

Self-trapped hole (V_K center) in NaCl-type alkali halides. Lattice relaxation and optical properties for $MX:X_2^-$ systems

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The equilibrium lattice configurations, electronic excitation energies, and systematic exploration of the V_K center in the 16 NaCl-type alkali halides, MX ($M = \text{Li, Na, K, Rb}$; $X = \text{F, Cl, Br, I}$) are calculated. The defect is regarded as a X_2^- molecular ion with the electronic structure perturbed by the ionic environment, but with the equilibrium bond length only slightly modified. The energy required to form a V_K center varies from ~ 4 eV (RbI) to ~ 7 eV (LiF), relatively large defect energies. The important relaxed ion positions are summarized, analyzed, and compared with experiment (for LiF and NaF). The V_K (X_2^-) electronic transition energies, ΔE_σ , ΔE_π , and ΔE_g , are predicted from theory and compared to experiment. There are clearly discerned trends in transition energies with the M^+ cation in the sequences MX which are discussed and compared with experiment.

I. INTRODUCTION

The self-trapped hole in alkali halide crystals is the archetype of the small-polaron system. All experimental and theoretical evidence is consistent with the picture of the V_K center as an X_2^- molecular anion embedded in a deformed alkali halide host crystal. The X_2^- anion results from the combination of a neutral halogen atom, X (the hole), with an adjacent halide anion, X^- , with both "atoms" moving off their regular lattice positions in the NaCl structure. The defect is completed with the associated lattice relaxation around the X_2^- anion. There is abundant experimental work on the preparation, alignment, optical and spin-resonance spectra, and temperature behavior of V_K centers. Kabler¹ and Stoneham² have reviewed hole centers in halides. Schoemaker³ has presented a detailed discussion of the experimental EPR data for V_K centers in alkali halides. The experimental work has emphasized V_K centers in normal alkali halides, e.g., $\text{KCl}:\text{Cl}_2^-$, but there is also useful information involving mixed, or hybrid, systems³ such as $MX:XY^-$ or $MX:Y_2^-$ (where X and Y are different halides), examples where a molecular cation (NH_4^+) is involved,⁴ and V_K centers are well known in other, non-NaCl-type ionic systems.⁵ Schoemaker *et al.*⁶ have reported a related center in KCl, involving a pseudohalide, i.e., $\text{KCl}:\text{XOH}^-$, although this system is apparently not a V_K center. From the ultraviolet and visible spectra, including polarization alignment, there is useful structural information available, but even more seems available from double-resonance spectra such as that of Mieher and co-workers.^{7,8} Goovaerts and Schoemaker⁹ have obtained Raman spectra due to the V_K center, in LiF, KCl, and RbCl, and there is work by Schoemaker and Lagendijk¹⁰ on librational motion associated with X_2^- in $MX:X_2^-$ in $MX:X_2^-$ systems. Experimental information about nuclear motion of the V_K center is, however, relatively sparse compared to information about molecules trapped in matrices. The characterization of the V_K center via nuclear quadrupole resonance (NQR) appears feasible in light of developments in

double-resonance techniques in NQR, but the specific NQR study of V_K centers in alkali halides has not appeared.¹¹ Positron-annihilation methods have also been applied¹² to study positron annihilation with V_K centers.

In addition to being a well-characterized system, the V_K center is generally important in characterizing defects in solids. It is the simplest example of self-trapping (the electron is not self-trapped in ionic crystals), it is a key "small-polaron" system, it is associated with relatively large lattice relaxation, it provides a basis for approaching excitons, and it offers a useful vehicle for considering electronic states of the defect as related to the band structure of the solid. The V_K center is also a convenient reference system for other, and more complicated, defects in alkali halides, e.g., the H center, the H_A center, and V_{KB} center.

The self-trapped hole in alkali halides has been the subject of a sequence of theoretical studies over the last two decades. The earliest efforts sought to explain the stability of this self-trapped hole and the general nature of the stability of the V_K center are summarized by Gilbert.¹³ Explicit calculations on V_K centers include those of Nettel¹⁴ (KCl), Das, Jette, and Knox¹⁵ (LiF), Song,¹⁶ Jette, Gilbert, and Das¹⁷ (MF, and MCl), Jette and Das¹⁸ (CaF_2), Norgett and Stoneham¹⁹ (CsCl, CsBr, and CsI), Diller²⁰ (MX), Monnier, Song, and Stoneham²¹ (CsX), and Oliveira and Maffeo²² (CsX). An overview of the "molecular model" of the V_K center has been given by Tasker and Stoneham.²³ In addition, Bartczak and Sugier²⁴ have explored calculations for V_K centers in NaCl and KCl on and near the crystal surface. The fundamental approach common to most of these calculations, beginning with that of Das, Jette, and Knox,¹⁵ has consisted of a relaxation calculation with assumed potentials and a molecular model for the V_K center. The basic results of these calculations are the equilibrium relaxed position of the V_K center and certain neighboring ions of the lattice. The resulting internuclear, or "core," separation for the X_2^- defect is then used to derive the uv and ir absorption energies from the corresponding *free* X_2^- molec-

ular potential curves. The various calculations have differed in the following respects.

- (i) The extent and nature of relaxation of neighboring anions and cations around the V_K center.
- (ii) The representation of the ("molecular") interaction potential between the V_K center (X_2^-) ions.
- (iii) The details of the interionic potentials (i.e., M^+-M^+ and X^-X^-) as well as the potentials active between the anions and the V_K center and the cations and the V_K center.

All such calculations represent the defect in terms of pair potentials and recognize the necessity of using a shell model to account for polarization effects in the ionic lattice. A more fundamental line, for example, as followed (with limited success) by Nettel,¹⁴ is certainly possible. It is likely that "cluster" methods, such as those recently reported by Oliveira and Maffeo,²² will encourage a more basic examination of V_K centers without assumption of pair potentials, with a direct calculation of the excitation energies and relaxation structure, and an examination of defect energy levels vis-à-vis the energy bands. Such calculations, however, pose formidable problems considering the size of the related region (the "cluster" size) required, serious termination questions, and the complexity involved. It is likely that considerable effort would be required to obtain the X_2^- geometry with good accuracy in a full *ab initio* cluster effort. On the other hand, the V_K center poses a promising test for "cluster" calculations.

The present study is intended to examine in depth the V_K center in the 16 NaCl-type alkali halides, MX ($M = \text{Li, Na, K, Rb}$; $X = \text{F, Cl, Br, I}$). We follow the basic approach employed by Das, Jette, and Knox,¹⁵ Jette, Gilbert, and Das,¹⁷ Norgett and Stoneham,¹⁹ Diller,²⁰ and Monnier, Song, and Stoneham,²¹ with the following general assumptions;

- (i) The V_K center consists of an essentially unperturbed, trapped X_2^- molecular anion. Hence theoretical (and experimental) results for the free X_2^- system are important. Approximate *ab initio* results characterize free X_2^- .
- (ii) All interactions between lattice ions, as well as those involving the X_2^- molecular anions' ions, are taken to be represented by pair-potentials. The resulting relaxation of the V_K center and lattice reflect this assumption as well as the specific potentials employed. A shell model is employed to characterize the polarization of all ions.
- (iii) The relaxation of the lattice can be effectively treated by following Mott and Littleton,²⁵ with a region I in which ions are explicitly relaxed and a region II where a simple harmonic relaxation is employed. The development of this technique by Lidiard and Norgett^{26,27} provides the foundation for this work. A feature of this work is a very generous (and variable) size for region I.

The present calculations represent, within these approximations, a state-of-the-art treatment. A comprehensive and systematic comparison with experimental results is provided. By examination of all 16 alkali halides, systematic trends are apparent not only for the transition energies of the V_K center and relaxation parameters, but also for V_K center hopping motion, dimensional changes,

electric field gradients, and other useful properties. In addition to the normal $MX:X_2^- V_K$ centers, results are presented elsewhere for representative $MX:Y_2^-$ and $MX:XY^- V_K$ -center systems, which provide an interesting new theoretical dimension to the understanding of V_K centers.

In this work the optical properties of the V_K centers and the details of lattice relaxation are presented. A planned second paper will summarize consideration of the hopping motion of V_K centers through the lattice, and a third paper will summarize optical properties and lattice relaxation of mixed V_K centers.

II. SUMMARY OF THE THEORETICAL MODEL EMPLOYED

The basic theoretical model rests on the three assumptions listed above. In this section these assumptions are discussed and specific choices, e.g., potentials, size of region I, are detailed. Except for the V_K -center potentials, the theoretical model is identical in nature to that successfully employed in many other defect problems, e.g., off-center displacements of univalent impurity ions in alkali halides by Catlow *et al.*²⁸ and Sangster,²⁹ and ion-migration barriers in alkali halides by Catlow *et al.*³⁰ and Uppal, Rao, and Sangster.³¹ Many other examples could be cited.^{32,33}

A. Interatomic potentials employed

The representation of interactions between atoms or ions in condensed media in terms of pairwise additive potentials is remarkably successful,³⁴ although there are well-known limitations to this approach. The principal difficulty is to obtain the requisite potentials. There are at least two major routes to interatomic potentials currently in use. (1) A functional form of the pair potential is assumed and experimental data are employed to determine potential parameters. Different experimental data do not always give the same potentials and the relative merits of different choices has been discussed.^{29,35} (2) Experimental data (e.g., scattering results) or *ab initio* calculation are used to determine the interaction potential between isolated atoms or molecules. There is no reason why potentials from various sources should always be similar; that obtained by fitting bulk solid properties may correspond to a "dressed atom," i.e., reflecting environmental effects on the free-atom (-ion) interactions.

In practice, the perfect-crystal potentials in alkali halides, e.g., M^+-M^+ , X^-X^- , and M^+-X^- , are accessible by both techniques. In dealing with a defect D , however, the M^+-D and X^-D potentials are more difficult to obtain. In principle, experimental data for the solid can still be used, but frequently there is insufficient independent data to determine all parameters unless unreasonable simplifications are introduced. Therefore M^+-D and X^-D potentials are most amenable to derivation from the pertinent diatomic systems. In many cases, different choices for the pair potentials give rise to relatively minor differences, but there are situations where the pair potential can be crucial to the phenomenon studied.

The lattice-ion potentials employed here, M^+-M^+ ,

M^+-X^- , and X^-X^- , are based on the extensive work of Catlow, Diller, and Norgett.³⁶ A useful description of the construction and merits of these potentials is given by Catlow *et al.*^{28,35} These pair potentials consist of the usual Coulomb potential together with the potentials described below. The electrostatic interaction incorporates a shell model; each ion is represented by a coupled core-and shell-charge pair such that ionic polarization is realized via the relative displacement dipole of the core and shell. A given ion is thus characterized by a shell charge and a force constant and these are chosen to reproduce the polarizability behavior of the ion in the crystal as well as possible. The remaining part of the potential is intended to represent short-range repulsion and a van der Waals attraction at large interionic distances. Catlow, Diller, and Norgett,³⁶ give two different forms. Their "set-1" potentials (CDN-1) are of the form

$$\begin{aligned} V_{+-}(r) &= A_{+-} \exp(-r/\rho_{+-}), \\ V_{++}(r) &= A_{++} \exp(-r/\rho_{++}) - C/r^6, \\ V_{--}(r) &= A_{--} \exp(-r/\rho_{--}) - C/r^6. \end{aligned} \quad (1)$$

Their "set-2" potentials (CDN-2) provide more flexibility between the short-range repulsive and long-range attractive regions, i.e., the following.

(a) For the anion-anion and cation-cation (second-neighbor) interactions, V_{++} and V_{--} , (i) for $r > r_a$, $V(r) = -C/r^6$; (ii) for $r_a > r > r_m$, $V(r)$ is a third-order polynomial, continuous in function and two derivatives with the potential in region (i) at r_a and with a minimum at r_m ; (iii) for $r_m > r > r_b$, $V(r)$ is a fifth-order polynomial, continuous in function and two derivatives with potential (ii) at r_m and potential (iv) at r_b ; and (iv) for $r_b > r$,

$$V(r) = A \exp(-r/\rho). \quad (2)$$

(b) For the anion-cation (nearest-neighbor interactions) V_{+-} ,

$$V(r) = A \exp(-r/\rho). \quad (3)$$

The anion-anion, V_{--} , cation-cation, V_{++} (next-nearest neighbors), and cation-anion, V_{+-} potentials, are different for each alkali halide, MX . The CDN-2 potentials have the advantage that the van der Waals interaction is not necessarily equally divided between next-nearest neighbors. The potentials are first fitted to the elastic constants of the crystal and the shell-charge parameters are determined by a least-squares fit to dielectric data. Catlow, Diller, and Norgett³⁶ present a full discussion of the derivation of these potentials, the recommended parameters, and their representation of the crystal data.

There are alternative ways to determine crystal potentials. The assumed form of the potential may vary, the crystal data employed may be of different types, and even using the same potential form and crystal data, fitting techniques may not be equivalent. As examples of an alternative approach, see Sangster and Dixon,³⁷ Sangster,³⁸ Sangster, Schroder, and Atwood,³⁹ and Sangster and Atwood.⁴⁰ Included in the various ideas explored by these authors is the notion of a generalized alkali-halide poten-

tial (entirely or partially) independent of system.⁴⁰ The critical compilation of Stoneham⁴¹ contains the potentials employed here as well as alternative potentials for each system.

The Catlow-Diller-Norgett potentials and shell-model parameters, set 2 (CDN-2), are used for all ion interactions, M^+-M^+ , X^-X^- , and M^+-X^- , except for those involving the defect X_2^- molecules. The potential between the halide (X) components of X_2^- (V_K) molecular anions are obtained from the valence-bond pseudopotential calculations of Tasker, Balint-Kurti, and Dixon.⁴² The X_2^- potential functions employed in computations were fits of the numerical $V(r)$ by a Buckingham (exponential-6), three-parameter function; these fits are given by Monnier, Song, and Stoneham.²¹ This analytical potential function for the X_2^- systems compares well with the Hartree-Fock-Roothaan (RHF) $V(r)$ curves for F_2^- and Cl_2^- given by Gilbert and Wahl.⁴³ The calculated dihalide anion potential curves are not definitive results, and hence can be improved, but they are probably reliable representations of the *shape* of the $(X-X)^-$ potential curve near the minimum. There is no experimental spectrum for free X_2^- in the usual sense, which permits a conventional [Rydberg-Klein-Rees (RKR)] determination of an "experimental" potential curve, but Lee *et al.*⁴⁴ have constructed portions of the potential curves for Cl_2^- from photodissociation cross sections. Their results are in reasonable agreement with theoretical results of Gilbert and Wahl.⁴³ The results⁴⁴ of Lee *et al.* do not yield the ground-state potential curve, however. The consistently successful interpretation of the V_K center as a trapped X_2^- molecule, suggests that the X_2^- potential curve is not a conspicuous weak point.

The most difficult potentials to characterize confidently are those between the lattice cations (M^+), or anions (X^-), and the X_2^- defect molecule. In general, defects do not give *changes* in the pertinent crystal properties (elastic constants or dielectric properties) sufficient to empirically define parameters of any assumed M^+-D and X^-D potentials. Alternatively, an *ab initio* calculation, e.g., a Kim-Gordon⁴⁵ electron-gas calculation, or a full many-electron Hartree-Fock configuration-interaction (HF-CI) or multiconfiguration Hartree-Fock (MCHF) calculation, may be necessary or desirable. For the present case, this corresponds to mapping the potential surface for the $X_2^-M^+$ and $X_2^-X^-$ interactions, involving a non-central potential and a rather substantial effort. In this work, following Norgett and Stoneham¹⁹ and Monnier, Song, and Stoneham,²¹ we employ a simpler approach, namely, we use the *same* potential forms between $M^+-X^{-0.5}$ and $X^-X^{-0.5}$ as we do between M^+-X^- and X^-X^- ions (in the lattice). The only difference arises from the Coulombic contribution to the potential between the lattice ions and the V_K center in which each "atom" of X_2^- is given a charge of $-\frac{1}{2}$, i.e., the hole is spread equally in the X_2^- anion. The Coulombic potential is certainly the dominant effect, and the representation of the short-range and long-range potentials is qualitatively consistent with the other potentials employed. There are further problems relating to the polarization of the V_K center, which are discussed below.

III. SUMMARY OF CALCULATIONS AND BASIC RESULTS

The basic results of this study of the NaCl-type alkali halides are defect energies E_D and the equilibrium configuration of the relaxed V_K center, i.e., the relaxed positions of the defect molecule X_2^- and the host-lattice ions included in the calculation. The ions in region I are relaxed explicitly until the forces acting on them are below a (small) threshold, and the remainder of the lattice ions included (in region II) are displaced so that the polarization of the crystal is the same as that of the material regarded as a dielectric continuum. A very detailed discussion of the relaxation technique has been given by Norgett.⁴⁶ All calculations were performed on the program HADES-II prepared by Norgett,⁴⁷ which is the culmination of extensive development. The numerical results for the 16 alkali halides (NaCl-type structure) appear in Table I. In Appendix A, a brief discussion is given in which we assess the accuracy and dependence on the basic parameters of the calculations.

A. Defect energy to form a V_K center in alkali halides

The energy required to form a V_K center may be considered as the sum of energies for several distinct steps. (i) The energy required to remove the two X^- lattice ions to infinity (separately)—the vacancy energy E_v . (ii) The

energy of formation of X_2^- (gaseous) $+e^-$ from two X^- anions. The internuclear separation R for X_2^- may be taken as R_e for free X_2^- , although other values of R do not change the final result. (iii) The energy associated with introducing X_2^- into the prepared (perfect) vacancy site—the interstitial energy E_I . (iv) The energy arising from relaxation of ions in region I, region II, and of course, within the V_K center—the relaxation (or lattice) energy E_R . Other energy cycles are also possible. If the internuclear separation for X_2^- (gaseous) is taken as R_0 (the normal X^-X^- crystal separation), then the energy associated with step (ii) is essentially $-A$, where A is the normal (gaseous) electron affinity of the halogen atom, X . However, it is desirable to take $R \approx R_e$ (for gaseous X_2^-) to ensure rapid and convergent relaxation results. Otherwise, it matters little what value of R is used since R is adjusted in step (iv) again. It is also necessary to consider the electron released in step (ii), and this is usually placed at the bottom of the conduction band of the MX crystal. The associated energy for this process is the electron affinity of the MX crystal, χ , and these values are not well known, but range from 0.1 to 1.5 eV.⁴⁸ The result is that the defect energy has a consistent reference point within a given MX crystal, but comparisons of defect energies involving different crystals, e.g., MX vs MY , do not have identical reference points. A more detailed discussion of absolute and relative aspects of the defect energies is given

TABLE I. Summary of $MX:X_2^- V_K$ -center results.

MX	$a_0(\text{\AA})^a$	$R_c(V_K)$	$R_s(V_K)$	$R_0(V_K)$	E_D^0 (eV) ^b
LiF	1.9960	1.926	1.964	2.823	6.866
NaF	2.2950	1.901	1.960	3.246	6.117
KF	2.648	1.881	1.951	3.745	4.950
RbF	2.789	1.875	1.948	3.944	4.447
(F_2^-)		1.90			
LiCl	2.539	2.674	2.732	3.166	5.461
NaCl	2.789	2.638	2.725	3.944	5.197
KCl	3.116	2.602	2.710	4.406	4.600
RbCl	3.259	2.586	2.701	4.609	4.259
(Cl_2^-)		2.71			
LiBr	2.713	2.836	2.919	3.837	5.082
NaBr	2.954	2.809	2.915	4.178	4.898
KBr	3.262	2.768	2.896	4.613	4.398
RbBr	3.410	2.755	2.889	4.822	4.155
(Br_2^-)		2.90			
LiI	2.951	3.182	3.280	4.173	4.751
NaI	3.194	3.193	3.297	4.517	4.517
KI	3.489	3.169	3.287	4.934	4.203
RbI	3.628	3.150	3.275	5.131	3.970
(I_2^-)		3.28			

^aLattice constant at 0° K for the alkali halides is given by a_0 in angstroms. $R_c(V_K)$ and $R_s(V_K)$ are, respectively, the core and shell distances for X_2^- in the relaxed crystal and $R_0(V_K)$ is the normal X^-X^- lattice separation in the NaCl-type structure. E_D is the defect energy as described in the text. The R_e distance for isolated X_2^- molecular ions are theoretical values given by Tasker, Balint-Kurti, and Dixon (Ref. 42).

^bAll calculations were performed on HADES-I [Norgett (Refs. 46 and 47)] using the Catlow-Diller-Norgett (Ref. 36) potential 2 (CDN-2). Region I contains 37 classes (196 ions) and the cutoff radius is $7a_0$ (~ 1250 ions in region II).

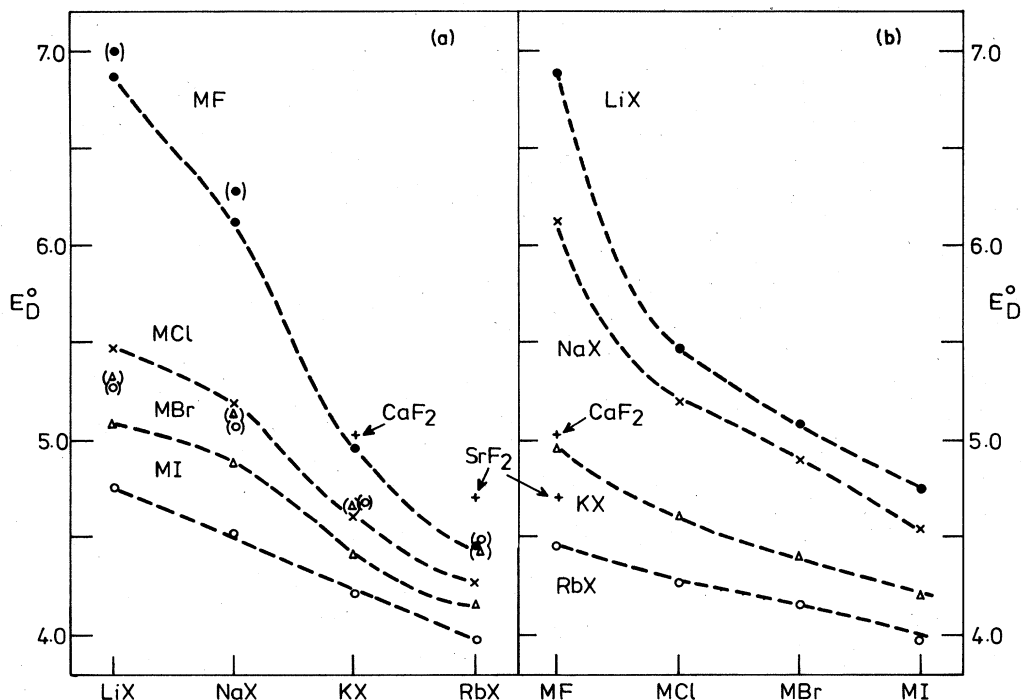


FIG. 1. Systematic trends in V_K -center defect energies E_D^0 (in eV) for $MX:X_2^-$ systems. (a) Variation with cations and (b) variation with anions. Points for CaF_2 and SrF_2 are from Ref. 19. The second set of points, in parentheses, reflect partial corrections for different zero-points [see text, Eqs. (6) and (7)].

in Appendix B. Specifically, for our purposes,

$$E_D = E_V + E_I + E_R + [A(X) - \chi(MX)] \quad (4)$$

on an absolute scale, or simply

$$E_D = E_V + E_I + E_R (= E_D^0), \quad (5)$$

referred to an energy scale with $A(X) = \chi(MX)$.

The calculated defect energy E_D^0 thus defined is given in Table I for the alkali halides MX ; Figs. 1 and 2 illustrate systematic trends. There are no measured defect-formation energies for V_K centers, but it is known³ that all alkali halide V_K centers form except for NaI, LiBr, and LiI. The latter two are perhaps precluded for technical reasons (high hygroscopy), but NaI has been shown to be unstable at 77 K. It is well known that above 77 K, the V_K center decays as the highly mobile hole center quickly finds an electron to annihilate the V_K center hole. The defect energies are energetically endothermic relative to the perfect MX crystal—the larger E_D , the larger the energy required to form the defect. Strictly speaking, a more realistic estimate of the thermodynamic defect energy associated with V_K -center formation should include the defect energy associated with the electron trap T usually doped into the crystal. If this were done, one expects that E_D would still be endothermic, but reduced in magnitude (see Appendix B).

The values for E_D reported in Table I for the alkali halides may be compared with results by Norgett and Stoneham¹⁹ for alkaline-earth fluorides [CaF_2 (5.04 eV), SrF_2 (4.75 eV), and BaF_2 (4.35 eV)] and calculations by

Monnier, Song, and Stoneham²¹ for cesium halides [$CsCl$ (3.64 eV), $CsBr$ (3.55 eV), and CsI (3.43 eV)]—all using HADES and the same potentials. Variable electron affinities χ between MX , AX_2 , and CsX are not included.

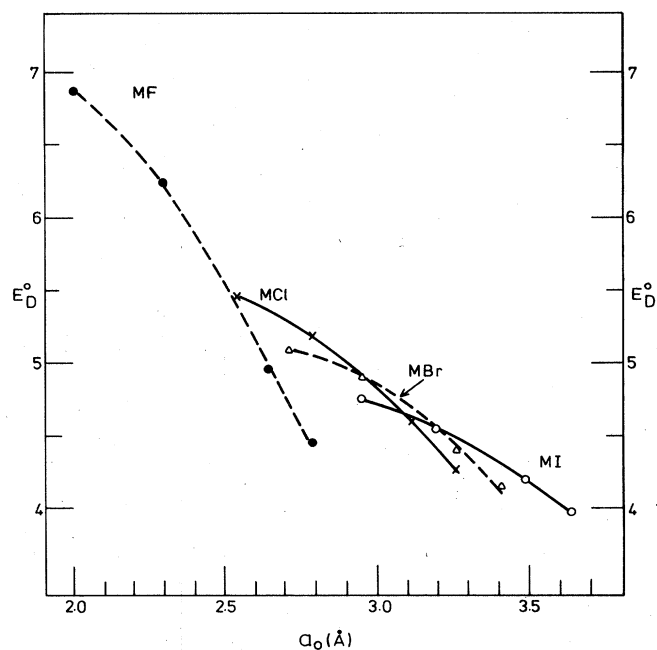


FIG. 2. Systematic trends in V_K -center defect energies E_D^0 (in eV) for $MX:X_2^-$ systems vs lattice constant a_0 (in Å) for MX crystals.

The comparison of the V_K -center defect energy, E_D or E_D^0 , with other defect energies for centers arising in alkali halides, i.e., H centers, V_{KA} centers, Shottky defects, etc., is handicapped by selection of the energy zero. A comparison of the V_K center and H center in the same MX crystal is the most favored case: $A(X)$ and $\chi(MX)$ are unchanged, but the H center defect energy includes the energy associated with placing the X^0 interstitial into the lattice. Dienes, Hatcher, and Smoluchowski⁴⁹ give (rough) values for H -center formation of 2.23 eV (NaCl) and 1.57 eV (KCl), Diller²⁰ reports H -center defect energies ranging from 0.3 eV (RbCl) to 0.42 eV (KCl) to 1.71 eV (LiI) with a slight $\langle 111 \rangle$ orientation favored, and in test calculations (with the same potentials as used here for the V_K center), we obtain an H -center defect energy of 0.78 eV for KCl. While the Diller results²⁰ are comparable in scope to the present calculations, the potentials employed in the earlier study are now felt to be unsatisfactory. The energy zero is identical for the V_K - and H -center systems, so that a direct comparison of defect energies is possible: The V_K -center energies are typically much larger, by a factor of ~ 2 – 4 , than the parallel H -center energies in the same crystal. Catlow *et al.*³⁰ have given a systematic study of the defect energy for Shottky defects in NaCl-type alkali halides and find most values near 2 eV (ranging from 1.54 to 2.91 eV). The large defect energy to form the V_K center can be understood in terms of the loss of a negative ion from the lattice, a loss which is not recovered by formation of X_2^- and the favorable relaxation of the lattice. The energy to create an anion vacancy is roughly comparable with V_K -center energies, and the negative charge that remains (on X_2^-) is a larger and more diffuse unit than a single X^- ion.

In Figs. 1(a) and 1(b) the systematic trends in E_D^0 are explored; results for the isoelectronic alkaline-earth fluorides¹⁹ CaF_2 and SrF_2 are included for comparison. The main trend appears associated with the "size" of the anion or cation; the defect energy is smaller for a fixed anion as the cation becomes larger or more polarizable, and smaller for a fixed cation as the anion becomes larger and more polarizable. The MF sequence appears distinct from the other alkali halides and only when a large cation is involved does the trend in fluorides seem "normal." In a more limited sense, the LiX and NaX systems appear distinct from the KX and RbX systems; again, the differences seem associated with the small, compact ions (Li^+ and Na^+) with small polarizabilities. The CaF_2 and SrF_2 points appear in reasonable perspective and suggest that ionic size and polarizabilities are the dominant factors with a lesser role for crystal structure. The dependence of E_D^0 on lattice constant a_0 is explored in Fig. 2. Indeed, except for the fluorides, the alkali halides' defect energies seem dominated by the lattice constant and a single broad line might include all alkali halides except fluorides. It might also be noted that the present results give E_D^0 values which are 10–20% larger than the earlier results of Diller.²⁰ However, the trends in the present study and that of Diller are very similar.

The comparisons just described are not corrected for their different energy zeros. For example, along the curve of E_D^0 vs MX for the MCl sequence [Fig. 1(a)], a correc-

tion $\chi(\text{std}) - \chi(MCl)$ is needed, where χ is the electron affinity of the crystal. Data to include these corrections are not available, but these corrections could easily be as large as the variation between the MCl and MBr sequences, for example. Poole *et al.*⁴⁸ do not describe any systematic trends in $\chi(MX)$ which are useful here. If we consider vertical points on different curves in Fig. 1(a), i.e., MF , MCl , MBr , and MI , then a correction of the form

$$[\chi(\text{std}) - \chi(MX)] - [A(X) - A(\text{std})] \quad (6)$$

(std denotes standard reference) is required. Again, the correction due to the different values of χ is unavailable, but the second correction is trivial, $A(X) - A(\text{std})$. Therefore, using (X variable, M fixed)

$$E_D(MX) \simeq E_D^0(MX) - [A(X) - A(\text{std})] \quad (7)$$

and MCl as the standard, the corrections in E_D involving A are given in Fig. 1(a). These corrections tend to make MCl , MBr , and MI very similar in behavior, but MF remains apart. This may indicate a "universal" aspect to V_K centers given suitable variables.

B. Lattice distortion associated with V_K -center formation

There is substantial lattice distortion near the V_K center. This distortion, i.e., the associated relaxed positions of various (symmetry-equivalent) classes of ions in the lattice, diminishes with distance from the defect, but a clear, symmetrical pattern is evident. In Fig. 3 the ion displacements around the V_K center are indicated in a general way—the HADES program gives relaxed core and shell positions in the final minimized results. In Table II the actual relaxed positions of the core and shell of the first several classes of ions about the V_K center are summarized for KCl. In our present analysis we focus primarily on the displacement of the ions forming and those near the V_K center.

The most important ion displacements in the lattice relaxation are those of the V_K -center halides (Table I), and when these are compared with the ideal anion positions in

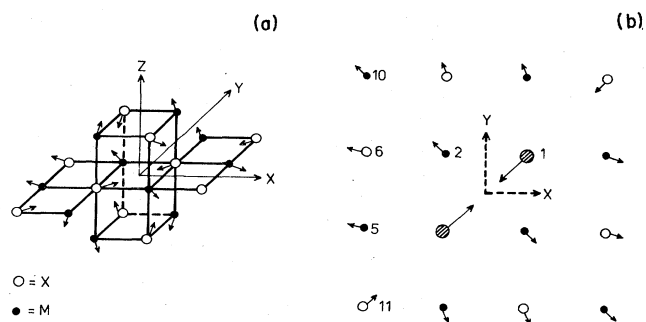


FIG. 3. Schematic relaxation of lattice-ion positions with formation of the V_K center in alkali-halide-type crystals MX . The anions forming the V_K center are the central open circles in (a) and (b). (a) Three-dimensional view with the definition of coordinate axes employed. (b) Relaxation near the V_K center in the (110) plane with lattice-ion classes (Table II) indicated.

TABLE II. Relaxed positions [all distances are given in units of a_0 , the basic crystal lattice separation, the shell displacements (X_s, Y_s, Z_s) are relative to the corresponding relaxed core positions (X_c, Y_c, Z_c), i.e., they are increments] of all ions in region I: $KCl:Cl_2^-$.

Class	(X, Y, Z)	R_0 (a_0)	Ion/No.	X_c	Y_c	Z_c	X_s	Y_s	Z_s
1	$(\frac{1}{2}, \frac{1}{2}, 0)$	$(\frac{1}{2})^{1/2} = 0.70710$	$V_K/2$	0.29513	0.29513	0.0	0.01224	0.01224	0.0
2	$(-\frac{1}{2}, \frac{1}{2}, 0)$	$(\frac{1}{2})^{1/2} = 0.70710$	$M/2$	-0.63402	0.63402	0.0	0.00000	0.00000	0.0
3	$(-\frac{1}{2}, -\frac{1}{2}, 1)$	$(\frac{3}{2})^{1/2} = 1.22474$	$M/4$	-0.48701	-0.48701	1.03363	0.00000	0.00000	0.00001
4	$(-\frac{1}{2}, \frac{1}{2}, 1)$	$(\frac{3}{2})^{1/2} = 1.22474$	$X/4$	-0.50890	0.50890	0.97731	-0.00020	0.00020	-0.00060
5	$(-\frac{3}{2}, -\frac{1}{2}, 0)$	$(\frac{5}{2})^{1/2} = 1.58114$	$M/4$	-1.54110	-0.49156	0.0	-0.00002	0.00000	0.0
6	$(-\frac{3}{2}, \frac{1}{2}, 0)$	$(\frac{5}{2})^{1/2} = 1.58114$	$X/4$	-1.56441	0.50211	0.0	0.00750	-0.00037	0.0
7	$(-\frac{1}{2}, \frac{1}{2}, 1)$	$(\frac{7}{2})^{1/2} = 1.87083$	$M/8$	-1.51887	0.50373	1.01118	0.00000	0.00000	0.00000
8	$(-\frac{3}{2}, -\frac{1}{2}, 1)$	$(\frac{7}{2})^{1/2} = 1.87083$	$X/8$	-1.48018	-0.49513	0.98528	0.00138	0.00065	-0.00219
9	$(-\frac{1}{2}, \frac{1}{2}, 2)$	$(\frac{9}{2})^{1/2} = 2.12132$	$M/4$	-0.50729	0.50729	2.00637	0.00000	0.00000	0.00000
10	$(-\frac{3}{2}, \frac{3}{2}, 0)$	$(\frac{9}{2})^{1/2} = 2.12132$	$M/2$	-1.52840	1.52840	0.0	-0.00001	0.00001	0.0
11	$(-\frac{3}{2}, -\frac{3}{2}, 0)$	$(\frac{9}{2})^{1/2} = 2.12132$	$X/2$	-1.47944	-1.47944	0.0	0.00213	0.00213	0.0
12	$(\frac{1}{2}, \frac{1}{2}, 2)$	$(\frac{9}{2})^{1/2} = 2.12132$	$X/4$	0.49437	0.49437	2.00463	-0.00040	-0.00040	-0.00391
13	$(-\frac{3}{2}, -\frac{3}{2}, 1)$	$(\frac{11}{2})^{1/2} = 2.34521$	$M/4$	-1.50072	-1.50072	1.00361	0.00000	0.00000	0.00000
14	$(-\frac{3}{2}, \frac{3}{2}, 1)$	$(\frac{11}{2})^{1/2} = 2.34521$	$X/4$	-1.49676	1.49676	0.99285	0.00081	-0.00081	-0.00104
15	$(-\frac{3}{2}, -\frac{1}{2}, 2)$	$(\frac{13}{2})^{1/2} = 2.54951$	$M/8$	-1.50154	-0.50047	2.00321	0.00000	0.00000	0.00000
16	$(-\frac{1}{2}, \frac{5}{2}, 0)$	$(\frac{13}{2})^{1/2} = 2.54951$	$M/4$	-0.50576	2.53492	0.0	0.00000	0.00000	0.0
17	$(-\frac{5}{2}, -\frac{1}{2}, 0)$	$(\frac{13}{2})^{1/2} = 2.54951$	$X/4$	-2.50941	-0.50013	0.0	0.00394	-0.00024	0.0
18	$(-\frac{1}{2}, \frac{3}{2}, 2)$	$(\frac{13}{2})^{1/2} = 2.54951$	$X/8$	-0.49902	1.50076	1.99918	-0.00027	-0.00095	-0.00167
19	$(-\frac{5}{2}, -\frac{1}{2}, 1)$	$(\frac{15}{2})^{1/2} = 2.73861$	$M/8$	-2.50380	-0.50020	1.00321	0.00000	0.00000	0.00000
20	$(-\frac{5}{2}, \frac{1}{2}, 1)$	$(\frac{15}{2})^{1/2} = 2.73861$	$X/8$	-2.50417	0.49860	1.00073	0.00118	-0.00032	-0.00001
21	$(-\frac{5}{2}, -\frac{3}{2}, 0)$	$(\frac{17}{2})^{1/2} = 2.91547$	$M/4$	-2.50258	-1.50356	0.0	0.00000	0.00000	0.0
22	$(-\frac{3}{2}, \frac{3}{2}, -2)$	$(\frac{17}{2})^{1/2} = 2.91547$	$M/4$	-1.50276	1.50276	-2.00272	0.00000	0.00000	0.00000
23	$(-\frac{3}{2}, -\frac{3}{2}, 2)$	$(\frac{17}{2})^{1/2} = 2.91547$	$X/4$	-1.49672	-1.49672	1.99676	0.00075	0.00075	-0.00115
24	$(-\frac{3}{2}, \frac{5}{2}, 0)$	$(\frac{17}{2})^{1/2} = 2.91547$	$X/4$	-1.50442	2.50782	0.0	0.00014	-0.00157	0.0
25	$(-\frac{1}{2}, -\frac{1}{2}, 3)$	$(\frac{19}{2})^{1/2} = 3.08220$	$M/4$	-0.49959	-0.49959	3.00566	0.00000	0.00000	0.00000
26	$(-\frac{5}{2}, \frac{3}{2}, -1)$	$(\frac{19}{2})^{1/2} = 3.08220$	$M/8$	-2.50478	1.50201	-1.00223	0.00000	0.00000	0.00000
27	$(-\frac{5}{2}, -\frac{3}{2}, 1)$	$(\frac{19}{2})^{1/2} = 3.08220$	$X/8$	-2.49485	-1.49699	0.99738	0.00114	0.00070	-0.00054

TABLE II. (Continued.)

Class	(X, Y, Z)	R_0 (a_0)	Ion/No.	X_c	Y_c	Z_c	X_s	Y_s	Z_s
28	$(-\frac{1}{2}, \frac{1}{2}, 3)$	$(\frac{19}{2})^{1/2} = 3.08220$	X/4	-0.50071	0.50071	2.99740	0.00004	-0.00004	-0.00115
29	$(-\frac{1}{2}, \frac{1}{2}, 2)$	$(\frac{21}{2})^{1/2} = 3.24037$	M/8	-2.50510	0.50073	2.00434	0.00000	0.00000	0.00000
30	$(-\frac{1}{2}, -\frac{1}{2}, 2)$	$(\frac{21}{2})^{1/2} = 3.24037$	X/8	-2.49600	-0.49972	1.99716	0.00096	0.00010	-0.00096
31	$(-\frac{1}{2}, \frac{1}{2}, 3)$	$(\frac{23}{2})^{1/2} = 3.39116$	M/8	-1.50195	0.50034	3.00386	0.00000	0.00000	0.00000
32	$(-\frac{1}{2}, -\frac{1}{2}, 3)$	$(\frac{23}{2})^{1/2} = 3.39116$	X/8	-1.49860	-0.49968	2.99675	0.00029	0.00011	-0.00095
33	$(-\frac{1}{2}, -\frac{1}{2}, 2)$	$(\frac{25}{2})^{1/2} = 3.53553$	M/8	-2.50166	-1.50152	2.00169	0.00000	0.00000	0.00000
34	$(-\frac{1}{2}, \frac{1}{2}, 0)$	$(\frac{25}{2})^{1/2} = 3.53553$	M/2	-2.50721	2.50721	0.0	0.00000	0.00000	0.0
35	$(\frac{1}{2}, \frac{1}{2}, 0)$	$(\frac{25}{2})^{1/2} = 3.53553$	M/4	0.50175	3.50849	0.0	0.00000	0.00000	0.0
36	$(-\frac{1}{2}, -\frac{1}{2}, 0)$	$(\frac{25}{2})^{1/2} = 3.53553$	X/2	-2.49739	-2.49739	0.0	0.00100	0.00100	0.0
37	$(-\frac{1}{2}, \frac{1}{2}, 2)$	$(\frac{25}{2})^{1/2} = 3.53553$	X/8	-2.49798	1.49894	1.99835	0.00069	-0.00032	-0.00059
38	$(-\frac{1}{2}, \frac{1}{2}, 0)$	$(\frac{25}{2})^{1/2} = 3.53553$	X/4	-0.49962	3.51183	0.0	-0.00010	-0.00214	0.0

the perfect lattice, R_0 , the $(X-X)^-$ distance has decreased from $\sim 15\%$ (LiCl) to $\sim 50\%$ (RbF) with most changes equaling $\sim 30\%$. [The relaxed positions of the core $R_e(V_K)$ are taken as the "nuclear" positrons of the ions.] This is a very substantial displacement and one expects lattice relaxation to reflect this large shift. In all cases, the final relaxed positions in the V_K center (i.e., X_2^-) closely approach the internuclear separation of the free X_2^- molecular anion. In general, $R_e(X-X)$ in the V_K center is smaller than $R_e(X_2^-)$, and for a given halide $R_e(X-X)$ slowly decreases with increasing cation radius (or lattice constant) and polarizability. It must be remembered that $R_e(X-X)$ is referred to *calculated* values for $R_e(X_2^-)$ and these could be in error by $\pm 0.05a_0$, but since the same *calculated* potential curves are the source of the V_K -center potential, internal consistency is assured. The deviations of $R_e(V_K)$ from $R_e(X_2^-)$ are small, i.e., 1–3%, and strongly support the idea of the V_K center as comprising X_2^- with very minor alteration. The $R_e(V_K)$ results are considered further below in relation to V_K -center spectra.

The V_K center possesses D_{2h} "site symmetry" in an unrelaxed alkali-halide-type lattice. This symmetry information has been used,³ in the analysis of the EPR and optical spectra of the V_K center; the reduced symmetry of X_2^- acts to split the π_u and π_g molecular-orbital levels. In addition, spin-orbit coupling mixes σ and π orbitals (or states). The substantial displacement of the anions forming the V_K center, and the associated lattice relaxation, might appear to further complicate the picture. In Fig. 3(a) the vector displacements of ions near the V_K center are illustrated in three-dimensions and the ion displacements in the (110) crystal plane are shown in Fig. 3(b). The overall character of the vector displacements of neighboring lattice ions, in response to V_K -center formation, is entirely determined by symmetry requirements with detailed specific effects for each MX system. In particular, the V_K center preserves D_{2h} site symmetry even with lattice relaxation, as long as the V_K center is aligned in the $\langle 110 \rangle$ direction. In this discussion on ion displacements, the ions will be identified by their class (Table II) and not by lettered symbols as used by Stoneham² and Miehler *et al.*⁷ This has the advantage of clearly associating the ion with a perfect-crystal lattice position and is general in scope.

The ion displacements in the (110) plane are most easily described. In Table II, the relaxed (equilibrium) positions of *all* classes of ions in region I are given for KCl as a representative example. Thus, relaxed positions of 196 lattice ions (including the V_K -center ions) out to a distance of $\sim 3.5a_0$ about the V_K center are explicitly given. The classes are defined with the origin (as shown) at the midpoint of the V_K center and the V_K center is taken to be in the $(x-y)$ plane. (The V_K center is taken to be aligned along the [110] direction, consistent with experiment.) The nearest neighbors are the (class-2) cations, M^+ which are displaced along the $\langle \bar{1}10 \rangle$ direction (or perpendicular (\perp) to the V_K -center axis—away from the V_K center. In Table III the systematic nature of class-2-cation displacements is summarized for all 16 MX cases. The vector from the origin to class-2 cations, \vec{r} , is in-

TABLE III. Summary of class-2, M^+ cation displacements in $MX(X_2^-)$ systems.

MX^a	$X_c = -Y_c$		Z_c	$X_s = -Y_s$		Z_s	Δr (%)
LiF	-0.625 16	0.625 16	0.0	-0.000 91	0.000 91	0.0	25
NaF	-0.631 43	0.631 43	0.0	-0.000 41	0.000 41	0.0	26.3
KF	-0.646 21	0.646 21	0.0	0	0	0.0	29.2
RbF	-0.655 03	0.655 03	0.0	0.000 03	-0.000 03	0.0	31
LiCl	-0.623 22	0.623 22	0.0	-0.000 64	0.000 64	0.0	24.6
NaCl	-0.625 02	0.625 02	0.0	-0.000 78	0.000 78	0.0	25
KCl	-0.634 02	0.634 02	0.0	0	0	0.0	26.8
RbCl	-0.644 13	0.644 13	0.0	0	0	0.0	28.8
LiBr	-0.628 87	0.628 87	0.0	-0.000 57	0.000 57	0.0	25.7
NaBr	-0.627 10	0.627 10	0.0	-0.000 77	0.000 77	0.0	25.4
KBr	-0.634 30	0.634 30	0.0	0	0	0	26.9
RbBr	-0.641 26	0.641 26	0.0	0	0	0	28.2
LiI	-0.629 13	0.629 13	0.0	-0.000 48	0.000 48	0	25.8
NaI	-0.626 52	0.626 52	0.0	-0.000 79	0.000 79	0	25.3
KI	-0.630 35	0.630 35	0.0	0	0	0	25.1
RbI	-0.636 71	0.636 71	0.0	-0.000 01	0.000 01	0	27.3

^aCalculations as described in the caption of Table I. Cation positions are given for cores (X_c, Y_c, Z_c) and shells (X_s, Y_s, Z_s) in units of a_0 . The M^+ cations are displaced in the $\langle 110 \rangle$ direction, i.e., perpendicular to the V_K -center axis. Δr is defined as $(r_R^2 - r_0^2)^{1/2}/r_0$. The shell displacements (X_s, Y_s, Z_s) are relative to the corresponding relaxed positions of (X_c, Y_c, Z_c) as in Table II.

creased in length by $\sim 25\%$ and there is little dependence on the particular anion or cation. For the M^+ (class-2) ions, there is a clear trend to larger displacements and smaller polarization as cation size (and a_0) increases, $Li^+ \rightarrow Cs^+$, for a fixed halide. In Fig. 4 the core and shell displacements for the M^+ (class-2) ions are plotted against a_0 for the MX sequence. The displacement of Li^+ (class-2) ions appears different for the MF, MCl sequence as compared with the MBr, MI sequence. It appears that a subtle interplay between ion displacement (r_c) and ion polarization, which depends critically on anion-cation pair, is present. It is apparent from Fig. 4 that the shell-polarization effect associated with the M^+ (class-2) relaxation for the KX and RbX crystals is entirely due to displacement of the core. In the other cases, LiX and NaX , polarization effects in the M^+ (class-2) relaxation involve interplay between movement of both core and shell charges.

In the (110) plane, class-10 cations and class-11 anions mimic the central M^+ (class-2) and X^- (class-1) ion displacements, respectively, and provide a comparison of the relative displacements differing only in distance from the origin. Thus the X^- (class-11) anions are displaced towards the origin, following the X_2^- motion in the $\langle 110 \rangle$ direction, by 1–1.5% and the M^+ (class-10) cations follow the V_K nearest-neighbor M^+ movement in the $\langle 110 \rangle$ direction (away from the origin) by 1.5–3%. A careful examination shows, however, that the shell motion is more significant in class-10 cations and class-11 anions than in the M^+ (class-2) cations. The polarization vectors for the M^+ (class-10) ions are in the same directions as those for M^+ (class-2) ions and as large or larger in most cases. Polarization vectors for the X^- (class-11)

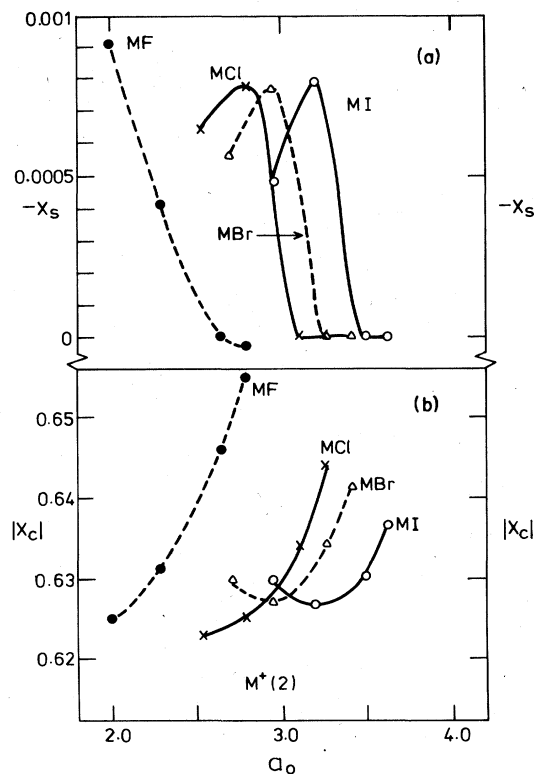


FIG. 4. Systematic trends in (a) shell and (b) core ion displacements of the class-2 cations M^+ near the V_K center in alkali halides; the displacements ($X = -Y$) in units of a_0 are plotted vs the MX lattice constant a_0 .

ions are such as to have the negative end of the "shell" dipole directed towards the origin (and V_K center); these X^- (class-11) polarization effects are substantially larger than those for the M^+ (class-10) or M^+ (class-2) cations.

In the ideal NaCl-type lattice, each anion (cation) occupies the center of a perfect octahedron (edge $\sqrt{2}a_0$) with local O_h symmetry due to six cations (anions) at the octahedral vertices, and all R_{M-X} distances are a_0 . In the relaxed crystal, following formation of a V_K center, the six cations (anions) are no longer all equivalent, but instead are grouped into several distinct classes depending on the central ion considered (the octahedron is also displaced from its original site following the shift of the central ion). One useful way to view lattice displacements associated with formation of a V_K center, is to describe the relaxed positions of the six nearest neighbors about particular anions or cations, i.e., to describe the distorted octahedral structure about key X^- and M^+ ions in the relaxed crystal. This perspective is most useful in considering how local structure has changed after relaxation, that is, it comprises a view from the relaxed central ion.

The local structure after ion relaxation is considered first for the X^- (class-1) ions forming the V_K center and the M^+ (class-2) ions which are adjacent and considerably shifted. The specific example used is KCl (Table II). The relaxed distances between the V_K -center chloride ion (class 1) and the six nearest-neighbor cations are $0.9890 a_0$ (K^+ , class 2), $1.0686 a_0$ (K^+ , class 3), and $1.2613 a_0$ (K^+ ,

class 5); these results using *core* displacements are within 1–2% of parallel results using *shell* displacements. The octahedron about Cl^- (class 1) is substantially distorted in the x - y plane by the large "apparent" shift of K^+ class-5 ions; this is true from a *local*, relative perspective, but, in fact, the K^+ , class-5 ions move slightly, and this pronounced octahedral distortion is due to the large displacement of the Cl^- (V_K) ion followed closely by the K^+ , class-2 ions. The octahedron about the K^+ , class-2 ions is much less distorted when the V_K center is formed. Thus the relaxed distances between the K^+ , class-2 ions (nearest neighbor of the V_K center) and its six nearest neighbors are $0.9890 a_0$ (Cl^- , class 1), $0.9932 a_0$ (Cl^- , class 4), and $0.9397 a_0$ (Cl^- , class 6).

The K^+ , class-3 and K^+ , class-5 ions are the other nearest-neighbor cations to the V_K -center Cl^- anion. In the relaxed crystal, these two ion classes are at the center of a slightly displaced, but distorted octahedron. These distorted octahedra are very similar to that for the K^+ , class-2 case, except that the latter is shifted more, following the V_K center. In addition, polarization aspects are more noticeable for anions about cations than for cations about anions. As an example, the relaxed distances between the K^+ , class-3 ion and its six nearest-neighbors are $1.0687 a_0$ (one Cl^- , class 1), $0.9977 a_0$ (two Cl^- , class 4), $0.9943 a_0$ (two Cl^- , class 8), and $0.9429 a_0$ (one Cl^- , class 12). The more distant ions are again at the center of almost perfect octahedra. The other alkali halides show

TABLE IV. Comparison of theory and experiment for ion displacements in V_K centers of LiF and NaF.

	LiF			NaF			Reference
	ΔX^a	ΔY	ΔZ	ΔX	ΔY	ΔZ	
V_K , class 1 (F^-)	0	0	-0.192	0	0	-0.193	b
	0	0	-0.180	0	0	-0.249	c
	0	0	-0.225	0	0	-0.293	d
A, class 2 (M^+)	0	0.141	0	0	0.270	0	b
	0	0.167	0	0	0.20	0	c
	0	0.177	0	0	0.186	0	d
B, class 4 (F^-)	0.24	0.13	0	0.081	0.081	0	b
	0.028	0.021	0	-0.005	0.020	0	d
C, class 3 (M^+)	0.063	0	-0.016	-0.026	0	0.086	b
	0.076	0	-0.014	0.045	0	-0.022	d
D, class 6 (F^-)	0	0.059	-0.127	0	-0.030	0.030	b
	0	0.013	0.013	0	0.030	0.030	d
E, class 5 (M^+)	0	0.083	0.051	0			b
	0	0.043	0.043		0.0396	0.0396	c
	0	0.052	0.049	0	0.045	0.035	d
F, class 11 (F^-)	0	0	-0.232	0	0	-0.111	b
	0	0	-0.033	0	0	-0.037	d

^aAll distances are in units of a_0 and correspond to shifts, ΔX , ΔY , and ΔZ , from normal lattice positions, X_0 , Y_0 , and Z_0 . Equivalent ions are correspondingly shifted. The ion designation A, B, C, . . . , and the coordinate system of Daly and Mieher (Ref. 8) given in their Fig. 1 are employed for the comparison; the corresponding class is also noted.

^b"Experimental" results of Daly and Mieher (Ref. 8) from their Tables II (LiF) and III (NaF).

^cResults due to T. P. Das, A. N. Jette, and T. L. Gilbert quoted by Daly and Mieher.

^dPresent theoretical results.

similar behavior and large-anion—small-cation or large-cation—small-anion cases may merit a closer examination.

It is desirable to compare the calculated ion displacements with experiment. The general symmetry features are known beyond doubt from ESR spectra.³ In addition, it is possible to measure volume changes associated with formation of the V_K center, but these do not provide a detailed analysis of the specific displacements. The most reasonable prospects for determination of specific ion displacements are with the use of various types of magnetic resonance, e.g., NQR or electron nuclear double-resonance (ENDOR) experiments or extended x-ray absorption fine-structure (EXAFS) studies. The full potential of NQR is yet to be realized in this context,¹¹ but Daly and Mieher⁸ have presented ENDOR results for the V_K centers in LiF and NaF. The ENDOR dipole-dipole hyperfine constants (measured) are sensitive to the relative positions of the X_2^- molecular ion and neighboring (ENDOR) ion nuclei (see Daly and Mieher,⁸ Fig. 1, for coordinate system and identification of ions). The ion displacements given by Daly and Mieher⁸ are *indirect* and depend on a theoretical calculation of the dipole-dipole interaction and other (theoretical) approximations, as they describe.⁸ In Table IV the ENDOR and theoretical ion displacements are compared for LiF and NaF, with the inclusion of theoretical results of Jette, Gilbert, and Das.¹⁷

For the V_K -center ions and the nearest-neighbor M^+ ions the agreement of theory with experiment is satisfactory in direction and magnitude of the ion shift. In the case of other ions, the agreement between theory and experiment is not impressive. The calculated displacement of the Li^+ ion in LiF, i.e., ions, *A*, *C*, and *E* are in good agreement with experiment; for the corresponding Na^+ ions in NaF there are significant sign differences for *C* ions. The most pronounced disagreement between the present calculated results and "experiment," however, is with the anion shifts (excepting the V_K center), i.e., ions of classes *B*, *D*, and *F*. The present calculations give Δr shifts for F^- which are much smaller than those reported by Daly and Mieher,⁸ this is most evident for the class-*F* anion which follows the V_K -center-ion motion. These discrepancies between calculated and "experimental" shifts of the F^- ions (excepting the V_K center ions) may indicate a serious shortcoming in the F^- - F_2^- potential used in this study. This is especially the case for the linear F^- - F_2^- - F^- (class-1 and class-11 X^- ions) arrangement where non-Coulombic elements associated with X_3^{2-} are active. The displaced-ion positions can also be employed in a detailed calculation of electric field gradients at various ions, and thus they offer an alternative check via NQR spectra.

C. Electronic absorption spectra of MX V_K centers

The present relaxation calculations can be employed to predict the maximum of the electronic absorption spectra due to V_K centers by accepting certain assumptions. The chief assumption is that the X_2^- molecular anions forming the V_K center behave as essentially free molecules regarding their electronic transitions, except for the shift in their equilibrium separation, R_e , required in the lattice relaxation. This view has been essential in the experimental

identification and characterization of V_K centers and is consistent with all previous experimental^{1,3} and theoretical² work. The matrix-trapping studies of Howard and Andrews,⁵⁰ in which the ir and uv spectra of $M^+X_2^-$ triatomic molecules trapped in argon at 4 K were observed, also support this perspective of X_2^- "molecules" in the MX crystal lattice. Other assumptions implicit in this approach are discussed below.

Therefore with the internuclear separations $R_c(V_K)$ obtained from the relaxation calculation (Table I) for X_2^- , and with the appropriate free- (X_2^-) molecule potential curves given by Gilbert and Wahl⁴³ (F_2^- and Cl_2^-) and Tasker, Balint-Kurti, and Dixon⁴² (Cl_2^- , Br_2^- , and I_2^-), the expected peaks in the $\Delta E_\pi(^2\Pi_g \leftarrow X^2\Sigma_u^+)$, $\Delta E_g(^2\Pi_u \leftarrow X^2\Sigma_u^+)$, and $\Delta E_\sigma(^2\Sigma_g^+ \leftarrow X^2\Sigma_u^+)$ electronic transitions can be predicted. Throughout, the values of $R_c(V_K)$ are used to obtain the predicted excitation energies for X_2^- ; it is taken as corresponding to R_e for X_2^- in the V_K center. In a comparison of calculated versus experimental transition energies, i.e., free- X_2^- -molecule ΔE_i versus measured spectra, Tasker and Stoneham²³ give plots of $\Delta E_\pi(R)$, $\Delta E_g(R)$, and $\Delta E_\sigma(R)$ with internuclear separation R so that ΔE_i can be directly read from their plots given $\Delta R_c(V_K)$. These results are summarized in Table V together with experimental values from various sources. The ΔE transition is strong, allowed and in the uv region (also denoted ΔE_{uv}), the ΔE_π transition is weak and located in the ir region (also denoted ΔE_{ir}), and the ΔE_g transition is dipole forbidden, but indirectly accessible from EPR spectra of the V_K center.

In previous V_K center studies, Norgett and Stoneham¹⁹ (HADES, CaF_2 , SrF_2 , and BaF_2), Monnier, Song, and Stoneham²¹ (HADES, CsCl, CsBr, and CsI), and Tasker and Stoneham²³ (X_2^- versus experiment) have emphasized the analysis of the V_K center in terms of free X_2^- molecular anions and the *common* spectra properties of MF_2 *vis-à-vis* free F_2^- or CsX compared to appropriate X_2^- . These probing studies did not address systematic trends. Without emphasizing details, the present investigation fully supports these earlier studies, i.e., the electronic transitions for $V_K(MX)$ are closely characteristic of the X_2^- molecule and the results are *not* very sensitive to the particular M^+ counterion involved. The changes in $R_c(V_K)$ relative to $R_e(X_2^-)$ are less than 1%, except for the fluorides where $R_c(V_K)$ differs from $R_e(X_2^-)$ by only $\sim 1\%$. These small changes in R_e (in the relaxed lattice) translate into small changes in ΔE_i compared to the free-ion transition energy, but these are detectable changes in many cases due to the steep slope of the $\Delta E_i(R)$ curves.

A useful new aspect is examination of systematic trends, i.e., trends in $R_c(V_K)$ and/or ΔE_i values with counterions and comparative behavior for the various halide sets. It must be emphasized that whereas the relaxation calculation is reliable to the significant figures given in Table I (and via translation also Table II), the physical significance of the numbers is less—the latter bearing the full weight of the model used and particular parameters employed. However, at the same time, we expect systematic trends to be reliable in their general features due to the tight consistency with which the relaxation calculation and key variables have been subject. This is support-

TABLE V. Summary of calculated and experimental excitation energies for NaCl-type V_K centers.

MX	$\Delta E_\pi(^2\Pi_g-X^2\Sigma_u^+)$		$\Delta E_g(^2\Pi_u-X^2\Sigma_u^+)$		$\Delta E_\sigma(^2\Sigma_g^+-X^2\Sigma_u^+)$	
	Theory ^a	Expt. ^b	Theory	Expt.	Theory	Expt. ^c
LiF	2.05	1.65	3.35	2.38	4.4	3.48
NaF	2.15		3.65	2.41	4.7	3.38
KF	2.25		3.85	2.55	4.9	
RbF	2.30		3.90		5.0	
(F ₂ ⁻)	(2.15)		(3.65)		(4.7)	
LiCl	2.10		3.11	2.09	3.95	3.16
NaCl	2.18		3.23	2.28	4.10	3.28
KCl	2.23	1.66	3.35	2.42	4.24	3.39
RbCl	2.26		3.37	2.44	4.27	3.40
(Cl ₂ ⁻)	(1.99)		(2.91)		(3.73)	
LiBr	2.04		3.07		3.86	
NaBr	2.12	1.44	3.18	1.95	4.03	2.90
KBr	2.18	1.51	3.29	2.19	4.10	3.22
RbBr	2.26		3.40	2.23	4.24	
(Br ₂ ⁻)	(1.90)		(2.83)		(3.56)	
LiI	1.71		2.61		3.43	
NaI	1.68	1.20	2.53	1.68	3.35	2.87
KI	1.71	1.31	2.61	2.03	3.43	3.10
RbI	1.77	1.33	2.67	2.12	3.51	3.06
(I ₂ ⁻)	(1.55)		(2.34)		(3.07)	

^aTheoretical results employ $R_c(V_K)$ as calculated from the present study projected onto the plots of Tasker and Stoneham (Ref. 23). The free X_2^- results included are also from the Tasker-Stoneham plots with theoretical R_e values used.

^bExperimental results are from the careful survey of Schoemaker (Ref. 3).

^cEnergy results are in eV. Energy values are vertical energy differences between the minimum R_e for the $X^2\Sigma_u^+$ state and the pertinent excited state.

ed by trends now considered.

In Fig. 5 the relaxed core and shell position shifts, $\Delta R_c(V_K)$ and $\Delta R_s(V_K)$, are plotted against a_0 —a conjectured fundamental variable here. Both sets of curves, $\Delta R_s(V_K)$ (upper) and $\Delta R_c(V_K)$ (lower), display a clear systematic nature and suggest that at least two factors influence the relaxed separations. Apparently, one factor dominates for fluorides and chlorides, whereas a second factor appears with bromides and iodides in association with the small (Li⁺) cation. Again, the fluorides, MF, appear to be atypical in the MX family. The key factors might well be associated with ion sizes and ion polarization. The most likely artifact would be related to a deterioration of the $M^+-X_2^-$ potential model with Br₂⁻ and I₂⁻. With these noted exceptions, the relaxed values R_c and R_s correlate in simple fashion with lattice constant and would appear dominated by purely electrostatic effects.

The previous V_K -center studies have emphasized the close similarity of the V_K center to the free X_2^- molecule. These earlier theoretical studies, as well as experimental results, have also noted the weak dependence on the M^+ counterion in halide systems. It is desirable to make a direct comparison with experiment and to carefully examine any dependence on M^+ ; this offers at the same time a critical assessment of the model used. In the detailed appraisal of the V_K -center model as compared to the free X_2^- molecule made by Tasker and Stoneham,²³

the experimental values for ΔE_π , ΔE_g , and ΔE_σ were placed on the appropriate calculated ΔE_i -vs- R curves, and any deviation in associated R_e values from $R_e(X_2^-)$ and from one another (in an MX set with fixed X) was attributed to "the influence of the crystal on the defect"—such deviations were present. In the summary of Schoemaker,³ certain experimental trends are also apparent in ΔE_i upon varying the counterion. These questions are examined in depth here in Fig. 6. ΔE_i -vs- a_0 curves are given for the chloride system with emphasis on a contrast of experiment against theory and a view toward internal trends. The experimental data are most complete for the chlorides, MCl, and they might be expected to be typical for other MX systems. Table V presents a complete picture.

It is very clear from Table V and Fig. 6 that the model used here consistently predicts transition energies which are too large, i.e., by as much as 1 eV, a very large difference in optical spectra. In particular, the adjacent curves in Fig. 6 are not for the same state—theory could lead to an incorrect assignment of transitions. The previous work by Monnier, Song, and Stoneham²¹ on the cesium halides, CsCl, CsBr, and CsI, also predict a larger ΔE_i than is observed. In contrast, the pioneering work of Jette, Gilbert, and Das¹⁷ consistently predicts transition energies that are smaller than experiments for alkali halide V_K center. The experimental values for ΔE_g , an indirect result employing a first-order perturbation calculation, is believed to be the

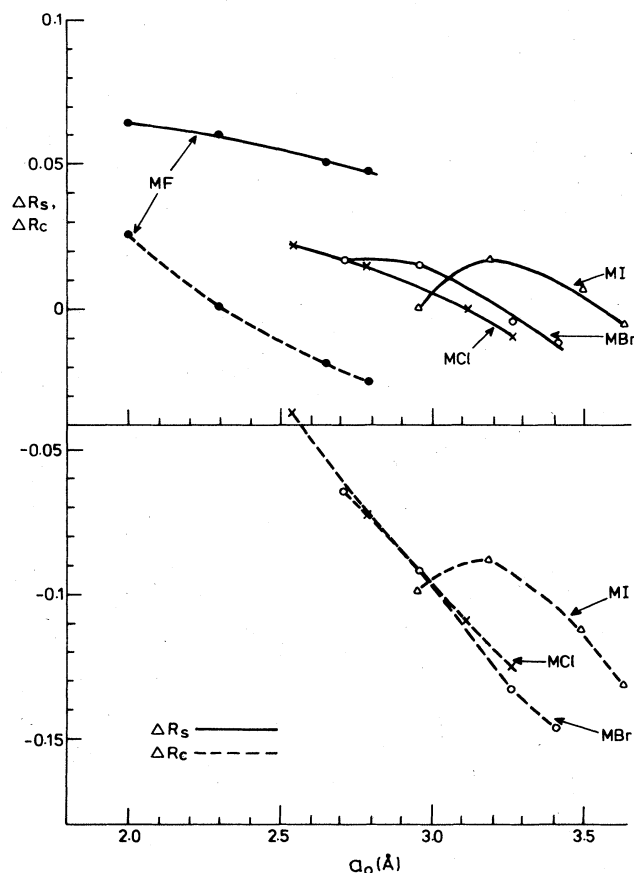


FIG. 5. Systematic trends in the shifts of $R_c(V_K)$ and $R_s(V_K)$, i.e., $\Delta R_c(V_K)$ and $\Delta R_s(V_K)$, for the $MX:X_2^-$ V_K -center nuclei plotted against the MX lattice constant a_0 . The upper shifts correspond to $\Delta R_s(V_K)$ and the lower shifts refer to $\Delta R_c(V_K)$.

least accurate, but these shortcomings are apparently below the scope of discrepancies between theory and experiment reported here.

The second key observation, most apparent in Fig. 6, is that experimental and theoretical trends within a family of halides, e.g., MCl, do appear similar—as previously noted in the basic relaxation positions, $R_c(V_K)$. The experimental data, although incomplete, shows an increase in transition energy ΔE_i as the lattice constant (or cation size, or cation polarizability) increases, but the increase tends to level off for larger a_0 . The theoretical curves show a parallel trend with M^+ , or a_0 . Theory predicts certain irregularities, however, in the iodide sequence; these irregularities are not confirmed by experiment.

The excitation-energy results presented here assume that the V_K center behaves essentially as a free X_2^- molecule, subject only to the adjustment of R_e required with lattice relaxation. A related implicit assumption is that the nature of the excited-state potential curves in the V_K center are essentially unchanged relative to the free X_2^- molecule. In the theoretical studies of Gilbert and Wahl⁴³ and Tasker, Balint-Kurti, and Dixon,⁴² the excited-state potential curves for $X_2^-(^2\Pi_u, ^2\Pi_g, ^2\Sigma_g^+)$ are all repulsive

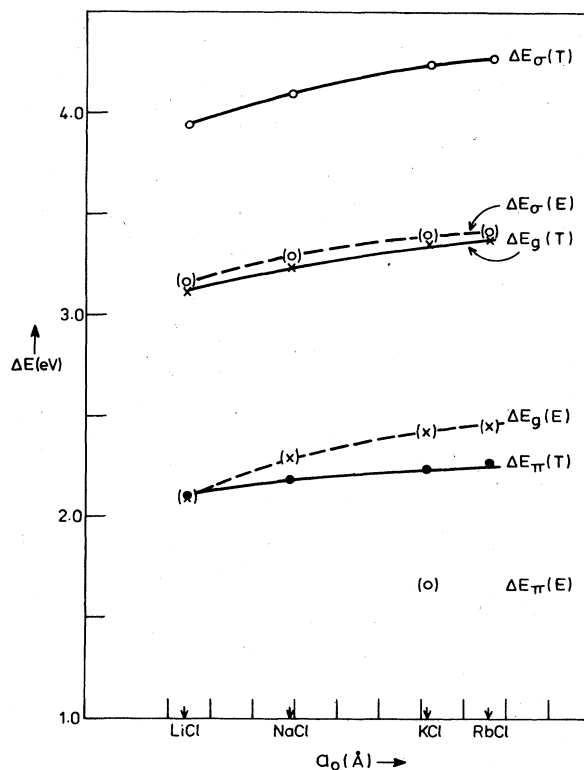


FIG. 6. Comparison of theoretical (T) and experimental (E) electronic transition energies for the σ , π , and g transitions of $Cl_2^-/MCl:Cl_2^-$ V_K centers. The relaxed "core" positions $R_c(Cl_2^-)$ are employed to determine the transition energy. All experimental values are taken from Ref. 3.

states. However, in the photodissociation cross-section measurements for Cl_2^- of Lee *et al.*⁴⁴ a potential curve was constructed for the $^2\Pi_g$ state which possessed a clear minimum—presumably required to agree with experimental results. Maessen and Cade⁵¹ have made theoretical calculations for $M^+X_2^-$ molecules and find that the excited states attributable to localized excitations on X_2^- , are shifted differentially relative to the ground state and may also show a minimum in the associated X_2^- potential curves. It is thus possible that when X_2^- is trapped into a distorted octahedral field of six nearest-neighbor cations, some excited states of the X_2^- moiety may possess a minimum with respect to R_{X-X} and, in addition, the relative separation of excited states from the ground, $X^2\Sigma_u^+$, state may be significantly shifted. One might not expect large shifts due to the unusual nature of this open-shell molecule, i.e., where the excited states considered here arise from transfer of a hole between nearly equivalent valence orbitals. The theoretical studies which provide the excitation energies are approximate in nature. The Gilbert-Wahl⁴³ results are near-HF calculations and the Tasker-Balint-Kurti-Dixon⁴² results are valence-bond pseudopotential calculations; but both may not give transition energies of very high accuracy even for the free X_2^- molecules. The predicted transition energies ΔE_i thus also bear this *ab initio* qualification. These aspects

raise the possibility that any discrepancies noted may arise from effects other than the relaxation calculation and/or associated pair potentials.

IV. DISCUSSIONS AND CONCLUSIONS

The present study has much in common with previous simple defect calculations using HADES—carefully constructed pair potentials and a well-honed relaxation procedure. However, the present (and past) V_K -center calculations also call upon certain new aspects, namely those dealing with an aspherical species, X_2^- , and consideration of an electronic aspect. Except for the use of a shell model, electronic aspects are usually avoided in relaxation calculations. There are two key aspects of the present work; (i) the success of the relaxation calculation and usefulness of the relaxed ion positions, and (ii) the ability to provide (indirectly) information on electronic effects.

The relaxed ion positions and calculated defect energy depend on the quality and sensitivity of the pair potentials employed. In the present studies the $M^+-X_2^-$ and $X^-X_2^-$ potential functions are probably the most crucial. Any errors in the final relaxed ion positions are probably not due in any significant measure to the general technique used (Mott-Littleton approach), an insufficient number of ions explicitly relaxed, or the details of numerical techniques employed. As Norgett and Stoneham,¹⁹ and as Appendix A illustrates, the basic relaxation results are not very sensitive to a modest variation of the pair potentials *within a common scope*. We believe that the present V_K -center results are therefore “state-of-the-art”, *vis-à-vis*, HADES relaxation calculations. Any improvements, within the Mott-Littleton approach, will be associated with improved $M^+-X_2^-$ and $X^-X_2^-$ potentials and a more realistic shell-model (or alternative) representation for the diatomic anion. A tractable means of improving $M^+-X_2^-$ and $X^-X_2^-$ potentials would involve *ab initio* calculation of an asymmetric potential for the triatomic interaction and then the seeking of a fit in terms of functions centered (only) on the two centers of the X_2^- anion. The representation of the polarization of the X_2^- system requires a new approach; the present treatment essentially considers X_2^- as two X^- ions and employs the same shell parameters for X_2^- components as for a normal X^- anion. It is not feasible to obtain polarization parameters for X_2^- , in a two-center perspective, from experiment, but perhaps *ab initio* calculations can again be employed to model the polarization of X_2^- within a modified shell model (e.g., with a new spring connecting valence shells of X_2^-).

The comparison of theoretical and experimental ion displacements for LiF and NaF is not very satisfying. The weakest aspect of the comparison might be expected to be in the ions near the V_K center, but there are glaring discrepancies rather far away (e.g., class-4 and -11 anions) and particularly for anions. It is very desirable to have more extensive experimental data for other alkali halides and perhaps NQR results as well. If all of the experimental ion displacements are correct, then the present relaxa-

tion calculation performs poorly in certain respects. While no clear trend is apparent in the comparison of experimental versus theoretical results, the small displacements calculated for some fluorides ions compared to experiment might be related to a poor representation of the polarization of X_2^- . These problems may be more pronounced for the fluorides and thus experimental results for other halides are most desirable.

The present investigations clearly demonstrate a discrepancy between predicted and observed transition energies. The most obvious suggestion is that the relaxed V_K -center ion positions are slightly in error, sufficiently so to shift predicted ΔE_i values to larger values—this in turn implies that the calculated $R_e(V_K)$ values are too small. This is certainly a possibility and is consistent with our reservations about the $M^+-X_2^-$ and $X^-X_2^-$ potentials, but we feel other explanations are also possible. It is thus possible that the V_K center is very close to the free X_2^- molecule and a relaxation calculation is entirely satisfactory, but the free X_2^- potential curves are not sufficiently accurate in the present *ab initio* calculations. The experimental photodissociation work of Lee *et al.*⁴⁴ suggests this explanation and this can be settled by state-of-the-art (post-Hartree-Fock) *ab initio* calculations for F_2^- and Cl_2^- . Finally, the resolution of the discrepancy in predicted versus observed ΔE_i values could be found in the effects of the local V_K -center site symmetry on the excited states of X_2^- molecules. In this circumstance the relative position and shape of the ground- and excited-state potential curves are significantly affected by the nearest-neighbor shell of M^+ cations. However, one must be very careful since an *ab initio* calculation for X_2^- in the relaxed field of six (cation) point charges might also be misleading. It would probably be necessary to include at least a matched pair of cation-anion shells to measure the effect of the local site symmetry on the X_2^- molecule. It appears that we are at the threshold of requiring a more detailed analysis of the V_K center; the recognition that the V_K center is very similar to a free X_2^- molecule is insufficient.

The disparity between the present calculations and experiments can be ascribed to a single key feature of the calculation, i.e., the details of the $X^-X_2^-$ potential. A potential function containing a chemical specificity, e.g., associated with an X_3^{2-} entity, which is now absent, might account for the major discrepancies. Thus a new attractive term, acting in addition to the simple adjusted anion-anion potential, would tend to displace class-10 (X^-) anions more and prevent $R_c(V_K)$ from taking the small values we now find. This would also be mirrored in other anion displacements. Further work is required to examine this conjecture.

There are other ramifications of this work that may be pursued in terms of the relaxed ion positions. Harding,⁵² for example, has calculated the local vibrational modes associated with the V_K center in alkali halides and related volume-change effects are also under investigation. As mentioned earlier, we also wish to consider the electric field gradients at various nuclei in a study using the relaxed ion positions, but which goes beyond the lattice-ion model of the relaxed crystal.

ACKNOWLEDGMENTS

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APPENDIX A: DISCUSSION OF THE ACCURACY OF RELAXATION CALCULATIONS FOR THE ALKALI HALIDES (NaCl-TYPE)

It is useful to have an indication of the sensitivity of the relaxation calculation, i.e., the defect energy and relaxed positions, on the model-dependent and model-independent (practical) parameters. The latter involves the size of regions I and II and other (technical) aspects of implementation. The former, the model, is defined by the HADES implementation of the Mott-Littleton (Lidiard-Norgett) relaxation method with fixed regions I and II and the defined pertinent interaction potentials employed. First we focus on the sensitivity of the relaxation calculation on the general form assumed by the potential, and then on the treatment of the lattice-ion- V_K -center potentials. As an example of the sensitivity of the relaxation calculation on the form of the interaction potentials, we performed relaxation calculations for NaCl, LiI, and RbF using both the CDN-1 and CDN-2 potentials³⁶ with substantially the same results. The defect energies change by less than 5% and the displacements from the ideal lattice positions are virtually identical; the CDN-1 and CDN-2 potentials are indistinguishable from this perspective. We use the CDN-2 potentials because of their edge in representation of the crystal properties and in particular because of their greater flexibility (and presumably more sensitive fit to experimental data), which may be vital in the hopping motion of the V_K center and in hybrid V_K -center calculations. There is no significant difference in behavior for the cases with a large-cation-small-anion system (RbF) or small-cation-large-anion system (LiI). This is not a very crucial test as the two potentials compared (CDN-1 and CDN-2) are not entirely independent representations; it would be desirable to compare interaction potentials which probe different forms or which encompass other experimental crystal properties.

Another model-dependent aspect involves the nature of the lattice-ion- V_K -center potential. This is the least satisfactory component defining the model employed. Norgett and Stoneham¹⁹ have explored several variants for handling the polarization of the V_K -center system, X_2^- , and the short-range potential between $X^{-1/2}$ ions and the lattice ions for alkaline-earth fluorides. Monnier, Song, and Stoneham²¹ continued this probe for the cesium halides. Their conclusion is that elaborate or special treatment of the polarization of the X_2^- specie, or the short-range $M^+X^{-1/2}$ and $X^-X^{-1/2}$ potentials, is not rewarded with convincing improvements. However, this is an area where further work is very desirable. This problem can be most satisfactorily treated by *ab initio* methods to produce a suitable potential for the $M^+X_2^-$ and

$X^-X_2^-$ interactions.

The basic Mott-Littleton model, and choice of potentials employed and their parameters, does not settle all pertinent variables in the relaxation calculation. A great deal of computing time is saved if the highest possible symmetry is used in the relaxation calculation (here with the crystal origin along the molecular axis of X_2^- midway between the ions). A significant variable of the relaxation is the size of region I, which can be expressed either in terms of the total number of ions involved or the number of classes (containing lattice equivalent ions) of ions, defining the number of unique (spatial) variables required in the relaxation calculation. In this work a systematic study was made for NaCl using the CDN-2 potentials, and Fig. 7 and Table VI summarize the results. "Convergence" is apparent, and although defect energies are given to 0.001 eV, this is for numerical comparisons and has no physical significance. A compromise between accuracy and computing time is easily struck, but the size of region I and the number of ions relaxed is substantial. In the production calculations, Tables I and II, we uniformly employ 38 classes and 196 ions in region I. (This includes the two "ions" in the V_K center, the first "class.") The total number of ions relaxed is fixed by the cutoff radius which is uniformly taken as $7a_0$, where a_0 is the lattice constant of the MX crystal. With this standard cutoff, region II contains about 1250 ions. The size of these calculations is clearly much larger than previous V_K -center studies of the alkali halides and parallels studies published for off-center displacements of univalent impurities in alkali halides,²⁸ etc. It is probable that the size of region I

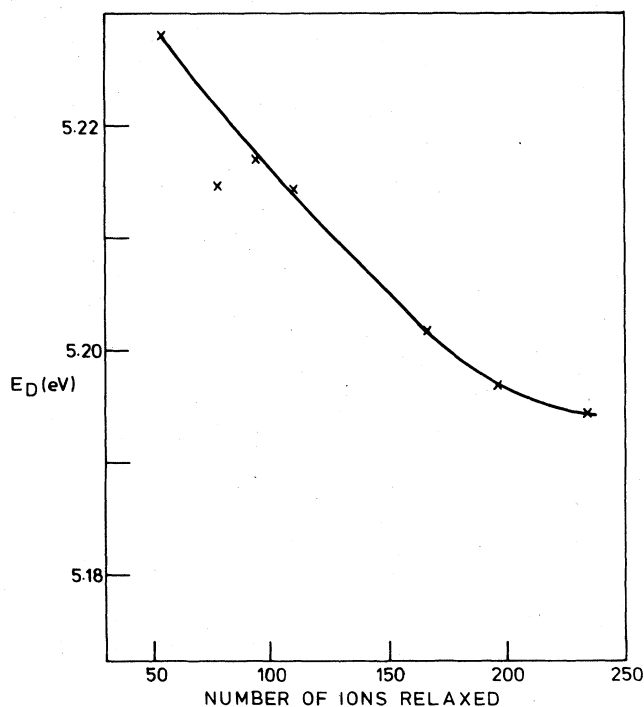


FIG. 7. Variation of V_K -center defect energy E_D for NaCl using the CDN-2 potentials with the size of region I, i.e., the number of ions explicitly relaxed.

TABLE VI. Summary of V_K centers for various-sized, region-I, NaCl, CDN-2 potentials.

Ions ^a	Size parameters		E_D (eV)	$X_c = Y_c$	$X_s = Y_s$
	Classes	Variables			
54	13	52	5.2279	0.3351	0.0112
78	17	72	5.2146	0.3351	0.0109
94	19	84	5.2168	0.3349	0.0110
110	23	100	5.2145	0.3346	0.0111
166	31	144	5.2018	0.3346	0.0110
196	37	168	5.1969	0.3344	0.0110
234	45	204	5.1942	0.3343	0.0111

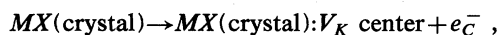
^a V_K -center internuclear distance is given by $R_i = 2\sqrt{2}a_0X_i$ ($i = c$ or s). The parent Cl^- -ion positions are $x = \frac{1}{2}a_0$, $y = \frac{1}{2}a_0$, and $z = 0$.

is an overestimate as far as a reliable defect energy and lattice displacement are concerned, but for other aspects, such as the hopping motion of the V_K center, electric field gradients, etc., it may be desirable. Computing times of the order of 1 to 2 min are standard for these (symmetric) relaxation calculations if the highest possible symmetry is employed (i.e., the number of coupled equations is minimal).

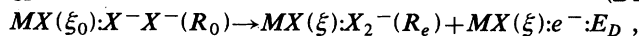
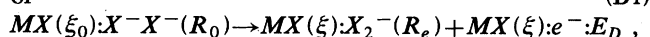
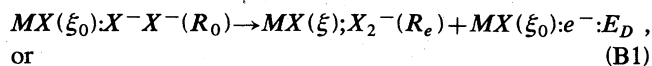
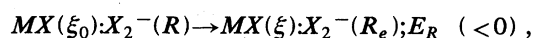
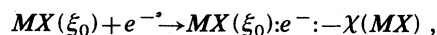
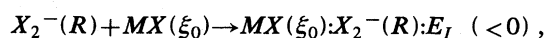
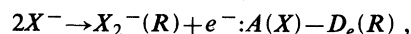
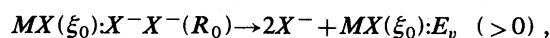
APPENDIX B: DEFINITION OF THE DEFECT ENERGY E_D

The energy associated with formation of a V_K center, the defect energy E_D , is defined with respect to an energy cycle which introduces an arbitrary reference energy. Comparisons of the magnitudes of defect energies, i.e., for various V_K centers or V_K centers versus H centers, must take the variable reference zero into account. Examples of comparisons of defect energies might include different V_K centers in the same crystal (e.g., Cl_2^- and Br_2^- in KCl), the same V_K center in different crystals (e.g., Cl_2^- in KCl, NaCl, CsCl, or CaCl_2), different V_K centers in different crystals (e.g., Cl_2^- in KCl and Br_2^- in KBr), or different types of X_2^- centers in the same, or different, crystal (e.g., Cl_2^- as V_K and H centers in KCl). The defect energies of V_K centers might also be compared to Shottky defects, cation substitutional defects, etc. Such comparisons are instructive in nature, perhaps assisting in understanding relative relaxation features, but they may also be crucial to consideration of the relative appearance, or stability, of mutually occurring defects. In this appendix a discussion of the definition of the defect energy is given paying particular attention to the dependence of the energy zero on the material, or energy cycle, employed. There is evidence that defect energies also depend on the crystal boundaries, but this aspect will not be discussed here.

The process of formation of a V_K center (X_2^-) in an ideal MX crystal can be represented as



where e_C^- corresponds to an electron at the bottom of the conduction band of MX . The defect energy is defined via the energy cycle,



so that

$$E_D = (E_D^e) = E_v + E_I + E_R + [A(X) - \chi(\text{MX})] - D_e(R) .$$

(B2)

In these expressions, $\text{MX}(\xi_0)$ and $\text{MX}(\xi)$ denote the perfect and defect-relaxed crystal, respectively, and R denotes the internuclear separation of the X_2^- or $X^- \cdots X^-$ systems; R_0 for $X^- \cdots X^-$ in the perfect crystal and R_e , the equilibrium-relaxed positions in the lattice. The electron affinity of the halide X , (A), and that of the crystal [$\text{MX}(\chi)$], as well as $D_e(R)$, the molecular dissociations energy, are taken to be positive quantities with a defined sense; on the other hand, E_v , E_I , and E_R take a sign, normally as indicated. It is clear that the value of R used in formation of X_2^- does not affect the deformation energy E_D (any variation is compensated in the host, relaxation step), and for convenience R can be considered large so that $D_e(R) \approx 0$. Thus the defect energy is

$$E_D(\text{MX}:X_2^-) = E_v(\text{MX}) + E_I(\text{MX}:X_2^-) + E_R(\text{MX}:X_2^-) + [A(X) - \chi(\text{MX})] . \quad (B3)$$

The HADES program calculates $E_v(\text{MX})$, $E_I(\text{MX}:X_2^-)$, and $E_R(\text{MX}:X_2^-)$ to form

$$E_D^0(\text{MX}:X_2^-) = E_v(\text{MX}) + E_I(\text{MX}:X_2^-) + E_R(\text{MX}:X_2^-) , \quad (B4)$$

which is the defect energy for formation of $X_2^-(R_e)$ in MX , and which takes the (zero) reference energy as $A(X) - \chi(\text{MX})$. These forms are not restricted to alkali halides.

If defect energies for X_2^- are compared for various crystals, then the reference energies are *not* necessarily identical, i.e., $A(X)$ is uniform, but $\chi(MX)$ depends on the particular crystal. Therefore, with AX as the reference crystal, the defect energy of MX referred to the same standard is

$$E_D = E_D^0 + [\chi(AX) - \chi(MX)], \quad (B5)$$

corrected by the difference between the electron affinities χ of AX and MX crystals. Poole *et al.*⁴⁸ discusses values of χ ; χ is not very well known and ranges from 0.1 to 1.5 eV for the alkali halides, a relatively small quantity compared to E_D .

The defect energies for X_2^- in MX can be compared with the defect energy of Y_2^- in MY by introducing the correction

$$A(X) - A(Y) - \chi(MX) + \chi(MY), \quad (B6)$$

and, of course, M can be different in MX and MY . The situation is unchanged since $A(X)$ are all well known [$A(F) = 3.45$ eV, $A(Cl) = 3.61$ eV, $A(Br) = 3.36$ eV, and $A(I) = 3.06$ eV].

The situation regarding different types of V_K centers, e.g., X_2^- , Y_2^- , and XY^- , in the same crystal (MX) is the most satisfactory situation and does *not* depend on relative χ values, although a correction with A 's is necessary. However, in the case of Y_2^- or XY^- in MX , the defect energy needs clear specification. In case of Y_2^- formed in MX , an energy cycle parallel to that given above leads to

$$\begin{aligned} MX(\xi_0): X^-X^-(R_0) + 2Y^- \rightarrow MX(\xi): Y_2^-(R_e) \\ + MX(\xi): e^- + 2X^-: E_D \end{aligned} \quad (B7)$$

and

$$E_D = E_v + E_I + E_R + [A(Y) - \chi(MX)] - D_e(R), \quad (B8)$$

as usual. The defect energy actually desired involves not $MX(\xi_0): X^-X^-(R_0)$, or even $MX(\xi_0): Y^-Y^-(R_0)$, but rather the *double-substitution* (DS) defect (including the relaxation) $MX(\xi'): Y^-Y^-(\bar{R}_e)$. Thus an additional energy cycle, also calculable by HADES, is required, i.e.,

$$\begin{aligned} MX(\xi_0): X^-X^-(R_0) + 2Y^- \rightarrow MX(\xi'): Y^-Y^-(\bar{R}_e) \\ + 2X^-: E_{DS} \end{aligned} \quad (B9)$$

and

$$E_{DS} = E'_v + E'_I + E'_R. \quad (B10)$$

By combining these two energy cycles (the second reversed), one obtains

$$\begin{aligned} MX(\xi'): Y^-Y^-(\bar{R}_e) \rightarrow MX(\xi): Y_2^-(R_e) + MX(\xi): e^- \\ (B11) \end{aligned}$$

and

$$E'_D = E_D - E_{DS} = E_D^0 - E_{DS} + [A(Y) - \chi(MX)], \quad (B12)$$

where E_D^0 is the Y_2^- V_K -center defect energy calculated by HADES and E_{DS} is the double-substitution defect ener-

gy, also calculated by HADES. To compare, on an absolute basis, the defect energy to form the Y_2^- center (with the required $Y^- \cdots Y^-$ defect already present) with the energy to form an X_2^- center in the same MX crystal, E'_D must then be corrected by subtracting $A(X) - \chi(MX)$ so that

$$\tilde{E}_D(Y_2^-) = E_D^0 - E_{DS} + [A(Y) - A(X)]. \quad (B13)$$

To include, on a common scale, the defect energy to form an XY^- V_K center in MX , the above argument (for Y_2^-) is repeated. Thus, via the energy cycle,

$$\begin{aligned} MX(\xi_0): X^-X^-(R_0) + Y^- \rightarrow MX(\xi): XY^-(R_e) \\ + MX(\xi): e^- + X^-: E_D \end{aligned} \quad (B14)$$

leads to the defect energy

$$\begin{aligned} E_D(XY^-) = E_v + E_I + E_R + [A(X) - \chi(MX)] - D_e(R), \\ A(X) < A(Y) \end{aligned} \quad (B15)$$

$$= E_v + E_I + E_R + [A(Y) - \chi(MX)] - D_e(X),$$

$$A(X) > A(Y)$$

i.e., the electron affinity A , corresponds to the *lesser* of $A(X)$ and $A(Y)$. The defect energy required to form the XY^- V_K center is relative to $MX(\xi'): X^-Y^-(\bar{R}_e)$, the relaxed substitutional defect ($X^- \rightarrow Y^-$). The associated substitutional defect energy

$$E_S = E'_v + E'_I + E'_R \quad (B16)$$

for

$$\begin{aligned} MX(\xi_0): X^-X^-(R_0) + Y^- \rightarrow MX(\xi'): X^-Y^-(\bar{R}_e) + X^-: E_S \\ (B17) \end{aligned}$$

is easily calculable from HADES. The desired process is thus obtained from the proper combination of Eqs. (B14) and (B17) to give

$$\begin{aligned} MX(\xi'): X^-Y^-(\bar{R}_e) \rightarrow MX(\xi): XY^-(\bar{R}_e) + MX(\xi): e^-: E'_D, \\ (B18) \end{aligned}$$

with the defect energy

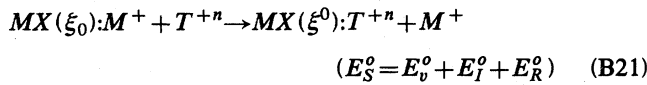
$$\begin{aligned} E'_D(XY^-) = E_D - E_S = E_D^0 - E_S + [A(X \text{ or } Y) - \chi(MX)], \\ (B19) \end{aligned}$$

where the smaller of the electron affinities, $A(X)$ or $A(Y)$, is used. To compare the defect energy to form an XY^- V_K center (with a relaxed substitutional Y^- defect *already* present) with the energy to form an X_2^- V_K center in the same MX crystal, $A(X) - \chi(MX)$ must then be subtracted from $E'_D(XY^-)$, i.e.

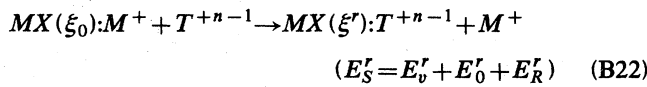
$$\begin{aligned} \tilde{E}'_D(XY^-) = E_D^0 - E_S, \quad A(X) < A(Y) \\ = E_D^0 - E_S + [A(Y) - A(X)], \quad A(X) > A(Y). \end{aligned} \quad (B20)$$

It is apparent that comparison of V_K -center defect energies for X_2^- , XY^- , and Y_2^- in a common MX crystal (practically speaking, in the *same* crystal), only differences in electron affinities of the free halogen atoms X are involved.

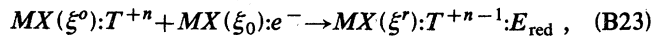
It has been mentioned that alternative energy cycles are possible and might be useful. In several of the comparisons given above, the electron affinity of the crystal, χ , appears, a quantity which is not well known. Although it appears small in magnitude relative to E_D , this electron affinity, $\chi(MX)$, can be eliminated from the energy reference by providing an additional energy cycle in which the electron is removed from the conduction band and placed on an "electron trap," i.e., it reduces a metal ion doped into the crystal for this purpose. Typically, for V_K -center formation, Pb^{2+} , Tl^+ , or Ag^+ cations are employed as electron traps. HADES defect calculations for substitutional defects of T^n and T^{n-1} (T denotes trap) are straightforward, in principle,



and



(the superscripts o denotes oxidized form, and the superscript r denotes reduced form of T). The reduction process with the electron in the conduction band of MX then becomes

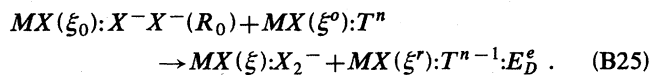


and the energy for reduction of the electron trap T by the electron in the conduction band is given by

$$E_{red} = E_S^r - E_S^o - I(T) + \chi(MX) \quad (B24)$$

where $I(T)$, the ionization potential of T^{+n} , is known from experiments, and E_S^o and E_S^r can be calculated using HADES.

If the reduction process is now combined with the usual energy cycle to form the V_K center, one obtains



The energy for V_K -center formation with allowance for placing the freed electron on the electron trap T is given by

$$E_D^o = E_D + E_{red} = E_D^0 + E_S^r - E_S^o + A(X) - I(T) \quad (B26)$$

where we let $D_e(R)$ go to zero as usual and $\chi(MX)$ has canceled out. We use ξ^r and ξ^o to denote relaxed ion positions around the substitutional defects T^{+n-1} and T^{+n} , respectively, but actually in the doped crystal there is only one set of relaxed positions; it is tacitly assumed that the V_K center (X_2^-) and T are far apart so that *independent HADES calculations are reliable*.

If various V_K centers are compared with the electron-trap (T) reference energy, we note the following.

(a) The same V_K center, X_2^- , in different crystals. Us-

ing crystal AX as the reference crystal, the defect energy in MX is

$$E_D^{(T)} = E_D^0 + [E_S^r(MX) - E_S^r(AX)] + [E_S^o(MX) - E_S^o(AX)] \quad (B27)$$

if the *same* electron trap, T , is employed for both crystals. The correction if *different* electron traps are used, namely T_1 and T_2 , is only slightly more complex, involving the difference $I(T_1) - I(T_2)$.

(b) Different V_K centers in different crystals, e.g., $MX(X_2^-)$ and $MY(Y_2^-)$, with $MY(Y_2^-)$ taken as the reference state leads to the expression, for the defect energy in MX , as

$$E_D^{(T)} = E_D^0 + [E_S^r(MX) - E_S^r(MY)] + [E_S^o(MX) - E_S^o(MY)] + A(X) - A(Y) \quad (B28)$$

with

$$T_1 = T_2.$$

(c) Different V_K centers in the *same* crystal, e.g., X_2^- , XY^- , and Y_2^- in MX with electron trap T . In this case, since T is common and only a single crystal (M) is involved, there is no *material-dependence* correction for V_K -center defect energies.

There are other energy reference points which might also be used, but material-dependent defect-energy scales cannot be freed of their material dependence by a choice of scale or zero. In certain comparisons, only the absolute defect energies will satisfy. We summarize as follows.

(i) The energy scale (zero) using the conduction-band electron is simple, convenient, and involves a relatively small correction. However, χ is not very well known or easy to calculate (see Poole *et al.*⁴⁸). An absolute scale based on use of χ will bear these uncertainties.

(ii) The energy scale (zero) involving an electron trap T does correspond to what is involved in practice in V_K -center formation, and in that sense, this zero point may be more satisfying. In addition, all the required substitution energies are, in principle, calculable from HADES and hence an absolute scale of defect energies is possible. In addition, the location of the electron on a trap recovers the neutrality of the system and permits comparison with uncharged defects on a common ground. There are serious drawbacks, however, to this energy scale; rather substantial work is implied to obtain E_S^o and E_S^r , not to mention the definition of appropriate potentials to employ, and it is likely that E_S^o and E_S^r for T^{+n} and T^{+n-1} , respectively, are probably not small numbers and their accuracy would deserve careful study to define uncertainties in this scale.

Finally, it might be mentioned that taking the common reference point as that of all the relevant (atomic) ions separated at infinity, and hence using the crystal binding energy, does not remove this material dependence from the energy scale except if different defects are studied in the same material.

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