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Schottky Defects in Alkali Halides*

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The method of lattice statics and the deformation-dipole model have been applied to Schottky defects in ionic crystals in approximations higher than zero order. For an isolated vacancy, all host-lattice–ion potential energy functions for short-ranged repulsive and Coulomb-defect forces were expanded to terms quadratic in the displacements and dipole moments, and the resulting forces were allowed to act on the first and/or second neighbors to the vacancy. The zero-order Coulomb force was allowed to act on the remainder of the host-lattice ions past first and/or second neighbors. The vacancy and Schottky-pair-formation energies in the 12 Na, K, Rb halides have been calculated. A comparison is made between the zero-order approximation and the one considered here. Fairly good agreement is obtained between our calculated values and the experimental values for the Schottky-pair-formation energies if the polarizations around the defect are properly treated with respect to deformation dipoles.

I. INTRODUCTION

For many years there has been widespread interest in the subject of ionic conductivity in solids.[1–4] Recent advances in conductivity measurements and data analysis have increased this interest in both experimental and theoretical areas. A review article by Lidiard[1] gives an excellent historical survey and a bibliography up to 1956. More recently Suptitz and Teltow,[2] and Fuller[3] have brought up to date advances and trends in the transport properties of ionic crystals. Fuller[3] has pointed out that there has been recent interest in solid electrolytes for use in electric automobiles and solid-state batteries. Thus there is an increased need for a continuing and deeper study of ionic conductivity and the types of defects which are important in transport processes. These types of defects, called point defects, are those formed by vacant lattice sites and interstitial ions. The important quantities needed are the formation energies since it is these energies which govern the concentrations of the defects.

Barr and Lidiard[4,5] have pointed out that Schottky-pair-formation energies tend to be ~ 10–20% low when compared with experiment (although the results of Scholz[6] are high possibly because polarization contributions are lost by assuming too small a crystal). They discuss several possible causes for the low values of the Schottky-pair-formation energy which may probably apply to the other types of defect calculations, e.g., interstitials, migrating ions, complexes of vacancies and interstitial ions, etc. Improvements discussed include the following: (i) a proper description of the repulsive potential, especially where the distance of approach between cations and anions is less than the equilibrium lattice spacing; (ii) a modification of the polarizabilities on neighbors close to charged defects because of the strong electric fields (~ 10^8 V/cm); (iii) a modification of polarizabilities when ionic overlap is large, e.g., when the ionic radii of cation and anion are very much different; (iv) the inclusion of dipoles as a result of distortions in the ionic-charge distributions due to the overlap of ions[7]; (v) extending the region of explicit relaxation to include more ions; (vi) and application of the lattice-statics method introduced by Matsubara[8] and later applied to vacancies in solid argon by Kanzaki.[9]

Since Kanzaki's work, the method of lattice statics has been used in many defect calculations for both metals and ionic crystals.[10–18]

The method of lattice statics consists essentially of minimizing the Fourier-transformed expression for the potential energy of a harmonically distorted superlattice containing supercells each having N unit cells and one defect. The assumption of periodic supercells allows the Fourier synthesis of the ionic displacements and dipole moments. Then the translational invariance of the force-constant matrices, which are contained in the potential-energy function of a harmonically distorted perfect lattice, is utilized and thereby the rank of these matrices is reduced. For example, the displacements and dipoles for a supercell containing N unit cells can be Fourier transformed in terms of N six-component Fourier amplitudes, one for each distinct allowed wave vector $\vec{q}$ in the first Brillouin zone obtained by applying periodic boundary conditions across the supercell. Then, in the case of ionic crystals with a diatomic unit cell, the $6N \times 6N$ array of linear equations can be decoupled into N 6×6 equations which subsequently determine the Fourier amplitudes. If the direct space displacements and dipoles are desired, back transformation is necessary. However, in problems involving charged defects, calculation of formation energies obtained directly from the Fourier amplitudes and generalized forces is much easier than using direct space quantities.

In this work, the formalism presented by Hardy and Lidiard[19] for treating point defects in ionic crystals using the deformation-dipole model and the method of lattice statics has been modified to include higher-order terms in the defect–host-lattice–ion interactions, and has been extended in some cases to allow for the explicit relaxation of both nearest and next-nearest defect neighbors. Schottky-pair-formation energies have been calculated for the 12 Na, K, and Rb halides.

II. VACANCY INTERACTION POTENTIAL ENERGY

A vacancy will interact with the host-lattice ions because of missing repulsive overlap, Coulomb-monopole and -dipole interactions, and deformation dipoles. In each of these cases, ψ will be the negative of the appropriate functions as they appear in the perfect crystal.

A. Repulsive Overlap

In considering the short-range overlap interactions, two separate types of potentials are used. If only first-neighbor (nn) interactions are to be considered, the Born-Mayer form

$$\psi^R(r) \equiv \phi_{ij}(r) = \lambda_{ij} e^{-r/\rho_{ij}}$$

between the ith and jth types of ions is used. The parameters λ and ρ are obtained from the equilibrium condition using the compressibility and the lattice constant. The compressibility β is obtained from the elastic constants C_{11} and C_{12} using the relation

$$\beta = 3/(C_{11} + 2C_{12}) \ .$$

When second-neighbor interactions (nnn) are included, both the nn and nnn repulsive potentials are assumed to be of the Huggins-Mayer form,[20]

$$\psi^R(r) \equiv \phi_{ij}(r) = \lambda'_{ij} e^{-r/\rho'_{ij}} \ ,$$

where

$$\lambda'_{ij} = b_{ij}(1 + z_i/n_i + z_j/n_j) e^{(r_i + r_j)/\rho'_{ij}} \ .$$

Here r_i, z_i, n_i, b_{ij}, and ρ' are, respectively, the ionic radius, net ionic charge, number of outer electrons, a constant characterizing the overlap between ions, and a screening parameter. The parameters λ' and ρ' were taken from Fumi and Tosi.[21]

In order to be consistent with the Fumi-Tosi parameters, we included van der Waals terms when considering the Huggins-Mayer potential-energy term. Thus to zero order in the ionic displacements,

$$\phi_{ij}(r_0) = -c_{ij}/r_0^6 - d_{ij}/r_0^8 + \lambda'_{ij} e^{-r_0/\rho'_{ij}} \ , \qquad (1)$$

and

$$\phi_{ii}(\sqrt{2}r_0) = c_{ii}/(\sqrt{2}r_0)^6 - d_{ii}/(\sqrt{2}\,r_0)^8 + \lambda'_{ii} e^{-\sqrt{2}r_0/\rho'_{ii}} \ ,$$

where c_{ij} and d_{ij} are the dipole-dipole and dipole-quadrupole van der Waals coefficients, respectively, calculated by Mayer.[22]

B. Coulomb Interactions

The contribution arising from the interaction between the defect electric field and the host-lattice monopole charges is written

$$\psi^c(|\vec{r}^{\lambda} + \vec{\xi}^{\lambda}|) = e_\kappa (e_D / |\vec{r}^{\lambda} + \vec{\xi}^{\lambda}|) \ ,$$

where e_D is the effective charge of the defect and $\vec{r}^{\lambda} + \vec{\xi}^{\lambda}$ is the relaxed-lattice separation between the defect and the λth ion, the defect being located at the origin. Here

$$\lambda \equiv \begin{pmatrix} l \\ \kappa \end{pmatrix} \ ,$$

i.e., κth ion in the lth unit cell.

The Coulomb-dipole contribution will be made up of separate parts arising from displacement, polarization, and deformation-dipole moments. Letting μ_α^λ be the αth component of the total dipole moment on the λth ion, we can write

$$\psi^{\mathrm{dipole}}(|\vec{r}^{\lambda} + \vec{\xi}^{\lambda}|) = -\sum_\alpha \mu_\alpha^\lambda E_\alpha(|\vec{r}^{\lambda} + \vec{\xi}^{\lambda}|) \ ,$$

where

$$E_\alpha(|\vec{r}^{\lambda} + \vec{\xi}^{\lambda}|) = -\frac{1}{e_\kappa}\left(\frac{\partial \psi^c(r)}{\partial x_\alpha^\lambda}\right)_{\mathrm{relaxed}}$$

is the defect electric field.

C. Missing Deformation Dipoles

The missing dipole contribution arises because each of the six nn anions about a cation vacancy is missing one of its six deformation-dipole moments. Following the lattice-dynamical studies by Hardy,[23] these dipoles are located entirely on the anions. The correction needs to be made for the missing "bonds" between dipoles and the remaining ions in the crystal. As a zero-order approximation, this correction will involve only the (200) neighbor-to-cation vacancies as shown in Fig. 1. The energy of the dipole P on the left in the presence of the field E of the ion at r_2 is

$$-P(r_1 + \xi_1) \times E(r_1 + \xi_1 - r_2) \ .$$

Here we have assumed that the vacancy center and the ion at r_2 remain at the unrelaxed-lattice configuration (the vacancy center will not move by symmetry). The contribution to the formation energy will be the negative of this or

$$\psi(|\vec{r} + \vec{\xi}|) = [P(r_1) + P'(r_1)\xi_1 + \cdots] \times [e/(r_1 - r_2)^2 - 2e\xi_1/(r_1 - r_2)^3 + \cdots]$$

upon expanding. The missing dipole correction is considered only to zero order in the force, so that

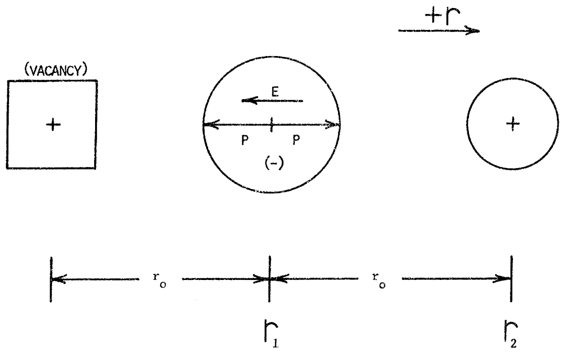

FIG. 1. Missing dipole configuration on cations about an anion vacancy.

in this approximation,

$$\psi^{\mathrm{MD}}(|\vec{\mathrm{r}}^{\lambda}+\vec{\xi}^{\lambda}|)=P(r_0)e/r_0^2+[P'(r_0)+2P(r_0)/r_0]e\xi/r_0^2 \ .$$

Here

$$P(r_0)=r_0(e-e^*)/[2(r_0/\rho-2)] \ ,$$

and

$$P'(r_0)=-P(r_0)/\rho \ ,$$

where e is the monopole charge, e^* is the "effective ionic charge," and $P(r_0)$ is taken to be the distortion-dipole moment which is the result of the mutual distortions of neighboring ions owing to their overlap and is to be distinguished from the deformation-dipole moment which is the unbalanced-dipole moment formed by the relative displacements of the ions against each other. The distortion dipoles are centered on the anions and are counted positive when directed toward the cation.

III. SCHOTTKY FORMATION ENERGY

The Schottky-pair-formation energy E_S is defined as the energy necessary to remove a well-separated anion-cation pair from the interior of the crystal and put it on the surface. Thus E_S is the sum of the formation energies for a cation vacancy and an anion vacancy, and cohesive energy per ion pair since the separated pair is placed on the surface of the crystal.

For both nn and nnn repulsive interactions, the cohesive energy can be written

$$W_L(r_0)=-\alpha_m e^2/r_0+6\phi_{ij}^{+-}+6\phi_{ii}^{++}+6\phi_{ii}^{--} \ ,$$

where the ϕ_{ij} are defined in Eq. (1), and α_m is the Madelung constant.

We have considered Schottky defects in two approximations; the zero-order and quadratic approximations which are referred to as I and II, respectively. In approximation I only the lowest-order terms are retained in the expansion of the forces for the defect–host-lattice-ion interactions (energy terms which are linear in the displacements and the dipole moments). In approximation II, force terms linear in the displacements and dipoles are retained. The expanded form has been chosen rather than evaluating the interactions at the relaxed-lattice configuration, since vacancy defects involve corrections to the perfect-lattice potential energy, and since the force-constant matrix contains interactions evaluated in the harmonic approximation.

The formalism for approximation I was first considered by Hardy and Lidiard,[19] and recently Karo and Hardy[24] (KH) have presented the results of calculations for alkali halides with nearest-neighbor repulsive overlap forces. In this work we have included repulsive overlap and higher-order Coulomb interactions between the defect and both its nn and nnn in approximations I and II.

In approximation I the deformation dipoles are considered to be "frozen" in as the defects are formed so that the missing-dipole contribution is zero. Thus, in this approximation,

$$\mu=C^{-1}\alpha[E_0+UH(1+U\tilde{S})\xi]+\tilde{S}\xi \ ,$$

$$M\xi=V_0+(U^{-1}+S)\tilde{C}^{-1}E_0 \ ,$$

and

$$E=\Phi_0^R+\Phi_0^c-\tfrac{1}{2}\tilde{E}_0C^{-1}\alpha E_0-\tfrac{1}{2}[\tilde{V}_0+\tilde{E}_0C^{-1}(U^{-1}+\tilde{S})]\xi$$

for the dipole moments $\vec{\mu}$, ionic displacements $\vec{\xi}$, and formation energy E, respectively.[24] Here Φ_0^R and Φ_0^c are the zero-order repulsive overlap and Coulomb interaction energies defined by the equation

$$\Phi_0=\textstyle\sum_\lambda\psi(|\vec{\mathrm{r}}^{\lambda}|) \ .$$

The subscript 0 indicates quantities that are to be evaluated at the relaxed or undistorted-lattice configuration.

In approximation II the interaction potential energy ψ is expanded to terms quadratic in the displacements. Thus, including a missing-dipole contribution, the above equations for the dipole moments, ionic displacements, and formation energy, respectively, become

$$\mu=C^{-1}\alpha(E_0+F_0\xi)+C^{-1}\alpha UH(1+U\tilde{S})\xi+\tilde{S}\xi \ ,$$

$$M\xi=D_0+V_0+G_0\xi+\tilde{F}_0\mu+(U^{-1}+S)\tilde{C}^{-1}(E_0+F_0\xi) \ ,$$

and

$$E=\Phi_0^R+\Phi_0^c+\Phi_0^{\mathrm{MD}}-\tfrac{1}{2}\tilde{E}_0C^{-1}\alpha E_0-\tfrac{1}{2}\tilde{D}_0\xi$$
$$-\tfrac{1}{2}\tilde{V}_0\xi-\tfrac{1}{2}\tilde{E}_0C^{-1}(U^{-1}+\tilde{S})\xi-\tfrac{1}{2}\tilde{E}_0C^{-1}\alpha F_0\xi \ .$$

Here the matrix elements for the harmonic repulsive overlap, Coulomb field gradient, and missing dipole moments are, respectively,

$$G^{\lambda}_{\alpha\beta,0} = -\left(\frac{\partial^2\psi^R(r)}{\partial x^{\lambda}_{\alpha}\partial x^{\lambda}_{\beta}}\right)_0 ,$$

$$F^{\lambda}_{\alpha\beta,0} = -\frac{1}{e_{\kappa}}\left(\frac{\partial^2\psi^c(r)}{\partial x^{\lambda}_{\alpha}\partial x^{\lambda}_{\beta}}\right)_0 ,$$

and

$$D^{\lambda}_{\alpha,0} = -[P'(r_0) + 2P(r_0)/r_0]e/r_0^2 .$$

These contributions are treated as short-range forces acting only on a few close neighbors.

The force-constant matrix M used in this work was the one considered by Jaswal and Hardy.[25] This matrix is in the dipole approximation and includes deformation dipoles and an angle-bending force.[26] This latter force is assumed to be proportional to the angular deviation from the 90° angle formed by an ion and two of its dissimilar nn ions.

IV. NUMERICAL RESULTS

The sum over the wave vectors $\vec{q}$ in the Fourier-transformed expression for the ionic displacements indicates a crystal of finite volume containing $N = n^3$ unit cells where n is the number of unit cells along an edge.[14] This sum is an approximation to an integral over the first Brillouin zone, and the sum approaches the integral as $N \to \infty$ in which case we would have an isolated defect in a lattice containing an infinite number of unit cells.

The sum requires that periodic boundary conditions be imposed on the displacements in a volume repeated throughout an infinitely extended medium. By doing this a representative sample of the permissible wave vectors can be obtained for the determination of the displacements and hence the formation energies. The sample becomes much improved as the size of the periodic volume is increased. The shape of this volume or "supercell" is taken to be the same as that of the unit cell. This is the same basic approach as used by Kellermann.[27]

The calculations were done on an IBM 360/65 computer for a uniform mesh of $N = 8000$ wave vectors in the first Brillouin zone and then extrapolated to $N = \infty$. The extrapolation was made possible because the ratio of the differences between relaxation energies for successive runs, having N values of 1000, 8000, 64 000, and 512 000, was found to be a constant. Therefore the extrapolated value could be found from the sum of a geometrical progression for an infinite number of terms from the values obtained for $n = 10$, 20, and 40. The results thus obtained are estimated to be within less than 2% of the values for $N = \infty$.[28]

In Table I values are given for the cohesive energy W_L and the energies needed to extract a cation, E_+, to extract an anion, E_-, and to form a Schottky pair, E_S, for both the nn and nnn models. The calculated values of E_S in this same approximation by KH[24] are also given for the nn model for comparison. Only neighbors as far as $3r_0$ have been included because we have found that for wave-vector samples larger than 8000, values of the displacements and dipole moments in this region do not change appreciably. In order to calculate accurately the displacements and dipole moments of more distant ions, the number of wave vectors must be increased, i.e., increase the size of the periodic volume, so that the influence of the other defects in the periodic lattice of defects becomes negligible. The calculated formation and Schottky energies in approximation II are given in Table II. The calculated values for Φ_0^{MD} for both the nn and nnn models along with some of the more recent experimental values of E_S are also given.

V. SUMMARY AND DISCUSSION

The formation energy of Schottky pairs in alkali halides has been calculated using the method of lattice statics and the deformation-dipole model. In this work the calculations of KH[24] have been repeated using the same model but different input data. This model, approximation I, was one in which all defect–host-lattice–ion forces were evaluated at the unrelaxed-lattice configuration. This approximation was considered for both nearest-neighbor Born-Mayer repulsive overlap and the more sophisticated Huggins-Mayer repulsive form which included the attractive van der Waals interactions. In this latter case, the dynamical matrix was modified to include nnn anion-anion repulsive interactions in addition to a noncentral angle-bending force, as opposed to the former case where only nn repulsive contributions were considered. This approximation was then modified to include higher-order terms in the expansion of the defect–host-lattice–ion potential energy. All terms up to and including those quadratic in the displacements and dipoles were considered significant. Calculations based on approximations I and II were carried out for both the nn and nnn models.

A comparison of E_S(nn) and E_S(KH) from Table I shows that the results of KH[24] have been satisfactorily repeated within the limitations of the input data used. A direct comparison of E_S(nn) and E_S(nnn) for either approximation is not too meaningful because the results for the former were found from experimental data for host-lattice–ion interactions while the latter were obtained using theoretically derived data as well as a modified force-constant matrix. However, within this limitation, the over-all choice of model does not seem to be significantly important when comparing the calculated E_S for the two models with the experimental values. Also, the lattice energies W_L given in Table I show no significant changes for the

TABLE I. Calculated cohesive energies W_L in the nn and nnn models, calculated energies to remove a cation and an anion to infinity, E_+ and E_-, and the Schottky-pair-formation energy E_S in approximation I. All energies are in eV.

	NaF	NaCl	NaBr	NaI	KF	KCl	KBr	KI	RbF	RbCl	RbBr	RbI
$-W_L$ (nn)	9.557	7.949	7.530	6.989	8.404	7.195	6.884	6.447	8.023	6.945	6.644	6.237
$-W_L$ (nnn)	9.451	7.976	7.610	7.141	8.388	7.296	7.001	6.613	8.001	7.049	6.780	6.425
E_+ (nn)	5.890	4.708	4.373	3.914	5.316	4.487	4.241	3.879	5.119	4.405	4.161	3.822
E_- (nn)	6.010	5.128	4.874	4.521	5.125	4.610	4.457	4.203	4.840	4.436	4.287	4.065
E_+ (nnn)	5.495	4.628	4.336	3.924	4.977	4.508	4.284	3.974	4.741	4.436	4.232	3.941
E_- (nnn)	5.903	5.140	4.938	4.678	5.186	4.772	4.641	4.477	4.855	4.587	4.479	4.339
E_S (nn)	2.342	1.888	1.718	1.446	2.037	1.902	1.814	1.636	1.936	1.896	1.805	1.650
E_S (nnn)	1.948	1.792	1.663	1.460	1.775	1.985	1.924	1.837	1.595	1.974	1.931	1.855
E_S (KH)[a]	2.399	1.904	1.657	1.441	2.070	1.935	1.811	1.621	1.804	1.900	1.770	1.638

[a] See Ref. 24.

different types of defect–host-lattice-ion interactions used. The values for E_S have a definite trend to increase on going from the first approximation to the second if one keeps the defect–host-lattice-ion interactions the same. This increase is markedly higher in the sodium halides (an increase of nearly 30% occurs for sodium iodide). The changes are smallest in the rubidium series, and within each of the three alkali-ion sequences the change was proportional to the anion ionic radius. In most cases, the difference between the two values of E_S is approximately equal to the zero-order missing-dipole energy Φ_0^{MD} which has a similar trend to the Schottky-defect-formation energies.

The over-all difference between the two approxi-

TABLE II. Calculated zero-order missing-dipole energies Φ_0^{MD} in the nn and nnn models, calculated energies to remove a cation and an anion to infinity, E_+ and E_-, and the Schottky-pair-formation energy E_S in approximation II. All energies are in eV.

	NaF	NaCl	NaBr	NaI	KF	KCl	KBr	KI	RbF	RbCl	RbBr	RbI
Φ_0^{MD} (nn)	0.515	0.503	0.518	0.464	0.205	0.336	0.355	0.380	0.099	0.271	0.295	0.305
Φ_0^{MD} (nnn)	0.624	0.555	0.530	0.368	0.142	0.339	0.336	0.294	0.040	0.217	0.251	0.243
E_+ (nn)	6.264	5.206	4.911	4.407	5.411	4.754	4.555	4.251	5.137	4.597	4.403	4.112
E_- (nn)	6.020	5.085	4.821	4.456	5.231	4.627	4.454	4.182	4.968	4.473	4.305	4.058
E_+ (nnn)	5.972	5.152	4.859	4.322	4.996	4.720	4.518	4.193	4.679	4.498	4.341	4.071
E_- (nnn)	5.967	5.087	4.865	4.586	5.317	4.772	4.613	4.420	5.011	4.601	4.465	4.295
E_S (nn)	2.727	2.343	2.203	1.873	2.239	2.186	2.124	1.986	2.081	2.126	2.063	1.933
E_S (nnn)	2.489	2.264	2.113	1.767	1.925	2.196	2.130	1.999	1.690	2.050	2.027	1.941
E_S (expt.)[a]	···	2.02	1.68	···	2.64[b]	2.22	2.53	1.60	···	2.0[c]	···	···
		2.09	1.74			2.30	1.99	1.58		2.04[d]		
		2.12				2.59[e]	2.00	1.56				
		2.34[f]				2.49[g]		2.21[h]				
						2.26[i]		1.90[j]				

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mations cannot be understood entirely in terms of zero-order missing-dipole contribution since in approximation II the forces acting on the host-lattice ions have been modified, especially on the nn as a result of the missing-dipole force.

A comparison of the displacements showed that the displacements past nn did not change significantly from one model to the other.[29] Even the displacements of the nn about an anion vacancy did not change to any great extent; however, in the case of a cation vacancy, where the additional repulsive missing-dipole force is acting on the nn anions, the change from approximation I to approximation II was significant. A similar behavior was found to occur for the dipole moments. The dipole moments are directed inward about cation vacancies because the polarization dipole generated by the defect electric field is dominant over the deformation-dipole moment which is directed away from the defect.

From these results we can conclude that the difference between the results of approximations I and II are mainly due to the missing-dipole contributions. Thus it appears that the consideration of the missing dipoles with the zero-order approximation in most cases should adequately describe the relaxation of the lattice about charged point defects in alkali halides, with the possible additional consideration of the missing dipole interacting with other ions in the vicinity of the defect.

An observation of the displacements of the nn anions about a cation vacancy in NaI showed that in zero-order (approximation I) the displacements were directed outward; however, the introduction of field-gradient dipole forces (which are included in approximation II) caused a contraction rather than an expansion for this nn shell. This effect can be attributed to the large-defect induced-polarization dipole moment in NaI which has the smallest ratio of the cation-to-anion ionic radius. The result is that there will be a large-defect electric field on the anion which has a large polarizability. Therefore in some cases approximation II contains important contributions which will be important especially in crystals like NaI and some of the lithium halides. Barr and Lidiard[4] discuss similar effects when the cations and anions are of very different size.

We would like to point out that large changes in the relative displacements of the nn and nnn along the (100) direction do occur. For cation vacancies, the general trend is for the (100) nn to displace inward as a result of the large Coulomb attraction. However, the opposite is true for anion vacancies as a result of the "pushing" caused by the large outward displacement of the nn cation. Therefore further useful information might be obtained by considering anharmonic forces between nn and nnn to a vacancy along the (100) direction.

The calculated values for E_S still tend to be somewhat low when compared to experimental values, although agreement is greatly improved in approximation II. Again we mention that Barr and Lidiard[4] have pointed out that because of the high electric fields due to charged defects, the assumption that the induced dipole moment is proportional to the electric field (linear approximation) may be an overconstraint resulting in an overestimation of the dipole moments. Also the deformation-dipole moments were considered to be centered on the ion rather than being located out near the region where the distortion is produced.

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Optical and EPR Studies of [Na]^0 and [Li]^0 Centers in CaO[†]

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We report EPR and optical studies of O^- ions located next to Li^+ and Na^+ impurities in calcium oxide. The oscillator strengths of the optical transitions ($f \sim 0.1$) are larger than expected for the $A(p_z) \rightarrow E(p_x, p_y)$ transitions of these centers. The hyperfine interaction with the impurity nuclei is interpreted as having a negative contact term a and a positive anisotropic term b. The results are discussed in terms of admixture of $O^- | 3s\rangle$ functions into the ground p_z state.

I. INTRODUCTION

The optical absorption bands of trapped electron and trapped hole centers in the alkali halides were studied long before models for the defects were accepted and before EPR and electron-nuclear double resonance (ENDOR) techniques were available to guide the choice of model. For the alkaline-earth oxides, the order of study was reversed and the EPR spectra of F^+ and V^- centers were identified first.[1] Presently the F^+ bands are reasonably well understood (albeit only after some controversy), but less attention has been given to the optical properties of trapped hole centers.

Trapped hole centers have very different structures in the isostructural alkali halides and alkaline-earth oxides. In the alkali halides, the intrinsic hole centers are the self-trapped X_2^- molecule ions, whose symmetry axes are parallel to the crystal $\langle 110 \rangle$ directions.[2] Although mixed molecule ions, $(OF)^{2-}$, have been observed in magnesium oxide crystals containing fluorine,[3] no EPR spectrum has been identified which can be attributed to O_2^{3-}, the analog of the X_2^- center in any of the alkaline-earth oxides. Instead, crystals of the alkaline-earth oxides irradiated with x rays, γ rays, or fast electrons show magnetic resonance absorption due to V^- centers, i.e., O^- ions adjacent to cation vacancies.[1] It can be seen in Fig. 1 that the V^- centers have tetragonal symmetry about the principal axes of the crystal.

The presence of trapped hole centers in MgO crystals subjected to ionizing radiation was first detected with EPR methods by Wertz *et al.*[1] These authors observed a three-line spectrum at arbitrary orientations with turning points about the $\langle 100 \rangle$ crystal direction. Analysis of the spectrum showed the g tensor to have cylindrical symmetry around the $\langle 100 \rangle$ axes with $g_\perp = 2.0385$ and $g_\parallel = 2.0033$. No central ion hyperfine pattern was reported. It was proposed that the spectrum was associated with the V^- center, an O^- ion adjacent to a cation vacancy. This proposed model was based upon the g values, saturation properties, and temperature dependence of the spectrum. Strong support came later from EPR and ENDOR measurements of the interactions between the trapped hole and neighboring OH^-, OD^-, or F^- impurities.[4] More recently, hyperfine interaction with the adjacent Mg^{2+} ions, of which only the 10% abundant ^{25}Mg nuclides are magnetic, has been observed.[5] Similarly, simple EPR spectra have now been observed for V^- centers in CaO[6] and SrO.[7,8] In all three oxides, the measured values of $g_\perp$ were significantly greater than the g value for free electrons. EPR spectra of O^- ions adjacent to substitutional Li^+ ions ($[Li]^0$ centers) in MgO, CaO, and SrO have also been reported.[9] A schematic representation of the structure of these and related defects in the alkaline-earth oxides is portrayed in Fig. 1. In the present paper, detailed optical and EPR resonance measurements on the $[Li]^0$ and $[Na]^0$ centers in CaO are discussed.

II. EXPERIMENTAL

Single crystals of CaO were grown from Mallinckrodt $CaCO_3$ powder, reagent grade, by submerged arc fusion.[10] The starting powder contained about 10% by weight of Na_2CO_3 or Li_2CO_3. An analysis of the resulting crystals showed there to be approximately 1300 ppm of Li or 70 ppm of Na present after melting. All crystals were annealed to 1100 °C and then quenched to room temperature. For EPR studies, trapped hole centers were produced by irradiation at 10 K with 2-MeV