Born Repulsive Potential in the Alkali Halide Crystals*

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Attempts are described to improve the current knowledge of the Born repulsive potential in the alkali halides in view of its critical role in the study of point imperfections by the Born model. The validity of various approximations to the equation of state of cubic solids, used in this connection, is clarified. Some evidence in favor of the Born-Mayer form of the Born repulsive potential is derived from the dependence of the experimental Born repulsive energy on interionic distance, as determined from a detailed analysis of high-pressure compression data. Some confirmation of the heuristic assumptions involved in the Huggins-Mayer procedure for the determination of the Born-Mayer repulsive parameters is obtained from the agreement between the crystal radii for the alkali and halogen ions in the individual alkali halides, derived from these repulsive parameters, and the experimental crystal radii, derived from the X-ray maps for the electron distribution in the solid. Finally, some insight into the manybody contributions to the Born repulsive energy is gained from a Born-model study of the polymorphic transitions of the alkali halides.

1. Introduction

The available calculations of the energies of motion of equilibrium point imperfections in the alkali halides and, to a lesser degree, the calculations of their energies of formation indicate that the form adopted for the Born repulsive potential, and the values used for the parameters entering the adopted form, represent rather critical factors in the theoretical study of point imperfections in the alkali halides by the Born model.¹⁾ The comparison of the results of these calculations with experiment provides, of course, a method of gaining some information about these factors, but this procedure is not particularly satisfactory because it does not distinguish the influence of the other factors which affect the accuracy of these calculations. It is thus desirable to try and improve our knowledge of the Born repulsive potential in the alkali halides by more direct methods, along the lines of the traditional procedure for the determination of the Born repulsive parameters from crystal data. To this end, we have attempted, first, to clarify the validity of various approximations to the equation of state of cubic solids²⁾ which are used in this connection, as the available literature was somewhat confused on this point. A trial

has then been made to test the functional form of the Born repulsive potential, which is merely assumed in the traditional procedure, against the dependence of the experimental lattice energy on interionic distance, over a range of linear compression of about 10%, and this has lead to results which appear to favor the Born-Mayer form.³⁾ We have also established a simple connection between the Born repulsive parameters in the Born-Mayer form, as determined by the Huggins-Mayer procedure, and the crystal radii of the ions in the individual alkali halides, and this has yielded some confirmation of the heuristic assumptions involved in the Huggins-Mayer procedure.⁴⁾ Finally, we have attempted to gain some insight into the many-body contributions to the Born repulsive energy by a Born model study of the polymorphic transitions of the alkali halides.⁵⁾ While the work on the equation of state and on the polymorphic transitions is largely completed, the remaining work is still in progress and thus the statements pertaining to it should be regarded as provisional.

2. Equation of State

The traditional procedure for the determination of the Born repulsive energy in an alkali halide crystal assumes a plausible functional form for the Born repulsive potential and then evaluates the pertinent parameters from crystal

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data at room temperature and atmospheric pressure by means of the vibrational Hildebrand equation of state and its volume derivative at constant temperature.⁶⁾ Born and Huang⁷⁾ and other authors have implied in recent years that this procedure should be refined by recurring to the vibrational Mie-Grüneisen equation of state, and quite recently Guggenheim et al.⁸⁾ have criticized rather strongly the traditional procedure in this connection.

A systematic investigation of the relative validity of these two approximate equations of state appeared thus to be in order. To carry it out, we established, first, the equivalence between these approximate equations of state and specific approximations in the functional form of the vibrational thermodynamic functions of the solid. Let us define

$$W_{vib}(V, T) = W(V, T) - W_L(V)$$

$$F_{vib}(V, T) = F(V, T) - W_L(V)$$

where W(V, T) and F(V, T) are the internal energy and the Helmholtz free energy of the crystal of volume V at temperature T, $W_{L}(V)$ is the lattice energy of the (static) crystal, and $W_{vib}(V, T)$ and $F_{vib}(V, T)$ are the vibrational internal energy and the vibrational Helmholtz free energy of the crystal. The equivalences in question are then as follows: Hildebrand

$$P V + \frac{dW_L}{d \ln V} = \frac{\alpha VT}{K} ; \quad W_{vib}(V, T) \equiv W_{vib}(T)$$

Mie-Grüneisen

$$P V + \frac{dW_L}{d \ln V} = \gamma(V) W_{vib}, \quad \gamma(V) = \frac{\alpha V}{KC_V} ;$$

$$F_{vib}(V, T) \equiv Tf\left(\frac{\Theta(V)}{T}\right)$$

where α and K are the coefficient of volume thermal expansion and the isothermal compressibility of the crystal, f is an arbitrary function and $\Theta(V)$ is a purely volume-dependent characteristic temperature. The problem is thus reduced to investigate the validity of these approximations in the functional form of the thermodynamic functions of the crystal. This can be done quite generally within the quasi-harmonic approximation to the statistical mechanics of the solid, without assuming any specific force model. The main results of interest here are the following: 1) The vibrational Mie-Grüneisen and Hildebrand equations of state are valid, in general, only at tempera-

tures somewhat above the Debye characteristic temperature $\Theta_2(V)$ for the high-temperature heat capacity at constant volume; 2)At somewhat lower temperatures, the vibrational Hildebrand equation of state is less accurate than the vibrational Mie-Grüneisen equation; and 3) In a number of solids (in particular sodium chloride) the vibrational Mie-Grüneisen equation of state remains reasonably valid down to temperatures of the order of $\Theta_2(V)/3$.

The first of these results allows us to say a priori that the vibrational Hildebrand and Mie-Grüneisen equations of state are essentially equivalent for most alkali halides at room temperature and atmospheric pressure, the thermodynamic conditions under which one carries out traditionally the determination of the Born repulsive parameters. To confirm this explicitly, we have shown that the use of the vibrational Hildebrand equation and the use of the vibrational Mie-Grüneisen equation in these thermodynamic conditions lead in fact to identical results for the Born repulsive energy [assumed to be of the form $A \exp(-r/\rho)$ in both sodium chloride and potassium chloride,9) the specific cases considered by Guggenheim et al. in their criticism of the traditional procedure for the determination of the Born repulsive parameters.

3. Functional Form of the Born Repulsive Potential

As we emphasized in Section 2, the traditional procedure for the determination of the Born repulsive parameters does not consider the problem of the functional form of the Born repulsive potential, but simply assumes a plausible form, such as the single exponential and inverse-power forms and the Born-Mayer form. We have attempted to devise tests of the validity of these plausible functional forms.

We noted, first, that the variation of the experimental Born repulsive energy with temperature at atmospheric pressure from 0°K to room temperature, as determined from the appropriate thermochemical cycles, and the corresponding variation of the experimental first volume derivative of the Born repulsive energy at constant temperature, as determined from the vibrational Mie-Grüneisen equation of state, do not provide meaningful

tests of the functional form of the Born repulsive potential. This is, in fact, rather obvious *a priori* because the slopes of the different forms at room temperature, as well as their curvatures, are at least approximately equal being fitted to experimental data, and the pertinent variation in interionic distance is quite small (of the order of 1% of the interionic distance at 300°K). Nevertheless, in view of the contrary statements made recently by Guggenheim *et al.*, we have provided an explicit verification of this fact for sodium chloride and potassium chloride.⁹⁾

An effective test is provided, at least in principle, by the variation of the experimental Born repulsive energy, and its first and second volume derivatives at constant temperature, over a relatively wide range of interionic distances, as determined from a detailed analysis of high-pressure compression data. Such a test is being carried out for sodium chloride, bromide and iodide, using Bridgman's compression data which extend up to 100.000 atmospheres at room temperature and up to 50.000 atmospheres at dry ice temperature. These data permit one to obtain directly the experimental values of the first and second volume derivatives of the lattice energy as a function of interionic distance up to linear compressions of almost 10%, by using the vibrational Mie-Grüneisen equation of state and its volume derivative at constant temperature at the various pressures and at room temperature, where they should still be reasonably accurate (see result No. 3 of Section 2). From the values of these derivatives, one can then construct the curve of the experimental lattice energy as a function of interionic distance, by means of Taylor expansions over limited ranges of compression. This yields the curves of the experimental Born repulsive energy as a function of interionic distance given in Fig. 1. A preliminary analysis of these results. reveals deviations of the experimental slope and curvature of the Born repulsive energy as functions of the interionic distance from the single exponential and inverse-power forms, which appear to be outside the limit of experimental error. On the other hand, the variation of the experimental Born repulsive energy itself with interionic distance appears to be represented rather well by the Born-Mayer form, with the values of the repulsive parameters obtained by a careful Huggins-Mayer fit of the cohesive properties of the alkali halides at atmospheric pressure.

Some further evidence in favor of the Born-Mayer form, with the repulsive parameters



Fig. 1. Variation of the experimental Born repulsive energy with interionic distance in NaCl, NaBr and NaI crystals, as obtained from high-pressure compression data (r_0 , equilibrium interionic distance at room temperature and atmospheric pressure).

determined by the Huggins-Mayer procedure, is provided by the result that this form leads to values for the crystal radii of the alkali and halogen ions in the individual alkali halides in rather good agreement with the values derived from the available experimental maps for the electron distribution in the crystals. The Born-Mayer form for the Born repulsive energy per ion pair in an alkali halide crystal with the NaCl structure reads as follows:

$$\begin{split} W_{R}(r) = & 6c_{+-}b_{+}b_{-}\exp\left(-r/\rho\right) \\ & + 6(c_{++}b_{+}^{2} + c_{--}b_{-}^{2})\exp\left(-2^{1/2}r/\rho\right) \\ & b_{+} = b^{1/2}\exp\left(r_{+}/\rho\right), \quad b_{-} = b^{1/2}\exp\left(r_{-}/\rho\right) \end{split}$$

where b_+ and b_- are parameters characteristic for each type of ion in the entire family of salts, r_+ and r_- are characteristic lengths for the ions, ρ and b are universal parameters, and the c's are the so-called Pauling Coefficients. The Huggins-Mayer procedure¹⁰⁾ permits a complete determination of the five parameters b_{\pm} for the five alkali ions, the four parameters b_{-} for the four halogen ions and the parameter ρ from crystal data at room temperature and atmospheric pressure, by using simultaneously the vibrational Hildebrand equation of state and its volume derivative at constant temperature for each of the salts in question. Once this set of parameters is determined, one has values for the differences r_--r_+ of the characteristic lengths for each pair of alkali and halogen ions:

$$r_--r_+=
ho\ln\frac{b_-}{b_+}$$

which are independent from the value of b. On the other hand, it is always possible to pick a value of b such that the equation for the equilibrium interionic separation r_0 in a particular alkali halide crystal takes the form

$$r_0 = r_+ + r_-$$

where now r_+ and r_- have the meaning of crystal radii in the salt in question. One can thus determine completely a set of crystal radii for the alkali and halogen ions in the individual alkali halides with the NaCl structure. Table I summarizes some of the result. The range of values given for each crystal radius is a measure of the uncertainty caused by the uncertainties in the crystal data entering the determination of the Born repulsive parameters. A note-worthy feature of the

crystal radii that we obtain from these parameters is that the radii of the alkali ions are significantly larger (typically by 0.2 Å) than the traditional crystal radii, while the radii of the halogen ions are correspondingly smaller.

Table I. Crystal radii of th alkali and halogen ions in some alkali halides (in Å)*

	F	C1	Br
Li	$0.86 \div 0.88$ $1.15 \div 1.13$	$0.94 \div 0.96 \\ 1.63 \div 1.61$	$0.96 \div 0.98$ $1.79 \div 1.76$
Na	$1.19 \div 1.20$ $1.13 \div 1.11$	$1.23 \div 1.24 \\ 1.59 \div 1.57$	$1.25 \div 1.26 \\ 1.74 \div 1.72$
К	$1.51 \div 1.52$ $1.16 \div 1.14$	$\begin{array}{c} 1.54 \div 1.55 \\ 1.61 \div 1.59 \end{array}$	$1.55 \div 1.56$ $1.75 \div 1.73$

* For each salt the first line gives the radius of the alkali ion and the second line gives the radius of the halogen ion.

This is physically quite reasonable if one considers that the traditional crystal radii refer to essentially free ions, since they were determined by means of the Wasastjerna-Pauling criterion,¹¹⁾ which fixes the relative sizes of isoelectronic alkali and halogen ions from the ionic refractivities in solution, while the new crystal radii are derived entirely from crystal data, and each halogen ion is "softer" than the isoelectronic alkali ion. In relation to our discussion, the significant feature of the new crystal radii is, of course, their fairly good agreement with the experimental crystal radii that have been derived from the available maps for the electron distribution in the alkali halides. These experimental crystal radii have the following values:

4. Many-Body Contributions to the Born Repulsive Energy

The Born repulsive energy in an alkali halide crystal under hydrostatic pressure is a function only of the interionic separation rbut is expected to contain contributions of a many-body nature. Thus the adoption of the same form for the Born repulsive potential with the same values of the pertinent parameters in different crystal phases of a given alkali halide should not be expected to be a

particularly accurate procedure. Nevertheless various attempts have been made to reproduce by means of the Born model the experimental values for the difference in lattice energy of the NaCl and CsCl phases of the alkali halides which undergo polymorphic transitions, using the same form for the Born repulsive potential in the two phases, with parameters determined from crystal data pertaining to the crystal phase stable under standard thermodynamic conditions.¹⁵⁾ A characteristic feature of these attempts is that they overestimate the lattice energy of the NaCl phase relative to the lattice energy of the CsCl phase by a few kilocalories per mole. The systematic character of this discrepancy induced us to analyze it within the framework of the Born model and we were lead to connect it with the treatment of the Born repulsive potential. To test this conclusion, we carried out a calculation for the alkali halides which undergo pressure transitions from the NaCl to the CsCl structure (the potassium and rubidium chlorides, bromides and iodides) in which we allowed the Born repulsive parameters to be different in the two phases of each salt. To this end, we adopted a single exponential form $A \exp(-r/\rho)$ for the Born repulsive potential and we determined the two pertinent parameters separately for the NaCl and CsCl phases of each salt from the observed values of the interionic separation and of the compressibility at the transition pressure and room temperature. The determination was carried out by means of the vibrational Hildebrand equation of state and its volume derivative at constant temperature, which should still be valid for the salts in question at the pertinent transition pressures and room temperature. The calculation leads us to values of the difference in lattice energy of the NaCl and CsCl phases of the various salts which agree with the experimental values within one or two tenths of a kilocalorie per mole (Table II). Further-

Table II. Lattice energy difference of the NaCl and CsCl phases of the potassium and rubidium halides at the transition pressure and 298°K (Kcal/mol)

	KC1	KBr	KI	RbC1	RbBr	RbI
Born model	2.2	2.0	2.0	0.9	0.8	0.9
Experiment	2.0	1.9	1.9	0.7	0.7	0.7

more, the values of the parameters A and ρ in the two phases of each salt display suggestive regularities. Specifically, the value of the parameter ρ in a CsCl phase is always smaller than the value in the corresponding NaCl phase by several per cent, and this implies that the Born repulsive potential is-"harder" at the equilibrium interionic separation in the (more compact) CsCl phase, even though the interionic separation in the NaCl phase is smaller. Similarly, the ratio between the values of the parameter A in the CsCl and NaCl phases of a given salt is always larger than the ratio 8/6 of the coordination numbers in the two structures, by a factor ranging roughly from 1.5 to 3. These results are summarized in Table III. This shows that

Table III. Born repulsive parameters for the form $A\exp(-r/\rho)$ in the NaCl and CsCl phases of the potassium and rubidium halides at the transition pressure and 298°K

	KC1	KBr	KI	RbC1	RbBr	RbI
$\frac{\rho(\text{CsCl})}{\rho(\text{NaCl})}$	0.96	0.96	0.94	0.93	0.92	0.91
A(CsCl) A(NaCl)	1.8	1.8	2.4	2.6	3.1	3.6

these "many-body effects" increase in going from the chloride to the iodide, and are larger in the rubidium than in the potassium salts.

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