

Lattice Energies and Bulk Moduli of Ionic Crystals

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Abstract

The Born-Landé equation has been used to calculate the lattice energy and bulk modulus of twenty one ionic crystals. These computations were carried out by means of a FORTRAN code, whose basic inputs are the name of crystal, the Born exponent, the number of charges and the lattice constant. The lattice energies obtained are in close agreement with both the theoretical and the experimental reported values. It has been found that as the ionic radii of either the cations or anions increases the lattice energy decreases. Similarly, ionic crystals consisting of divalent ions have much larger lattice energies than those with monovalent ions.

PACS: 61.66Bi, 61.50.Lt, 71.15.Nc

Introduction:

The lattice energy of an ionic crystal is the energy required to separate one mole of a solid into the gases of its ions. It has the same magnitude but different sign with energy of crystallization, which is the energy released when the ions condensed from gaseous state to a solid state [1]. Lattice energy has not been measured directly, experimental values are obtained from thermodynamic data using the Born-Haber cycle [2]. However, theoretical values for lattice energy can be calculated by considering the effective attractive forces between the ions.

If the ions are treated as point charges the Coulombic attractive energy, U between any two ions of opposite charge is given by

$$U = -\frac{(Ze)^2}{4\pi\epsilon_0 r}, \quad (1)$$

where Z is an integer, e is the electronic charge, Ze is the absolute value of the charge on each ion, ϵ_0 is the permittivity of free space and r is the inter-ionic distance. For more than two pair of ions, the electrostatic energy depends on the number of ions and also on A , their arrangement in space. For one mole of the ionic pair the attractive energy is [3]

$$U = -\frac{NZ^2Ae^2}{4\pi\epsilon_0 r}, \quad (2)$$

where N is the Avogadro number and A is a dimensionless constant called Madelung constant [4]. The electrostatic energy given by Eq (2) is not the actual energy required to separate a mole of the solid into gases of its ions. Real ions are not rigid spheres, the equilibrium separation of a cation and an anion in an ionic crystal is fixed when the attractive forces are balanced by repulsive forces. The attractive forces are Coulombic and follow strictly a $\frac{1}{r^2}$ law. The repulsive forces follow an inverse r^n law and vary with the nature of the particular ions. The total repulsive energy per mole at any value of r is given by [5] $E_{rep} = \frac{NB}{r^n}$,

where B is the Born constant and n is the Born exponent. The net electrostatic energy, U is

$$U = -\frac{Z^2NAe^2}{4\pi\epsilon_0 r} + \frac{NB}{r^n}. \quad (3)$$

Bulk modulus, κ is a property of a substance that is related to its hardness, and can be defined as the resistance of a substance to compression. It is given by [6] $\kappa = -V \frac{\partial P}{\partial v}$, where V is the volume of the substance, and P is the pressure exerted by its atoms/molecules. Bulk modulus is related to energy U via the relation [7] $\kappa = v \frac{\partial}{\partial v} \left(\frac{\partial u}{\partial v} \right)$, where v is the specific volume (volume per particle) and u is the specific internal energy.

In this work, a first-principle calculations of lattice energies and bulk moduli of some ionic crystals has been done. Essentially, a FORTRAN codes was written and executed in order to get the lattice energies and bulk moduli. A fundamental input in these calculations is the value of the madelung constant for a crystal. The expressions that are employed by the code are described below in section two.

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2 LATTICE ENERGY AND BULK MODULUS

2.1 Lattice Energy

At ionic separation, r the lattice energy is given by

$$U = -\frac{NZ^2 Ae^2}{4\pi\epsilon_0 r} + \frac{NB}{r^n} \quad (4)$$

At equilibrium, when $r = r_0$, U is a minimum by definition. The derivative of U with respect to r , evaluated at $r = r_0$ must equal to zero. Differentiating Eq (4) with respect to r we get:

$$\left(\frac{dU}{dr}\right)_{r=r_0} = \frac{NZ^2 Ae^2}{4\pi\epsilon_0 r^2} - \frac{nNB}{r^{n+1}} = 0.$$

Solving the above equation for B gives:

$$B = \frac{Z^2 Ae^2}{4\pi\epsilon_0 n} r_0^{n-1} \quad (5)$$

When Eq (5) is substituted in Eq (4), we obtain:

$$U(r_0) = -\frac{NZ^2 Ae^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right) \quad (6)$$

The above equation is the Born-Landé equation which involves the electrostatic energy of a 'reference ion' resulting from electrostatic interactions with an infinite number of ions surrounding it in the crystal lattice. The value of the Born exponent, n is dependent upon the electronic configuration of the closed shell ion^[8]. The Madelung constant plays a vital role in incorporating this infinite number of interactions into the Eq (6).

2.2 Bulk Modulus of Rock Salt (NaCl) Structure

For a rock salt crystal structure of lattice constant, a the nearest neighbour distance is given by $r = \frac{a}{2}$, [9]. Since there are four molecules per unit cell for a rock salt crystal structure [10], the specific volume is given by: $v = \frac{a^3}{4}$. In terms of the nearest neighbour distance, r the specific volume can be written as: $v = 2r^3$.

Differentiating the above expression gives: $dv = 6r^2 dr$ thus the differential $\frac{\partial}{\partial v}$ can be written as $\frac{\partial}{\partial v} = \frac{1}{6r^2} \frac{\partial}{\partial r}$, and the bulk modulus can then be written as:

$$k = 2r^3 \left(\frac{1}{6r^2} \frac{\partial}{\partial r}\right) \left(\frac{1}{6r^2} \frac{\partial u}{\partial r}\right) = \frac{r}{3} \frac{\partial}{\partial r} \left(\frac{1}{6r^2} \frac{\partial}{\partial r}\right) = \frac{r}{18} \frac{\partial}{\partial r} \left(\frac{1}{r^2} \frac{\partial u}{\partial r}\right) \quad (8)$$

The bulk modulus at the equilibrium separation r_0 is:

$$K = \frac{r}{18} \left(\frac{-1}{r^2} \frac{\partial u}{\partial r} \Big|_{r=r_0} + \frac{1}{r^2} \frac{\partial^2 u}{\partial r^2} \Big|_{r=r_0} \right)$$

Using the derivative $\frac{\partial u}{\partial r} \Big|_{r=r_0} = 0$, therefore

$$K = \frac{1}{18r_0} \left(\frac{\partial^2 u}{\partial r^2} \Big|_{r=r_0} \right). \quad (9)$$

From Eq (4), the energy per particle is $u = -\frac{AZ^2 e^2}{4\pi\epsilon_0 r} + \frac{B}{r^n}$, and using this in Eq (9) gives:

$$K = \frac{AZ^2 e^2}{4\pi\epsilon_0 r} \left(\frac{n-1}{18r_0^4} \right). \quad (10)$$

2.3 Bulk Modulus of CsCl Structure

For a CsCl crystal structure of lattice constant, a the nearest neighbour distance is [7] $r = \frac{a\sqrt{3}}{2}$. Since there is one molecule per unit cell for a CsCl crystal structure [10], the specific volume, v is given by: $v = a^3$. In terms of the nearest neighbour distance, r the specific volume can be written as: $v = \frac{8r^3}{3\sqrt{3}}$.

Differentiating, gives $dv = \frac{8r^2}{\sqrt{3}} dr$ Thus the differential $\frac{\partial}{\partial v} = \frac{\sqrt{3}}{8r^2} \frac{\partial}{\partial r}$, and the bulk modulus can then be written

as:

$$K = \frac{8r^3}{3\sqrt{3}} \left(\frac{\sqrt{3}}{8r^2} \frac{\partial}{\partial r} \right) \left(\frac{\sqrt{3}}{8r^2} \frac{\partial u}{\partial r} \right) = \frac{r}{3} \frac{\partial}{\partial r} \left(\frac{\sqrt{3}}{8r^2} \frac{\partial u}{\partial r} \right) = \frac{r\sqrt{3}}{24} \frac{\partial}{\partial r} \left(\frac{1}{r^2} \frac{\partial u}{\partial r} \right). \tag{11}$$

The bulk modulus at the equilibrium separation r_0 is:

$$K = \frac{r\sqrt{3}}{24} \left(\frac{-1}{r^3} \frac{\partial u}{\partial r} \Big|_{r=r_0} + \frac{1}{r^2} \frac{\partial^2 u}{\partial r^2} \Big|_{r=r_0} \right). \text{ Using the derivative } \frac{\partial u}{\partial r} \Big|_{r=r_0} = 0 \text{ therefore,}$$

$$K = \frac{r\sqrt{3}}{24} \frac{1}{r^2} \frac{\partial^2 u}{\partial r^2} \Big|_{r=r_0}. \tag{12}$$

Also, from Eq (4) the energy per particle u is: $u = -\frac{AZ^2 e^2}{4\pi\epsilon_0 r} + \frac{B}{r^n}$, using this in Eq (12) gives:

$$K = \frac{AZ^2 e^2}{4\pi\epsilon_0} \left(\frac{\sqrt{3}}{24} \frac{(n-1)}{r_0^4} \right). \tag{13}$$

3. PROCEDURE

Eq (6) was employed to compute the lattice energy, while Eqs (10) and (13) were used to calculate the bulk modulus of ionic crystals having the NaCl and CsCl structures respectively. These computations were carried out by means of a FORTRAN code. When executed, the program prompts for the following inputs: the name of crystal, the Born exponent, the number of charges and the lattice constant. The results are printed out in a file.

4. RESULTS AND DISCUSSION

The lattice energies and bulk moduli of twenty ionic crystals having the NaCl or CsCl crystals structures are calculated. Table 1 below, contains the computed values of lattice energies and bulk moduli.

TABLE 1 lattice energy and bulk modulus

S/N	Ionic Crystal	Lattice energy (KJ/mol)			Bulk modulus (10^{10} Nm ⁻²)	
		This work	Theoretical value[11,12]	Experimental value[12]	This work	Experimental value[13]
1	NaCl ^s	752.4814	766	788	2.5420691	2.40
2	MgO ^s	3950.287		3580	2.7545810	
3	RbF ^s	749.0868	774	784	2.5374837	2.62
4	KI ^s	620.8500	631	615	1.2625105	1.17
5	NaBr ^s	717.6126	731	719	2.2105209	1.99
6	NaI ^s	670.0281	686	670	1.8094244	1.51
7	KCl ^s	674.4526	692	718	1.4901142	1.75
8	KBr ^s	658.0125	667	656	1.5064721	1.48
9	LiCl ^s	806.9651	834	862	3.7171352	2.98
10	LiF ^s	1033.996	1030	1037	6.7188563	6.71
11	CsCl ^c	620.0477	657	672	3.3175034	
12	CsBr ^c	597.5823	632	603	2.9558758	
13	CsI ^c	566.4877	600	568	2.5399986	
14	CaO ^s	3528.511	-	3465	1.8837989	
15	TiO ^s	3999.257	-	3882	3.1087493	
16	VO ^s	4151.189	-	3917	3.6087667	
17	CsF ^s	720.4196	744	729	2.3268176	2.35
18	KF ^s	794.4115	808	817	3.0976382	3.05
19	LiI ^s	711.6325	-	729	2.0667963	1.72
20	LiBr ^s	763.9139	730	785	4.7239557	2.38
21	NaF	898.7650	910	918	3.0700124	4.65

Structure: ^s = NaCl Structure, ^c = CsCl Structure

The lattice energies and bulk moduli obtained are in close agreement with both of the theoretical and the experimental values reported. Taking the case of NaCl and NaI: The calculated (i.e. this work), theoretical and experimental values in KJ mol^{-1} are; 752.48, 766 and 788 for NaCl crystal, and 670.0281, 686 and 670 for NaI crystal the respectively.

From the Table 2 below, it can be observed that as the ionic radii of either the cations or anions increases the lattice energy decreases. It is also obvious from the values in Table 1 that ionic crystals consisting of divalent ions have much larger lattice energies than those with monovalent ions.

TABLE 2 Variation of lattice energies with change in ionic radii

Increase in ionic radii	→				
	Ions	F ⁻	Cl ⁻	Br ⁻	I ⁻
↓	Li ⁺	1033.996	806.9651	763.9139	711.6325
	Na ⁺	898.7650	752.4814	717.6126	670.0281
	K ⁺	794.4115	674.4526	658.0125	620.8500
	Cs ⁺	720.4196	620.0477	597.5823	566.4877

More accurate calculations can done by considering a quantum mechanical description of the interactions in ionic crystals and particularly effecting corrections for van der Waal energy, and the zero point energy.

5. CONCLUSION

The lattice energy and bulk modulus of twenty one ionic crystals have been calculated. The values obtained agree with theoretical and experimental values reported. It has been found that as the ionic radii of either the cations or anions increases the lattice energy decreases. Similarly, ionic crystals consisting of divalent ions have much larger lattice energies than those with monovalent ions. It is hoped that in the near future calculations in which all the interactions in these crystals are considered will be undertaken.

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