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: $1s^22s$, F: $1s^22s^22p^5$. The singly charged ions have the configurations Li^+:$1s^2$, F^-: $1s^22s^22p^6$, 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).

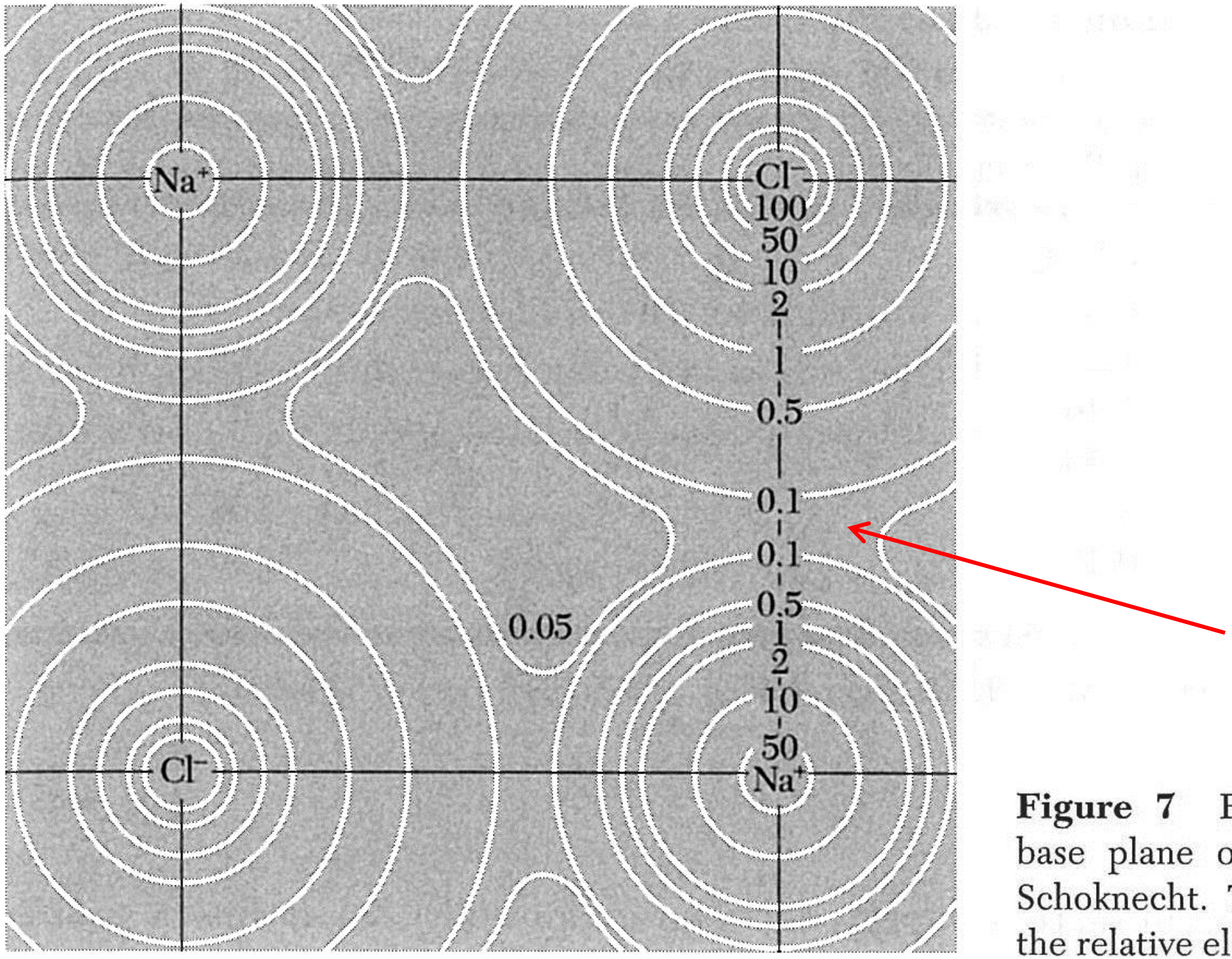
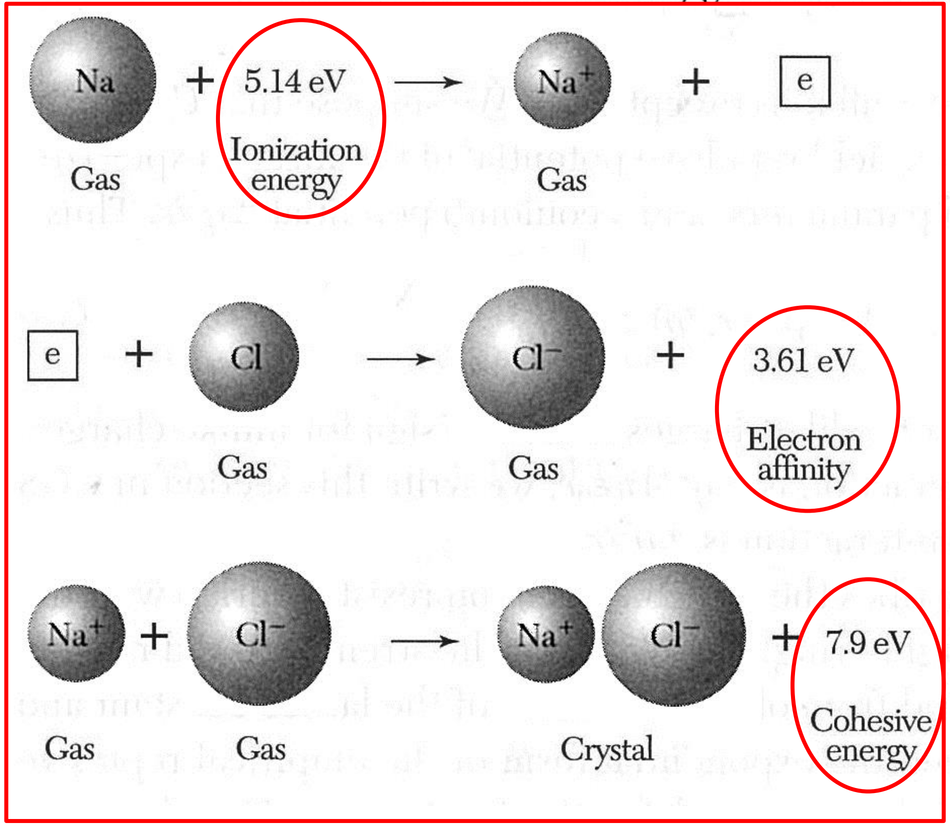


Figure 7 Electron density distribution in the base plane of NaCl, after x-ray studies by G. Schoknecht. The numbers on the contours give the relative electron concentration.

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.



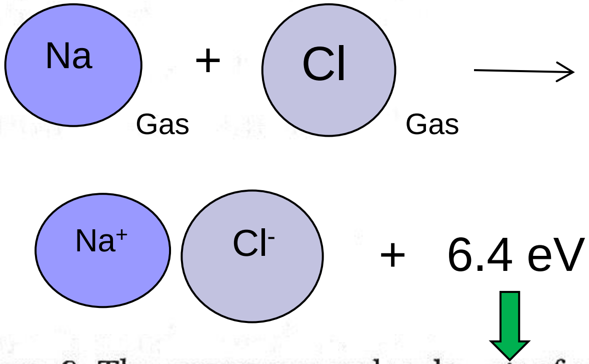


Figure 8 The energy per molecule unit of a crystal of sodium chloride is (7.9 − 5.1 + 3.6) = 6.4 eV lower than the energy of separated neutral atoms. The lattice energy with respect to separated ions is 7.9 eV per molecule unit. All values on the figure are experimental. Values of the ionization energy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

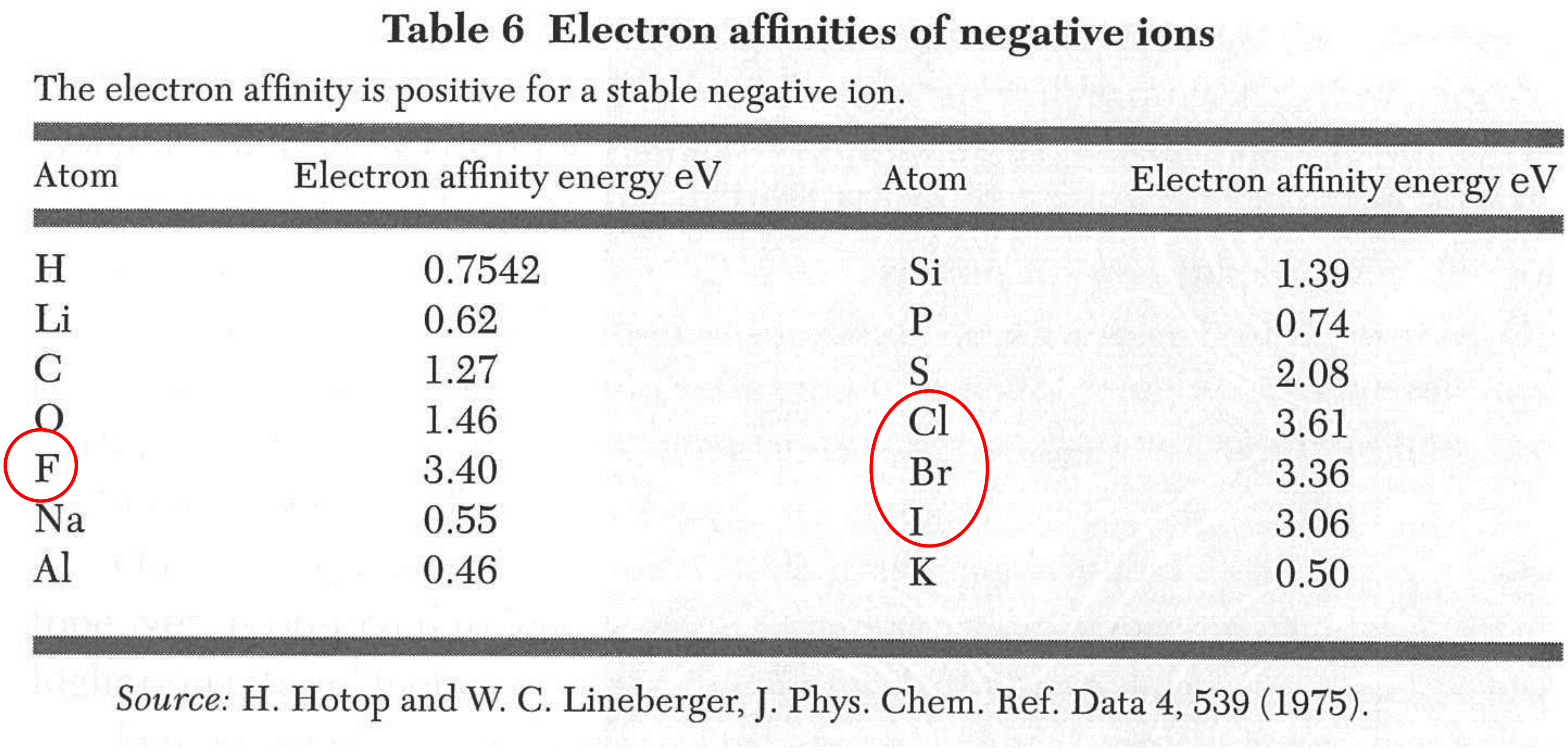
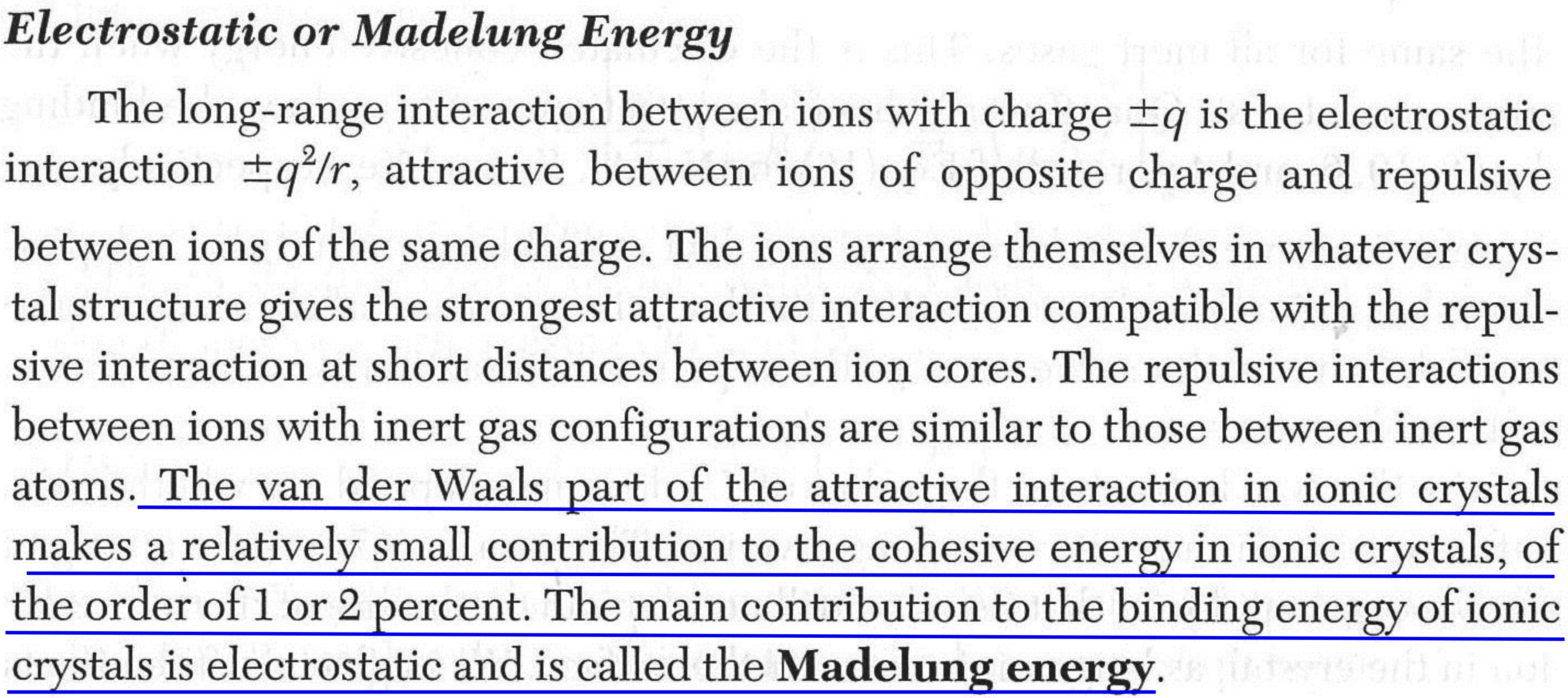


Table 6 Electron affinities of negative ions

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:

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

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

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

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 $U_{tot} = NU_i$. 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

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

Thus

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

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. 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 $dU_{tot}/dR = 0$, so that

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

or

(CGS) At R =R$_o$ $$R_0^2 \exp(-R_0/\rho) = \rho\alpha q^2/z\lambda\ . \tag{23}$$

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

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

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.

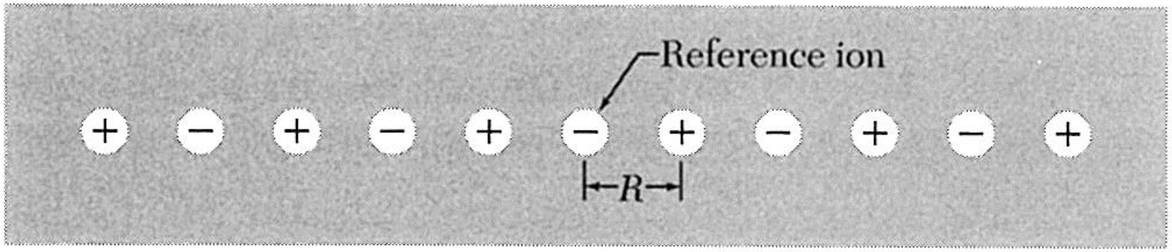


Figure 9 Line of ions of alternating signs, with distance R between ions.

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

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

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.

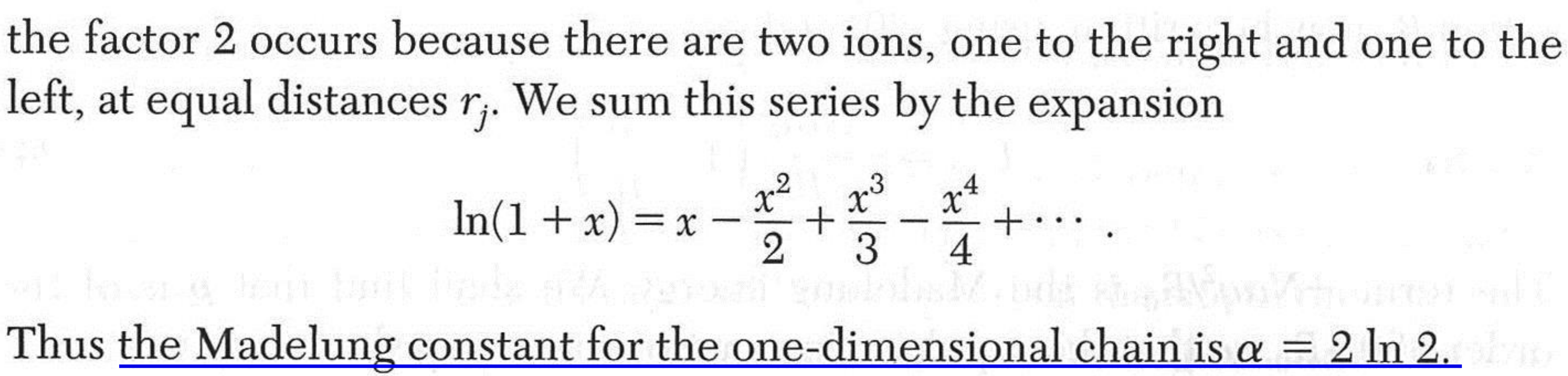
As an example, we compute the Madelung constant for the infinite line of ions of alternating sign in Fig. 9. Pick a negative ion as reference ion, and let R denote the distance between adjacent ions. Then

1-D

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

or

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

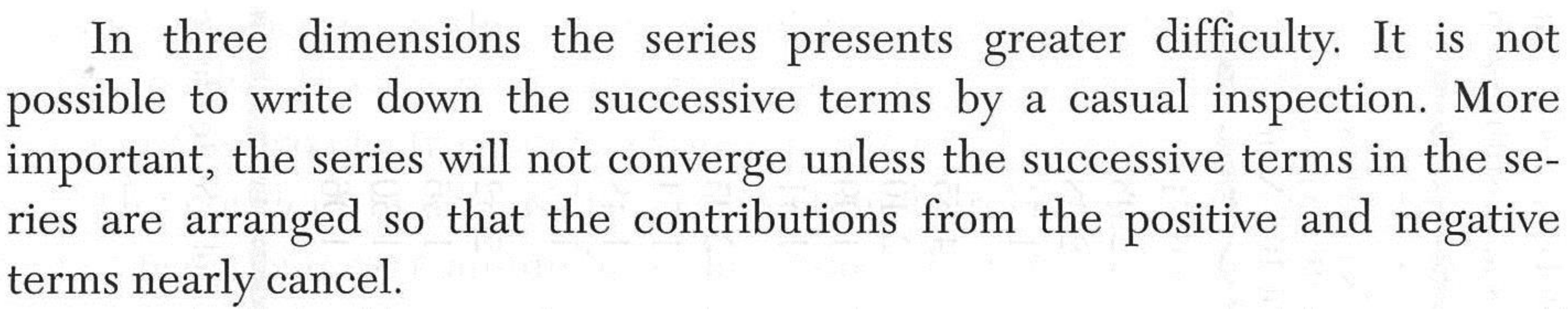


the factor 2 occurs because there are two ions, one to the right and one to the left, at equal distances r_j. We sum this series by the expansion

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

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

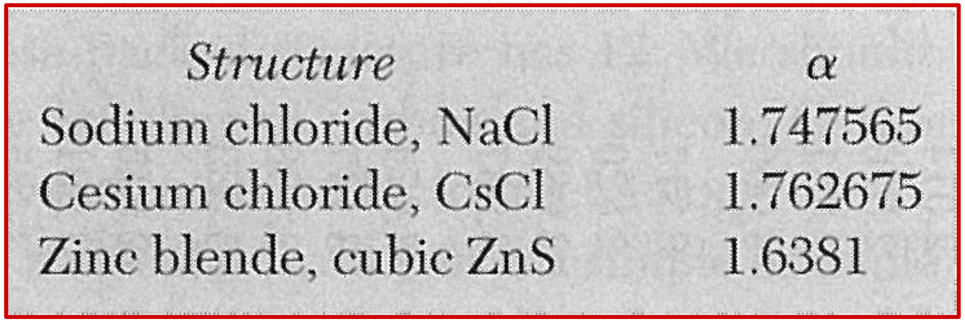
For X =1



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.

3-D ???

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.

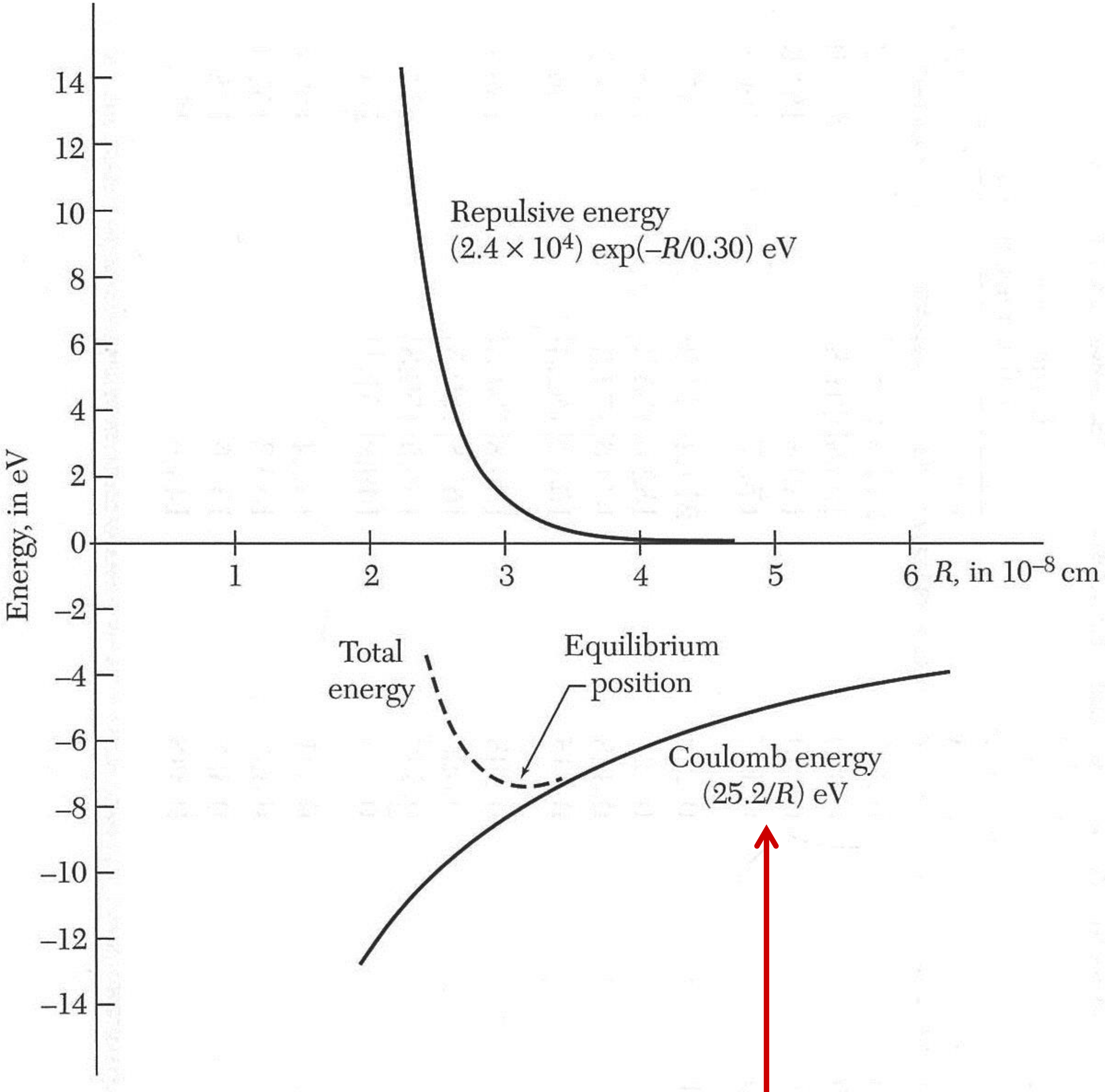


Figure 10 Energy per molecule of KCl crystal, showing Madelung (coulomb) and repulsive contributions.

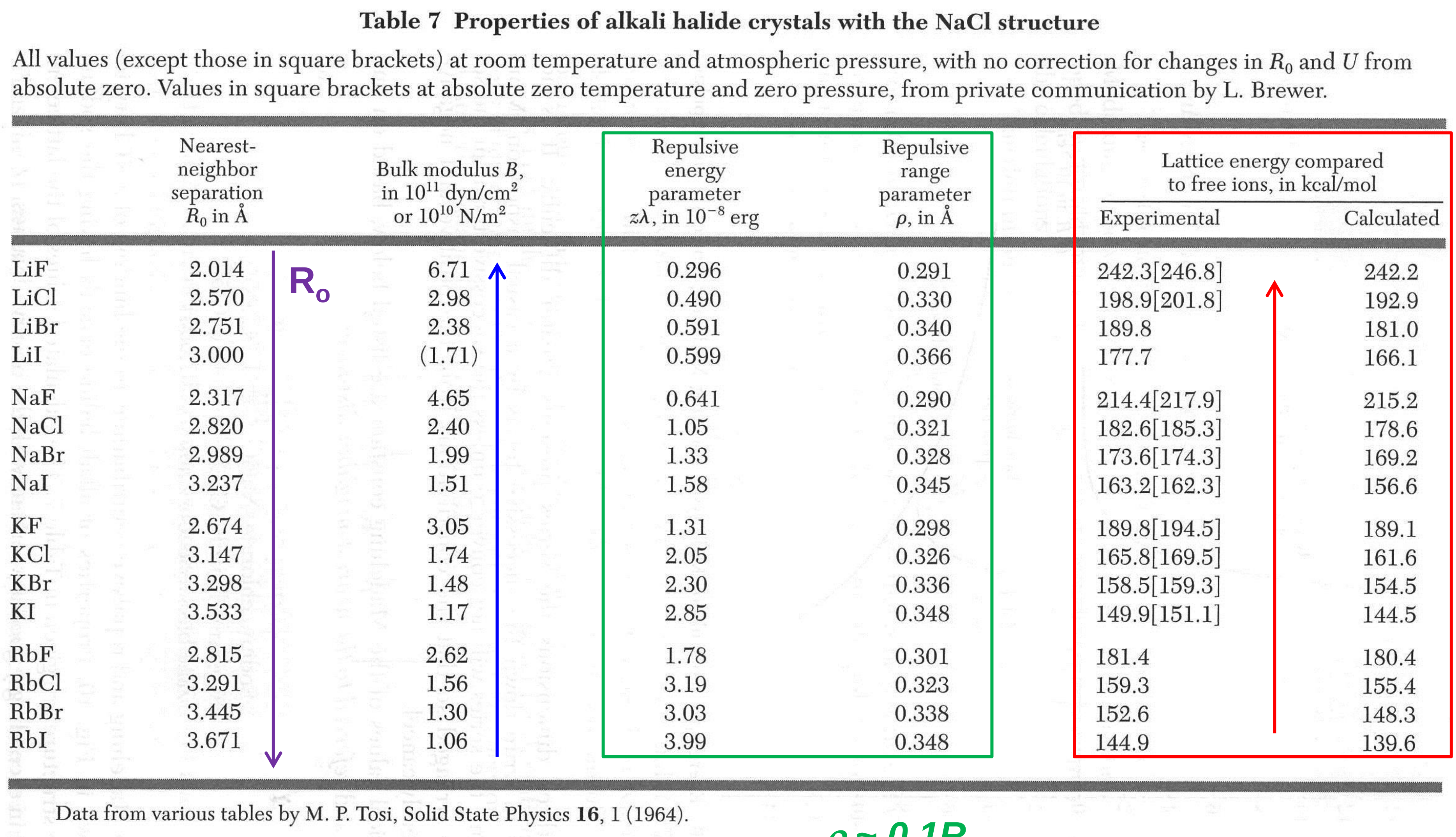


Table 7 Properties of alkali halide crystals with the NaCl structure

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).

$\rho \sim 0.1R_o$