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Off-center displacements of univalent impurity ions in alkali-halide crystals

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We report calculations of the structures and energies of monovalent ions (mainly Li^+ and F^-) dissolved in a number of alkali-halide hosts. Our results are used to discuss the observation of such ions in certain crystals at positions displaced from the regular lattice sites. The calculations use the HADES program together with recently derived interionic potentials. In contrast to previous theoretical studies in this field, we obtain good agreement with experiment in a substantial majority of cases, without making any arbitrary alterations to the potentials. Moreover, our results agree with recent experimental investigations of the effect of pressure on Li^+-doped KCl; calculations with a contracted lattice show that the Li^+ ion goes on center, in agreement with the experimental findings at higher pressures. Such calculations therefore provide a highly critical test of our potentials and the generally good agreement between theory and experiment reported in our study therefore confirms the accuracy of our lattice models. Our results are also used to discuss in general terms those factors that determine whether off-center displacements occur in specific alkali halides. We show how the observed trends are determined by a balance between short-range repulsion and polarization terms.

I. INTRODUCTION

Experimental evidence obtained using various techniques[1-3] has shown that a small univalent impurity ion, when substituted for a larger host ion in an alkali-halide crystal, may adopt an off-center postion. Matthew[4] first identified the origin of this effect: the small substitutional ion has only weak overlap interactions with its neighbors; such reduced repulsive forces are therefore insufficient to oppose the displacement of the foreign ion to an off-center site which is stabilized by the resulting polarization energy of the lattice. It should therefore be possible to reproduce this observed effect in defect calculations that use a satisfactory lattice model and a proper description of the interaction of the substitutional ion and the host crystal. In this paper we report such calculations for a wide range of systems in which the foreign ion is an alkali or halide ion and the host crystal is an alkali halide; we have used potentials recently derived by Catlow *et al.*,[5] which are based on the shell model.

This displacement of small substitutional ions to off-center sites depends on a balance between overlap and polarization terms in the lattice energy, and the successful prediction of this effect in lattice calculations is therefore a very critical test of the lattice model used. The various difficulties that may indicate limitations in the chosen model are well illustrated in a survey of earlier calculations. Thus when Dienes *et al.*[6] used a Born-Mayer potential for Li^+ in KCl with potential parameters from Tosi and Fumi,[7] they at first found no stable minimum-energy configuration when the foreign ion was displaced along the $\langle 100\rangle$ axis; indeed, using a polarizable point-ion model to calculate the polarization energy, this term dominated the repulsion between the Li^+ and the nearest Cl^- ion at all separations—such an instability in the model is termed a polarization castastrophe. Dienes *et al.* could only find a stable minimum along $\langle 100\rangle$, with the Li^+ displaced to $0.12a$ (a is the cation-anion separation) if, at close separations, they replaced the Born-Mayer interaction for Li^+-Cl^- with a steep linear potential. In contrast, the unmodified model did predict minima in the lattice energy for displacements of the Li^+ along $\langle 110\rangle$ and $\langle 111\rangle$ directions; but the deeper minima were along $\langle 110\rangle$, at variance with the experimental results of Byer and Sack[8,9] and Alderman and Cotts.[10] In a later paper, Wilson *et al.*[11] therefore modified the Born-Mayer potential $V(r)=b\exp[(r_+ + r_- - r)/\rho]$ for the Li^+-Cl^- interaction; the ionic radii r_+ and r_- were unchanged but the hardness parameter ρ was set at 0.317 Å in place of the value 0.342 Å appropriate to LiCl. They found minima in the $\langle 111\rangle$ direction that were 0.0073 eV more stable than those along $\langle 110\rangle$. The use of this harder potential also eliminated the polarization castastrophes found for displacements of the substitutional Li^+ ion along $\langle 100\rangle$.

These results were also obtained using a model with a lattice parameter appropriate to room temperature; they need not therefore describe phenomena observed at low temperature, particularly as it is clear that the predicted behavior is very sensitive to small changes in the model.

Quigley and Das[12] made a more thorough investigation of the characteristic polarization catastrophes found when Li^+ in KCl is displaced from a lattice site along a ⟨100⟩ axis. They used a model with potential parameters from Born and Huang[13] and a lattice parameter appropriate to room temperature, and found shallow minima in the plot of lattice energy against the displacement of the substitutional ion; however, the potential energy decreased without limit at larger displacements. Quigley and Das showed how this difficulty could be avoided if the Born-Mayer-Verwey[14] form $V(r) = A + Br^{-12}$ was used for the Li^+-Cl^- interaction when $r < a$, or if the anion polarizability was reduced when the ions were separated by a distance less than the lattice constant of the host crystal. With such models Quigley and Das[15] found minima along ⟨100⟩ and ⟨111⟩ for Li^+ in both KCl and KBr, with the deeper minima along the ⟨111⟩ axes. Subsequently, Quigley and Das[16] also performed calculations for Li^+ in KCl and KBr at reduced values of the lattice parameter to simulate lattice contraction at low temperature and to study the effect of pressure on the paraelectric properties of these defects. They found that at 4 K the minima in KBr are too shallow to localize the Li^+ at an off-center position but that KCl requires an additional pressure of 7 kbar before the substitutional ion returns to a preferred on-center site; this is qualitatively in agreement with the different behavior of these two systems. Finally, Quigley and Das[17] have reported calculations on F^- substituted in NaBr using similar models; but the prediction of a preferred displacement along ⟨111⟩ is at variance with the results of Rollefson,[18] which are best explained assuming strongly localized potential wells along the ⟨110⟩ axes.

We can identify two general deficiencies in these calculations: first, they are restricted to a very limited number of systems; and second, they give satisfactory results only after arbitrary adjustments to the lattice models which are introduced in order to secure particular agreement with known experimental results. In this paper we have greatly extended the scope of the calculations to consider a broad range of systems. We have also used two new lattice models that we believe are a substantial improvement on those that were available for the earlier work; the models are used without modification because our aim is not only to study an interesting range of defects and predict their properties, but also to test these new models in calculations which will critically expose their remaining limitations.

The potentials used in the calculations are the subject of Sec. II: these models of Catlow *et al.*,[5] which are based on the shell model, provide a more realistic description of the ionic polarization than the polarizable point-ion model, and of the effect that the polarization of the ions has in modifying the overlap interactions. We also believe that these new potentials are valid over a wider range of ionic separations than those used in earlier studies, and they are thus more suitable for reliable studies of off-center substitutional ions. We describe the calculations in Sec. III; we use the HADES program, which is a package available for economical and general studies of defects in ionic solids. We have considered all those systems, where the substitutional ion is an alkali or halide ion, that have been investigated experimentally for off-center effects, or in which such behavior might be expected; then we have studied a number of less likely systems for comparison. The actual list comprises Li^+ in all halides with other alkali host cations and Na^+ in KF. We have also studied F^- substituted in LiCl, NaCl, and KCl, in NaBr, and KBr, and RbBr, and in NaI, KI, and RbI. Finally, we have considered Cl^- in KBr, KI, and RbI. Our calculations apply essentially to a lattice at absolute zero but we have also studied the effect of reducing the lattice parameter in calculations for Li^+ in KCl.

Section IV discusses the results of these studies; we provide some simple qualitative explanations of the observed behavior of these systems, in particular of the pattern of occurrence of paraelectric centers only within a limited range of halides. Section V contains a detailed comparison of our results with experimental studies of appropriate systems which may contain small substitutional ions at off-center sites. In general, we find complete agreement for the series of systems with Li^+ as the substitutional ion but the results for anion substitutionals are still not wholly satisfactory.

II. POTENTIALS

We have seen in Sec. I how, in early calculations for alkali halides containing small cation substitutionals, it was necessary to make modifications to standard lattice models in order to predict the observed off-center displacements. In our own calculations we have used new shell-model potentials derived by Catlow *et al.*[5] in place of the polarizable point-ion models with Tosi and Fumi[7] potentials that were utilized in the earlier studies. We now show that these new models include the particular features that were introduced arbitrarily in previous calculations as necessary for accurate prediction of the off-center behavior of small foreign ions.

For present purposes, the most important feature of these new descriptions of the alkali halides is their use of the shell model of Dick and Overhauser[19]; each ion is then represented by a coupled core and shell with separate charges so that ionic polarization corresponds to a differential displacement of the core and shell. Because the short-range interactions represent the effect of the overlap of electron shells, there is coupling between ionic polarization and the effective repulsion between adjacent ions. For example, as a small Li^+ ion approaches an adjacent anion, the negatively charged electron shell of the polarizable ion is drawn into the region between the interacting ions; the overlap is increased and the effective interaction is harder than that between unpolarized or polarized point ions. This feature is essential in any model that describes both the elastic and dielectric properties of ionic crystals; in this respect, the shell model is satisfactory but the polarizable point-ion model is not. Moreoever, the increased overlap of ions caused by their polarization also removes the necessity for any separate strengthening of the repulsive potential between the substitutional ion and the surrounding lattice. Dienes *et al.*[6] and Quigley and Das[12,15] had to introduce just such adjustments in their polarizable point-ion calculations to avoid polarization catastrophes and to secure deeper minima along the $\langle 111 \rangle$ axes in simulations of Li^+ in KCl.

The two sets of shell-model potentials of Catlow *et al.*[5] have shell charges and core-shell coupling constants fitted to the dielectric properties of the halides. The models, as fitted, assign negative shell charges to all the anions and thus provide a physically realistic description of the polarization of the negative ions. However, it is quite usual in such fitted models to obtain positive shell charges for the cations, and Bilz *et al.*[20] have suggested that this simulates properties of the crystals that are not, in fact, associated physically with the cation polarizability. We would therefore expect the models to be most satisfactory for the case of small unpolarizable cation substitutionals, where the polarization of adjacent anions stabilizes the off-center configuration; less satisfactory results are to be expected for anion substitutionals when polarization of the adjacent cations may be more significant.

However, these detailed and subtle difficulties do not invalidate the main conclusion that the shell model is a satisfactory description of the ionic polarization and its coupling to the overlap interaction. Moreover, the particular form of this repulsive potential is itself of considerable significance and calculations for off-center substitutional ions provide a critical test, especially of the form of the interaction of the substitutional ion with the adjacent lattice ions. Any potential for the interaction of a substitutional ion with the nearest neighbors of opposite charge can of course be defined from data on an appropriate halide. Thus the Li^+-Cl^- potential for Li^+ substituted in KCl is deduced from equilibrium and elastic data on LiCl; such data define the interaction only at the equilibrium separation, while the calculations for the substitutional ion demand knowledge of the potential over a much wider range of separations. We believe the new models of Catlow *et al.*[5] are more satisfactory in this respect than the earlier models of Tosi and Fumi[7] used in many of the original studies of these systems; it is worth considering why, as well as providing a more complete description of the potentials used in this study.

As Tosi and Fumi did, Catlow *et al.* used a Born-Mayer representation of the dominant overlap repulsion between the ions. Tosi and Fumi, however, invoked a radius scheme to relate the overlap interactions between first and second neighbors; they then included Mayer[21] Van der Waals interactions and fitted the equilibrium condition and compressibility of each crystal. However, Catlow *et al.*[5] found that the usual radius relation does not take account of the different hardness factors required for the different first- and second-neighbor interactions. They therefore retained the usual empirical Born-Mayer potential only between nearest neighbors, fitting to equilibrium and elastic data for the crystal; the second-neighbor overlap interactions were computed using the electron-gas methods proposed by Wedepohl[22] and Gordon and Kim.[23]

An enlarged Van der Waals term was then added to the second-neighbor potentials to account for the observed elastic properties of the alkali halides. This was done in two different ways: in the first set of potentials (potential set I), the Van der Waals potential is chosen specifically for each substance; however, the crystal data give no indication as to how this term should be divided between the equivalent cation-cation and anion-anion Van der Waals interactions, which were therefore arbitrarily made equal. The second set of potentials (potential set II) used a much more flexible form of second-neighbor interaction with limiting overlap and Van der Waals forms joined by polynomials in the intervening region; these potentials are specific to each interaction and are defined over a range of separations by considering their contribution, at various interionic distances, to the elastic and equilibrium properties of a series of halides.

The second-neighbor interactions are not directly very important in the present calculations; how ever, they make significant contributions to the elastic and equilibrium properties of the halides and thus have a substantial influence on the prediction of the near-neighbor interactions when these are fitted to crystal data. Because of the more detailed treatment of both first- and second-neighbor potentials, the new models are apparently valid over a wide range of interionic separations and are thus generally satisfactory in predicting the off-center properties of substitutional ions. They are certainly quite satisfactory for calculations of the formation and migration energies of intrinsic defects in alkali halides (Catlow *et al.*[24,25]), which also require potentials valid for crystals in which ions are displaced from normal lattice positions.

Potentials for all the alkali halides give models not only for the host lattices but also define the interaction of any substitutional ion with its immediate neighbors of opposite charge. However, crystal data do not fix the appropriate potential for a substutional ion with its next-nearest neighbors in the crystal. For Li^+ substitutional, these interactions are very small but there may be more significant contributions from Van der Waals interactions with substitutional anions. We were particularly aware that this small term might yet be sufficient to reorder the energies of the off-center minima along different crystal axes. We have generally used routine interpolation methods to find the unknown potentials. We have used a Buckingham potential when this is the form appropriate for the host lattice (the set I potential of Catlow *et al.*) and generally used a geometric-mean rule for both the overlap and Van der Waals parts to deduce the potential $\phi_{ij}(r)$ from the known homogeneous interactions $\phi_{ii}(r)$ and $\phi_{jj}(r)$ of like ions. This in particular gives overlap potentials in excellent agreement with alternative values calculated using the electron-gas method. In the same way, the substitution of an arithmetic mean for the Van der Waals interaction has very little effect. And when the more complex polynomial potentials are appropriate (with the use of the Catlow *et al.* set II potential for the host), the details of the joining of the various potential forms have no significant influence on the results.

TABLE I. Calculated energies and displacements for alkali halide crystals containing substitutional Li^+ or Na^+ ions. E is the change in lattice energy (in eV) when the impurity cation is constrained to a lattice site. ΔE is the energy difference (in eV) between this value and that of the off-center equilibrium site of the impurity; this is at $\delta, 0, 0$ for displacements along $\langle 100 \rangle$, at $\delta, \delta, 0$ for displacements along $\langle 110 \rangle$, and at δ, δ, δ for displacements along $\langle 111 \rangle$; δ is in units of the nearest-neighbor cation-anion separation a.

			$\langle 100 \rangle$		$\langle 110 \rangle$		$\langle 111 \rangle$		
System	Potential	E	ΔE	δ	ΔE	δ	ΔE	δ	Experimental
$NaF:Li^+$	I	−0.782	0.000	0.000	0.000	0.000	0.000	0.000	
$NaCl:Li^+$	I	−0.562	0.000	0.000	0.000	0.000	0.000	0.000	on center [a]
	II	−0.655	0.000	0.000	0.000	0.000	0.000	0.000	
$NaBr:Li^+$	I	−0.491	0.000	0.000	0.000	0.000	0.000	0.000	on center [b]
$NaI:Li^+$	I	−0.514	0.000	0.000	0.000	0.000	0.000	0.000	
$KF:Li^+$	I	−1.179	0.102	0.153	0.208	0.165	0.321	0.174	
	II	−1.190	0.80	0.139	0.172	0.151	0.269	0.167	
$KCl:Li^+$	I	−0.926	0.015	0.103	0.033	0.111	0.050	0.117	$\langle 111 \rangle$ [a]
	II	−0.807	0.002	0.066	0.005	0.069	0.008	0.073	
$KBr:Li^+$	I	−0.850	0.003	0.077	0.008	0.084	0.011	0.085	on center [a]
	II	−0.728	0.000	0.000	0.000	0.001	0.000	0.001	
$KI:Li^+$	I	−0.799	0.000	0.000	0.000	0.001	0.000	0.000	
$RbF:Li^+$	I	−1.410	0.178	0.164	0.409	0.177	0.545	0.193	
	II	−1.150	0.070	0.016	0.350	0.172	0.499	0.192	
$RbCl:Li^+$	I	−1.066	0.051	0.130	0.121	0.143	0.156	0.156	on center [a]
	II	−0.804	0.027	0.114	0.059	0.124	0.095	0.140	
$RbBr:Li^+$	I	−1.004	0.029	0.118	0.068	0.130	0.091	0.142	
	II	−0.704	0.009	0.089	0.019	0.097	0.031	0.108	
$RbI:Li^+$	I	−0.963	0.000	0.015 [c]	0.000	0.000	0.000	0.000	
$KF:Na^+$	I	−0.991	0.000	0.000	0.000	0.000	0.000	0.000	
	II	−0.728	0.000	0.000	0.000	0.000	0.000	0.000	

[a] F. Bridges, Crit. Rev. Solid State Sci. 5, 1 (1975).

[b] R. J. Rollefson, Phys. Rev. B 5, 3235 (1972).

[c] Run did not converge completely.

III. CALCULATIONS

The principles of the HADES program, which was used throughout this study, have been described by Lidiard and Norgett[26] and Norgett.[27,28] In the present calculations for neutral defects, an inner region I is relaxed explicitly, subject only to constraints imposed by a predetermined defect symmetry. The distortion in an additional finite region surrounding region I is then calculated assuming that the lattice behaves as a dielectric continuum; the lattice responds to the electric-displacement field of the dipole formed by any off-center displacement of the substitutional ion. The remainder of the lattice is held fixed.

The potential models used in these studies hold the perfect crystal in equilibrium at the interionic separation expected for a static lattice; such values of the lattice parameter used in these calculations were obtained by extrapolating measured values to absolute zero.[29] These dimensions differ only slightly from the observed low-temperature lattice parameters and our calculations are thus directly comparable with experimental results obtained in this temperature range.

We first calculated the energy required to substitute a foreign ion at a lattice site, allowing only symmetric relaxation about the defect. The values of this substitution energy E are collected in Tables I and II, which contain results for cation and anion substitutionals. We then performed three further sets of calculations with the foreign ion displaced along the $\langle 100\rangle$, $\langle 110\rangle$, or $\langle 111\rangle$ axes of the crystal; both the substitutional and surrounding lattice ions were relaxed but with the inital defect symmetry retained. In these calculations, the foreign ion moved either to an energetically favored off-center site, if this existed, or it relaxed directly to the lattice site. The results of these calculations are also given in Tables I and II; there we report first the displacement energy ΔE, which is the difference in energy of the symmetric and off-center defect configurations, and then the coordinates of the stable off-center substitutional ion; the displacement energy and the displacement are both zero if there are no off-center energy minima of the appropriate symmetry. In either situation, we found no difficulties with instabilities in the models and the calculations generally converged very smoothly to well-defined energy mini-

TABLE II. Calculated energies and displacements for alkali-halide crystals containing substitutional F^- or Cl^-. The meaning of the symbols is explained in the caption to Table I.

			$\langle 100\rangle$		$\langle 110\rangle$		$\langle 111\rangle$		
System	Potential	E	ΔE	δ	ΔE	δ	ΔE	δ	Experimental
$LiCl:F^-$	I	−1.031	0.084	0.132	0.178	0.139	0.271	0.151	
	II	−1.128	0.040	0.108	0.091	0.117	0.121	0.116	
$NaCl:F^-$	I	−0.987	0.001	0.046	0.001	0.041	0.001	0.025	on center[a]
	II	−0.992	0.000	0.000	0.000	0.000	0.000	0.000	
$KCl:F^-$	I	−0.668	0.000	0.000	0.000	0.000	0.000	0.000	on center[b]
	II	−0.697	0.000	0.000	0.000	0.000	0.000	0.000	
$NaBr:F^-$	I	−0.094	0.042	0.112	0.099	0.124	0.110	0.119	$\langle 110\rangle$[a, c]
	II	−1.060	0.034	0.113	0.077	0.124	0.085	0.117	
$KBr:F^-$	I	−0.874	0.000	0.000	0.000	0.001	0.000	0.000	on center[c, d]
	II	−0.774	0.000	0.000	0.000	0.000	0.000	0.000	
$RbBr:F^-$	I	−0.660	0.000	0.000	0.000	0.000	0.001	0.000	on center[c,d]
	II	−0.673	0.000	0.000	0.000	0.000	0.000	0.000	
$NaI:F^-$	I	−1.276	0.145	0.153	0.356	0.172	0.456	0.118	on center[d]
	II	−0.992	0.071	0.026	0.324	0.173	0.404	0.179	
$KI:F^-$	I	−0.937	0.048	0.116	0.104	0.133	0.097	0.134	$\langle 110\rangle$[c,d]
	II	−0.778	0.039	0.122	0.093	0.138	0.134	0.154	
$RbI:F^-$	I	−0.794	0.001	0.013	0.048	0.118	0.040	0.118	$\langle 110\rangle$[c,d]
	II	−0.708	0.001	0.028	0.026	0.105	0.039	0.117	
$KBr:Cl^-$	I	−0.369	0.000	0.000	0.000	0.000	0.000	0.000	
	II	−0.269	0.000	0.000	0.000	0.000	0.000	0.000	
$KI:Cl^-$	I	−0.614	0.000	0.000	0.000	0.000	0.000	0.000	
	II	−0.482	0.000	0.000	0.000	0.000	0.000	0.000	
$RbI:Cl^-$	I	−0.535	0.000	0.000	0.000	0.000	0.000	0.000	
	II	−0.428	0.000	0.000	0.000	0.000	0.000	0.000	

[a] R. J. Rollefson, Phys. Rev. B 5, 3235 (1972).

[b] G. Lombardo and R. O. Pohl, Bull. Am. Phys. Soc. 11 212 (1966).

[c] A. Gongora and F. Luty, Bull. Am. Phys. Soc. 20, 469 (1975).

[d] J. Wahl and F. Luty, Bull. Am. Phys. Soc. 20, 469 (1975).

ma.

In such studies, we should stress that it is essential when comparing energies of these different defect configurations, that the various calculations use exactly the same sizes for the inner region I. This is particularly important in the present study because the energies of the various off-center configurations may differ very little; such differences are only of the order of the uncertainties in the absolute defect energies arising from any variation in the size chosen for the explicitly relaxed region. Thus to fix the relative magnitudes of these different errors, we made several studies with Li^+ as impurity ion and used two sizes of relaxed region: the standard region contained 81 ions and the enlarged region contained 123 ions. The absolute values of the energies of substitution differed in these calculations by up to 0.02 eV; however, any change in displacement energy was less than 0.007 eV. Moreoever, the relative energies of the different off-center minima were also unchanged by the increase in size of the relaxed region and the calculated displacements of the substitutional ion agreed to within 0.01 times the cation-anion separation. Thus the smaller relaxed region, if used consistently for all defect symmetries, is quite adequate for studying off-center displacements; it was used for all calculations of cation and anion substitutional defects described in Secs. IV A and IV B.

IV. RESULTS AND DISCUSSION

A. Cation-substitutional results

We made calculations for Li^+ substituted in all alkali halides in which Li^+ is not the host cation and studied Na^+ substituted in KF. We used potential set I described in Sec. II for all these calculations but potential set II for a more restricted number of comparative studies. In various materials, the Li^+ substitutional relaxes to a preferred off-center site and there are in such cases well-defined energy minima along the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions; the minima along the ⟨111⟩ axes are always deepest. In the next paragraph we consider explicitly the pattern of occurrence of this behavior within the halide series. We observe first, however, that the calculated values of the displacement energy in Table I depend quite sensitively on the chosen potential but the calculated displacements of the Li^+ substitutional ion are generally less affected by the choice of model. Most important, the two comparable calculations, with one exception, predict the same ordering of the energies of the different configurations; only for Li^+ in KBr is there any qualitative difference in the results obtained with different potentials, and here the displacement energies are certainly very small. The basic pattern of the results is therefore not affected by the chosen interionic potentials.

These results for Li^+ substituted in a series of halides show two distinct trends. There is first a clear change in the preferred site of the substitutional ion depending on the size of the displaced cation. For example, in a series of chlorides, Li^+ substitutes at a lattice site in NaCl, and in the same way Na^+ adopts a lattice site in KCl. However, Li^+ is certainly located at an energetically favored off-center site in KCl and RbCl; thus off-center substitution occurs in systems where Li^+ replaces a substantially larger ion. As expected, the various displacement energies are greater for RbCl than KCl because of the larger difference in the ionic radii of the substitutional and host cations.

There is also a second trend found where Li^+ replaces a particular cation in a series of halides; this trend is apparent only for potassium and rubidium salts but not, of course, in the sodium halides where the Li^+ substitution always occupies a lattice site. Thus in the two series with larger host cations, the magnitude of the displacement energies and the equilibrium displacements of the substitutional ion decrease on passing from any fluoride to the corresponding chloride. The values for the appropriate bromide are even smaller and KBr in particular is an intermediate case where calculations with the different lattice potentials indicate either an on-center Li^+ ion or only very shallow off-center minima. Finally, in the iodides, Li^+ is restricted to a lattice site in both KI and RbI. We can thus summarize both trends in the observation that Li^+ substitutes at an off-center site in those halides with large cations but small anions; this pattern is illustrated most clearly in Table III, which records our predictions of off-

TABLE III. Summary of calculated off-center behavior of Li^+ and F^- substitutional ions. All the systems calculated to be off-center are indicated by writing the substitutional ion (Li^+ or F^-) in the relevant host-crystal position in the table. Where these symbols do not appear the systems were calculated to be on-center except for those cases marked ··· where no calculation was made for an F^- substitutional ion. § indicates a marginal case where the results differ for the two potentials used in this study.

	F	Cl	Br	I
Li		F^-	···	···
Na			F^-	F^-
K	Li^+	Li^+	Li^+ §	F^-
Rb	Li^+	Li^+ ···	Li^+	F^-

center substitution of both Li^+ and F^- in all members of the alkali-halide series.

Both trends can be explained in terms of the balance of overlap and polarization energies associated with the substitutional ion. The first trend, which follows the difference in radii of the substitutional and host ions, is clearly associated with the reduced overlap repulsion between the foreign ion and the surrounding lattice when the substitutional displaces a host ion of much greater radius. However, such a variation in overlap interaction has very little effect in determining the second trend which, for Li^+ substitution, depends on the anion radius of the host. To show this, we may represent the overlap interactions in all alkali halides approximately using a radius scheme; the potential $V(r)$ is then written

$$V(r)=b\exp[(r_+ + r_- - r)/\rho]\,.$$

Common values of b and ρ serve for all halides and the radii of cation and anion, r_+ and r_-, sum to give the lattice constant of the appropriate halide. Thus the interaction of a substitutional ion of radius $\tilde{r}_+$ with adjacent anions, where the foreign ion replaces a host cation of radius r_+ in a crystal with interionic separation $r_+ + r_-$, is a function of $\tilde{r}_+ - r_+$; in particular, it is independent of the radius of the lattice anion.

The second observed trend depending on just this radius must therefore be determined by changes in the polarization energy of the lattice. The trend is therefore at first sight anomalous because the lattice polarization must depend on the polarizability of the anions surrounding the substitutional Li^+ ion; the polarizability is greater for the heavy anions but the iodides, in particular, always have Li^+ substituted at a lattice site. A more rigorous argument removes this apparent anomaly; the induced polarization energy E of the adjacent anions is a product of the ionic polarizability α_- and the square of the effective electric field F:

$$E=-\tfrac{1}{2}\alpha_- F^2\,.$$

The polarizability α_- depends approximately on the cube of the anion radius. However, for proportional lattice distortions in different crystals, the electric field will depend on the inverse square of the lattice constant $r_+ + r_-$. Hence with r_+ less than r_-, the polarization energy, which attracts the substitutional ion to an asymmetric site, decreases as the radius of the adjacent lattice ion increases; this is just the second trend found in our results.

Both the overlap and polarization energies increase in magnitude if the lattice is compressed but the overlap repulsion varies more rapidly with the interionic separation. Compression of the lattice may therefore destabilize off-center sites for a small substitutional ion. To study this effect, we have made calculations for Li^+ in KCl at reduced values of the lattice parameter; the results are collected in Table IV. The Li^+ moves to a symmetric lattice site when the lattice contracts by about 2% for calculations made with the first potential; with the second potential, the displacement of the Li^+ along the $\langle 111\rangle$ direction reaches zero when the lattice contraction is less than 1%. Figure 1 shows this decrease in the displacement of the Li^+ substitutional ion from a lattice site as a function of the lattice parameter. In Sec. V we compare these results with experiment; the successful prediction of this delicate effect is a particularly satisfactory confirmation of the vali-

TABLE IV. Effect of lattice contraction on the off-center behavior of Li^+ in $\mathrm{KCl{:}Li}^+$. Symbols are defined in the caption to Table I. Lattice constant in Å.

Potential	Lattice constant	E	$\langle 100\rangle$ ΔE	$\langle 100\rangle$ δ	$\langle 110\rangle$ ΔE	$\langle 110\rangle$ δ	$\langle 111\rangle$ ΔE	$\langle 111\rangle$ δ
I	3.116	−0.926	0.015	0.103	0.033	0.111	0.050	0.117
	3.105	−0.993	0.011	0.096	0.024	0.103	0.035	0.107
	3.096	−1.030	0.007	0.088	0.016	0.094	0.022	0.096
	3.085	−1.078	0.004	0.075	0.008	0.080	0.010	0.077
	3.075	−1.117	0.001	0.062	0.001	0.042	0.001	0.034
	3.066	−1.157	0.000	0.040	0.000	0.033	0.000	0.027
	3.060	−1.184	0.000	0.002	0.000	0.002	0.000	0.000
	3.054	−1.217	0.000	0.001	0.000	0.000	0.000	0.000
II	3.116	−0.807	0.002	0.066	0.005	0.069	0.008	0.073
	3.110	−0.827	0.001	0.057	0.003	0.063	0.004	0.061
	3.105	−0.845	0.000	0.045	0.001	0.047	0.001	0.050
	3.100	−0.862	0.000	0.017	0.000	0.023	0.000	0.028
	3.097	−0.873	0.000	0.000	0.000	0.002	0.000	0.001
	3.096	−0.878	0.000	0.000	0.000	0.000	0.000	0.000
	3.085	−0.921	0.000	0.000	0.000	0.000	0.000	0.000

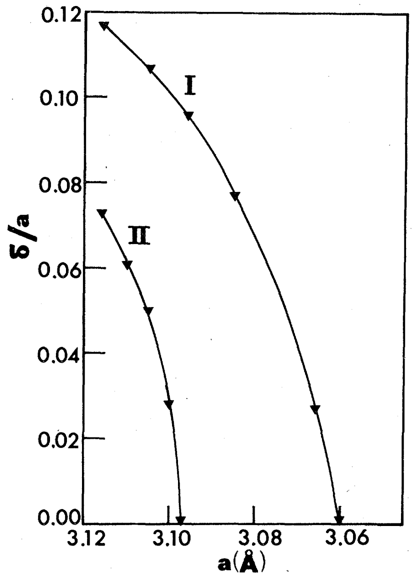

FIG. 1. Variation of the parameter δ, which defines the equilibrium displacement of Li^+ in KCl along ⟨111⟩, with decreasing lattice constant a. The symbols I and II signify the potentials used in the calculations.

dity of the models.

We have thus provided simple explanations of the trends observed in the occurrence of off-center Li^+ substitution in only certain particular members of the halide series; we have also described and explained the effect of pressure on such a system. For Li^+ substitution it is also possible to understand why the preferred displacement of the foreign ion is always along the ⟨111⟩ axis; the substitutional ion is then attracted towards three adjacent anions. The validity of this simple model is supported by a significant observation: for all but a few calculations, the displacement energies for the three directions ⟨100⟩, ⟨110⟩, and ⟨111⟩ are quite accurately in a ratio of 1:2:3. The displacements along the separate coordinate axes are thus in some sense independent and make equal and additive contributions to the total displacement energy. In Sec. V A we shall see how this observation is consistent with the use of simple potential models to explain the low-frequency vibrational modes of the substitutional Li^+ ion. However, the anion-substitutional results discussed in Sec. V B indicate that such simple descriptions are not always completely satisfactory.

B. Anion-substitutional results

The results for F^- substituted in various alkali halides show just the trends that might be expected from an analogy with the results of our calculations where Li^+ replaced a host cation. Thus F^- occupies an off-center site in halides with large anion but small cation. This first trend is exemplified by a series of potassium salts: F^- is on-site when substituted in KCl and KBr but off-center in KI. The second trend is illustrated by comparing results for salts with a common host anion: in the chlorides, F^- occupies an off-center site in LiCl but is on-site in KCl; NaCl is an intermediate case with ambiguous results depending on the chosen potential. The tendency for the F^- substitutional ion to occupy a displaced site is naturally more developed in the bromides: F^- is definitely off-center in NaBr but on-site in KBr and RbBr. The trend continues in the iodides where the F^- always substitutes at an off-center site, in NaI, KI, and RbI, but there is the same regular trend of reduced displacement energies in the systems with heavier cation. The same general principles are apparent in the brief study made with Cl^- as the substitutional ion. When Cl^- replaced Br^- in KBr and I^- in KI and RbI we found no stable off-center configurations for the substitutional ion.

For the anion substitutionals, we found much more ambiguity in the order of the various energy minima along the principal symmetry directions of the crystal than when Li^+ was the foreign ion: for F^- in Li^+ and Na^+ salts, the deepest minima are along the ⟨111⟩ axes, although the magnitude of the minima along ⟨110⟩ are not much smaller. However, for KI and RbI, the results are particularly uncertain because the different potential models predict deepest minima either along ⟨110⟩ or ⟨111⟩. We will need to consider this point in the subsequent discussion of the experimental results for these systems.

We can offer the same qualitative arguments to explain the basic pattern of these results that we used for the results obtained with Li^+ as the substitutional ion. Some parts of the discussion must be modified, however, because in some systems, for example F^- substituted in LiCl, the displacement of the F^- must result from the polarization induced in the substitutional ion itself rather than in the adjacent Li^+ ions of the host crystal. These details do not alter the basic interpretation of the trends in the results but it is much more difficult to offer confident explanations of the orientation of the displacement dipole. We may list a number of complications: for systems such as F^- in KI, both the substitutional and lattice ions are polarized; we have remarked that the description of the cation polarization in our model is suspect; in addition, the model may include quite substantial Van der Waals interactions between the substitutional ion and more distant lattice ions. Finally, the shell model is itself deficient. Kleppmann[30] has shown how more complex ionic distortions may have substantial influence in deciding the favored displacement of a substitutional ion.

V. COMPARISON OF THEORY AND EXPERIMENTAL DATA

A. Cation dopants

The most marked feature of comparison between theory and experiment is the generally satisfactory nature of the agreement. For certain dopants we predict on-center behavior in those systems where this is suggested by the experimental data (Li^+ in NaCl, Li^+ in NaBr, and Na^+ in KCl)[3]. We find ⟨111⟩ off-center behavior for Li^+ in KCl in agreement with abundant experimental information summarized by Bridges[1]; ⟨111⟩ off-center Li^+ is also predicted for KF, RbF, and RbBr for which there are at present no experimental data. We find, as commented in Sec. IV A, that $KBr:Li^+$ is a marginal case, with on-center behavior predicted by potential set II, while potential set I predicts an off-center displacement with a very flat minimum along ⟨111⟩. Bridges[1,31] has reported paraelectric spectra for $KBr:Li^+$ in accord with the results for potential I; such behavior is, however, inconsistent with the infrared data of Sievers[32] and co-workers,[33] who speculate that extra absorption which they observed in Bridges's crystals may be due to Li^+ pairs or Li^+ complex centers. Our theoretical prediction of marginal behavior indicates that the occurrence of off-center Li^+ ions in KBr may be determined by local strains in the crystal.

Serious disagreement between theory and experiment for cation-doped systems is found only in one case, i.e., $RbCl:Li^+$ where we predict ⟨111⟩ displacements, although Bridges reports no paraelectric behavior for this system. We are puzzled by this result, particularly in view of the success of the other calculations on lithium-doped crystals. Moreoever, since our prediction for $RbCl:Li^+$ is in line with the trends discussed in Sec. IV, a reexamination of the experimental data on this system might be worthwhile.

Our results in Table IV on the effect of contracting the lattice also shows fair agreement with experimental observation. For both potentials the locations of the minima move smoothly back towards the origin as the lattice parameter is decreased. There is no evidence of any change in the symmetry of the lowest minimum as the lattice contracts. The shift of the ⟨111⟩ minimum with decrease in lattice constant is shown in Fig. 1 in which δ is plotted against the lattice constant a. The lines for potential I and II intersect the abscissa at $a = 3.060$ and 3.097 Å, respectively, which correspond to hydrostatic pressures of 9.0 and 3.1 kbar. We may compare these predictions with the experimental results of Holland and Lüty[34] who have measured the pressure dependence of the dipole contribution to the relative permittivity ϵ_D of $KCl:Li^+$ at 1 kHz. ϵ_D decreases with increasing pressure and is almost zero at $P = 4.57$ kbar. Their plot of dipole moment $\langle p \rangle$ against the pressure extrapolates to zero $\langle p \rangle$ at 5.4 kbar—a value which is intermediate between our two calculated values for the pressure at which Li^+ goes on-center. More recently Kahan *et al.*[23] have studied the effects of hydrostatic pressure on the far-infrared properties of lattice resonant modes in a number of systems. For $KCl:Li^+$ they find that Li^+ goes on-center at a strain of 0.5% which corresponds to a pressure of ~3.8 kbar and is thus also in rather good agreement with our prediction using potential II.

Further aspects of this recent work[33] are the interpretation of the spectroscopic information in an effort to probe the detailed shape of the multiwell potential associated with the off-center ion and a detailed comparison of the experiments with particular models. A rather simple potential in which

$$V(x, y, z) = V(x) + V(y) + V(z) ,$$

where $V(x)$ has two minima at $\pm a$, and $V(x, y, z)$ therefore has eight minima at $(\pm a, \pm a, \pm a)$ along the ⟨111⟩ directions was found to have general validity and, as we have remarked previously, such a form is in good agreement with many of our results, expecially for KCl and KBr.

B. Anion dopants

For these dopants we again find good agreement between theory and experiment. On-center behavior is precluded for F^- in KCl, KBr, and RbBr in agreement with the studies of Rollefson,[18] Góngora and Lüty,[35] and Wahl and Lüty[36]; in addition, our calculations find on-center structures for Cl^- in KBr, KI, and RbI, for which there is at present no experimental information.

Off-center displacements along the ⟨110⟩ axis have been clearly demonstrated for F^- in NaBr, KI, and RbI by the experimental work of Góngora and Lüty[35] and Wahl and Lüty.[36] For these systems our calculations also suggest off-center behavior. As discussed earlier, we find shallow minima along both ⟨110⟩ and ⟨111⟩ directions, with a very slight energetic preference for the observed ⟨110⟩ configuration for $KI:F^-$ and $RbI:F^-$ with potential I although the reverse is true for potential II. For $NaBr:F^-$, ⟨111⟩ displacements are predicted to be more stable by a narrow margin. Thus even our present potentials may fail in the exacting task of distinguishing between almost equivalent minima in certain systems. Indeed these inadequacies may be inherent in the use of the simple two-body shell-model potentials discussed in Sec. II, and satisfactory agreement with experiment may only be possible if more sophisticated potentials are used, including, for example, ion-deformation terms, whose importance has been demonstrated recently by Kleppmann[30] in a study of Ag$^+$-doped rubidium halides.

There is one disagreement between theory and the currently available experimental data. Wahl and Lüty[36] failed to find any paraelectric effects in low-temperature experiments ($<$20K) on NaI:F$^-$ for which we predict pronounced off-center displacements with deep potential wells. However, such stable off-center locations would not be expected to display orientation effects at very low temperatures so that these results are not necessarily inconsistent.

In general, however, it is clear that our calculations have achieved a large measure of success for both cation and anion dopants. Such results are most encouraging as predictions of off-center behavior provide a stringent test of our new potentials. Out of the 26 systems studied, serious discrepancies have been found in only one case. Moreover, this success has been achieved without any arbitrary modification of our potential; it may be attributed to our use of the shell model description of ionic polarization, and our improved short-range potential discussed in Sec. II.

VI. CONCLUSIONS

Two results of general importance have emerged from the study. First, we have shown that the complex interplay of short-range repulsion and polarization terms gives rise to unexpected variations in the properties of Li$^+$ and F$^-$ doped crystals with the lattice parameter of the host lattice. We may best describe these by reference to Table III, where if we imagine a diagonal drawn from LiF to RbI, then off-center behavior of Li$^+$ is generally found below the diagonal and that of F$^-$ above the diagonal. Calculation and experiment are in accord regarding these trends, which can be rationalized in terms of the simple arguments presented in Sec. V.

Second, the good measure of agreement between theory and experiment, provides strong evidence for the general validity of our recently derived potentials for the alkali halides. There are inadequacies but any remedy will require more sophisticated potentials than those employed in our present study.

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