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Formation Energies of Schottky Defects in Alkaline Earth Oxides

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Schottky defect formation energies of alkaline earth oxides have been calculated by the procedure of Mott and Littleton, employing two parameter repulsive potentials. It is found that the polarizability of oxygen ion must be substantially lower in the case of MgO to obtain meaningful defect formation energy. Use of both displacement and anion polarizabilities, obtained from respective dielectric data, for each oxide, yields defect formation energies that are in fair agreement with more recent experimental values, for all the alkaline earth oxides.

Introduction

Alkaline earth oxides, with the exception of beryllium oxide, crystallize in face centered cubic structures of the NaCl type. They are essentially ionic (*1–3*) and it has been shown (*4*) that the Born model of ionic solids is applicable to them. In such ionic solids therefore, it should be possible to calculate the Schottky defect formation energies by the procedure of Mott and Littleton. Two significant attempts (*4*, *5*) have been made earlier to obtain theoretical values of Schottky energies. In their investigation, Yamashita and Kurosawa (*5*) found that the defect formation energies in alkaline earth oxides become negative (and hence absurd) unless very low values of oxygen ion polarizabilities are used for the oxygen ions immediately surrounding the defect. However, in solving for repulsive parameters they obtained negative like-ion (oxygen–oxygen) interactions, which they ignored. Later, Boswarva and Franklin (*4*) encountered very similar difficulties. They obtained either an attractive oxygen–oxygen interaction, which is not justified in the Born model, or they obtained anomalous (negative) Schottky defect formation energies. Such difficulties have been attributed by the authors to the possible incorrectness of the exponential repulsive functions. Therefore, the implications of the failure of theoretical defect energy calculations in these oxides remain unresolved.

The defect formation energies in these oxides have since been redetermined experimentally. The available experimental data on Schottky defect energies (*6–15*) have been summarized in Table I. However, there are not enough confirmatory measurements of these energies. The formation energies obtained from the more recent self-diffusion data are considered as reliable enough for purposes of comparison with the theoretically calculated values, in this communication.

In a previous publication (*16*) from this laboratory the adequacy and implication of two-parameter repulsive potentials have been discussed. The method of obtaining these parameters and some relevant aspects of such a procedure are presented very briefly in the following section. In this communication, we have reinvestigated the problem of defect formation energies in alkaline earth oxides, employing two-parameter repulsive potentials and assuming the applicability of the Born model. The defects have been assumed to be doubly charged Schottky defects corresponding to Mg^{2+} and O^{2-}. Polarizabilities obtained from different sources are used and the effect

TABLE I

LITERATURE VALUES OF THE DEFECT ENERGIES OF ALKALINE EARTH OXIDES

Substance	Method of study	$\frac{1}{2}E^s + E_a$ (eV)	E^s (eV)	E_a (eV)	Reference
MgO	^{28}Mg self-diffusion	3.46	3.80	1.56	*(6)*
	A.C. electrical conductivity	3.50	5.20	0.92	*(7)*
	^{18}O self-diffusion	2.71	—	—	*(8)*
	^{28}Mg self-diffusion	—	—	3.40	*(9)*
	Conductivity with doped samples	2.00	—	—	*(10)*
CaO	^{45}Ca self-diffusion	—	—	3.50	*(11)*
	^{45}Ca self-diffusion	1.22	3.08	2.76	*(12)*
SrO	^{85}Sr self-diffusion	4.60	3.60	2.80	*(13)*
	Electrical conductivity (for O interstitial)	—	3.00	0.60	*(14)*
BaO	^{133}Ba self-diffusion	—	—	4.00	*(15)*

on defect formation energy has been discussed. An attempt has been made to resolve the problem of defect energy calculations in alkaline earth oxides by the use of polarizabilities obtained from experimental dielectric data for individual oxides.

Method of Calculation

Overlap Potentials

The repulsive potential used in these calculations has the form

$$B(r) = 6b \exp(-r/\rho). \tag{1}$$

b and ρ were obtained by solving the following two equations:

$$u(r) = -\frac{z^2 e^2 \alpha_m}{r} + B(r), \qquad u(r) < 0 \tag{2}$$

$$r_0[\partial u(r)/\partial r]_{r=r_0} = 0, \tag{3}$$

where $u(r)$ is the thermochemical lattice energy obtained from Kapustianski et al. *(17)*; and r_0 is the lattice parameter at 0°K and it was estimated from the knowledge of volume thermal expansivities. It has been shown elsewhere by the authors *(16)* that ρ calculated by this procedure is the lower critical value for the hardness parameter and that the expression (1) is equivalent to

$$B(r) = 6b_1 \exp(-r/\rho_c) + 12b_2 \exp(-ar/\rho^c), \tag{4}$$

where $\rho_c \equiv \rho$ and $\rho^c \equiv a\rho_c$, and a is the ratio of the interionic distances of like and unlike neighbors, b_1 and b_2 are the strength parameters for unlike and like neighbor interactions. The b of Eq. (1) also may be partitioned (since $b = b_1 + 2b_2$) into contributions from like and unlike ion repulsions in proportion to the radius ratio R (using Pauling formula *(18)*):

$$\frac{2b_2}{b_1} = f(R) = \frac{1}{(\sqrt{2})^9}\left[1.25\left(\frac{2R}{1+R}\right)^8 + 0.75\left(\frac{2}{1+R}\right)^8\right]. \tag{5}$$

Later, we will be using such values of b_1 and b_2 to investigate the effect of including second neighbor interactions explicitly.

Defect Energies

Once the parameters for repulsive interactions are known, Schottky point defect formation energies may be calculated using the force balance method of Mott and Littleton *(19)*. Briefly, the procedure is as follows. The defect configuration in equilibrium is as shown in Fig. 1. If the energies of the lattice site when the ions are held rigidly is E_0 and when the surrounding ions are relaxed and the ions throughout the lattice are polarized, is E, then the energy for creation of the defect is equal to $\frac{1}{2}(E_0 + E)$ for small values of relaxations

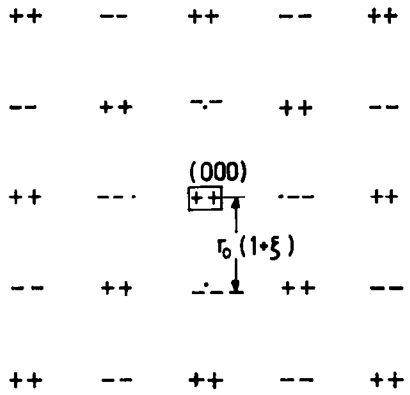

FIG. 1. Defect configuration in equilibrium.

(*20*). The value of the equilibrium relaxation ξr_0 is found by equating the net force on an ion adjacent to the defect in the lattice to zero. If F_e and F_r are the electrostatic and short-range repulsive forces then

$$F_e + F_r = 0, \qquad (6)$$

while both F_e and F_r are functions of the relaxation, F_e is also a function of μ (= *mea*), the dipole moment induced on the immediate neighbors of the defect. The effect of these ions is treated explicitly in the Mott–Littleton model (*19*). Using the expression

$$\mu = \frac{\alpha_\pm F_e}{ze}, \qquad (7)$$

μ is eliminated from the expression for F_e and the forces are then calculated as a function of ξ. One can obtain graphically the value of ξ for which $F_e = -F_r$ and then μ may be evaluated for the particular value of F_e.

Results and Discussion

The data employed for the calculations (*17*, *21–25*) are given in Table II. Three sets of reported polarizabilities for these substances due to (a) Pauling (*18*), (b) Tessmann, Kahn and Shockley (*24*) (TKS), and (c) Fajans and Joos (*25*) (FJ) are given, in that order. Defect energies were initially determined using only two repulsive parameters. No van der Waals terms were used in these calculations. The defect parameters so obtained are summarized in Table III. (Calculations were performed

TABLE II

DATA EMPLOYED FOR THE CALCULATION OF SCHOTTKY DEFECT ENERGIES

	u (kcal/mole) (*17*)	(År at 298°K) (*21*)	b (10^{-12} ergs)	ρ (Å)	η^a (10^{-6} deg^{-1}) (*22*)	Static dielectric constant (*23*)	Cation polarizability (10^{-24} cm^3)			Anion polarizability (10^{-24} cm^3)		
							Pauling (*18*)	TKS (*24*)	Fajans and Joos (*25*)	Pauling (*18*)	TKS (*24*)	Fajans and Joos (*25*)
MgO	934	2.106	1229.8	0.3268	10.3	9.8	0.094	—	0.12	3.88	—	2.75
CaO	845	2.405	3607.8	0.3061	11.6	11.8	0.47	1.1	0.51	3.88	1.8	2.75
SrO	789	2.580	3507.6	0.3262	13.7	13.3	0.86	1.6	0.86	3.88	2.0	2.75
BaO	751	2.769	11377.8	0.2970	13	34	1.55	2.5	1.68	3.88	2.5	2.75

[a] Thermal expansivities.

TABLE III

SCHOTTKY DEFECT PARAMETERS[a]

	ξ_-	m_-	ξ_+	m_+	M'_+	M'_-	M'	E^v_+ (eV)	E^v_- (eV)	E^s (eV)
MgO	0.0575	0.1501	0.0920	0.0044	0.0357	0.1072	0.0339	16.87	23.59	−0.11
	—	—	—	—	—	—	—	—	—	—
	0.0715	0.1135	0.0933	0.0056	0.0424	0.1006	0.0397	18.80	23.63	1.86
CaO	0.0608	0.1157	0.0770	0.0157	0.0433	0.1024	0.0351	17.69	21.79	2.77
	0.0735	0.0585	0.0758	0.0365	0.0655	0.0802	0.0425	20.22	21.12	4.63
	0.0675	0.0863	0.0783	0.0172	0.0505	0.0951	0.0404	19.11	21.82	4.22
SrO	0.0645	0.0965	0.0760	0.0232	0.0507	0.0965	0.0376	17.29	20.03	3.05
	0.0730	0.0531	0.0745	0.0428	0.0702	0.0770	0.0426	19.05	19.42	4.19
	0.0715	0.0719	0.0765	0.0236	0.0574	0.0898	0.0426	18.32	20.15	4.19
BaO	0.0573	0.0834	0.0640	0.0351	0.0599	0.0946	0.0368	17.23	18.89	3.50
	0.0615	0.0557	0.0615	0.0557	0.0772	0.0772	0.0384	18.23	18.23	3.84
	0.0625	0.0615	0.0645	0.0382	0.0684	0.0861	0.0408	18.07	18.66	4.30

[a] The three sets of values were obtained in order by using polarizabilities due to Pauling, TKS, and Fajans and Joos.

with $r = r_0$ itself because the repulsive parameters were obtained at $r = r_0$.) The three sets of values in Table III were obtained by the use of the three different polarizabilities mentioned above.

The defect formation energies in Tables I and III may be compared. It is seen that the E^s values obtained using Pauling polarizabilities for CaO and SrO are close to more recent experimental values (*12*, *13*). But in the case of MgO the value of E^s is negative, and hence, meaningless. Use of TKS or FJ polarizability data give substantially higher values of E^s in general. In the case of MgO, E^s is even then lower than any experimental data. Defect formation energy values may be obtained from the empirical linear relationship that exists between the defect formation energies and the melting temperatures for a large class of materials (*3*). (Though such a relation has been derived theoretically for the case of point defects in metals (*26*), it is only an empirical relation in the case of ionic salts.) Defect formation enthalpies obtained this way (*3*) are very much higher than the experimental values. They may be taken as upper limits of the formation energies. The principal result of this comparison is that in the case of MgO, the above procedure yields anomalously low values of Schottky defect energy, while for CaO and SrO fairly high values of defect formation energies are obtained.

The factors responsible for such results are many. They may be (a) the neglect of van der Waals forces, (b) neglect of explicit consideration of second neighbor interactions, or (c) choice of improper polarizabilities—both anion and displacement. It is therefore essential to discuss the influence of these factors individually and ascertain which of them is largely responsible for the discrepancy. The necessary calculations were performed on MgO. For purposes of evaluating the influence of factors (a) and (b) above, the calculations were performed with an arbitrary oxygen ion polarizability of 2.0 Å^3. (This choice has no particular sanctity.)

The effect of the neglect of van der Waals term was tested by introducing the terms $[C/r^6 + D/r^8]$ into Eq. (2) (for reevaluating b and ρ and in the calculations of F_e and F_r). C and D are the van der Waals constants and were obtained from (*27*). For the test case of MgO, the inclusion of van der Waals terms affects the defect formation energies adversely. Without and with the inclusion of van der Waals terms, the defect energies were found to be 3.3 and 2.30 eV, respectively.

The repulsive parameters employed in these calculations have been shown by the present authors (*16*) to be satisfactory in many solid state calculations involving the Born model. The constraint of the thermochemical lattice energy produces bounds for the hardness parameter. Still lower hardness parameters will require negative strength parameters for the anion–anion interaction if the total lattice energy constraint is to be simultaneously satisfied. Indeed, if hardness parameters reported in the literature (*28*) are used to solve for strength parameters holding the lattice energy as a constraint, a negative (attractive) value is obtained for one of the strength parameters. Though such negative values of b_2 have been used by Norgett and Catalow (*29*) for point defect calculations in fluorite lattices, there is no clear theoretical basis for such use. However, if the repulsive energy expression is inadequate, it would affect E^s for two reasons: (i) due to the apparent neglect of second neighbor interactions in these calculations, and (ii) due to incorrect estimate of displacement polarizabilities. To assess the effect of considering like neighbor interactions explicitly, three parameters, b_1 and b_2, and ρ, were used for calculating F_r and E^s. b_1 and b_2 were obtained using Eq. (5). But the value of E^s for the test case of MgO was found to decrease as:

$b_1(10^{-12}\text{ ergs})$—1229.8, 1014.8; $b_2(10^{-12}\text{ ergs})$—0, 107.5; $\rho(10^{-8}\text{ cm})$—0.3268, 0.3268; E_+ (eV)—20.17, 19.99; E_- (eV)—23.78, 23.32; E^s (eV)—3.38, 2.73.

The extent to which incorrect repulsive parameters influence the displacement polarizability and hence E^s may be understood as follows. The polarization of the lattice outside of the first neighbors is treated in the procedure of Mott and Littleton (*17*) by a continuum approximation. The required displacement polarizability α is determined by using the expressions

$$\alpha = [z^2 e^2/p] \tag{8}$$

and

$$p = 4b[1/\rho^2 - 2/\rho r]. \tag{9}$$

The error in α thus obtained may be estimated by considering the dielectric relation (*3*),

$$\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} + \frac{8\pi\alpha}{3v_m}, \tag{10}$$

where ε_0 and ε_∞ are experimental low and high frequency dielectric constants and v_m is the volume per pair of ions. α calculated using expressions (8) and (10) are given in Table IV. For comparison, the values of α obtained by alternative expressions (*5*) are also given. There is considerable disagreement in the values of α so obtained. The extent of disagreement may be reflected as effective charge, e^*, calculated using Szigeti relation (*30*), $\alpha = z^2 e^{*2}/p$. The values of e^*/e are also shown in Table IV. The displacement polarizabilities obtained from repulsive parameters are therefore considerably lower than those of Yamashita and Kurosawa (*5*). The defect calculations may be performed by incorporating α calculated from Eq. (10). It is found for the test case of MgO, that E^s value is decreased by using such α values. (The defect formation energy of MgO decreased from 3.38 to 3.26 eV.)

However, a consideration of Eq. (10) immediately suggests that the oxygen ion

TABLE IV

POLARIZABILITIES FROM DIELECTRIC DATA

Substance	α from Eq. (10)	α from Eq. (8)	α from Ref. (*5*)	e^*/e (Present work)	e^*/e from Ref. (*5*)
MgO	0.785	1.795	1.016	0.661	0.88
CaO	1.165	2.028	3.689	0.758	0.76
SrO	1.513	2.476	5.421	0.782	0.58

TABLE V

SCHOTTKY DEFECT PARAMETERS USING POLARIZABILITIES FROM DIELECTRIC DATA

	α_-	ξ_-	m_-	ξ_+	m_+	M'_+	M'_-	M'	E^v_+ (eV)	E^v_- (eV)	E^s (eV)
MgO	1.663	0.0875	0.0755	0.0920	0.0044	0.0378	0.1052	0.0337	20.92	23.65	4.00
CaO	2.398	0.0730	0.0775	0.0780	0.0158	0.0458	0.0999	0.0327	19.56	21.80	4.65
SrO	2.708	0.0725	0.0713	0.0760	0.0232	0.0530	0.0942	0.0338	18.41	20.09	4.23

polarizability employed in these calculations may also be similarly inconsistent with the dielectric equation

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{4\pi N}{3v_m}(\alpha_+ + \alpha_-). \qquad (11)$$

The smaller cation polarizability, α_+, from the literature may be assumed to be accurate and oxygen ion polarizabilities consistent with Eq. (11) may be determined for each oxide. The effect of using such value of α_-, together with the values of α obtained from Eq. (10) on the values of E^s may now be tested. The values of α_- and E^s so obtained are presented in Table V for the cases of MgO, CaO, and SrO. The agreement between the calculated defect energies and the more recent experimental values (Table I) seems to be, *on the whole*, very much improved. (Because, though better agreement is achieved in the cases of CaO and SrO by the use of Pauling polarizabilities, the procedure fails in the case of MgO.)

The above calculations therefore indicate that polarizability of the anion is the most important factor in determining the defect energies. To explore this influence in greater detail, α_- was treated as a variable and the defect parameters were determined over a whole range of α_- values. In Fig. 2, variations of F_e and F_r with ξ for various values of α_- are given. It also reveals how the equilibrium value of ξ varies with α_-. The variation of E^s as a function of α_-, for the three oxides, MgO, CaO, and SrO, is shown in Fig. 3. The arrows marked P, TKS, and FJ correspond to the respective polarizabilities. The line marked BF corresponds to oxygen ion polarizability of 1.657 Å^3 due to Boswarva and Franklin.

The disagreement in the displacement polarizabilities obtained from Eqs. (8) and (10) could be eliminated by a reformulation of the procedure by which the repulsive parameters are determined. b and ρ may be obtained from the equations

$$p = \frac{z^2 e^2}{\alpha} = 4b\left[\frac{1}{\rho^2} - \frac{2}{\rho r}\right]\exp(-r/\rho) \qquad (12)$$

$$0 = \frac{\alpha_m z^2 e^2}{r^2} - 6b\exp(-r/\rho) \qquad (13)$$

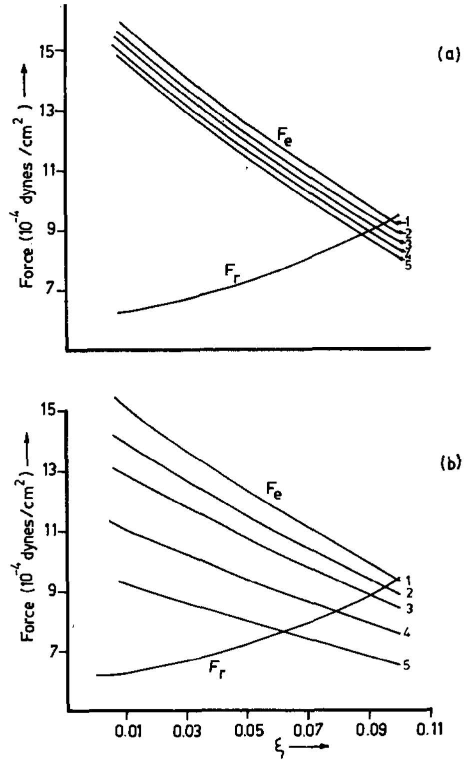

FIG. 2. Variation of F_e and F_r with variation of α_- and ξ. (a) For anion vacancy; (b) for cation vacancy. (1) $\alpha_- = {}_{-}= 0.50$ Å^3, (2) $\alpha_- = 1.00$ Å^3, (3) $\alpha_- = 1.66$ Å^3, (4) $\alpha_- = 2.5$ Å^3, (5) $\alpha_- = 3.88$ Å^3.

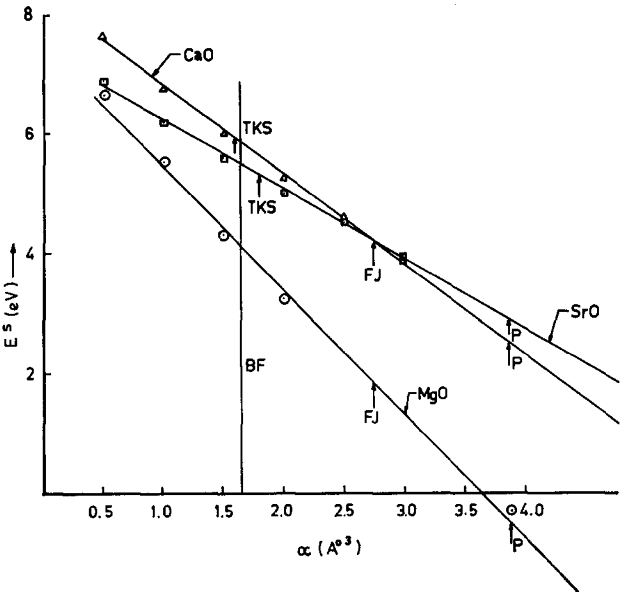

FIG. 3. E^s as a function of α_-. Arrows at P, TKS, and FJ indicate the E^s values obtained using oxygen ion polarizabilities due to Pauling; Tessmann, Kahn and Shockley; and Fajans and Joos, respectively.

in which α from Eq. (10) is employed. But b and ρ obtained from this procedure lead to very high values of E^s (14.02 eV for MgO). Also the repulsive energy varies from 171.4 to 90.5 kcal/mole. Therefore, such procedures may have to be abandoned.

Hence, theoretical values of defect energies which are comparable to experimental values are obtained when use is made of polarizabilities determined individually from dielectric data. These values are substantially different from the free ion polarizabilities reported in the literature. In the case of MgO it is much lower than P, TKS, and FJ polarizabilities, but very close to that value reported by Boswarva and Franklin.

The reasons for the disagreement between the displacement polarizabilities from repulsive energy expression and dielectric data are not very obvious. The e^*/e values from Table IV are somewhat lower than in the case of alkalihalides (*31*). e^* is generally taken as a measure of the distortion of the charge cloud in the lattice and is obtained phenomenologically by replacing ze by ze^* in the expression, $\alpha = z^2e^2/p$. This could be quite satisfactory if p (Eq. (12)) is not erroneous. But there are no strong reasons at present to believe that p derived from a two-parameter repulsive potential is very accurate. This is further strengthened by the fact that e^*/e of the last column of Table IV, calculated using the lattice optical frequency and dielectric data only (and therefore independent of the repulsive energy models), are larger than the e^*/e values from the present work. Thus, it supports indirectly the limitation of exponential description of repulsive energies pointed out by Boswarva and Franklin.

There are at least two qualitative explanations to account for the discrepancies in the negative ion polarizability. The polarizability may be decreased because the electron states of the oxygen ions nearest to the defect are very highly perturbed by the static fields of the defects (*32*). The perturbation presumably affects the relative separation of the energy levels of the oxygen ion excited states. Quantum mechanical expression for polarizability (*33*) is

$$\alpha = 2e^2 \sum_m \frac{|\langle\psi_0|\,Q\,|\psi_m\rangle|^2}{E_m - E_0}, \qquad Q = \sum_i q_i \qquad (15)$$

where q_i are the electron coordinates, and

ψ_0 and ψ_m are the wave functions of the ground and excited states. The dominating contribution to α is usually from one of the m states and it is entirely possible that the perturbation due to the intense static field of the Mg^{2+} vacancy (of the order of 10^8 V/cm) increases $E_m - E_0$. In the classical dielectric theory, this amounts to a change in the fundamental frequencies of the oscillators (*33*) in the field of defect. That the values of α_- increase with the size of the cation also supports this argument because the perturbing field decreases with the size of the vacancy.

Another possible source of error may be due to the fact that MgO is not sufficiently ionic, and hence, the covalent contributions limit the validity of the ionic model calculations. Indeed the failure of the Cauchy relation (*34*) and the negative stress coefficient of high frequency dielectric constant (*35*) have been cited as indications of covalency effects (*36*) in MgO. But, as pointed out earlier, the ionic nature of these oxides and the applicability of the Born model has been reliably established (*4*). It would be very interesting if covalency is the principal cause which fails the calculations of defect energies in MgO. It should be remembered that the ionicity of MgO is as high as 0.88 on Pauling scale and 0.84 on Philips scale (*37*). The ionicities of KI or RbI, where defect energy calculations are successful, are 0.92 on Paulings' and 0.95 on Phillips' scales (*37*). Another curious factor which may be noted in this context is that the values of α_- do not need to be very low (compare Tables II and V) in the cases of CaO and SrO, where the ionicities are more than 0.92 and comparable to those of alkali halides.

Conclusions

The displacement and anion polarizabilities that yield fairly acceptable values of the defect formation energies in alkaline earth oxides are obtained from individual susceptibility data. Even in the case of oxides like MgO, where covalency and the possibility of inaccurate repulsive energy descriptions complicate the situation, this procedure of obtaining the polarizabilities eliminates the anomalies and reduces the quantitative discrepancies in the calculated defect formation energies.

Acknowledgments

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