

Effect of the crystal potential on electronic polarizabilities of ions in alkaline earth chalcogenides

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Abstract. The electronic polarizabilities of ions in alkaline earth chalcogenides are estimated by taking account of the effect of the crystalline potential. The polarizabilities thus obtained are found to present a good agreement with experimental data. It has been shown that the polarizabilities and radii of alkaline earth and chalcogenide ions follow the polarizability-radius cube relation approximately well.

Keywords. Electronic polarizabilities; alkaline earth chalcogenides; ionic radii.

1. Introduction

The electronic polarizabilities of ions in alkaline earth chalcogenides were obtained by Tessman *et al* (1953) by performing an analysis of the crystal refraction data on the basis of the Lorentz-Lorenz relation employing the additivity rule. A careful revision of this analysis has been presented by Boswarva (1970). The electronic polarizabilities of ions in alkaline earth chalcogenide crystals obtained by Tessman *et al* and by Boswarva differ from the free state values (Fajans and Joos 1924, Pauling 1927), being larger for cations and smaller for anions. In the present paper we estimate the effect of the crystalline potential on the electronic polarizabilities of ions following Ruffa (1963). It has thus been possible to provide an explanation for the observed differences between free ion and crystalline state polarizabilities.

2. Analysis of the effect of crystal potential

When the ions are transported from free state to a crystal their polarizabilities are changed. According to Ruffa (1963) we can write

$$\frac{\alpha_{c+}}{\alpha_{f+}} = \frac{E_{f+}^2}{E_{c+}^2} \quad (1)$$

where $E_{c+} = E_{f+} - eV_M$. α_{f+} and α_{c+} are respectively the free state and crystalline state polarizabilities of a cation. V_M is the madelung potential, E_f is an energy parameter defined as

$$E_{f+}^2 = \frac{e^3 \hbar^3 n}{m \alpha_{f+}} \quad (2)$$

where e and m are the electronic charge and mass respectively. n is the number of electrons in the ion. \hbar is Planck's constant divided by 2π . An equation similar to (1) cannot, however, be used for anions because of the contribution of excitation levels to the anion polarizability in the crystal which has no counterpart in free state. In addition, quantum states above the first ionization continuum contribute substantially to the free anion polarizabilities. Ruffa (1963), therefore, obtained a different expression for anion polarizabilities which is as follows

$$\frac{\alpha_{c-}}{\alpha_{f-}} = \frac{E_{f-}^2}{E_{c-}^2} \quad (3)$$

where α_{c-} and α_{f-} are respectively the crystalline and free state polarizabilities of an anion. E_{f-} is the energy parameter analogous to E_{f+} . Crystalline state parameter E_{c-} is

$$E_{c-} = \frac{1}{4} [(\Delta - e^2/R) + 3(E_{f-} + \Delta - E)] \quad (4)$$

with

$$\Delta = 2e(V_M - V_R) + E - I + Q \quad (5)$$

where R is the interionic separation, eV_R is the repulsive energy, E the electron affinity of anions, I the ionization potential of cations and Q is the energy of interaction between the free atoms and the crystal environment.

We have calculated the values of crystalline state electronic polarizabilities α_{c+} and α_{c-} in 16 alkaline earth chalcogenides. The madelung energies, repulsive energies and electron affinities necessary to perform these calculations were obtained from the results of Huggins and Sakamoto (1957), while the ionization potentials used are those quoted by Herzberg (1944). Following Von Hippel (1936), the interaction energy Q necessary for the calculation of Δ is set equal to -1 eV for all cases.

3. Results and discussions

In table 1 we have listed the free ion polarizabilities of Pauling (1927) along with the

Table 1. Values of free ion data

Ion	α_f (\AA^3)	n	E_f (eV)
Mg ²⁺	0.094	10	108.00
Ca ²⁺	0.47	18	64.81
Sr ²⁺	0.87	36	67.72
Ba ²⁺	1.56	54	61.69
O ²⁻	3.92	10	16.77
S ²⁻	10.31	18	13.87
Se ²⁻	10.63	36	19.32
Te ²⁻	14.12	54	20.53

Table 2. Values of crystalline state polarizabilities and energy parameters

Crystal	E_{c+} (eV)	α_{c+} (\AA^3)	E_{c-} (eV)	α_{c-} (\AA^3)
MgO	83.97	0.16	28.50	1.36
MgS	88.59	0.14	22.02	4.09
MgSe	89.52	0.14	25.15	6.28
MgTe	90.77	0.13	23.94	10.38
CaO	44.29	1.01	28.26	1.38
CaS	47.04	0.90	23.29	3.66
CaSe	47.76	0.87	26.82	5.52
CaTe	48.89	0.83	26.67	8.36
SrO	48.09	1.71	28.61	1.35
SrS	50.56	1.55	23.94	3.46
SrSe	51.55	1.49	26.79	5.53
SrTe	52.15	1.46	27.48	7.88
BaO	43.41	3.16	28.23	1.38
BaS	45.82	2.83	23.44	3.61
BaSe	46.45	2.77	26.92	5.48
BaTe	47.27	2.66	26.83	8.26

Table 3. Comparison of theoretical and experimental molar polarizabilities (in \AA^3).

Crystal	Molar polarizabilities	
	Theoretical	Experimental
MgO	1.51	1.77
MgS	4.23	4.85
MgSe	6.41	6.03
MgTe	10.51	11.26
CaO	2.39	2.86
CaS	4.55	5.89
CaSe	6.39	7.15
CaTe	9.19	9.71
SrO	3.06	3.52
SrS	5.01	6.45
SrSe	7.02	8.20
SrTe	9.34	9.99
BaO	4.54	4.96
BaS	6.44	8.38
BaSe	8.23	10.04
BaTe	10.92	12.67

values of E_f calculated from eq. (2). The calculated values of E_{c+} , α_{c+} , E_{c-} and α_{c-} are given in table 2. A comparison of theoretical and experimental molar polarizabilities of alkaline earth chalcogenides has been presented in table 3. Theoretical values of molar polarizabilities are the sum of calculated α_{c+} and α_{c-} whereas the experimental molar polarizabilities are those corresponding to the Lorentz-Lorenz relation (Boswarva 1970). It is evident from the data compiled by Tessman *et al* (1953) that the free state polarizabilities reported by Pauling are not accurate to better than 15% for alkaline earth and chalcogenide ions. This fact should be kept in mind in comparing the calculated and experimental polarizabilities since our cal-

Table 4. Average values of polarizabilities (in Å³) and radii (in Å) of ions.

Ion	α_c			r_c	r_f
	(a)	(b)	(c)		
Mg ²⁺	0.14	—	0.29	0.95	0.65
Ca ²⁺	0.90	1.21	1.04	1.29	0.99
Sr ²⁺	1.55	1.92	1.75	1.43	1.13
Ba ²⁺	2.85	3.51	2.85	1.65	1.35
O ²⁻	1.37	1.69	1.90	1.10	1.40
S ²⁻	3.70	4.71	6.05	1.54	1.84
Se ²⁻	5.70	6.18	6.49	1.68	1.98
Te ²⁻	8.72	8.45	9.12	1.91	2.21

(a) based on eqs (1) and (3).

(b) based on experimental data (Boswarva 1970).

(c) calculated from eq. (6).

culations strongly depend upon free ion polarizabilities. In table 4 we compare the average values of crystalline state polarizabilities calculated in the present study with those obtained empirically by Boswarva from experimental refraction data. The agreement is fair particularly in view of the uncertainty in the data on free ion polarizabilities used in the calculations.

Recently Jai Shanker and coworkers (1973, 1975, 1976, 1977) have investigated a relation between electronic polarizabilities and ionic radii. According to this relation we can write for a given ion

$$\frac{\alpha_c}{\alpha_f} = \left(\frac{r_c}{r_f}\right)^3. \quad (6)$$

Values of α_c calculated from eq. (6) have been included in table 4 along with the radii r_c and r_f corresponding to crystalline and free states respectively. According to the criterion of Tosi and Fumi (1964), the values of r_c are larger for cations and smaller for anions than the free state values by 0.30 Å. Ionic radii reported by Pauling (1928) correspond to free state for reasons discussed at length by Tosi (1964). Values of α_c for alkaline earth and chalcogenide ions calculated from eq. (6) present reasonable agreement with the polarizabilities obtained from Ruffa's theory as well as with those reported by Boswarva. The polarizability-radius cube relation (eq. 6) can, therefore, be used for an approximate but quick estimate of crystalline state polarizabilities.

4. Conclusions

The loosening of cations and the tightening of anions in crystalline state relative to the free state, as evident from the analysis of Tessman *et al* and Boswarva, have been explained by using Ruffa's theory in alkaline earth chalcogenides. A reasonable agreement between theoretical and experimental polarizabilities has been achieved. It has been demonstrated that the polarizability radius cube relation is approximately valid in the family of crystals under study.

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