

# An Ionic Model for Metallic Bonding

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Bonding in metals is usually described as resulting from the electrical attractions among positively charged metal ions and the "sea of electrons" belonging to the lattice as a whole. Such a qualitative description can be a basis for a quantitative model by giving the "sea of electrons" a well-defined structure. This has been accomplished using the tangent-spheres model developed by Bent (1).

This model has previously been applied to a quantitative study of the ionic bonding in LiH (2). The purpose of this paper is to describe a similar ionic model for metallic bonding. The tangent-spheres approach, combined with several simplifying assumptions, enables one to calculate the lattice energy, the lattice constant and the density of metals.

## An Ionic Model for Metals

The tangent spheres model for a metal assumes that the metal lattice sites are occupied by cations and anions. The cations are the positively charged metal ions; the anions are spherical electron charge clouds. The electron charge clouds are assumed to have uniform charge density. On the basis of this picture the energy of the metallic solid is

$$E(M,s) = E(M(n^+),s) + nE(e^-,s) + E(\text{coul}) \quad (1)$$

where  $E(M(n^+),s)$  is the internal energy of the metal ion in the solid state,  $E(e^-,s)$  is the energy of the spherical electron charge clouds in the solid state and  $E(\text{coul})$  is the coulombic inter-ion potential energy of the ions in the solid state.

This model will be checked by comparing the calculated lattice energy with the experimental value. The calculated value of the lattice energy,  $U$ , is given by

$$U = E(M(n^+),g) + nE(e^-,g) - E(M,s) \quad (2)$$

whereas, the experimental value of the lattice energy is just the enthalpy of formation of 0 K of the gas-phase metallic ion.

$$U = \Delta H_{\text{form}}(M(n^+),g) \quad (3)$$

Substitution of eqn. (1) into eqn. (2) and using the convention that the energy of a free electron in the gas phase is zero yields,

$$U = E(M(n^+),g) - E(M(n^+),s) - nE(e^-,s) - E(\text{coul}) \quad (4)$$

In addition, the cation radius is assumed to be the same in the gas phase and the solid state. That is, the cation does not change size under the influence of  $E(\text{coul})$  in the formation of the solid. Therefore, the internal energy of the cation is the same in the gas phase and solid state,  $E(M(n^+),g) = E(M(n^+),s)$ . Equation (4) becomes,

$$U = -nE(e^-,s) - E(\text{coul}) \quad (5)$$

The calculation of the metallic lattice energy requires the calculation of the internal energy of the electrons in the solid and their inter-ionic coulombic interaction with the cations. These calculations are described below for a specific example.

## Metallic Calcium

Calcium metal crystallizes in the face-centered cubic structure at room temperature and below. The calculations are valid for absolute zero.

$E(e^-,s)$

The internal energy of a single spherical electron charge cloud of uniform charge density is its kinetic energy and de-

pends on the charge cloud radius. In atomic units this is

$$E(e^-,s) = 9/8R_a^2 \quad (6)$$

If the charge cloud consists of two interpenetrating electrons, the energy is

$$E(e^-,s) = 9/4R_a^2 + 6/5R_a \quad (7)$$

Here the second term is due to the electron-electron repulsions of the interpenetrating spherical charge clouds. The origin of eqns. (6) and (7) is discussed in ref. (2).

$E(\text{coul})$

The net coulombic interaction of a lattice of cations and anions is expressed in terms of the charges of the ions, the inter-ion separation,  $R_{ac}$ , and the Madelung constant characteristic of the lattice geometry. The inter-ion separation depends on the relative sizes of the ions and the crystal structure. The coulombic term is,

$$E(\text{coul}) = -M/R_{ac} \quad (8)$$

If the ions touch,  $R_{ac}$  is the sum of the radii,  $R_a + R_c$ . If the cation rattles in the holes created by the anions,  $R_{ac} = C \times R_a$ , where  $C$  will be determined by the geometry of the hole in which the cation resides.

## Lattice Energy

Because calcium has two valence electrons, two face-centered structures are possible. If the anions consist of two interpenetrating charge clouds, the appropriate structure is the NaCl form. In this form the cations occupy octahedral holes created by the spherical anion charge clouds. The lattice energy is

$$U = 2.25/R_a^2 + 1.2/R_a - 4 \times 1.75/(R_a + R_c) \text{ for } R_c/R_a \geq 0.414 \quad (9)$$

$$U = 2.25/R_a^2 + 1.2/R_a - 4 \times 1.75/(1.41R_a) \text{ for } R_c/R_a < 0.414 \quad (10)$$

where 1.75 is the Madelung constant for the NaCl structure and 0.414 is the smallest radius ratio for which the cations and anions are in contact.

If the anions are singly charged, then the  $\text{CaF}_2$  structure is appropriate. To form the metallic lattice replace the fluoride ions with spherical electron charge clouds. The calcium ions are in holes created by the spherical charge clouds located at the corners of a cube. For this structure the lattice energy is

$$U = 2.25/R_a^2 - 5.04/(R_a + R_c) \text{ for } R_c/R_a \geq 0.732 \quad (11)$$

$$U = 2.25/R_a^2 - 5.04/(1.732R_a) \text{ for } R_c/R_a < 0.732 \quad (12)$$

where 5.04 is the Madelung constant and 0.732 is the smallest radius ratio for which the cations and anions are in contact.

To calculate the lattice energy, the radius of the calcium ion

	NaCl Structure	CaF <sub>2</sub> Structure	Literature
Cation radius/Å	0.99	0.99	0.99 (3)
Anion radius/Å	1.61	1.35	...
Lattice energy/e.v.	21.4	21.6	19.8 (4)
Lattice constant/Å	5.20	5.40	5.58 (5)
Density/(g/cm <sup>3</sup> )	1.89	1.69	1.53 (5)

is given the literature value of  $0.99 \text{ \AA}$  (3) and the electron charge cloud radius is varied until an energy minimum is located. The listing of a Basic program which accomplishes this task is available from the author.

Once the minimum lattice energy and the optimum anion radius are found, the lattice constant and density can be calculated from the crystal structure. All three calculated results can then be compared to literature values. A summary of the results of these calculations and a comparison with literature values is provided in the table.

The author wishes to thank Mike Kenney and Dave Funk,

who, while undergraduates at St. John's, helped with the calculations on which this paper is based.

#### Literature Cited

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