A check is made of the applicability of an interpolation equation proposed for the binding energy in mixed ionic–covalent crystals having the sphalerite structure. It is shown that the parameters of the equation can be adjusted for most such crystals to match the physical properties. The equation reveals that the covalent interaction makes a large contribution to the total lattice energy.

1. Introduction and Formulation of the Problem

We previously carried out a qualitative analysis of the binding forces in mixed ionic–covalent crystals having the wurtzite lattice and proposed an interpolation equation for the binding energy [1]. The structure of the interpolation equation permitted the covalent contribution to the total lattice energy to be singled out.

A general study of this equation showed that it could be used to describe stable lattices having the wurtzite structure. It was subsequently used to study the mechanical properties and energies of several crystals having this structure, in particular, the ZnS wurtzite crystal.

This interpolation equation for the binding energy is

\[ \varphi(r) = -\frac{e^2}{r} + \frac{\alpha}{r^n} + \frac{\beta}{r^\sigma} \] (1a)

for the interaction with particles in the first coordination spheres,

\[ \varphi(r) = \frac{e^2}{r} + \frac{\beta'}{r^\epsilon} \] (1b)

for the interaction with particles of the second coordination spheres, and

\[ \varphi(r) = \frac{e_1 e_2}{r} \] (1c)

for the interaction with all other particles.

A further study of interpolation equation (1) for the binding energy should be made by extending the equation to other systems. An interesting possibility is to use this equation to describe the binding forces in crystals having the sphalerite structure, which are of higher symmetry than the wurtzite crystals but which have binding forces similar in nature. It seems quite interesting to try to apply this interpolation equation to both modifications of ZnS, wurtzite, and sphalerite, and to determine as much as possible about the subtler features of the interaction, which are responsible for the particular modification.

2. Application of the Interpolation Equation to Wurtzite

Interpolation equation (1) contains seven parameters, \( m, n, k, \alpha, \beta, \beta', \) and \( e, \) which must be determined from experimental data and from the equilibrium equations. We have three equilibrium equations for the wurtzite crystals, so we can eliminate three parameters of the interpolation equation: \( \alpha, \beta, \) and \( \beta'. \)

The parameters $m$, $n$, and $k$ are determined from the values corresponding to stable wurtzite lattices by choosing the form for the elastic-modulus diagram which best approximates the experimental one. The parameter $e$ (the effective ionic charge) is determined by equating one of the elastic moduli ($c_{11}$) to its experimental value. In this manner, the following parameters are obtained for the interpolation equation for wurtzite on the basis of the experimental elastic moduli [2]:

$$m = 1, \ n = 2, \ k = 10, \ \frac{a}{e^2} = -1.263; \ \frac{\beta}{e^2} = 1.598; \ \frac{\beta'}{e^2} = 6243; \ e = 1.24e_0,$$

where $e_0$ is the magnitude of the electronic charge. The lattice energy calculated from these parameters is

$$U = 355 \left( -1 - 2.90 + 1.30 + 0.20 \right) = -851 \text{ kcal/mole}, \quad (2)$$

where the first term ($-1$) describes the Coulomb contribution to the lattice energy, the second ($-3.08$) describes the contribution of covalent attraction of the first coordination spheres, the third ($+0.97$) describes the contribution of the repulsive forces of the first coordination spheres, and the fourth term ($+0.76$) describes the contribution of the interaction of the particles of the second coordination spheres. This value differs from the experimental value of $U = -851 \text{ kcal/mole}$ [3] by 3%.

We note that Eq. (2) shows the large covalent-attraction contribution characteristic of covalent crystals.

Experimental data [4] yield an effective charge of $e = 1.29e_0$ for wurtzite. The calculated energy differs from the experimental energy by 6%, while the relative contributions of the various terms in Eq. (1) are the same.

3. Application of the Interpolation Equation to Sphalerite

As a first step, we tried to determine whether interpolation equation (1) could be applied to the binding forces in sphalerite through the use of the interpolation-equation parameters determined for wurtzite. We found that this procedure resulted in an unstable sphalerite lattice.

Because of the higher symmetry of the sphalerite lattice, the direct determination of the interpolation-equation parameters for sphalerite is carried out by a procedure different from that for wurtzite. Using the sole equilibrium equation for the sphalerite lattice, the experimental elastic moduli $c_{11}$, $c_{12}$, and $c_{44}$, and the experimental lattice constant, we eliminated the parameters $\alpha$, $\beta$, $\beta'$, and $e$. We determined the $m$, $n$, and $k$ values from the set of possible values through the requirement that the numerical lattice energy approximate the experimental energy as well as possible; the set of $m$, $n$, and $k$ values was chosen in the same manner as for the wurtzite lattice.

From the calculations and from an analysis of the results obtained for five versions of the experimental elastic moduli of ZnS sphalerite (Table 1) with $a = 5.42 \text{ Å}$ [5], we found the energy values to agree best for the set of values $m = 2, n = 4, k = 2$. The energies calculated for this case differ from the experimental energy of $U = -851 \text{ kcal/mole}$ [3] by no more than 6.5%. An approximately unit effective charge is found.

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The calculated energy is most nearly equal to the experimental value in version I in Table 1. The effective charge for ZnS sphalerite turns out to be $1.24e_0$, i.e., approximately equal to the charge which we evaluated for ZnS wurtzite ($e_w = 1.24e_0$ or $e_w = 1.29e_0$). The sphalerite energy written for the parameters in column I of Table 1 is

$$U = 355 \left( -1 - 2.90 + 1.30 + 0.20 \right) = -851 \text{ kcal/mole}. \quad (3)$$