

## Sizes and electronic polarizabilities of divalent ions in crystals

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**Abstract.** The Pauling's form for the overlap repulsive energy is used to calculate the sizes of isoelectronic divalent ions in MgO, CaS, SrSe and BaTe crystals by minimising the next nearest neighbour repulsive interaction. The radii calculated by this method differ significantly from the conventional sets of ionic radii in a consistent way, being larger for cations and smaller for anions. The polarizability-radius cube relation is also utilized to calculate the electronic polarizabilities of ions. The electronic polarizabilities, thus obtained agree with the values determined from the refractivity measurements.

**Keywords.** Electronic polarizabilities; ionic radii.

### 1. Introduction

Recently Fumi and Tosi (1964) have criticised the traditional determination of crystal radii for the ions in the NaCl type alkali halides by means of the Wasastjerna (1923) and Pauling (1960) criterion, stressing that this criterion fixes the radii ratios of the alkali and halogen ions with reference to a state in which the ions are nearly free. Fumi and Tosi (1964) have shown that the Born model of ionic solids permits a complete determination from solid state data of crystal radii for the ions in the individual NaCl type alkali halides. The crystal radii determined by Fumi and Tosi unlike the traditional radii are directly comparable with those deducible from the x-ray diffraction measurements from the location of the minimum charge density between nearest neighbours in alkali halide crystals.

Bansigir (1969) has also suggested an empirical method for determining the radii ratio in alkali halides using the Pauling's form for the repulsive energy including first and second neighbour contributions. The radii determined by this simple empirical approach agree closely with the studies of Fumi and Tosi. We shall determine the crystal radii in the alkaline earth compounds following the method of Bansigir.

### 2. Crystal radii

The ratio  $u$  of the next nearest neighbour ( $W_{NNN}$ ) to the nearest neighbour ( $W_{NN}$ ) contributions of the repulsive energy can be expressed as

$$u = \frac{W_{NNN}}{W_{NN}} = \frac{1}{\beta_{p,p'}(\sqrt{2})^n} \left\{ \beta_{p,p} \left( \frac{2\rho}{\rho+1} \right)^{n-1} + \beta_{p',p'} \left( \frac{2}{\rho+1} \right)^{n-1} \right\} \quad (1)$$

which is a function of the radii ratio  $\rho = (r_+/r_-)$ . Choosing the value of  $n = 7$  for the divalent crystals like MgO (Tosi 1964) we can deduce a value of  $\rho$  which minimizes the magnitudes of  $u$ , i.e.,

$$du/d\rho = 0. \tag{2}$$

The value of  $\rho$  determined from equations (1) and (2) comes out to be 0.81. The value of  $\rho = 0.81$  can be chosen as the radii ratio of positive and negative ions for the crystals with isoelectronic divalent ions (MgO, CaS, SrSe and BaTe), as the second neighbour repulsive interactions become predominant in crystals with large difference in ionic sizes (Pauling 1960). The values of basic radii determined by dividing the observed interionic separations in the above radii ratio are listed in table 1.

It is illustrated in table 2 that like the sum of Pauling's radii, the sum of basic radii obtained in this paper is also nearly equal to the observed lattice parameter in each crystal. In order to deduce a set of crystal ion radii ( $R_{\pm}$ ) which should exactly restore the observed interionic separation, one can assume that

$$R_+/R_- = r_+/r_-$$

where ( $r_{\pm}$ ) are the basic radii (table 1). The crystal ion radii thus calculated are listed in table 3.

Using an empirical relationship between electronic polarizability and ionic radius (Jai Shanker *et al.* 1973) according to which the electronic polarizability of an ion can be assumed to be directly proportional to the cube of its radius in different crystalline or free states, we have calculated the crystal electronic polari-

Table 1. Basic radii in Å

	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>	O <sup>2-</sup>	S <sup>2-</sup>	Se <sup>2-</sup>	Te <sup>2-</sup>
Calculated	0.95	1.26	1.39	1.56	1.15	1.57	1.72	1.94
(a)	0.65	0.99	1.13	1.35	1.40	1.84	1.98	2.21
(b)	0.75	1.02	1.20	1.40	1.32	1.69	1.77	1.91

(a) From Pauling (1964); (b) From Wasastjerna (1923)

Table 2. The sum of radii and observed interionic separation in Å

Compound	R (observed)	( $r_+ + r_-$ )	Pauling's sum of radii	Compound	R (observed)	( $r_+ + r_-$ )	Pauling's sum radii
MgO	2.10	2.10	2.05	SrO	2.54	2.54	2.53
MgS	2.54	2.52	2.49	SrS	3.00	2.96	2.97
MgSe	2.72	2.67	2.63	SrSe	3.11	3.11	3.11
CaO	2.40	2.41	2.39	SrTe	3.33	3.33	3.34
CaS	2.83	2.83	2.83	BaO	2.75	2.71	2.75
CaSe	2.96	2.98	2.97	BaS	3.18	3.13	3.19
CaTe	3.17	3.20	3.20	BaSe	3.31	3.28	3.33
				BaTe	3.50	3.50	3.56

**Table 3.** Calculated values of crystal ion radii\* (in Å) and crystal electronic polarizabilities\* in Å of ions

	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>
	Crystal ion radii				Crystal electronic polarizabilities			
O <sup>2-</sup>	0.95	1.25	1.39	1.58	0.29	0.94	1.60	2.48
	1.15	1.15	1.15	1.17	2.15	2.15	2.15	2.27
S <sup>2-</sup>	0.96	1.26	1.41	1.59	0.30	0.96	1.67	2.53
	1.58	1.57	1.59	1.59	6.46	6.34	6.58	6.58
Se <sup>2-</sup>	0.98	1.25	1.39	1.58	0.32	0.94	1.60	2.48
	1.74	1.71	1.72	1.73	7.12	6.76	6.88	7.00
Te <sup>2-</sup>	..	1.25	1.39	1.56	..	0.94	1.60	2.39
	..	1.92	1.94	1.94	..	9.18	9.47	9.47

\* For each crystal the first row value gives the radius or electronic polarizability for positive ion and the second row value gives the same for negative ion.

**Table 4.** The arithmetic averages of the calculated electronic polarizabilities (in Å<sup>3</sup>)

	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>	O <sup>2-</sup>	S <sup>2-</sup>	Se <sup>2-</sup>	Te <sup>2-</sup>
Calculated	0.30	0.95	1.62	2.47	2.17	6.49	6.94	9.37
(a)	..	1.10	1.60	2.50	2.10	5.13	6.70	9.44
(b)	0.09	0.47	0.86	1.55	3.88	10.20	10.50	14.00

(a) The average values from Tessman *et al.* (1953); (b) Free ion polarizabilities from Pauling (1927).

zabilities (table 3). The arithmetic averages of the electronic polarizabilities for each ion are listed in table 5 and compared with the values of Tessman *et al* 1953) and Pauling (1927).

## Conclusion

The crystal radii for positive ions are larger and for negative ions are smaller than the corresponding radii of Pauling and Wasstjerna which essentially refer to free ions. This result is consistent with the quantum mechanical prediction of Petrashen *et al* (1960) who have used a point-ion approximation to the crystal potential. The calculated values of electronic polarizabilities (table 4) present a good agreement with the average values of Tessman *et al* (1953) and therefore the present study reinforces the validity of the polarizability radius cube relation in divalent ionic crystals.

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