Dimension changes due to aligned V_k centres and H centres in ionic crystals

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Abstract. When anisotropic defects are aligned, the dimensions of the host crystal parallel and perpendicular to the defect axis are changed, an effect observed previously for H centres and V_k centres in KCl. We have calculated the effect for H centres and V_k centres in several crystal structures. The contribution from long-range Coulomb interactions has been obtained in all cases, with less-detailed estimates of short-range repulsion and covalency effects in special cases. The predictions are in good agreement with experiment for H centres in KCl, but agree only poorly for V_k centres in the same host. The discrepancy appears to arise from modifications of the local repulsive forces near the defect. Measurements of dimension changes show great promise for studies of such interatomic forces.

1. Introduction

The long-range elastic displacements associated with defects in solids have two obvious macroscopic effects. In all cases, the total volume is changed. If anisotropic defects are aligned, the dimensions of the crystal parallel and perpendicular to the defect axis are changed. We consider the latter effect here, and look at the difference $(L_{\parallel} - L_{\perp})$ for elementary defects in ionic crystals. The cases we shall consider are the self-trapped hole (V_k centre) in the NaCl, CsCl and CaF_2 structures, and the neutral interstitial anion (H centre) in the NaCl and CsCl lattices.

The reason why $(L_{\parallel} - L_{\perp})$ measurements are useful is that they give information on the microscopic forces near defects. In particular, we shall show that one should be able to extract details of the repulsive forces between ions close to defects. This is especially interesting because of the conjecture of Norgett and Stoneham (1973) that the axial repulsive parameters near V_k centres differ from the usual bulk values, with consequent effects on reorientation behaviour. In analysing repulsive (and other) forces, the static $(L_{\parallel} - L_{\perp})$ measurements have an advantage over the local- and resonance-mode discussions (see e.g. Dienes 1968) in that no complications of dynamics are involved.

2. Method

Our treatment follows the discussion given earlier by Stoneham (1973). In essence, we regard the crystal containing the defect as a perfect crystal on which certain 'defect forces' are imposed and which determine any lattice distortion. This description involves some subtle aspects which are not immediately apparent. These problems appear when the

3059

defect is one which changes the number of sites, for example when a molecule with several atoms is substituted for a single anion; the question of the internal forces then arises. Another problem occurs if there is substantial lattice distortion, for the microscopic defect forces vary as the lattice relaxes. We discuss these cases in the context of the two types of centre considered in detail later.

2.1. Changes in number of atoms

The H centre consists of a neutral interstitial halogen atom. In a crystal, the centre adopts a crowdion configuration which can be regarded as a $(\text{halogen})_2^-$ molecular ion replacing an anion.

It is clear that a simple substitutional ion (e.g. Cl^- replacing F^- in a fluoride) can be described without difficulty by defect forces on the other lattice ions. The same description can be used for the H centre, with the complication that an X_2^- molecular ion has replaced X^-. It is as if one had a substitutional defect which was anisotropic. In particular, it is clear that the internal forces between the components of the X_2^- ion are not to be counted as defect forces. These internal forces play a different rôle: they determine the equilibrium X_2^- separation, and this, in turn, decides the forces the X_2^- molecular ion exerts on the surrounding crystal.

2.2. Large lattice distortion

The V_k centre, or self-trapped hole, also involves an X_2^- molecular ion. In the self-trapping distortion which localizes the hole, two adjacent halogens are pulled together strongly by covalent forces.

The lattice distortion near a V_k centre is substantial, sufficient to change the defect forces (there is no ambiguity about internal forces, which must be included here) and to introduce anharmonic terms. Any problems of principle can be resolved by recalling that the defect forces are those forces which, acting on a perfectly harmonic lattice, produce the same distortion field. This definition can be hard to put into practice; it is simple to do the pure point-charge contribution, but some of the other terms are more difficult.

3. Microscopic model

We now define the defect forces and make comments on their origin and the convergence of the Coulomb part. As a general description there are three main contributions to the forces:

(i) Point-charge interactions, giving Coulomb forces;

(ii) Short-range repulsive interactions, usually of the Born–Mayer form;

(iii) Covalent bonding within the X_2^- molecular ion. This term is taken to include *all* interactions within X_2^-, including repulsive terms.

In principle, electronic polarization of the ions is important. We shall not discuss it here, for it is not our aim to produce results of the highest possible accuracy. The point is that accurate calculations of $(L_{\parallel} - L_{\perp})$ are only possible when one has also made really accurate calculations of the equilibrium geometry. Such calculations themselves are substantial, and there are few documented cases for H centres and V_k centres in the literature (Dienes *et al* 1968, Jette *et al* 1969, Norgett and Stoneham 1973). So we have chosen to do two things. First, we calculate the Coulomb contributions. These involve

awkward lattice sums, and will be of use in subsequent, more detailed treatments. Secondly, we make estimates of the other contributions (ii) and (iii) within the rigid-ion model. This allows us to see the relative sizes of different terms, to check orders-of-magnitude, and to judge the utility of $(L_{\parallel} - L_{\perp})$ measurements.

3.1. Coulomb forces

The expression which we have to evaluate involves sums of the sort

$$S \equiv \sum_i \phi_{\alpha\beta} F_{i\alpha} R_{i\beta}$$

where i labels the site and (α, β) are Cartesian components. F is a defect force, R the site at which it acts, and ϕ is a matrix of coefficients given by Stoneham (1973). Expressions for S are listed in Appendix 1. In the case of the long-range Coulomb forces the way in which S converges is important. Indeed, convergence is only achieved simply if one groups the terms in S in a convenient way. As in the well known method of Evjen, we group the host lattice ions in a way which give units whose lowest multipole moment is the octopole. However, instead of taking clusters centred on an interstitial site, we follow a suggestion of Dr M J Norgett (1973 private communication) and take groups centred on the lattice sites. The choices are listed in table 1.

Table 1. Groupings of ions for lattice sum. In the Coulomb sums, the point charges $Z_i e$ are replaced by a charge $Z_c e$ on the ion in question and $Z_N e$ on the nearest neighbours. Here e is the proton charge, and $(-Z_c/Z_N)$ is equal to the number of neighbours.

Lattice	Ion	Z_c	Z_N
NaCl	anion	$-\frac{1}{2}$	$+1/12$
	cation	$+\frac{1}{2}$	$-1/12$
CsCl	anion	$-\frac{1}{2}$	$+1/16$
	cation	$+\frac{1}{2}$	$-1/16$
CaF_2	anion	$-\frac{1}{2}$	$+1/8$
	cation	$+1$	$-1/8$

In the case of the V_k centre, which has a net charge, the monopole–octopole interaction is needed: $F(R)$ falls off as R^{-5}. Thus, if the lattice sum is continued out to distance R_L, the residue in S is proportional to $\int_{R_L}^{\infty} dr\, r^2 r^{-5}\, r$, or to R_L^{-1}. In the case of the H centre, a quadrupole–octopole interaction dominates at large distances. The R^{-7} fall-off of $F(R)$ leads to an R_L^{-3} dependence of the residue. We have been able to carry the sums in S sufficiently far that the asymptotic régime has been reached, so that the trends with R_L can be exploited to give accurate results.

The Coulomb sums have been made regarding the V_k centre as two X^- ions plus a central charge $|e|$ and regarding the H centre as two $X^{-1/2}$ ions replacing a single X^- ion.

3.2. Short-range forces

The short-range forces come from the differences between the interatomic forces in the perfect lattice and those in the defect lattice. These contributions are particularly

sensitive to the local geometry. In calculating them we shall assume that all atoms remain at their perfect lattice sites except for a small number (see Appendix 2) which are displaced. The repulsive parameters used were those of Born and Huang (1954). Covalent contributions were deduced from the work of Gilbert and Wahl (1971).

3.2.1. V_k centre. The changes in forces, apart from the modified Coulomb interaction between X_2^- and the rest of the lattice, are these:

(*a*) The altered geometry changes the short-range repulsive forces between X_2^- and its neighbours.
(*b*) The repulsive interaction between two X^- ions has been replaced by a more complicated potential energy curve for X_2^- (e.g. Gilbert and Wahl 1971).

The main effect of these short-range contributions is to give inward forces on the two $X^{-1/2}$ ions.

3.2.2. H centre. In this case we are not interested in the internal force between the X_2^- ions, for the X_2^- molecular ion is regarded as a particularly complex substitutional defect. The only short-range terms of interest are those from the altered Coulomb and repulsive interactions. These are actually more complex than one might expect in the NaCl structure because of the particular geometry. If the X_2^- axis is (110), then there are two planes of atoms normal to this axis which almost pass through the two H-centre ions. A slight shift of the positions of the H-centre ions can alter the sign of their forces on these planes.

4. Results

We shall present two types of result. The first includes only the Coulomb contributions to $(L_\parallel - L_\perp)$ or, more strictly, to the terms S, S' or S'' of Appendix 1 which appear in $(L_\parallel - L_\perp)$. The Coulomb terms are awkward to calculate, but can be presented once and for all. They are given for a variety of geometries in the NaCl, CsCl and CaF$_2$ structures. In all cases the ions apart from those in the X_2^- molecular ion are held at the perfect lattice sites. The second type of result involves the Coulomb, repulsive and covalent contributions for the few cases where local lattice distortions are available. In two cases, comparison with experiment is possible.

Table 2. Coulomb contributions for V_k centres in the CsCl and fluorite structures. The spacing is in units of the anion–anion separation in the perfect crystal. The values of S include the term $S_1 = -\sqrt{3}/2 \simeq -0.8660$ which enters because the initial-state Coulomb repulsion between the two anions has been removed. S_{eff} includes the effects of local atomic displacements (Appendix 2). Apart from a small covalent contribution, the length change is $(\rho e^2/a) S_{eff}/(C_{11} - C_{12})$, where a is the nearest-neighbour distance.

Spacing	1·0	0·7	0·66	0·62	0·58	0·54	0·50	0·454	0·4
S	−2·85	−1·13	−1·03	−0·84	−0·64	−0·42	−0·18	+0·07	+0·38
S_{eff}		−1·57 (CaF$_2$)							
System	Perfect crystal	CaF$_2$ CsBr	SrF$_2$	BaF$_2$ CsCl					

Table 3. The V_k centre in the NaCl structure. (a) This lists the Coulomb contributions only in a crystal in which the V_k ions alone are displaced. Their spacing is in units of the perfect-crystal anion–anion separation. S' and S'' are defined in the text; S_{eff} is $S' + [(C_{11} - C_{12})/C_{44}]S''$, so that the Coulomb contribution to the length change is $(\rho e^2/a)S_{eff}/(C_{11} - C_{12})$. (b) This gives results for NaCl and KCl in more detail, including contributions for local distortion (references a, b, . . . refer to details in Appendix 2) and from repulsive and covalent forces. Here covalent forces include any forces within the Cl_2^- molecular ion.

(a)

Spacing	S' (Coulomb)	S'' (Coulomb)	S_{eff} (Coulomb)
1·0	0·707	-0·51	(perfect crystal geometry)
0·7	0·282	-0·40	-0·18 (LiF) -0·91 (NaBr)
0·54	0·218	-0·35	-0·724 (NaCl)
0·62	0·168	-0·31	-1·60 (KBr)
0·60	0·137	-0·28	-1·80 (KCl)
0·56	0·07	-0·23	
0·54	0·04	-0·19	-1·02 (KF)
0·45	-0·097	-0·05	-0·624 (NaF)

(b)

Crystal	Distortion	S'				S''				S_{eff}
		Coulomb	Repulsive	Covalent	Total	Coulomb	Repulsive	Covalent	Total	
NaCl	a	0·199	0·254	-0·094	0·359	-0·23	0·138	-0·141	-0·233	-0·312
	b	0·065	0·387	—	0·452	-0·25	0·141	—	-0·11	+0·135
KCl	a	0·115	0·476	-0·076	0·515	-0·210	0·288	-0·115	-0·037	+0·315
	b	0·005	0·555	—	0·561	-0·165	-0·021	—	-0·186	-0·447
	Expt				0·147				0·049	0·412

Table 4. Coulomb contributions for H centres in the CsCl structure. The spacing is in units of the anion–anion separation in the perfect crystal. The length change is $(\rho e^2/a)S/(C_{11} - C_{12})$ where a is the nearest-neighbour distance. For CsCl, the appropriate H centre spacing is about 0·454.

Spacing	0·64	0·60	0·56	0·50	0·454	0·40	0·0
Coulomb part of S	1·691	1·533	1·377	1·133	0·850	0·771	0

The Coulomb contributions alone are summarized in tables 2, 3(*a*), 4 and 5(*a*). In all cases there is a simple monotonic trend with the separation of the components of the X_2^- molecular ion, so interpolation is straightforward.

The cases treated in more detail are the V_k and H centres in NaCl and KCl. The effects of local distortion on the Coulomb part alone have also been obtained for the V_k centre in CaF$_2$; as seen from table 2, the value of S is changed from $-1\cdot13$ to $-1\cdot57$.

Table 5. The H centre in the NaCl structure. As in table 3, we give Coulomb contributions to S' and S'' for a variety of spacings of the X_2^- molecular ion, other ions being at their perfect lattice sites. We also give results for all contributions in KCl and NaCl. Notation is as in table 3; as before, the spacings are in units of the X–X separation in the perfect crystal.

(*a*)

Spacing	S'	S''	S_{eff}
0·7	−0·3313	1·3487	
0·66	−0·3127	1·2816	
0·62	−0·2916	1·2175	3·20 (NaCl)
0·60	−0·2801	1·1870	6·13 (KCl)
0·54	−0·2436	1·1051	
0·50	−0·2179	1·0611	
0·0	0	0	

(*b*)

Crystal	Distortion	S' Coulomb	S' Repulsive	S' Total	S'' Coulomb	S'' Repulsive	S'' Total	S_{eff}
NaCl	c	−0·242	1·300	1·058	1·033	−0·370	0·663	1·966
KCl	c	−0·240	1·183	0·943	0·987	−0·556	0·431	3·277
	Expt			0·98			0·33	2·77

4.1. V_k centres in NaCl and KCl

Two sets of local distortions have been used. One is that of Jette *et al* (1969). The other recognises that the lattice relaxation obtained by these authors is not adequate. This is shown both by analysis of the observed spectra of the V_k centre (see, for example, Stoneham 1975) and by explicit calculations (M J Norgett, K Lumb and A M Stoneham 1971 unpublished). For convenience we have obtained a second set of distortions by scaling those of Jette *et al* so as to give a Cl$_2^-$ spacing equal to that of a free Cl$_2^-$ ion. The two sets of distortions should bracket the correct ones.

The results are given in table 3(*b*). They show that the repulsive forces dominate in S',

although there is a sizeable Coulomb contribution to S'' and S_{eff}. The results are sensitive to the local geometry and presumably to the choice of repulsive parameters. Thus it is not too surprising that agreement with experiment is only fair. The values of S'' and S_{eff} for KCl lie slightly outside the broad ranges covered by the two models, and S' (which is dominated by the short-range repulsion) is too large by about a factor four.

Some of the discrepancies may be eliminated when lattice polarization and more up-to-date repulsive parameters are used. But others may result from local modifications of the repulsive interactions, the sort of effect proposed by Norgett and Stoneham from their analysis of V_k centre reorientation in CaF_2. One of the virtues of measuring $(L_{\parallel} - L_{\perp})$ is that it is sensitive to very localized effects like this, and so could be used to measure local changes in forces. A third possibility is that the discrepancy arises from the same unknown source which leads to apparently anomalous volumes of formation for isolated vacancies (Faux and Lidiard 1971). The anomalies occur only for the charged vacancies, not for their neutral analogue, the F centre (Lord and Stoneham 1974). This raises an obvious analogy with the present case, where discrepancies occur for the charged V_k centres and not for the neutral H centres.

4.2. H centres in NaCl and KCl

As for the V_k centres, the repulsive terms dominate in S'. But for the H centre, agreement with experiment is good. For KCl, S' is predicted as 0·94 and observed as 0·98 (Balzer *et al* 1973); S'' is predicted to be 0·43, and the measured value is 0·33. The success may be partly fortuitous, for we have used a very simple rigid-ion model for the repulsive terms. Nevertheless, it is gratifying accord, and it suggests that our analysis is basically sound.

5. Conclusions

We have calculated the Coulomb contributions to $(L_{\parallel} - L_{\perp})$ for H centres and V_k centres in ionic crystals. These have been supplemented by estimates of the other contributions in special cases to permit comparison with experiment. Very good agreement is found for H centres in KCl, with less satisfactory accord for V_k centres in KCl. The discrepancies are probably a result of simplifying assumptions about the short-range repulsions between ions near the defect. Since measurements of $(L_{\parallel} - L_{\perp})$ can show up such discrepancies in a particularly simple and conspicuous way, it is clear that measurements of length changes due to aligned defects can be a powerful method in analysing interatomic forces in crystals.

Appendix 1. Expressions for the length change and dipole tensor

Consider a density ρ of defects in a cubic crystal with nearest-neighbour distance a and elastic constants C_{ij}. If the defects are aligned along [001], then the length change is:

$$L_{\parallel} - L_{\perp} = \frac{e^2}{a} \frac{\rho}{C_{11} - C_{12}} S_0 \qquad (A1.1)$$

with

$$S_0 = \tfrac{1}{2} \sum_i (2F_{zi}R_{zi} - F_{xi}R_{xi} - F_{yi}R_{yi}). \qquad (A1.2)$$

For alignment along [110] we have

$$L_\parallel - L_\perp = \frac{e^2}{a}\left[\frac{\rho}{(C_{11} - C_{12})}\,S' + \frac{\rho}{C_{44}}\,S''\right] \tag{A1.3}$$

with

$$S' = \tfrac{1}{4}\sum_i (F_{xi}R_{xi} + F_{yi}R_{yi} - 2F_{zi}R_{zi}) \tag{A1.4}$$

$$S'' = \tfrac{3}{8}\sum_i (F_{xi}R_{yi} + F_{yi}R_{xi}). \tag{A1.5}$$

Balzer *et al* (1974) work with the dipole tensor in the NaCl structure, giving three components $(P_{\xi\xi}, P_{\eta\eta}, P_{\zeta\zeta}) = (P_{xx} + P_{xy}, P_{zz}, P_{xx} - P_{xy})$. The relation to the components above is

$$\frac{e^2}{a}\,S' = \tfrac{1}{2}(P_{xx} - P_{zz}) \tag{A1.6}$$

$$\frac{e^2}{a}\,S'' = \tfrac{3}{4}P_{xy} \tag{A1.7}$$

or, alternatively

$$S' = [\tfrac{1}{4}(P_{\xi\xi} + P_{\zeta\zeta}) - \tfrac{1}{2}P_{\eta\eta}]/[e^2/a] \tag{A1.8}$$

$$S'' = \tfrac{3}{4}(P_{\xi\xi} - P_{\zeta\zeta})/(e^2/a). \tag{A1.9}$$

Appendix 2. Displacements of ions near defects

The specific displacements used are listed here in the form:

(coordinates in perfect crystal) → (coordinates in defect crystal)

(i) V_k *centres in NaCl and KCl*
(a) Jette *et al* (1969) results.

	NaCl	KCl
$(\tfrac{1}{2}, \tfrac{1}{2}, 0) \rightarrow$	$(0\cdot364, 0\cdot364, 0)$	$(0\cdot333, 0\cdot333, 0)$
$(\tfrac{1}{2}, -\tfrac{1}{2}, 0) \rightarrow$	$(0\cdot627, -0\cdot627, 0)$	$(0\cdot644, -0\cdot644, 0)$
$(\tfrac{3}{2}, \tfrac{1}{2}, 0) \rightarrow$	$(1\cdot557, 0\cdot5, 0)$	$(1\cdot526, 0\cdot5, 0)$

(b) (Cl_2^-) in equilibrium $(2\cdot47\,\text{Å}$ separation), with other displacements scaled from Jette *et al* (1969).

	NaCl	KCl
$(\tfrac{1}{2}, \tfrac{1}{2}, 0) \rightarrow$	$(0\cdot31, 0\cdot31, 0)$	$(0\cdot285, 0\cdot285, 0)$
$(\tfrac{1}{2}, -\tfrac{1}{2}, 0) \rightarrow$	$(0\cdot644, -0\cdot644\ 0)$	$(0\cdot625, -0\cdot625, 0)$
$(\tfrac{3}{2}, \tfrac{1}{2}, 0) \rightarrow$	$(1\cdot539, 0\cdot5, 0)$	$(1\cdot546, 0\cdot5, 0)$

(ii) H centres in NaCl and KCl
(c) Dienes *et al* (1968) results

	NaCl	KCl
$(0, 0, 0) \rightarrow$	$(\pm 0.31, \pm 0.31, 0)$	$(\pm 0.285, \pm 0.285, 0)$ H centre ions
$(1, 1, 0) \rightarrow$	$(1.08, 1.08, 0)$	$(1.045, 1.045, 0)$ axial anions
$(2, 2, 0) \rightarrow$	$(2.025, 2.025, 0)$	$(2, 2, 0)$ axial anions
$(0, 1, 1) \rightarrow$	$(-0.010, 1.010, 1.010)$	$(0, 1, 1)$ anion
$(1, 0, 0) \rightarrow$	$(1.105, -0.05, 0)$	$(1.01, -0.095, 0)$ cation
$(1, -1, 0) \rightarrow (1, -1, 0)$		$(1.035, -1.035, 0)$ anion
$(1, 0, 1) \rightarrow$	$(1, 0, 1)$	$(1.01, -0.01, 1.01)$ anion

(iii) V_k centre in CaF_2
(d) Norgett and Stoneham (1973) results

$(0, 0, \frac{1}{2}) \rightarrow$	$(0, 0, 0.35)$	V_k ions
$(0, 0, \frac{3}{2}) \rightarrow$	$(0, 0, 1.43)$	axial anions
$(0, 1, \frac{1}{2}) \rightarrow$	$(0.015, 0.98, 0.50)$	anion
$(1, 1, \frac{1}{2}) \rightarrow$	$(1.021, 1.021, 0.509)$	anion
$(\frac{1}{2}, \frac{1}{2}, 0) \rightarrow$	$(0.577, 0.577, 0)$	cation
$(-\frac{1}{2}, \frac{1}{2}, 1) \rightarrow$	$(-0.518, 0.518, 1.012)$	cation

Note added in proof. It has been suggested (C P Flynn 1971 *Z. Naturf.* **26a** 99 and private communication) that the errors for volume changes for charged centres are an electrostriction effect involving volume derivatives of the static dielectric constant. Explicit calculations (M J Norgett) show that the shell models of Faux and Lidiard correctly reproduce the derivatives, so this plausible explanation cannot be correct.

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