Crystal Bindings

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Content

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

References

Introduction to Solid State Physics – Charles Kittel
Solid State Physics – Neil W. Ashcroft, N. David Mermin
Elementary Solid State Physics: Principles and Applications – M. Ali Omar

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Crystal Binding and Elastic Constants

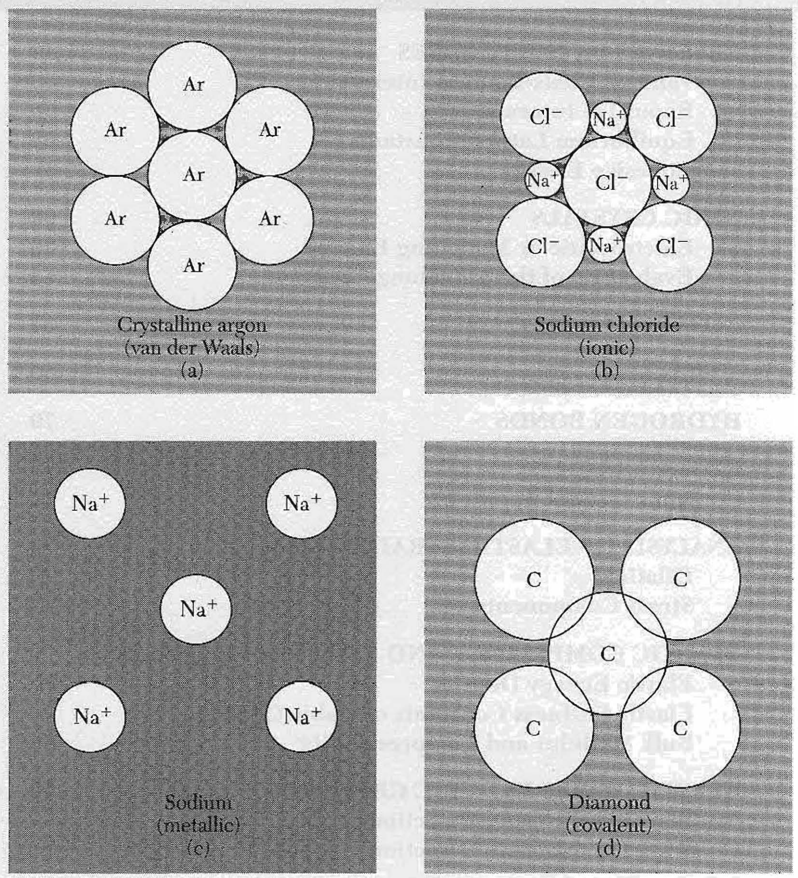

Figure 1 The principal types of crystalline binding. In (a) neutral atoms with closed electron shells are bound together weakly by the van der Waals forces associated with fluctuations in the charge distributions. In (b) electrons are transferred from the alkali atoms to the halogen atoms, and the resulting 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.

CHAPTER 3: CRYSTAL BINDING AND ELASTIC CONSTANTS

In this chapter we are concerned with the question: What holds a crystal together? 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 observed differences between the forms of condensed matter are caused in the final analysis by differences in the distribution of the outermost electrons and the ion cores (Fig. 1).

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.*

Values of the cohesive energy of the crystalline elements are given in Table 1. Notice the wide variation in cohesive energy between different columns of the periodic table. The inert gas crystals are weakly bound, with cohesive energies less than a few percent of the cohesive energies of the elements in the C, Si, Ge . . . column. The alkali metal crystals have intermediate values of the cohesive energy. The transition element metals (in the middle columns) are quite strongly bound. The melting temperatures (Table 2) and bulk modulii (Table 3) vary roughly as the cohesive energies.

CRYSTALS OF INERT GASES

The inert gases form the simplest crystals. The electron distribution is very close to that of the free atoms. Their properties at absolute zero are summarized in Table 4. The crystals are transparent insulators, weakly bound, with low melting temperatures. The atoms have very high ionization energies (see Table 5). 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[1]: the

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[1] Zero-point motion of the atoms (kinetic energy at absolute zero) is a quantum effect that plays a dominant role in He^3 and He^4. They do not solidify at zero pressure even at absolute zero temperature. The average fluctuation at 0 K of a He atom from its equilibrium position is of the order of 30 to 40 percent of the nearest-neighbor distance. The heavier the atom, the less important the zero-point effects. If we omit zero-point motion, we calculate a molar volume of 9 $cm^3\ mol^{-1}$ for solid helium, as compared with the observed values of 27.5 and 36.8 $cm^3\ mol^{-1}$ for liquid He^4 and liquid He^3, respectively.

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.

← 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**

Table 2 Melting points, in K.

(After R. H. Lamoreaux)

Li 453.7	Be 1562											B 2365	C	N 63.15	O 54.36	F 53.48	Ne 24.56
Na 371.0	Mg 922											Al 933.5	Si 1687	P w 317 r 863	S 388.4	Cl 172.2	Ar 83.81
K 336.3	Ca 1113	Sc 1814	Ti 1946	V 2202	Cr 2133	Mn 1520	Fe 1811	Co 1770	Ni 1728	Cu 1358	Zn 692.7	Ga 302.9	Ge 1211	As 1089	Se 494	Br 265.9	Kr 115.8
Rb 312.6	Sr 1042	Y 1801	Zr 2128	Nb 2750	Mo 2895	Tc 2477	Ru 2527	Rh 2236	Pd 1827	Ag 1235	Cd 594.3	In 429.8	Sn 505.1	Sb 903.9	Te 722.7	I 386.7	Xe 161.4
Cs 301.6	Ba 1002	La 1194	Hf 2504	Ta 3293	W 3695	Re 3459	Os 3306	Ir 2720	Pt 2045	Au 1338	Hg 234.3	Tl 577	Pb 600.7	Bi 544.6	Po 527	At	Rn
Fr	Ra 973	Ac 1324															

Ce 1072	Pr 1205	Nd 1290	Pm	Sm 1346	Eu 1091	Gd 1587	Tb 1632	Dy 1684	Ho 1745	Er 1797	Tm 1820	Yb 1098	Lu 1938
Th 2031	Pa 1848	U 1406	Np 910	Pu 913	Am 1449	Cm 1613	Bk 1562	Cf	Es	Fm	Md	No	Lw

Table 3 Isothermal bulk modulii and compressibilities at room temperature

After K. Gschneidner, Jr., Solid State Physics 16, 275–426 (1964); several data are from F. Birch, in *Handbook of physical constants*, Geological Society of America Memoir 97, 107–173 (1966). Original references should be consulted when values are needed for research purposes. Values in parentheses are estimates. Letters in parentheses refer to the crystal form. Letters in brackets refer to the temperature:

[a] = 77 K; [b] = 273 K; [c] = 1 K; [d] = 4 K; [e] = 81 K.

Bulk modulus in units 10^{12} dyn/cm² or 10^{11} N/m²

Compressibility in units 10^{-12} cm²/dyn or 10^{-11} m²/N

H [d] 0.002 500																	He [d] 0.00 1168
Li 0.116 8.62	Be 1.003 0.997											B 1.78 0.562	C [d] 4.43 0.226	N [e] 0.012 80	O	F	Ne [d] 0.010 100
Na 0.068 14.7	Mg 0.354 2.82											Al 0.722 1.385	Si 0.988 1.012	P (b) 0.304 3.29	S (r) 0.178 5.62	Cl	Ar [a] 0.013 79
K 0.032 31.	Ca 0.152 6.58	Sc 0.435 2.30	Ti 1.051 0.951	V 1.619 0.618	Cr 1.901 0.526	Mn 0.596 1.68	Fe 1.683 0.594	Co 1.914 0.522	Ni 1.86 0.538	Cu 1.37 0.73	Zn 0.598 1.67	Ga [b] 0.569 1.76	Ge 0.772 1.29	As 0.394 2.54	Se 0.091 11.0	Br	Kr [a] 0.018 56
Rb 0.031 32.	Sr 0.116 8.62	Y 0.366 2.73	Zr 0.833 1.20	Nb 1.702 0.587	Mo 2.725 0.366	Tc (2.97) (0.34)	Ru 3.208 0.311	Rh 2.704 0.369	Pd 1.808 0.553	Ag 1.007 0.993	Cd 0.467 2.14	In 0.411 2.43	Sn (g) 1.11 0.901	Sb 0.383 2.61	Te 0.230 4.35	I	Xe
Cs 0.020 50.	Ba 0.103 9.97	La 0.243 4.12	Hf 1.09 0.92	Ta 2.00 0.50	W 3.232 0.309	Re 3.72 0.269	Os (4.18) (0.24)	Ir 3.55 0.282	Pt 2.783 0.359	Au 1.732 0.577	Hg [c] 0.382 2.60	Tl 0.359 2.79	Pb 0.430 2.33	Bi 0.315 3.17	Po (0.26) (3.8)	At	Rn
Fr (0.020) (50.)	Ra (0.132) (7.6)	Ac (0.25) (4.)															

Ce (γ) 0.239 4.18	Pr 0.306 3.27	Nd 0.327 3.06	Pm (0.35) (2.85)	Sm 0.294 3.40	Eu 0.147 6.80	Gd 0.383 2.61	Tb 0.399 2.51	Dy 0.384 2.60	Ho 0.397 2.52	Er 0.411 2.43	Tm 0.397 2.52	Yb 0.133 7.52	Lu 0.411 2.43
Th 0.543 1.84	Pa (0.76) (1.3)	U 0.987 1.01	Np (0.68) (1.5)	Pu 0.54 1.9	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

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

crystal structures (Fig. 2) 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.

Van der Waals-London Interaction

Consider two identical inert gas atoms at a separation R large in comparison with the radii of the atoms. What interactions exist between the two neutral 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.

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

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

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

Table 5 Ionization energies

The total energy required to remove the first two electrons is the sum of the first and second ionization potentials. (*Source:* National Bureau of Standards Circular 467.)

← Energy to remove one electron, in eV →

← Energy to remove two electrons, in eV →

H 13.595																	**He** 24.58 78.98
Li 5.39 81.01	**Be** 9.32 27.53											**B** 8.30 33.45	**C** 11.26 35.64	**N** 14.54 44.14	**O** 13.61 48.76	**F** 17.42 52.40	**Ne** 21.56 62.63
Na 5.14 52.43	**Mg** 7.64 22.67											**Al** 5.98 24.80	**Si** 8.15 24.49	**P** 10.55 30.20	**S** 10.36 34.0	**Cl** 13.01 36.81	**Ar** 15.76 43.38
K 4.34 36.15	**Ca** 6.11 17.98	**Sc** 6.56 19.45	**Ti** 6.83 20.46	**V** 6.74 21.39	**Cr** 6.76 23.25	**Mn** 7.43 23.07	**Fe** 7.90 24.08	**Co** 7.86 24.91	**Ni** 7.63 25.78	**Cu** 7.72 27.93	**Zn** 9.39 27.35	**Ga** 6.00 26.51	**Ge** 7.88 23.81	**As** 9.81 30.0	**Se** 9.75 31.2	**Br** 11.84 33.4	**Kr** 14.00 38.56
Rb 4.18 31.7	**Sr** 5.69 16.72	**Y** 6.5 18.9	**Zr** 6.95 20.98	**Nb** 6.77 21.22	**Mo** 7.18 23.25	**Tc** 7.28 22.54	**Ru** 7.36 24.12	**Rh** 7.46 25.53	**Pd** 8.33 27.75	**Ag** 7.57 29.05	**Cd** 8.99 25.89	**In** 5.78 24.64	**Sn** 7.34 21.97	**Sb** 8.64 25.1	**Te** 9.01 27.6	**I** 10.45 29.54	**Xe** 12.13 33.3
Cs 3.89 29.0	**Ba** 5.21 15.21	**La** 5.61 17.04	**Hf** 7. 22.	**Ta** 7.88 24.1	**W** 7.98 25.7	**Re** 7.87 24.5	**Os** 8.7 26.	**Ir** 9.	**Pt** 8.96 27.52	**Au** 9.22 29.7	**Hg** 10.43 29.18	**Tl** 6.11 26.53	**Pb** 7.41 22.44	**Bi** 7.29 23.97	**Po** 8.43	**At**	**Rn** 10.74
Fr	**Ra** 5.28 15.42	**Ac** 6.9 19.0															
			Ce 6.91	**Pr** 5.76	**Nd** 6.31	**Pm**	**Sm** 5.6	**Eu** 5.67	**Gd** 6.16	**Tb** 6.74	**Dy** 6.82	**Ho**	**Er**	**Tm**	**Yb** 6.2	**Lu** 5.0	
			Th	**Pa**	**U** 4.	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**	

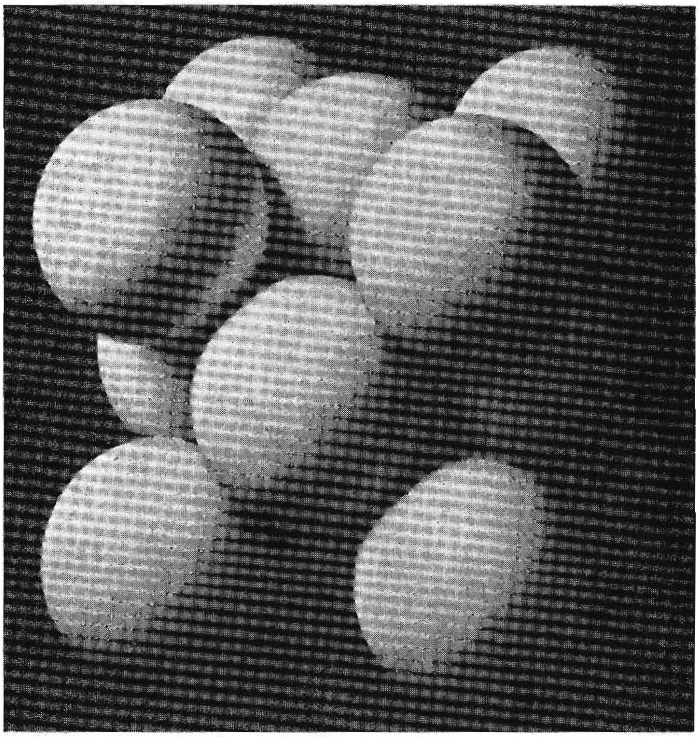


Figure 2 Cubic close-packed (fcc) crystal structure of the inert gases Ne, Ar, Kr, and Xe. The lattice parameters of the cubic cells are 4.46, 5.31, 5.64, and 6.13 Å, respectively, at 4 K.

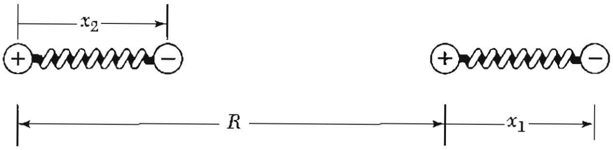


Figure 3 Coordinates of the two oscillators.

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

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

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

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

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. It is the principal attractive interaction in crystals of inert gases and also in crystals of many organic molecules. The interaction is a quantum effect, in the sense that $\Delta U \rightarrow 0$ as $\hbar \rightarrow 0$. Thus the zero point energy of the system is lowered by the dipole-dipole coupling of Eq. (3). The van der Waals interaction does not depend for its existence on any overlap of the charge densities of the two atoms.

An approximate value of the constant A in (9) for identical atoms is given by $\hbar\omega_0\alpha^2$, where $\hbar\omega_0$ is the energy of the strongest optical absorption line and α is the electronic polarizability (Chapter 15).

Repulsive Interaction

As the two atoms are brought together, their charge distributions gradually overlap (Fig. 4), 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.

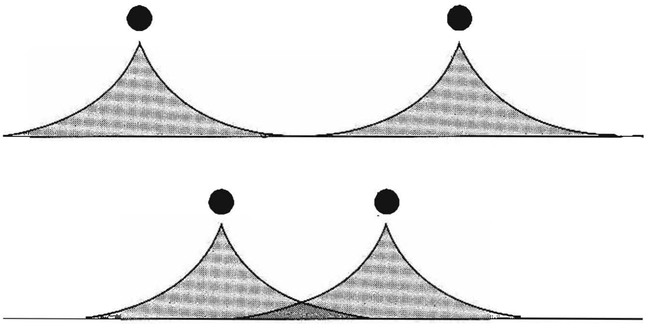
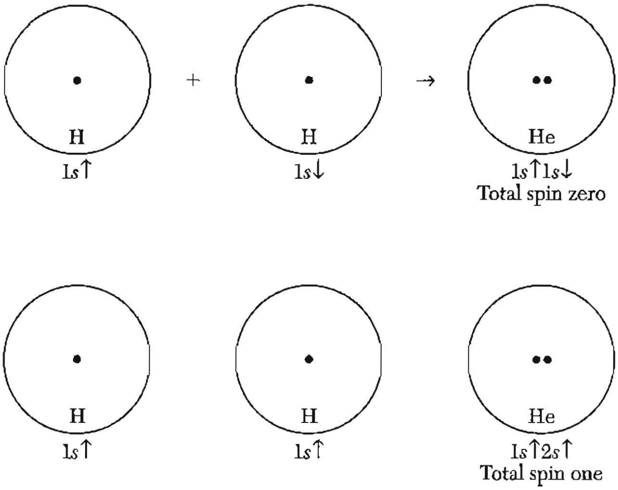


Figure 4 Electronic charge distributions overlap as atoms approach. The solid circles denote the nuclei.



(a)
Total electron energy: −78.98 eV

(b)
Total electron energy: −59.38 eV

Figure 5 The effect of Pauli principle on the repulsive energy: in an extreme example, two hydrogen atoms are pushed together until the protons are almost in contact. The energy of the electron system alone can be taken from observations on atomic He, which has two electrons. In (a) the electrons have antiparallel spins and the Pauli principle has no effect: the electrons are bound by −78.98 eV. In (b) the spins are parallel: the Pauli principle forces the promotion of an electron from a 1s ↑ orbital of H to a 2s ↑ orbital of He. The electrons now are bound by -59.38 eV, less than (a) by 19.60 eV. This is the amount by which the Pauli principle has increased the repulsion. We have omitted the repulsive coulomb energy of the two protons, which is the same in both (a) and (b).

The Pauli principle prevents multiple occupancy, and electron distributions of atoms with closed shells can overlap only if accompanied by the partial promotion of electrons to unoccupied high energy states of the atoms. Thus the electron overlap increases the total energy of the system and gives a repulsive contribution to the interaction. An extreme example in which the overlap is complete is shown in Fig. 5.

We make no attempt here to evaluate the repulsive interaction[2] 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

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[2] The overlap energy naturally depends on the radial distribution of charge about each atom. The mathematical calculation is always complicated even if the charge distribution is known.

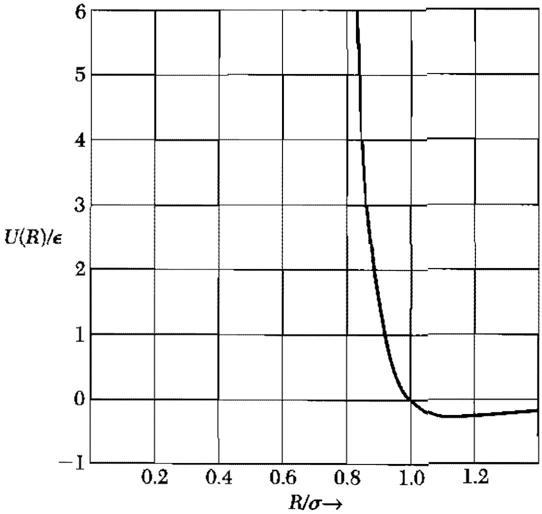

Figure 6 Form of the Lennard-Jones potential (10) which describes the interaction of two inert gas atoms. The minimum occurs at $R/\sigma = 2^{1/6} \cong 1.12$. Notice how steep the curve is inside the minimum, and how flat it is outside the minimum. The value of U at the minimum is $-\epsilon$; and $U = 0$ at $R = \sigma$.

together with a long-range attractive potential of the form of (9). 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

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

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.

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

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

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.

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.

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 .

The agreement with (14) is remarkable. The slight departure of R_0/σ for the lighter atoms from the universal value 1.09 predicted for inert gases can be explained by zero-point quantum effects. From measurements on the gas phase we have predicted the lattice constant of the crystal.

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

Ionic crystals are made up of positive and negative ions. The ionic bond results from the electrostatic interaction of oppositely charged ions. Two common crystal structures found for ionic crystals, the sodium chloride and the cesium chloride structures, were shown in Chapter 1.

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. 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 2.81×10^{-8} 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.

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

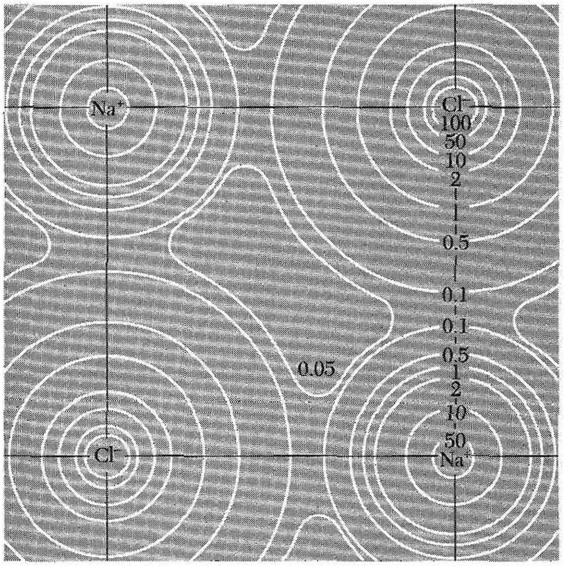

Figure 7 Electron density distribution in the base plane of NaCl, after x-ray studies by G. Schoknecht. The numbers on the contours give the relative electron concentration.

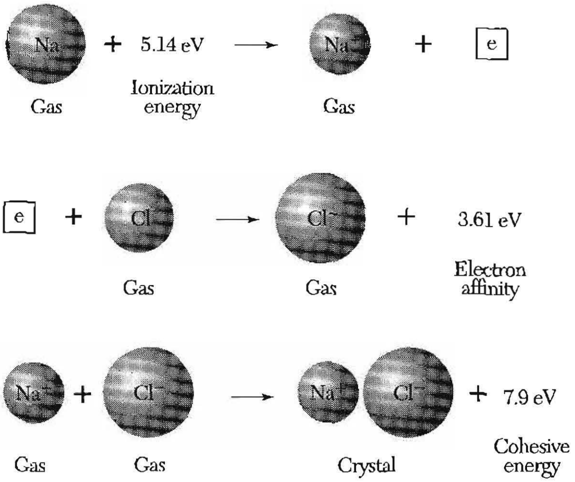

Figure 8 The energy per molecule unit of a crystal of sodium chloride is (7.9 − 5.1 + 3.6) = 6.4 eV lower than the energy of separated neutral atoms. The lattice energy with respect to separated ions is 7.9 eV per molecule unit. All values on the figure are experimental. Values of the ionization energy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

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**.

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).

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

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

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 $\pm q^2/r$.

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. The change is made because it may give a better representation of the repulsive interaction. For the ions, we do not have gas-phase data available to permit the independent determination of λ and ρ. We note that ρ 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. The sum in (17) can be arranged to converge rapidly, so that its value will not depend on the site of the reference ion in the crystal, as long as it is not near the surface. We neglect surface effects and write the total lattice energy U_{tot} of a crystal composed of N molecules or $2N$ ions as $U_{\mathrm{tot}} = NU_i$. 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

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

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. The ($\pm$) sign is discussed just before (25). The value of the Madelung constant is of central importance in the theory of an ionic crystal. Methods for its calculation are discussed next.

At the equilibrium separation $dU_{\mathrm{tot}}/dR = 0$, 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

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

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.

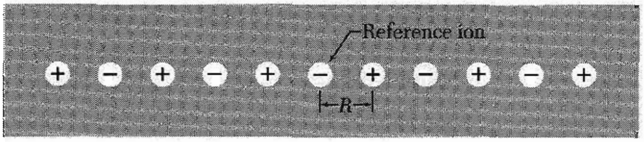

Figure 9 Line of ions of alternating signs, with distance R between ions.

Evaluation of the Madelung Constant

The first calculation of the coulomb energy constant α was made by Madelung. A powerful general method for lattice sum calculations was developed by Ewald and is developed in Appendix B. Computers are now used for the calculations.

The definition of the Madelung constant α is, by (21),

$$\alpha = \sum_j{}' \frac{(\pm)}{p_{ij}} \ .$$

For (20) to give a stable crystal it is necessary that α be positive. If we take the reference ion as a negative charge, the plus sign will apply to positive ions and the minus sign to negative ions.

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.

As an example, we compute the Madelung constant for the infinite line of ions of alternating sign in Fig. 9. Pick a negative ion as reference ion, and let R denote the distance between adjacent ions. Then

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

or

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

the factor 2 occurs because there are two ions, one to the right and one to the left, at equal distances r_j. We sum this series by the expansion

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

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

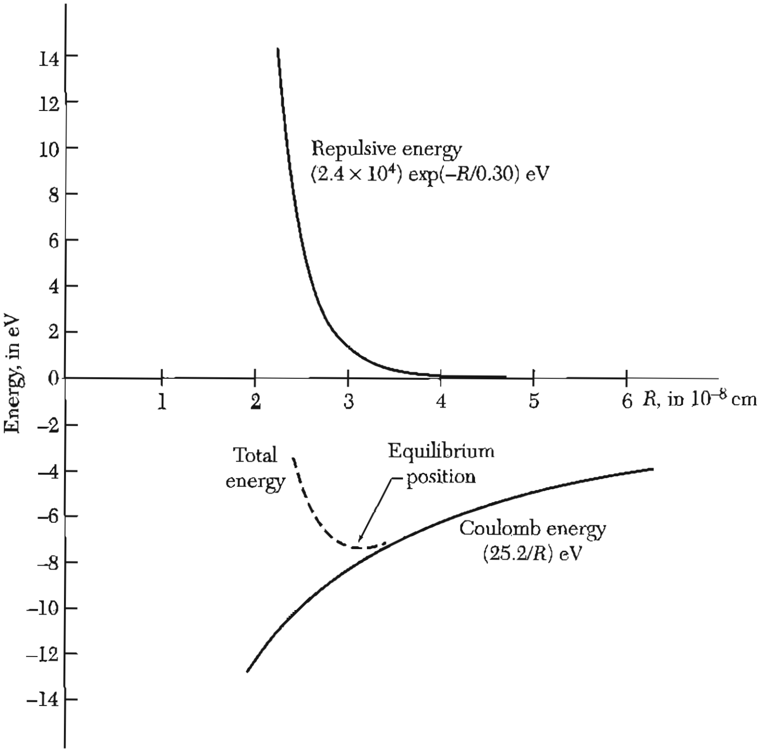

Figure 10 Energy per molecule of KCl crystal, showing Madelung (coulomb) and repulsive contributions.

In three dimensions the series presents greater difficulty. It is not possible to write down the successive terms by a casual inspection. More important, the series will not converge unless the successive terms in the series are arranged so that the contributions from the positive and negative terms nearly cancel.

Typical values of the Madelung constant are listed below, based on unit charges and *referred to the nearest-neighbor distance:*

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

The Madelung and repulsive contributions to the binding of a KCl crystal are shown in Fig. 10. Properties of alkali halide crystals having the sodium chloride structure are given in Table 7. The calculated values of the lattice energy are in exceedingly good agreement with the observed values.

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).

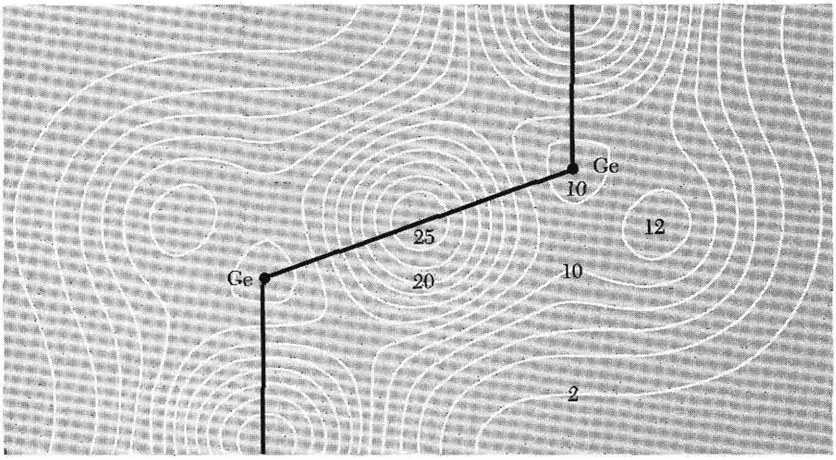

Figure 11 Calculated valence electron concentration in germanium. The numbers on the contours give the electron concentration per primitive cell, with four valence electrons per atom (eight electrons per primitive cell). Note the high concentration midway along the Ge-Ge bond, as we expect for covalent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

COVALENT CRYSTALS

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 (Fig. 11). 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 (Fig. 12) 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**.

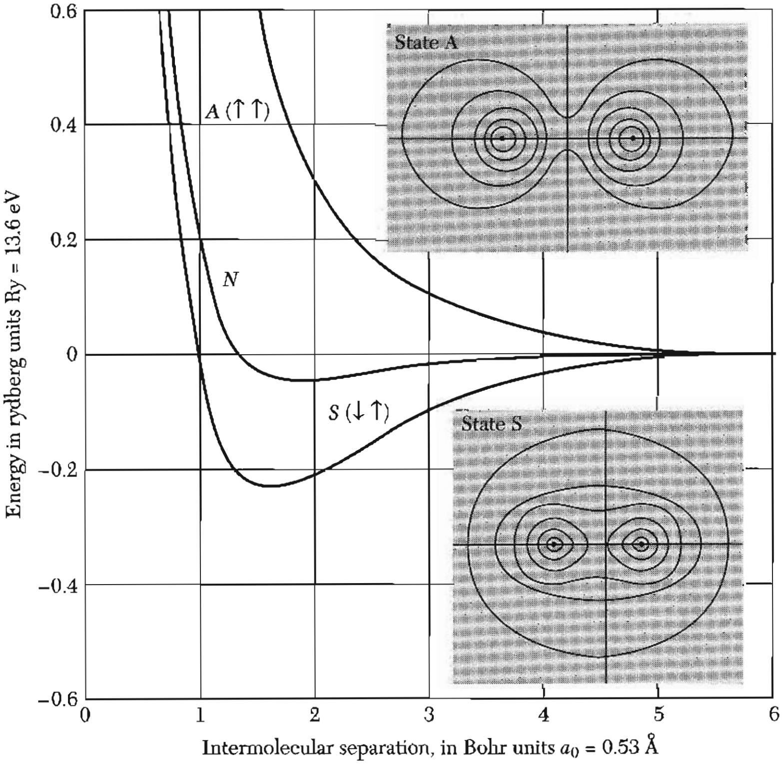

Figure 12 Energy of molecular hydrogen (H_2) referred to separated neutral atoms. A negative energy corresponds to binding. The curve *N* refers to a classical calculation with free atom charge densities; *A* is the result for parallel electron spins, taking the Pauli exclusion principle into account,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

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 3*p* 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.

Table 8 Fractional ionic character of bonds in binary crystals

Crystal	Fractional ionic character	Crystal	Fractional ionic character
Si	0.00		
SiC	0.18	GaAs	0.31
Ge	0.00	GaSb	0.26
ZnO	0.62	AgCl	0.86
ZnS	0.62	AgBr	0.85
ZnSe	0.63	AgI	0.77
ZnTe	0.61	MgO	0.84
CdO	0.79	MgS	0.79
CdS	0.69	MgSe	0.79
CdSe	0.70		
CdTe	0.67	LiF	0.92
		NaCl	0.94
InP	0.42	RbF	0.96
InAs	0.36		
InSb	0.32		

After J. C. Phillips, *Bonds and bands in semiconductors.*

There is a continuous range of crystals between the ionic and the covalent limits. It is often important to estimate the extent a given bond is ionic or covalent. A semiempirical theory of the fractional ionic or covalent character of a bond in a dielectric crystal has been developed with considerable success by J. C. Phillips, Table 8.

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

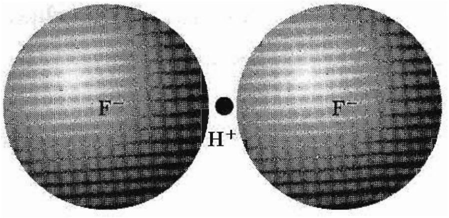

Figure 13 The hydrogen difluoride ion HF_2^- is stabilized by a hydrogen bond. The sketch is of an extreme model of the bond, extreme in the sense that the proton is shown bare of electrons.

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 BONDS

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.

ATOMIC RADII

Distances between atoms in crystals can be measured very accurately by x-ray diffraction, often to 1 part in 10^5. Can we say that the observed distance between atoms may be assigned partly to atom A and partly to atom B? Can a definite meaning be assigned to the radius of an atom or an ion, irrespective of the nature and composition of the crystal?

Strictly, the answer is no. The charge distribution around an atom is not limited by a rigid spherical boundary. Nonetheless, the concept of an atomic

Table 9 Atomic and ionic radii

Values approximate only. Units are 1 Å$=10^{-10}$ m. For original references see W. B. Pearson, *Crystal chemistry and physics of metals and alloys*, Wiley, 1972.

← Standard radii for ions in inert gas (filled shell) configuration →

← Radii of atoms when in tetrahedral covalent bonds →

← Radii of ions in 12-coordinated metals →

H																	**He**
2.08																	
Li	**Be**											**B**	**C**	**N**	**O**	**F**	**Ne**
0.68	0.35											0.23	0.15	1.71	1.40	1.36	1.58
	1.06											0.88	0.77	0.70	0.66	0.64	
1.56	1.13											0.98	0.92				
Na	**Mg**											**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
0.97	0.65											0.50	0.41	2.12	1.84	1.81	1.88
	1.40											1.26	1.17	1.10	1.04	0.99	
1.91	1.60											1.43	1.32				
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
1.33	0.99	0.81	0.68								0.74	0.62	0.53	2.22	1.98	1.95	2.00
										1.35	1.31	1.26	1.22	1.18	1.14	1.11	
2.38	1.98	1.64	1.46	1.35	1.28	1.26	1.27	1.25	1.25	1.28	1.39	1.41	1.37	1.39			
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
1.48	1.13	0.93	0.80	0.67						1.26	0.97	0.81	0.71	2.45	2.21	2.16	2.17
										1.52	1.48	1.44	1.40	1.36	1.32	1.28	
2.55	2.15	1.80	1.60	1.47	1.40	1.36	1.34	1.35	1.38	1.45	1.57	1.66	1.55	1.59			
Cs	**Ba**	**La**	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
1.67	1.35	1.15								1.37	1.10	0.95	0.84				
											1.48						
2.73	2.24	1.88	1.58	1.47	1.41	1.38	1.35	1.36	1.39	1.44	1.57	1.72	1.75	1.70	1.76		
Fr	**Ra**	**Ac**															
1.75	1.37	1.11															
			Ce	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	
			1.01														
			1.71–1.82	1.83	1.82	1.81	1.80	2.04^{2+}–1.80^{3+}	1.80	1.78	1.77	1.77	1.76	1.75	1.94^{2+}–1.74^{3+}		
			Th	**Pa**	**U**	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**	
			0.99	0.90	0.83												
			1.80	1.63	1.56	1.56	1.58–1.64	1.81									

radius is fruitful in predicting interatomic spacing. The existence and probable lattice constants of phases that have not yet been synthesized can be predicted from the additive properties of the atomic radii. Further, the electronic configuration of the constituent atoms often can be inferred by comparison of measured and predicted values of the lattice constants.

To make predictions of lattice constants it is convenient to assign (Table 9) sets of self-consistent radii to various types of bonds: one set for ionic crystals with the constituent ions 6-coordinated in inert gas closed-shell configurations, another set for the ions in tetrahedrally-coordinated structures, and another set for 12-coordinated (close-packed) metals.

The predicted self-consistent radii of the cation Na^+ and the anion F^- as given in Table 9 would lead to 0.97 Å + 1.36 Å = 2.33 Å for the interatomic separation in the crystal NaF, as compared with the observed 2.32 Å. This agreement is much better than if we assume atomic (neutral) configurations for Na and F, for this would lead to 2.58 Å for the interatomic separation in the crystal. The latter value is $\frac{1}{2}$(n.n. distance in metallic Na+ interatomic distance in gaseous F_2).

The interatomic distance between C atoms in diamond is 1.54 Å; one-half of this is 0.77 Å. In silicon, which has the same crystal structure, one-half the interatomic distance is 1.17 Å. In SiC each atom is surrounded by four atoms of the opposite kind. If we add the C and Si radii just given, we predict 1.94 Å for the length of the C-Si bond, in fair agreement with the 1.89 Å observed for the bond length. This is the kind of agreement (a few percent) that we shall find in using tables of atomic radii.

Ionic Crystal Radii

Table 9 gives the ionic crystal radii in inert gas configurations for 6-fold coordination. The ionic radii can be used in conjunction with Table 10. Let us

Table 10 Use of the standard radii of ions given in Table 9

The interionic distance D is represented by $D_N = R_C + R_A + \Delta_N$, for ionic crystals, where N is the coordination number of the cation (positive ion), R_C and R_A are the standard radii of the cation and anion, and Δ_N is a correction for coordination number. Room temperature. (After Zachariasen.)

N	Δ_N(Å)	N	Δ_N(Å)	N	Δ_N(Å)
1	−0.50	5	−0.05	9	+0.11
2	−0.31	6	0	10	+0.14
3	−0.19	7	+0.04	11	+0.17
4	−0.11	8	+0.08	12	+0.19

consider $BaTiO_3$ with a lattice constant of 4.004 Å at room temperature. Each Ba^{++} ion has 12 nearest O^{--} ions, so that the coordination number is 12 and the correction Δ_{12} of Table 10 applies. If we suppose that the structure is determined by the Ba-O contacts, we have $D_{12} = 1.35 + 1.40 + 0.19 = 2.94$ Å or $a = 4.16$ Å; if the Ti-O contact determines the structure, we have $D_6 = 0.68 + 1.40 = 2.08$ or $a = 4.16$ Å. The actual lattice constant is somewhat smaller than the estimates and may perhaps suggest that the bonding is not purely ionic, but is partly covalent.

ANALYSIS OF ELASTIC STRAINS

We consider the elastic properties of a crystal viewed as a homogeneous continuous medium rather than as a periodic array of atoms. The continuum approximation is usually valid for elastic waves of wavelengths λ longer than 10^{-6} cm, which means for frequencies below 10^{11} or 10^{12} Hz. Some of the material below looks complicated because of the unavoidable multiplicity of subscripts on the symbols. The basic physical ideas are simple: we use Hooke's law and Newton's second law. **Hooke's law** states that in an elastic solid the strain is directly proportional to the stress. The law applies to small strains only. We say that we are in the **nonlinear region** when the strains are so large that Hooke's law is no longer satisfied.

We specify the strain in terms of the components e_{xx}, e_{yy}, e_{zz}, e_{xy}, e_{yz}, e_{zx} which are defined below. We treat infinitesimal strains only. We shall not distinguish in our notation between isothermal (constant temperature) and adiabatic (constant entropy) deformations. The small differences between the isothermal and adiabatic elastic constants are not often of importance at room temperature and below.

We imagine that three orthogonal vectors $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ of unit length are embedded securely in the unstrained solid, as shown in Fig. 14. After a small uniform deformation of the solid has taken place, the axes are distorted in orientation and in length. In a uniform deformation each primitive cell of the crystal is deformed in the same way. The new axes $\mathbf{x}'$, $\mathbf{y}'$, $\mathbf{z}'$ may be written in terms of the old axes:

$$\begin{aligned}
\mathbf{x}' &= (1 + \epsilon_{xx})\hat{\mathbf{x}} + \epsilon_{xy}\hat{\mathbf{y}} + \epsilon_{xz}\hat{\mathbf{z}} \ ; \\
\mathbf{y}' &= \epsilon_{yx}\hat{\mathbf{x}} + (1 + \epsilon_{yy})\hat{\mathbf{y}} + \epsilon_{yz}\hat{\mathbf{z}} \ ; \qquad (26) \\
\mathbf{z}' &= \epsilon_{zx}\hat{\mathbf{x}} + \epsilon_{zy}\hat{\mathbf{y}} + (1 + \epsilon_{zz})\hat{\mathbf{z}} \ .
\end{aligned}$$

The coefficients $\epsilon_{\alpha\beta}$ define the deformation; they are dimensionless and have values $\ll 1$ if the strain is small. The original axes were of unit length, but the new axes will not necessarily be of unit length. For example,

$$\mathbf{x}' \cdot \mathbf{x}' = 1 + 2\epsilon_{xx} + \epsilon_{xx}^2 + \epsilon_{xy}^2 + \epsilon_{xz}^2 \ ,$$