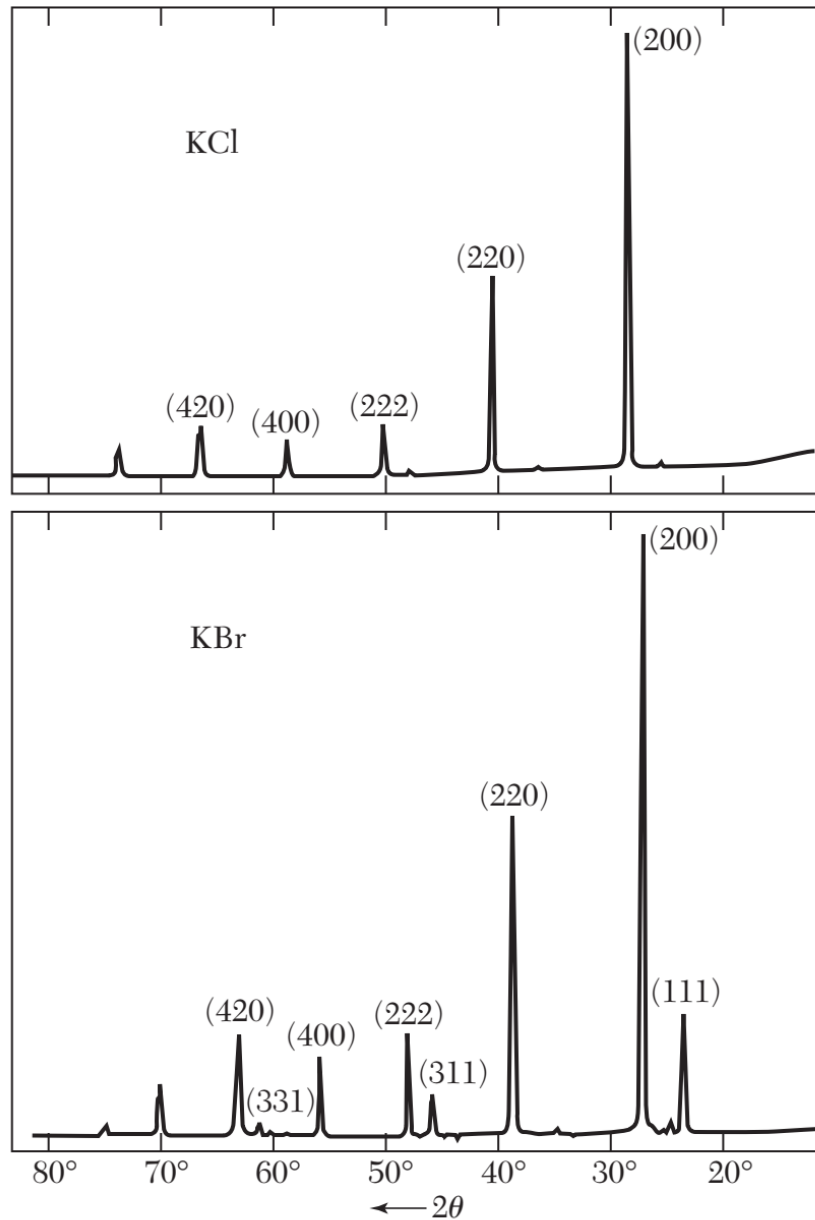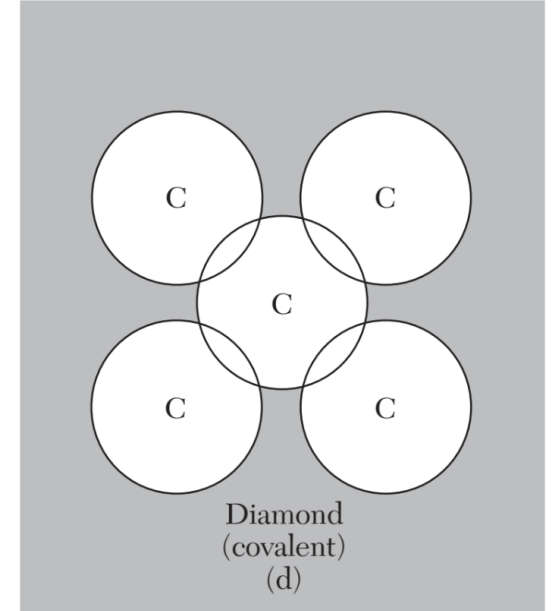
Crystal Bindings

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?
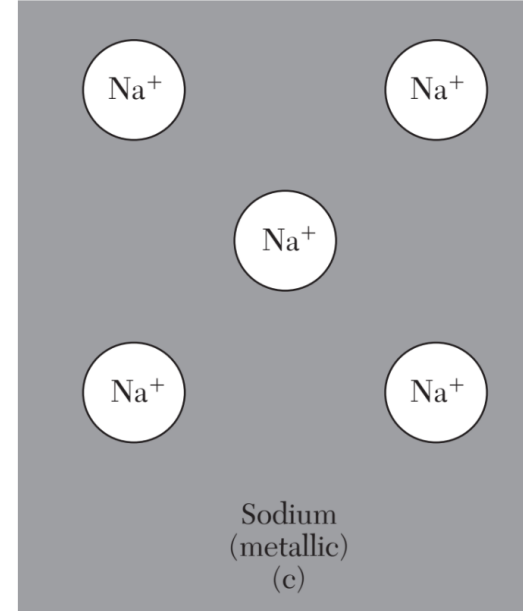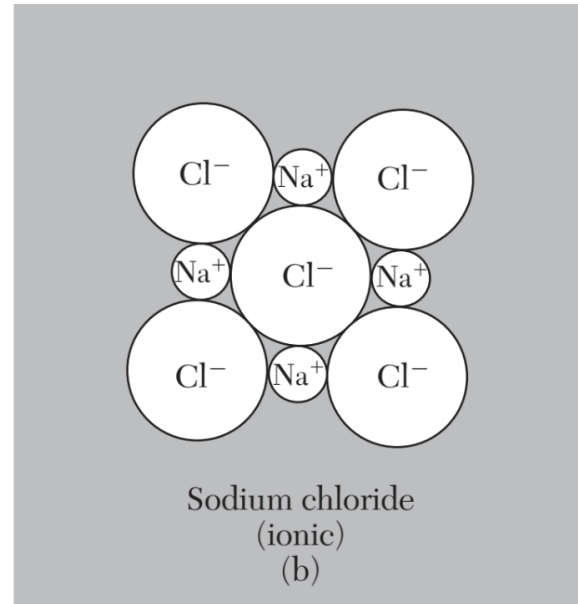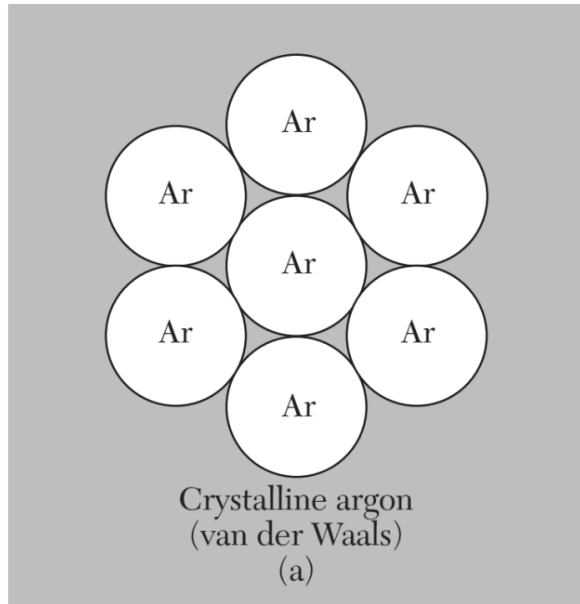
The principal types of crystalline binding. In (a) neutral atoms with closed electron shells are bound together weakly by the van der Waals forces associated with fluctuations in the charge distributions. In (b) electrons are transferred from the alkali atoms to the halogen atoms, and the resulting ions 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.

Values listed per element as: kJ/mol, eV/atom, kcal/mol

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

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.
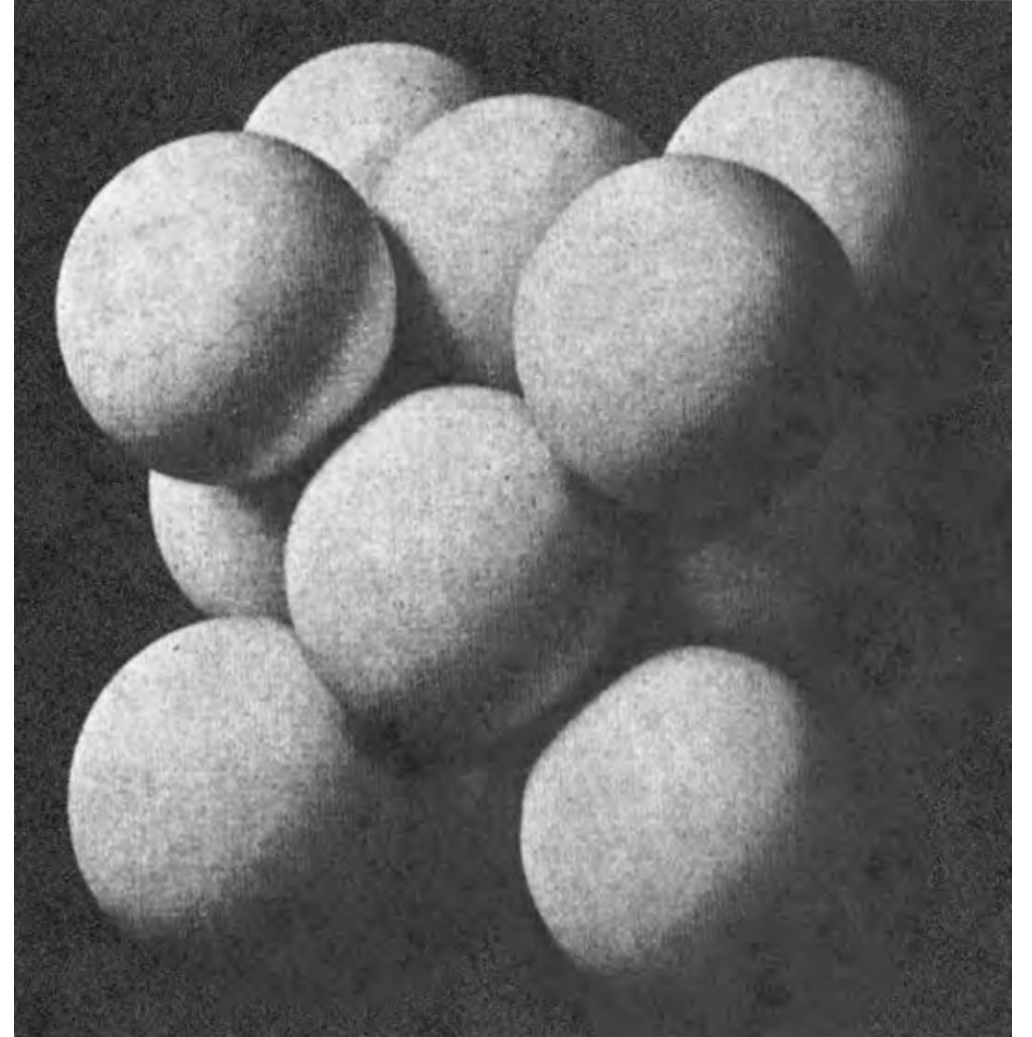
Crystals of inert gas

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.
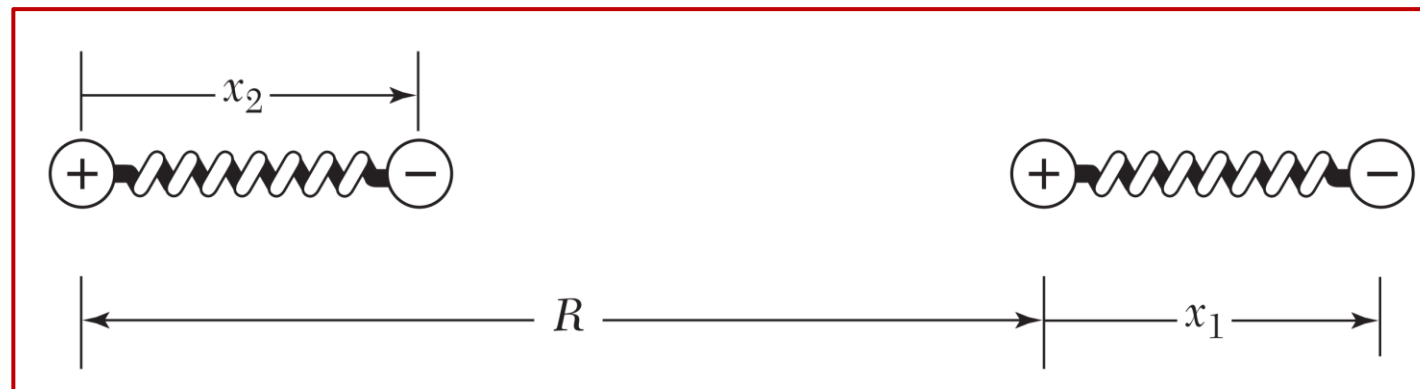
Van der Waals-London Interaction

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

$$\mathscr{H}_0 = \frac{1}{2m}\, p_1^2 + \tfrac{1}{2}Cx_1^2 + \frac{1}{2m}\, p_2^2 + \tfrac{1}{2}Cx_2^2 \ . \tag{1}$$

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

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

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

$$\mathcal{H}_1 \cong -\frac{2e^2 x_1 x_2}{R^3} \; . \qquad (3)$$

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

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

or, on solving for x_1 and x_2,

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

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:

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

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.
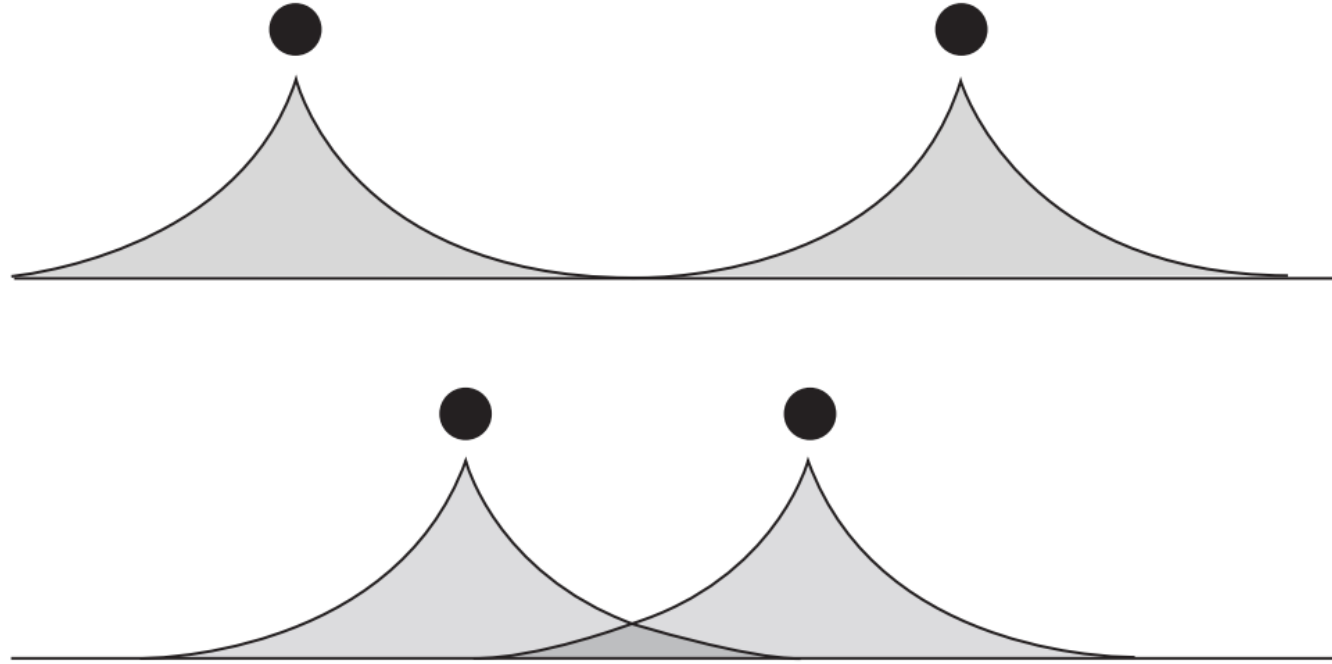
Repulsive Interaction

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.
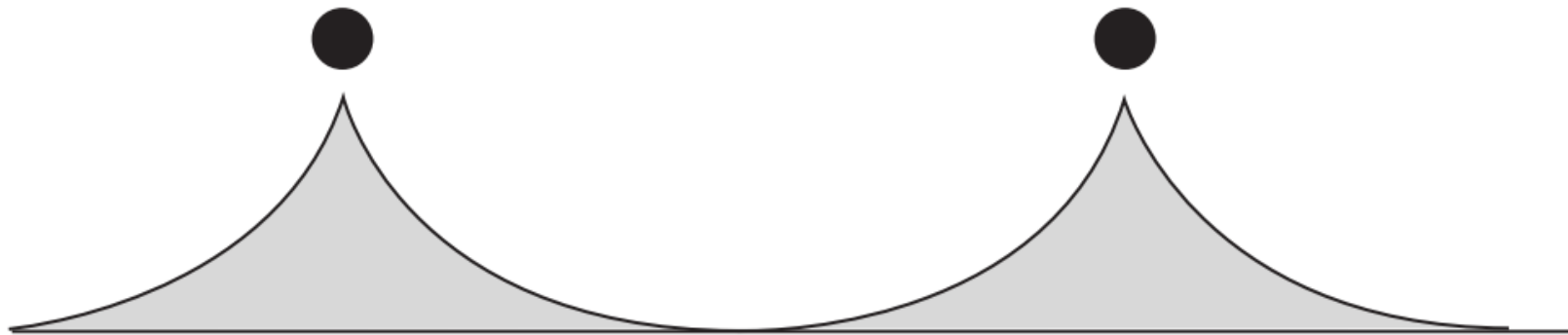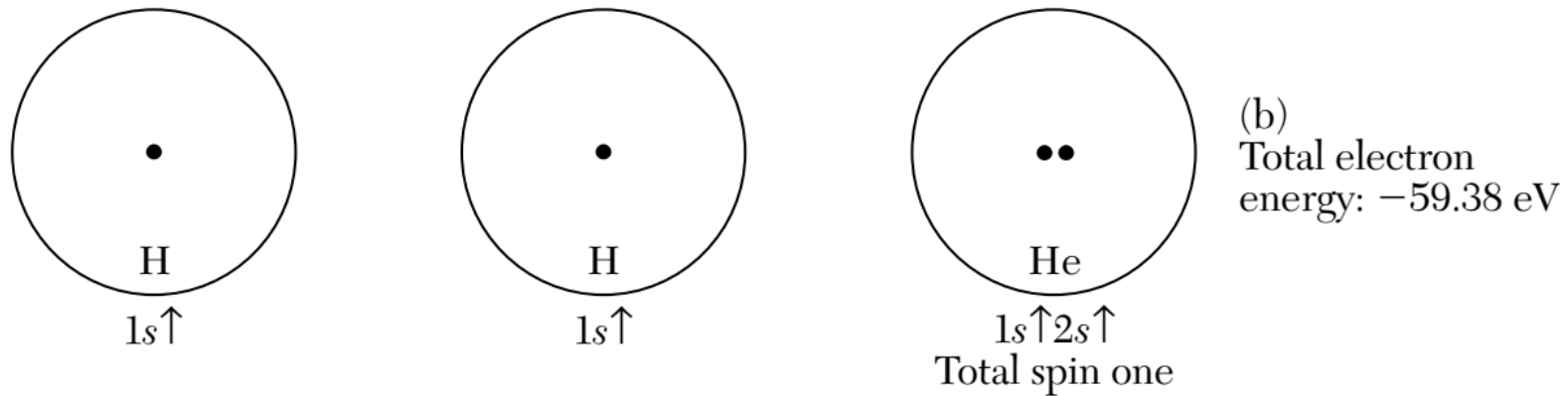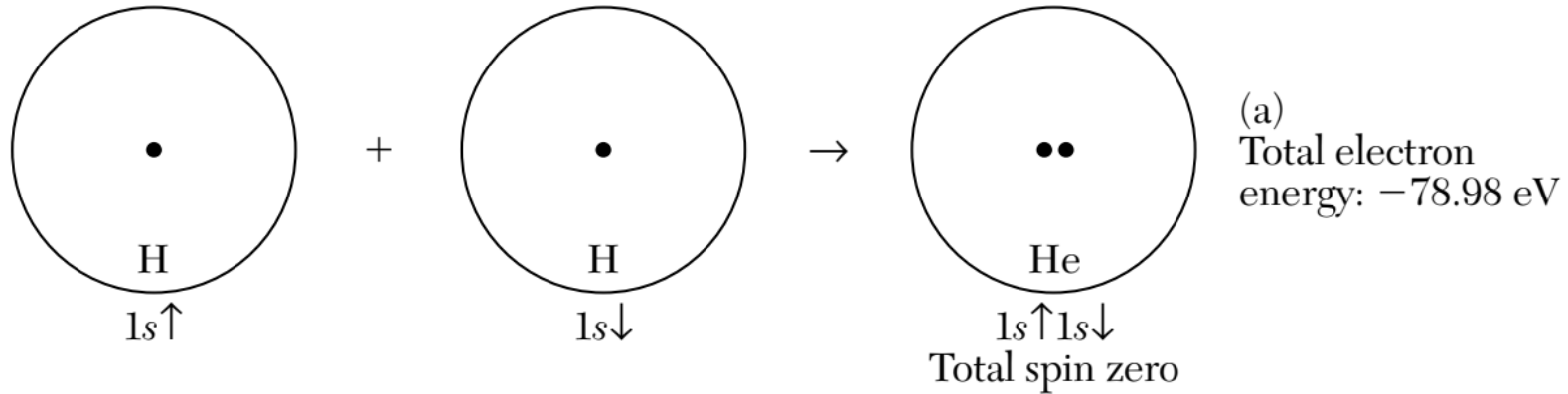
Repulsive Interaction: Pauli exclusion principle

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

Repulsive Interaction: Pauli exclusion principle

(a) Total electron energy: -78.98 eV

(b) Total electron energy: -59.38 eV

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

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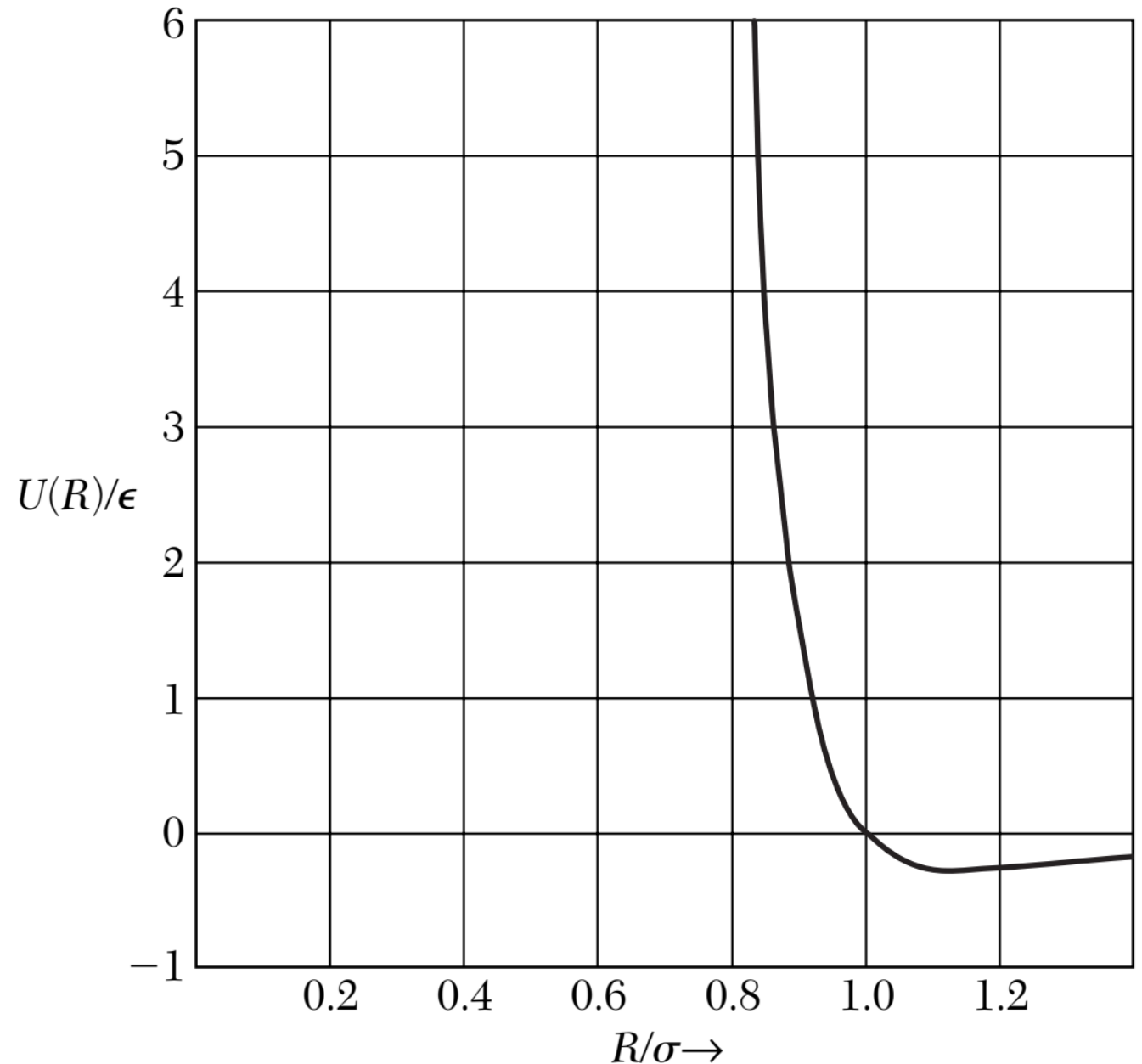
Equilibrium Lattice Constants

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

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

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 $\tfrac{1}{2}$ 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:

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

whence

$$R_0/\sigma = 1.09 , \tag{14}$$

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):

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

and, at $R = R_0$,

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

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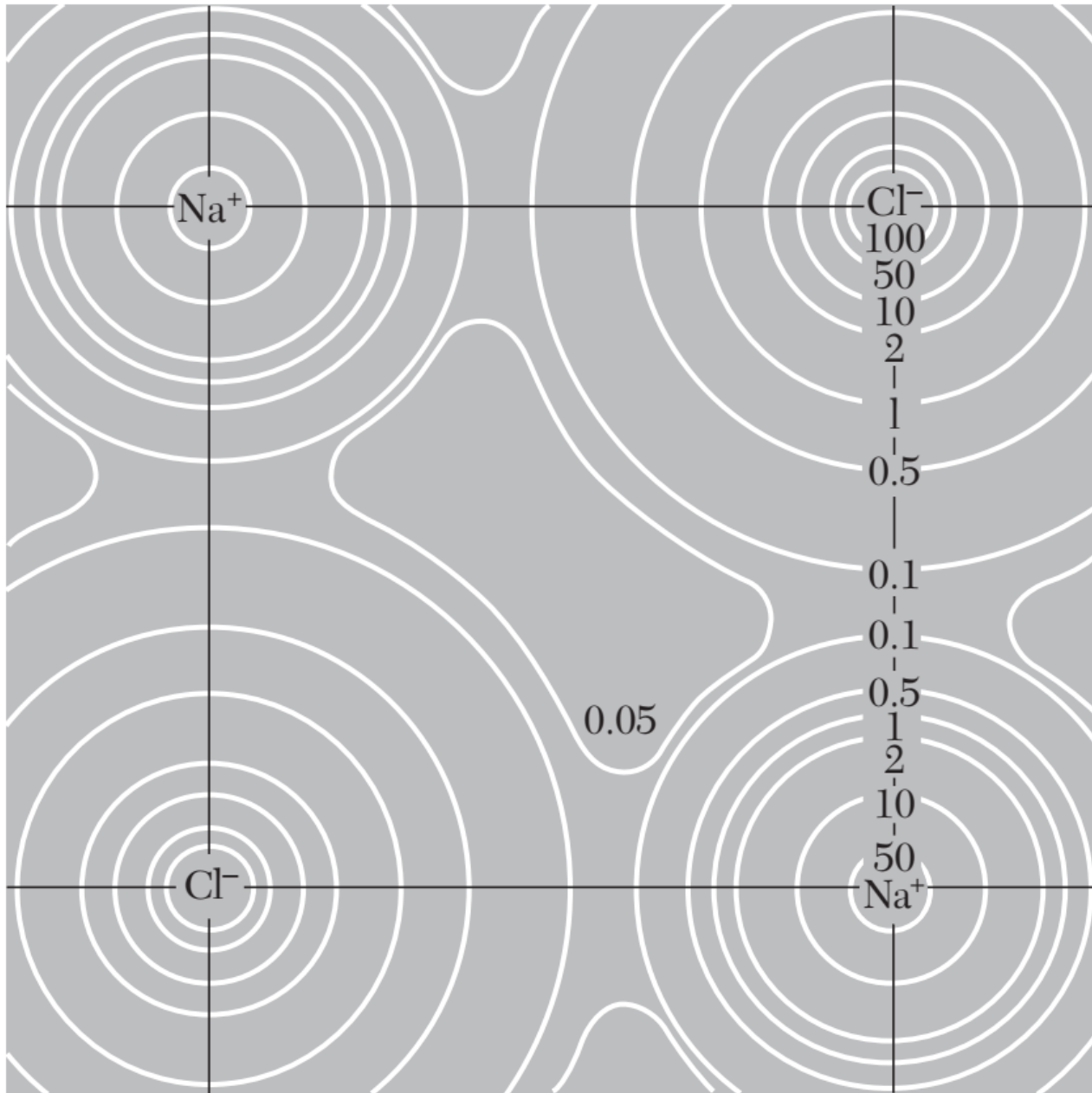
Figure 7 Electron density distribution in the base plane of NaCl, after x-ray studies by G. Schoknecht. The numbers on the contours give the relative electron concentration.

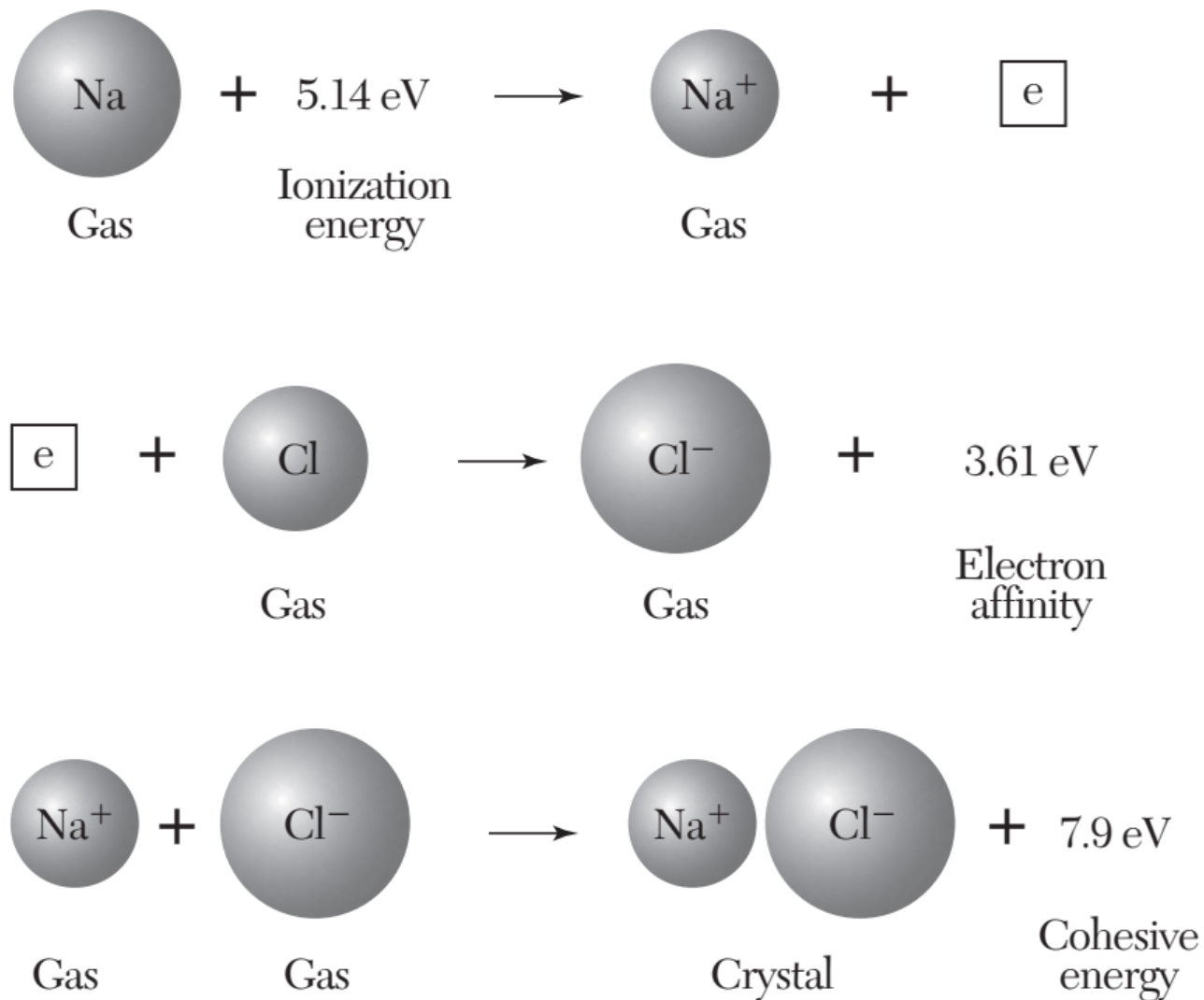**Figure 8** The energy per molecule unit of a crystal of sodium chloride is $(7.9 - 5.1 + 3.6) = 6.4$ eV lower than the energy of separated neutral atoms. The lattice energy with respect to separated ions is 7.9 eV per molecule unit. All values on the figure are experimental. Values of the ionization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

If U_{ij} is the interaction energy between ions i and j, we define a sum U_i which includes all interactions involving the ion i:

$$U_i = \sum_j{}' U_{ij} \ , \tag{17}$$

where the summation includes all ions except $j = i$. We suppose that U_{ij} may be written as the sum of a central field repulsive potential of the form $\lambda \exp(-r/\rho)$, where λ and ρ are empirical parameters, and a coulomb potential $\pm q^2/r$. Thus

$$(\text{CGS}) \qquad\qquad U_{ij} = \lambda \exp(-r_{ij}/\rho) \pm q^2/r_{ij} \ , \tag{18}$$

where the $+$ sign is taken for the like charges and the $-$ sign for unlike charges. In SI units the coulomb interaction is $\pm q^2/4\pi\epsilon_0 r$; we write this section in CGS units in which the coulomb interaction is $\pm q^2/r$.

Electrostatic or Madelung Energy

The repulsive term describes the fact that each ion resists overlap with the electron distributions of neighboring ions. We treat the strength λ and range ρ as constants to be determined from observed values of the lattice constant and compressibility; we have used the exponential form of the empirical repulsive potential rather than the R^{-12} form used for the inert gases. We note that r is a measure of the range of the repulsive interaction; when $r = \rho$, the repulsive interaction is reduced to e^{-1} of the value at $r = 0$.

In the NaCl structure the value of U_i does not depend on whether the reference ion i is a positive or a negative ion. We neglect surface effects and write the total lattice energy U_{tot} of a crystal composed of N molecules or $2N$ ions as U tot 5 NU_i. Here N, rather than $2N$, occurs because we must count each *pair* of interactions only once or each bond only once. The total lattice energy is defined as the energy required to separate the crystal into individual ions at an infinite distance apart.

It is convenient again to introduce quantities p_{ij} such that $r_{ij} \equiv p_{ij}R$, where R is the nearest-neighbor separation in the crystal. If we include the repulsive interaction only among nearest neighbors, we have

$$(\text{CGS}) \qquad U_{ij} = \begin{cases} \lambda \exp(-R/p) - \dfrac{q^2}{R} & (\text{nearest neighbors}) \\ \\ \pm\dfrac{1}{p_{ij}}\dfrac{q^2}{R} & (\text{otherwise}). \end{cases} \qquad (19)$$

Thus

$$(\text{CGS}) \qquad U_{\text{tot}} = NU_i = N\left(z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R}\right), \qquad (20)$$

where z is the number of nearest neighbors of any ion and

$$\boxed{\alpha \equiv \sum_j{}' \frac{(\pm)}{p_{ij}} \equiv \textbf{Madelung constant} } . \qquad (21)$$

The sum should include the nearest-neighbor contribution, which is just z.

At the equilibrium separation $dU_{\text{tot}}/dR = 0$, so that

$$\text{(CGS)} \qquad N\frac{dU_i}{dR} = -\frac{Nz\lambda}{\rho}\exp(-R/\rho) + \frac{N\alpha q^2}{R^2} = 0 \ , \qquad (22)$$

or

$$\text{(CGS)} \qquad R_0^2\exp(-R_0/\rho) = \rho\alpha q^2/z\lambda \ . \qquad (23)$$

This determines the equilibrium separation R_0 if the parameters ρ, λ of the repulsive interaction are known. For SI, replace q^2 by $q^2/4\pi\epsilon_0$.

The total lattice energy of the crystal of $2N$ ions at their equilibrium separation R_0 may be written, using (20) and (23), as

$$\text{(CGS)} \qquad U_{\text{tot}} = -\frac{N\alpha q^2}{R_0}\left(1 - \frac{\rho}{R_0}\right) \ . \qquad (24)$$

The term $-N\alpha q^2/R_0$ is the Madelung energy. We shall find that ρ is of the order of $0.1R_0$, so that the repulsive interaction has a very short range.

Evaluation of the Madelung Constant

The definition of the Madelung constant α is,
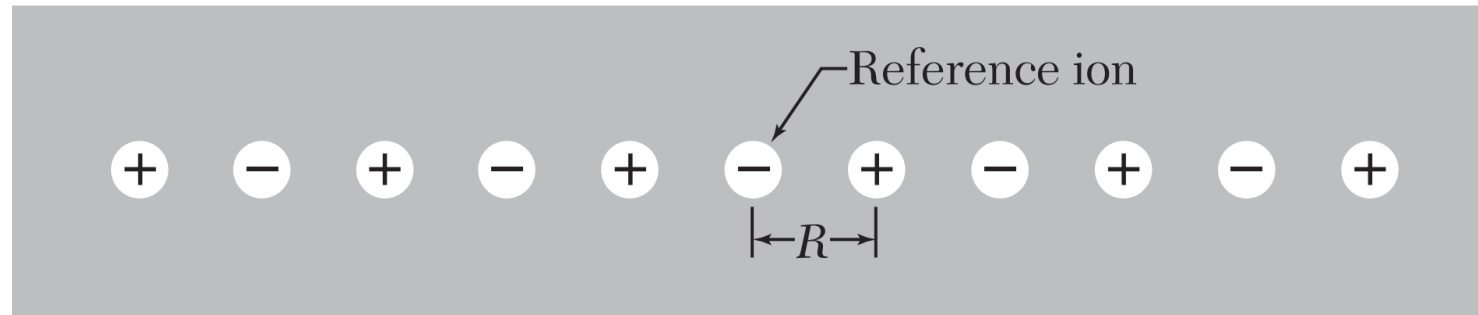
$$\alpha = \sum_j{}' \frac{(\pm)}{p_{ij}} \; .$$

An equivalent definition is

$$\frac{\alpha}{R} = \sum_j{}' \frac{(\pm)}{r_j} \; , \tag{25}$$

where r_j is the distance of the jth ion from the reference ion and R is the nearest-neighbor distance. The value given for α will depend on whether it is defined in terms of the nearest-neighbor distance R or in terms of the lattice parameter a or in terms of some other relevant length.

Evaluation of the Madelung Constant

As an example, we compute the Madelung constant for the infinite line of ions of alternating sign in figure. Pick a negative ion as reference ion, and let R denote the distance between adjacent ions. Then

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

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

The factor 2 occurs because there are two ions, one to the right and one to the left, at equal distances r_j.

Evaluation of the Madelung Constant

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

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

Thus the Madelung constant for the one-dimensional chain is $\alpha = 2\ln 2$.

Structure	α
Sodium chloride, NaCl	1.747565
Cesium chloride, CsCl	1.762675
Zinc blende, cubic ZnS	1.6381

Energy per molecule of KCl crystal, showing Madelung (coulomb) and repulsive contributions.

Repulsive energy
$(2.4 \times 10^4) \exp(-R/0.30)$ eV

Energy, in eV

Total energy

Equilibrium position

Coulomb energy
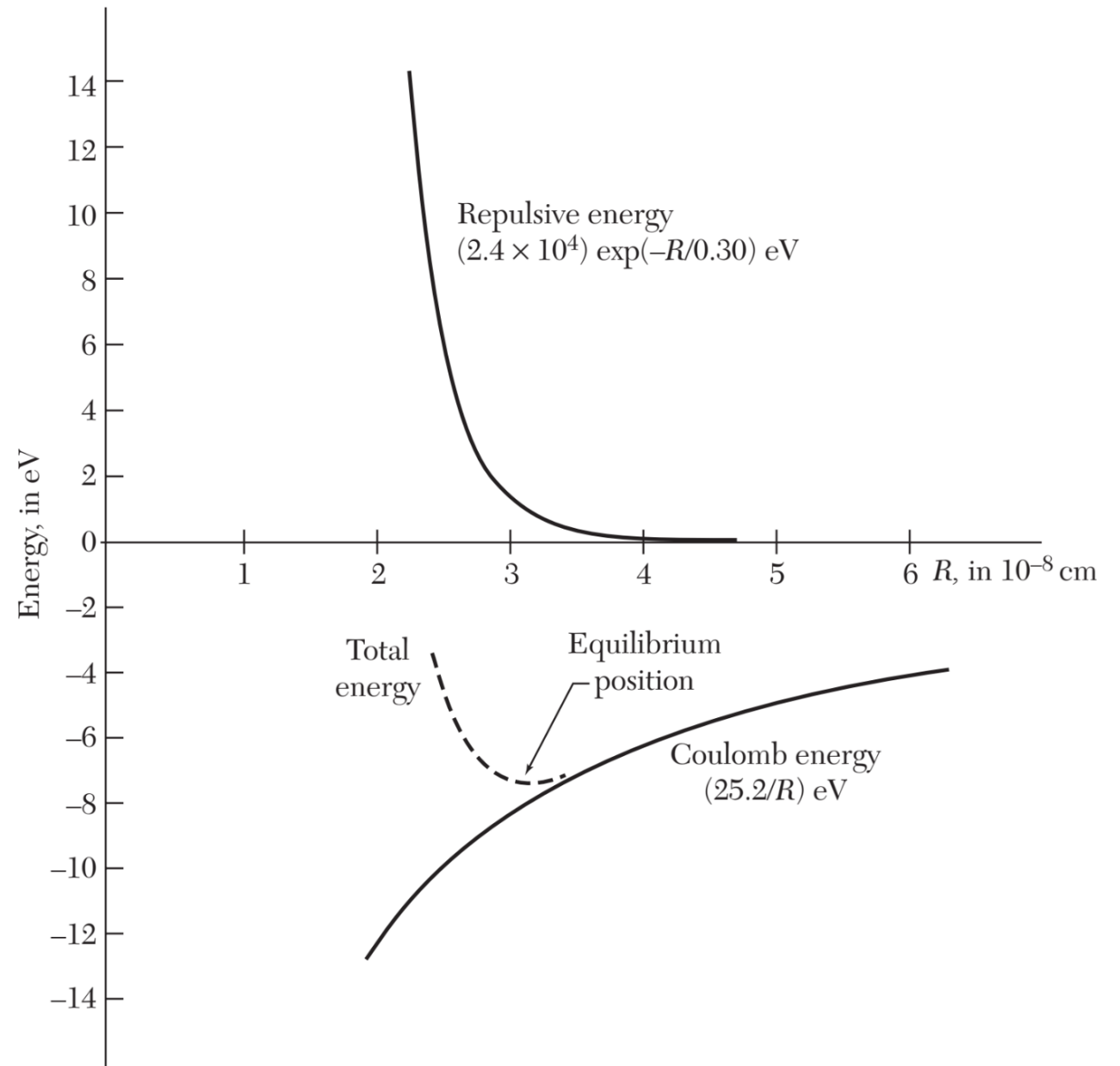$(25.2/R)$ eV

R, in 10^{-8} cm

Table 7 Properties of alkali halide crystals with the NaCl structure

All values (except those in square brackets) at room temperature and atmospheric pressure, with no correction for changes in R_0 and U from absolute zero. Values in square brackets at absolute zero temperature and zero pressure, from private communication by L. Brewer.

	Nearest-neighbor separation R_0 in Å	Bulk modulus B, in 10^{11} dyn/cm^2 or 10^{10} N/m^2	Repulsive energy parameter $z\lambda$, in 10^{-8} erg	Repulsive range parameter ρ, in Å	Lattice energy compared to free ions, in kcal/mol	
					Experimental	Calculated
LiF	2.014	6.71	0.296	0.291	242.3[246.8]	242.2
LiCl	2.570	2.98	0.490	0.330	198.9[201.8]	192.9
LiBr	2.751	2.38	0.591	0.340	189.8	181.0
LiI	3.000	(1.71)	0.599	0.366	177.7	166.1
NaF	2.317	4.65	0.641	0.290	214.4[217.9]	215.2
NaCl	2.820	2.40	1.05	0.321	182.6[185.3]	178.6
NaBr	2.989	1.99	1.33	0.328	173.6[174.3]	169.2
NaI	3.237	1.51	1.58	0.345	163.2[162.3]	156.6
KF	2.674	3.05	1.31	0.298	189.8[194.5]	189.1
KCl	3.147	1.74	2.05	0.326	165.8[169.5]	161.6
KBr	3.298	1.48	2.30	0.336	158.5[159.3]	154.5
KI	3.533	1.17	2.85	0.348	149.9[151.1]	144.5
RbF	2.815	2.62	1.78	0.301	181.4	180.4
RbCl	3.291	1.56	3.19	0.323	159.3	155.4
RbBr	3.445	1.30	3.03	0.338	152.6	148.3
RbI	3.671	1.06	3.99	0.348	144.9	139.6

Data from various tables by M. P. Tosi, Solid State Physics **16**, 1 (1964).
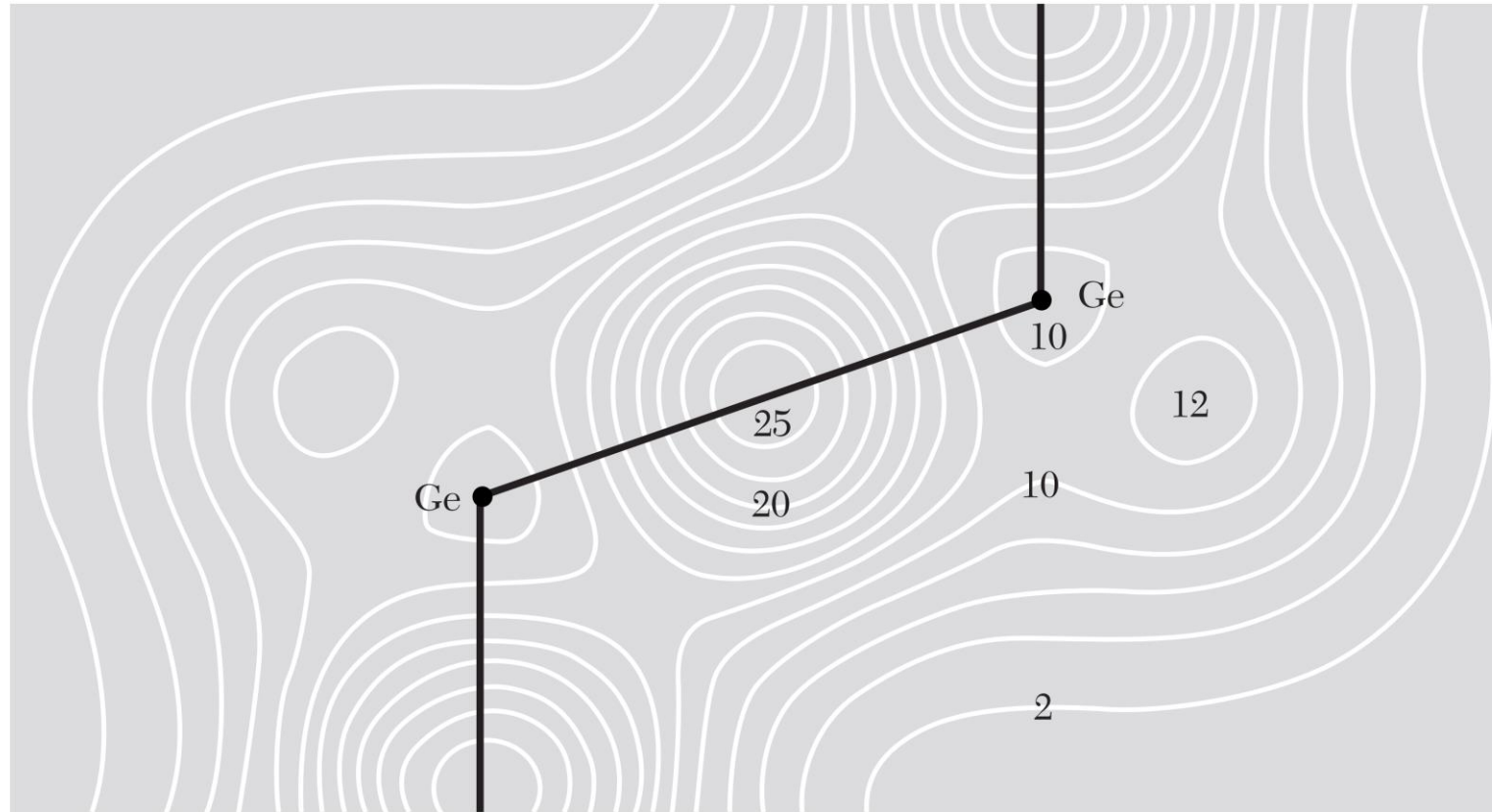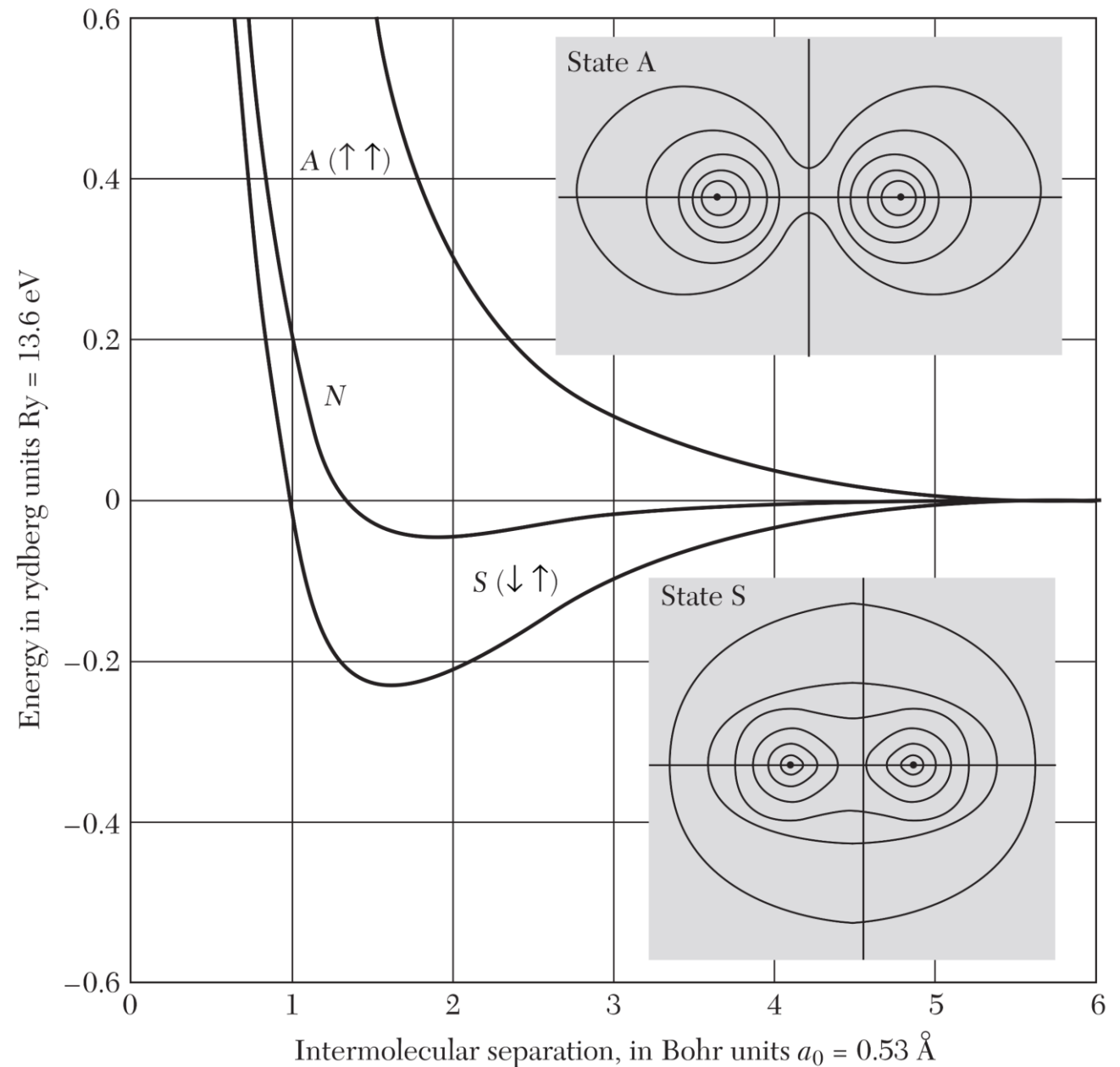
Covalent Crystals

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.)

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.

State A

State S

$A\ (\uparrow\uparrow)$

N

$S\ (\downarrow\uparrow)$

Energy in rydberg units Ry = 13.6 eV

Intermolecular separation, in Bohr units $a_0 = 0.53\ \mathring{A}$

Covalent bond

The covalent bond is the classical electron pair or homopolar bond of chemistry, particularly of organic chemistry. It is a strong bond: the bond between two carbon atoms in diamond with respect to separated neutral atoms is comparable with the bond strength in ionic crystals.

The covalent bond is usually formed from two electrons, one from each atom participating in the bond. The electrons forming the bond tend to be partly localized in the region between the two atoms joined by the bond. The spins of the two electrons in the bond are antiparallel.

The covalent bond has strong directional properties. Thus carbon, silicon, and germanium have the diamond structure, with atoms joined to four nearest neighbors at tetrahedral angles, even though this arrangement gives a low filling of space, 0.34 of the available space, compared with 0.74 for a close-packed structure. The tetrahedral bond allows only four nearest neighbors, whereas a close-packed structure has 12. We should not overemphasize the similarity of the bonding of carbon and silicon. Carbon gives biology, but silicon gives geology and semiconductor technology.

The binding of molecular hydrogen is a simple example of a covalent bond. The strongest binding occurs when the spins of the two electrons are antiparallel. The binding depends on the relative spin orientation not because there are strong magnetic dipole forces between the spins, but because the Pauli principle modifies the distribution of charge according to the spin orientation. This spin-dependent coulomb energy is called the **exchange interaction**.

The Pauli principle gives a strong repulsive interaction between atoms with filled shells. If the shells are not filled, electron overlap can be accommodated without excitation of electrons to high energy states and the bond will be shorter. Compare the bond length (2 Å) of Cl_2 with the interatomic distance (3.76 Å) of Ar in solid Ar; also compare the cohesive energies given in Table 1. The difference between Cl_2 and Ar_2 is that the Cl atom has five electrons in the $3p$ shell and the Ar atom has six, filling the shell, so that the repulsive interaction is stronger in Ar than in Cl.

The elements C, Si, and Ge lack four electrons with respect to filled shells, and thus these elements (for example) can have an attractive interaction associated with charge overlap. The electron configuration of carbon is $1s^2 2s^2 2p^2$. To form a tetrahedral system of covalent bonds the carbon atom must first be promoted to the electronic configuration $1s^2 2s 2p^3$. This promotion from the ground state requires 4 eV, an amount more than regained when the bonds are formed.

Metals

Metals are characterized by high electrical conductivity, and a large number of electrons in a metal are free to move about, usually one or two per atom. The electrons available to move about are called conduction electrons. The valence electrons of the atom become the conduction electrons of the metal. In some metals the interaction of the ion cores with the conduction electrons always makes a large contribution to the binding energy, but the characteristic feature of metallic binding is the lowering of the energy of the valence electrons in the metal as compared with the free atom.

The binding energy of an alkali metal crystal is considerably less than that of an alkali halide crystal: the bond formed by a conduction electron is not very strong. The interatomic distances are relatively large in the alkali metals because the kinetic energy of the conduction electrons is lower at large interatomic distances. This leads to weak binding. Metals tend to crystallize in relatively close packed structures: hcp, fcc, bcc, and some other closely related structures, and not in loosely-packed structures such as diamond.

In the transition metals there is additional binding from inner electron shells. Transition metals and the metals immediately following them in the periodic table have large d-electron shells and are characterized by high binding energy.

Hydrogen bond

Figure 13 The hydrogen difluoride ion HF_2^- is stabilized by a hydrogen bond. The sketch is of an extreme model of the bond, extreme in the sense that the proton is shown bare of electrons.
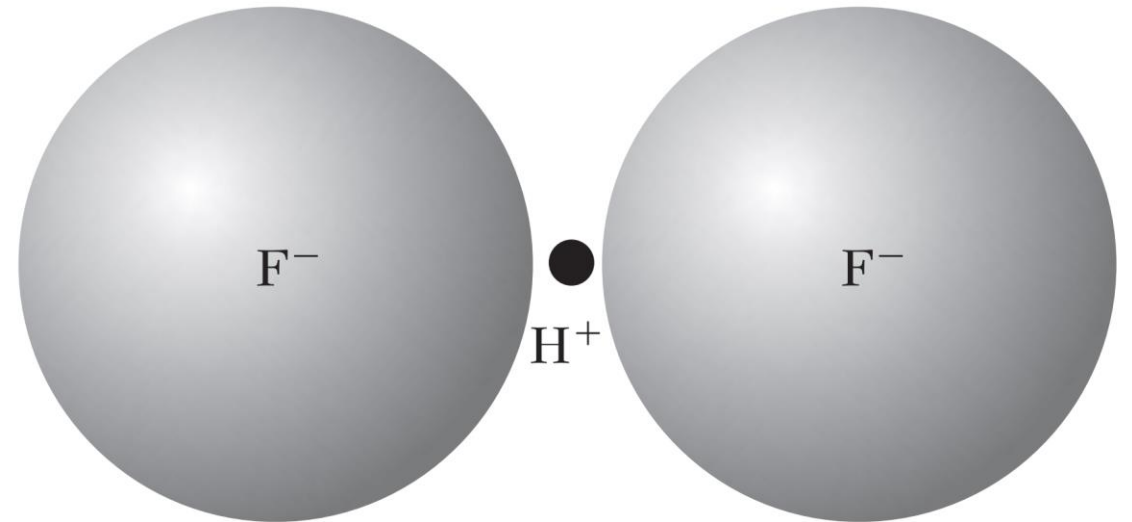
Because neutral hydrogen has only one electron, it should form a covalent bond with only one other atom. It is known, however, that under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, thus forming a **hydrogen bond** between them, with a bond energy of the order of 0.1 eV. It is believed that the hydrogen bond is largely ionic in character, being formed only between the most electronegative atoms, particularly F, O, and N. In the extreme ionic form of the hydrogen bond, the hydrogen atom loses its electron to another atom in the molecule; the bare proton forms the hydrogen bond. The atoms adjacent to the proton are so close that more than two of them would get in each other's way; thus the hydrogen bond connects only two atoms (Fig. 13).

The hydrogen bond is an important part of the interaction between H_2O molecules and is responsible together with the electrostatic attraction of the electric dipole moments for the striking physical properties of water and ice. It is important in certain ferroelectric crystals and in DNA.