

A NEW APPROACH TO REPULSION IN IONIC CRYSTALS

II. Further Refinement on the Alkali Halides

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ABSTRACT

The repulsion parameters in the formulation by the authors (*J. Phys. Chem. Solids*, 1976, 37, 395; *Curr. Sci.*, 1976, 45, 357) for the alkali and the halogen ions have been refined using more experimental data. These parameters could be used to calculate the repulsion potential in any crystal of any structure in which these ions may occur. The r.m.s. error in the alkali halides between the measured and calculated values of the nearest neighbour distance is 0.712% and that in d^2W_r/dr^2 is 7.40%. The corresponding values in the theory of Tosi and Fumi (*J. Phys. Chem. Solids*, 1964, 25, 45) are 1.381% and 6.06%. Our earlier claim that our values were much better than Tosi and Fumi arose out of a computational error and is hence retracted here. Our present repulsion parameters indicate that the alkali ions are (as is to be expected) much less compressible compared to the halogen ions.

RECENTLY we proposed a new approach to repulsion in ionic crystals¹⁻³ based on the following three postulates:

(a) A specific compression energy is associated with each ion and the repulsion between ions arises solely from the resistance of the ions to compression.

(b) The compression energy function of an ion is independent of the neighbouring ions that compress it.

(c) The compression energy of an ion is directly proportional to the number of nearest neighbours.

In the present formulation of repulsion, the compression energy function of an ion that has been determined in one crystal in one structure, can be used for that ion in any other crystal (of any other structure) in which it occurs. This lends predictive power to our approach, in contrast to earlier approaches to repulsion which require the refinement of new parameters in each new crystal.

For the compression energy of the ion, the specific exponential form ($Ae^{-r/\rho}$) was chosen arbitrarily², where r is the radius of the ion and A and ρ are repulsion parameters to be refined for each ion. In this form, 18 parameters are enough to describe all the 20 alkali halides in all their structural modifications and over a range of pressures. In contrast, the widely accepted repulsion potentials of Tosi and Fumi⁴ require 27 parameters to describe just the atmospheric pressure behaviour of 17 alkali halides (they omit CsCl, CsBr and CsI).

The refinement of the repulsion parameters A and ρ for the alkali and the halogen ions using the data on the alkali halides involves the simultaneous optimization of a large number of strongly correlated parameters. The parameters presented earlier²⁻³ were obtained using a graphical method. Although the refinement there was not

complete, those parameters are sufficiently accurate for the calculation of repulsion potentials. Further refinement was, however, undertaken because of our interest in the correlations among the repulsion parameters of different ions. In addition to the experimental data used earlier², new high pressure data^{5,6} on LiF and NaF were also included. We shall not discuss here the actual procedure followed for the refinement except to mention that the computations were quite tedious and the convergence very slow.

Table I lists the repulsion parameters obtained for the alkali and the halogen ions. The values of A and ρ given in papers (2) and (3) are now to be replaced by the values given here. The r.m.s. error, for all the alkali halides, between the measured values of r , the nearest neighbour distance, and the values calculated with the repulsion parameters of Table I, is 0.712%. The r.m.s.

TABLE I
Repulsion parameters for the alkali and the halogen ions

Ion	A (erg)	ρ (Å)
Li ⁺	0.1544×10^{-5}	0.04158
Na ⁺	0.1211×10^{-7}	0.09029
K ⁺	0.5600×10^{-7}	0.1078
Rb ⁺	0.3980×10^{-8}	0.08883
Cs ⁺	0.5604×10^{-8}	0.09977
F ⁻	0.7506×10^{-10}	0.2152
Cl ⁻	0.2958×10^{-9}	0.2240
Br ⁻	0.3724×10^{-9}	0.2352
I ⁻	0.4407×10^{-9}	0.2538

error in d^2W_r/dr^2 , which depends on the bulk modulus, is 7.40%. The corresponding r.m.s. errors in the values predicted by the potentials of

TABLE II
Ionic radii (in Angstroms) in the alkali halides at atmospheric pressure

	F ⁻		Cl ⁻		Br ⁻		I ⁻	
Li ⁺	0.727	1.271	0.760	1.800	0.770	1.990	0.786	2.270
Na ⁺	1.066	1.259	1.105	1.706	1.111	1.849	1.144	2.114
K ⁺	1.425	1.272	1.457	1.688	1.461	1.826	1.481	2.040
Rb ⁺	1.563	1.255	1.598	1.693	1.610	1.851	1.611	2.025
Cs ⁺	1.766	1.230	1.844	1.752	1.845	1.886	1.846	2.060

Tosi and Fumi⁴ are 1.381% for r and 6.06% for d^2W_v/dr^2 .

In earlier papers^{2,3} we claimed that the r.m.s. fit in r and d^2W_v/dr^2 obtained with our potentials is superior to that obtained with the potentials of Tosi and Fumi⁴. This claim is not correct since the r.m.s. errors (for the potentials of Tosi and Fumi) 1.435% and 15.40% quoted there arose from a computational error. The present comparison indicates that the fit in the two theories are of the same order. However, the advantages of the present formulation mentioned at the beginning of this paper are still valid.

The repulsion parameters listed in Table I are different from those listed in references 2 and 3. However, the ionic radii (listed in Table II) predicted by the new set of parameters are not significantly different. During the refinement, the radii of the ions remained almost the same while the compressibility of the ions, which is qualitatively measured by the parameter ρ , varied considerably. The essential difference of the present set of repulsion parameters from the earlier set^{2,3} is that the alkali ions are much harder and the halogen ions much softer than predicted by the earlier parameters.

As a consequence, the present repulsion parameters indicate that the alkali ions are much less compressible than the halogen ions. For instance, calculations show that in CsI, between 0 and 40 kbars, the radius of Cs⁺ decreases by 0.062 Å while the radius of I⁻ decreases by 0.159 Å. In LiF, between 0 and 150 kbars, the radius of Li⁺ decreases by only 0.017 Å while the radius of F⁻ decreases by only 0.017 Å while the radius of F⁻ consistent with the relatively large polarizabilities of the halogen ions. The compressibilities of ions will be discussed in some detail in a later communication.

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