# The Volumes of Formation of Schottky Defects in Ionic Crystals *

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In this paper we calculate the volumes and energies of formation of Schottky defects in the alkali halides NaCl, NaBr, KCl and KBr. Both the polarisable point-dipole and a simple shell model are evaluated. The calculation uses a generalised and extended Mott-Littleton approach in conjunction with results derived previously by the lattice statics method of Kanzaki. The polarisable point-dipole model, as might be expected, is bad, but the shell model leads to good values for the Schottky formation energies, which not only compare well with experiment but are insensitive to the size of the region ('region I') around the defect for which the lattice displacements are computed explicitly (i. e. as distinct from the outer Mott-Littleton region, 'region II'). The predicted volumes of formation of Schottky defects are less than the molecular volume, $v_m$, i. e. the volumes of relaxation are negative (NaCl, $-0.69\,v_m$; NaBr, $-0.73\,v_m$; KCl, $-0.52\,v_m$; KBr, $-0,51\,v_m$ in the static lattice approximation). This is in conflict with the results of experiments on the effect of pressure upon the ionic conductivity of these crystals although some other experimental data are consistent with negative relaxation volumes. The disagreement is briefly discussed and the possibility that temperature effects are greater than is implied by the quasi-harmonic model is noted as a possible explanation.

## § 1. Introduction

In non-ionic solids, such as metals, valence crystals and solid inert gases, theory and experiment appear to agree that the elastic relaxation associated with vacancies is inwards (conventionally negative), thus leading to a volume of formation less than the corresponding atomic volume. Another well-known consequence of this inward relaxation is that the lattice parameter of such solids containing vacancies is less than that of the corresponding perfect solid.

In ionic crystals the situation is not quite so clear. Thus a number of detailed calculations of the lattice relaxation and polarisation around ionic vacancies have been made [1] and these agree that the displacements of the nearest neighbours to the vacancy are generally outwards. It has thus often been assumed that the presence of vacancies in an ionic lattice will lead to an increase of volume and an increase in lattice parameter. However, this outward relaxation of nearest neighbours is mainly a polarisation effect, the sense of relaxation of an ion being principally determined by its charge. It is thus not obvious what the aggregate effect on the lattice parameter and lattice volume of these alternating displacements will be.

Experimentally there are indications of both positive and negative volume and lattice parameter changes on forming vacancies. Thus some of the early radiation damage studies on LiF led to the inference of a net contraction [2]. More recent work [3] on MgO, agrees with this and sets the associated volume change per Schottky pair of vacancies in the range 0.2 to 0.4 of the molecular volume $v_m$. In addition, PICK and WEBER [4] had earlier shown by density measurements that there was a net contraction of the lattice of KCl on doping with $CaCl_2$ and $SrCl_2$. Of course, in these studies not only cation vacancies but also divalent cations are added to the latice, but the effects may be somewhat similar to those caused by adding anion and cation vacancies together. The volume changes which the PICK and WEBER measurements gave were $\Delta V = -0.11\,v_m$ for

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[1] See, e. g., the review by L. W. BARR and A. B. LIDIARD, Physical Chemistry, an Advanced Treatise, Vol. X, Academic Press, New York 1970, p. 151.

[2] See D. S. BILLINGTON and J. H. CRAWFORD, Radiation Damage in Solids, University Press, Princeton 1961, p. 290 et seq.

[3] B. S. HICKMAN and D. G. WALKER, Phil. Mag. **11**, 1101 [1965].

[4] H. PICK and H. WEBER, Z. Phys. **128**, 409 [1950].

$CaCl_2$ and $\Delta V = -0.08\, v_m$, for $SrCl_2$, per molecule added. In contrast to these results indicating contractions, experiments on the effect of pressure on the ionic conductivity of several alkali halides in both the intrinsic and extrinsic regions[5–8] yield volumes of formation of Schottky defects greater than $v_m$, i. e. a net expansion due to the lattice relaxation around the vacancies. This was also inferred to be true for anion vacancies from some experiments studying directly the volume change occurring in $U \rightarrow \alpha$ colour centre conversions[9].

In this situation it seems important to attempt a reliable theoretical analysis. Previously published attempts to evaluate the elastic strengths of vacancies and thus the associated volume changes have been based on elementary intuitive ideas[10, 11] and are, we believe, misleading. As the basis of our calculations we use instead an analysis derived from the method of KANZAKI[12]. This analysis is a revision of that given previously by HARDY and LIDIARD[13]. We show how the results of this analysis can be incorporated into an extended Mott-Littleton calculation to yield both defect energies and volumes of relaxation. In this paper we present the results of such detailed calculations for four alkali halides, viz. NaCl, NaBr, KCl and KBr, for which we use two different models (a) the polarisable point-dipole model and (b) a simple shell model. Both agree in predicting negative relaxation volumes, i. e. contraction of the lattice, but only the shell model gives acceptable defect energies. As has been noted before, the polarisable point-dipole model considerably overestimates the polarisation energy (a negative term) and thus leads to Schottky energies which are far too low. The shell model energies, however, agree well with experiment. This agreement lends force to our prediction of negative relaxation volumes for vacancies in these substances.

## § 2. General Theory for an Ionic Crystal

The general theory relating the details of the forces and displacements around a point defect to the macroscopic volume change and lattice parameter change for an assembly of point defects has been discussed by a number of authors[12–15]. A discussion of these relations for vacancies in ionic crystals in particular was given by HARDY and LIDIARD[13], but unfortunately was not correct in some particulars. In the present section we correct the omissions of that previous discussion (hereafter referred to as H. L.) and show how the results can be incorporated into detailed numerical calculations, e. g., of the generalised Mott-Littleton kind. It is not necessary to repeat all the details of the previous derivations and it will be sufficient to limit ourselves here simply to a statement of corrections and additions to the previous arguments.

### *2.1. Elastic Strengths and Volume Changes*

The most important correction is that to the form assumed for $X$, the term in the energy of the defect solid expressing the interaction of the defect with the (perfect) lattice. It will be recalled that, following KANZAKI[12], the potential energy of the defect solid was written as

$$W = X + Y(\xi, \mu), \tag{1}$$

where $Y(\xi, \mu)$ is the potential function for the perfect lattice ($\xi$ standing for the ion displacements and $\mu$ for the electronic moments) and $X$ stands for all the remaining terms, i. e. for the defect-lattice interactions. Explicit expressions for $X$ for the polarisable point-dipole model, for example, are obtainable from the paper by BOSWARVA and LIDIARD[11]. From these or otherwise it will be seen that the discussion by HARDY and LIDIARD[13] [their Eq. (2.13) et seq] omits the term in $X$ corresponding to the electrostatic interaction of the effective charge on the vacancy with the dipoles, $\boldsymbol{\mu}$, on the ions of the lattice. The correct expression for $X$ is thus

$$X = -\sum_{l,k} \Phi\left(\left|\boldsymbol{R}\binom{l}{k} + \boldsymbol{\xi}\binom{l}{k}\right|\right) + q_0 \sum_{l,k} \frac{\boldsymbol{\mu}\binom{l}{k} \cdot \left(\boldsymbol{R}\binom{l}{k} + \boldsymbol{\xi}\binom{l}{k}\right)}{\left|\boldsymbol{R}\binom{l}{k} + \boldsymbol{\xi}\binom{l}{k}\right|^3}, \tag{2}$$

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[15] V. K. TEWARY, A.E.R.E. Report TP. 388 [1970].

where $q_0$ is the charge on the ion which was removed to form the vacancy and $\boldsymbol{\xi}\binom{l}{k}$ specifies the vector displacement of the ion originally at the lattice site $\boldsymbol{R}\binom{l}{k}$. Here $l$ is the cell index, while $k=1$, 2 specifies the particular ion in the cell, cation or anion. It follows that there is an additional term in $\boldsymbol{T}_\xi$ of the form

$$-\nabla_{\boldsymbol{\xi}} X = -q_0 \nabla_{\xi} \left( \frac{\boldsymbol{\mu} \cdot (\boldsymbol{R} + \boldsymbol{\xi})}{|\boldsymbol{R} + \boldsymbol{\xi}|^3} \right). \tag{3}$$

This term must be added to Eqs (2.14) und (3.1) of H. L.

The analysis for the long-range elastic distortion around the vacancy then follows the same path as before (but with the addition of the extra term to H. L. Eq. (3.3)] and the expression for the elastic strength of the equivalent point defect becomes

$$G = \sum_{l,k} R\binom{l}{k}_\alpha \frac{\partial}{\partial \xi \binom{l}{k}_\alpha} \Phi\left(\boldsymbol{R}\binom{l}{k} + \boldsymbol{\xi}\binom{l}{k}\right) - q_0 \sum_{l,k} R\binom{l}{k}_\alpha \frac{\partial}{\partial \xi \binom{l}{k}_\alpha} \left\{ \frac{\boldsymbol{\mu}\binom{l}{k} \cdot \left(\boldsymbol{R}\binom{l}{k} + \boldsymbol{\xi}\binom{l}{k}\right)}{\left|\boldsymbol{R}\binom{l}{k} + \boldsymbol{\xi}\binom{l}{k}\right|^3} \right\}. \tag{4}$$

where, as before, $\Phi\left(\boldsymbol{R}\binom{l}{k} + \boldsymbol{\xi}\binom{l}{k}\right)$ is the potential of interaction of the ion at the displaced position $\boldsymbol{R}\binom{l}{k} + \boldsymbol{\xi}\binom{l}{k}$ with the ion at the origin which was removed to form the vacancy. An exactly equivalent expression holds for the shell model. For defects other than vacancies $-\Phi$ would be replaced by the actual potential of interaction with the defect. However, in the case of the vacancy a simplification of the above expression for $G$ is possible, firstly, by expanding in powers of $\boldsymbol{\xi}$ and, secondly, by making use of the condition of lattice stability. For a static lattice ** the necessary condition is that the potential function $Y$ be minimal at the observed lattice spacing, $r_0$ (zero external pressure). Thus to first order in $\xi$, $\mu$

$$G = \tfrac{1}{3} \sum_{l,k} \left\{ R\binom{l}{k}\, \Phi'\left(R\binom{l}{k}\right) + \boldsymbol{R}\binom{l}{k} \cdot \boldsymbol{\xi}\binom{l}{k}\, \Phi''\left(R\binom{l}{k}\right) \right\} + \frac{2\,q_0}{3} \sum_{l,k} \frac{\boldsymbol{R}\binom{l}{k} \cdot \boldsymbol{\mu}\binom{l}{k}}{R\binom{l}{k}^3} \equiv G^{(0)} + G^{(1)}. \tag{5}$$

To embody the lattice stability condition we separate $\Phi$ into Coulombic and non-Coulombic terms ($\Phi_{\mathrm{C}}$ and $\Phi_{\mathrm{NC}}$ respectively) and make use of the special nature of Coulomb forces. The result is that the zero-order term in (5) becomes

$$G_1{}^{(0)} = \tfrac{1}{6} \left\{ \sum_l{}^{(1)} R^{(1)}\binom{l}{1}\, \Phi'_{\mathrm{NC}}\left(R^{(1)}\binom{l}{1}\right) - \sum_l{}^{(2)} R^{(2)}\binom{l}{2}\, \Phi'_{\mathrm{NC}}\left(R^{(2)}\binom{l}{2}\right) \right\}, \tag{6}$$

for a positive ion vacancy (1), with a corresponding expression for $G_2{}^{(0)}$ $(=-G_1{}^{(0)})$. The symbol $\boldsymbol{R}^{(1)}\binom{l}{1}$ specifies the position of the cation in cell $l$ relative to a central cation (cell 0) while $R^{(2)}\binom{l}{2}$ is the position of the anion in cell $l$ relative to a central anion (cell 0). For Schottky defects in a static lattice therefore $G_1{}^{(0)} + G_2{}^{(0)} = 0$, the analogue of the result $G^{(0)} = 0$ for a monatomic static lattice in equilibrium. However, for an ionic crystal $G_1{}^{(0)}$ and $G_2{}^{(0)}$ are not separately zero (although they are very small) unless the non-Coulombic interactions do not extend beyond nearest neighbours.

For a quasi-harmonic lattice in thermal equilibrium at zero pressure and temperature $T$ one may extend the above argument to obtain an additional term on the r.h.s. of (6) of $6\,\gamma\,k\,T/v_{\mathrm{m}}$ where $\gamma$ is the average Grüneisen constant ($\sim 1.5$ for alkali halides) and $k$ is Boltzmann's constant. If the displacements and moments of the ions surrounding the vacancies are known we may thus calculate their elastic strengths $G_1$ and $G_2$ from (5) and (6).

The corresponding macroscopic volume changes are simply related to the strengths, $G$. The argument is basically that given in H. L. Appendix II. Firstly, the volume change $\Delta V$ on creating the defect and allowing the lattice to relax and polarise is

$$\Delta V = -\frac{r_0\,\varkappa}{6} \frac{\partial X}{\partial r_0} \tag{7}$$

where $\varkappa$ is the isothermal compressibility and $r_0$ is the anion-cation lattice constant. This is true for harmonic lattices, both static and in thermal equilibrium, provided only that the small changes in $\varkappa$ and $\gamma$ caused by the defect can be neglected. By inserting the correct expression for $X$ we then obtain

$$\Delta V_{1,2} = \varkappa\, G_{1,2}\,. \tag{8}$$

It should be noted that his expression includes the Eshelby term in the lattice dilatation resulting from the tractions exerted on the surface of the solid by the defect [12].

### 2.2. Extension of Mott-Littleton Method

The term (2) which was omitted from $X$ by HARDY and LIDIARD [13] does not affect the expressions which they deduced for the limiting polarisation of the lattice and which thus confirmed and extended the Mott-Littleton approach. The reason is

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** The changes required for a quasi-harmonic lattice in thermal equilibrium are noted below.

that the omitted terms in the transformed forces $F_1 - F_2$ are $O(\boldsymbol{q})$ at small $\boldsymbol{q}$ and are thus quite unimportant compared to the dominant Coulomb part which is $O(1/q)$.

We are therefore now in a position to extend the Mott-Littleton method so that it provides values for the volumes $\Delta V_1$, $\Delta V_2$ and thus $\Delta V_S$, which can be compared directly with experiment. In this method we divide the defect lattice into two regions, I and II. The inner region I contains the defect and a number of neighbouring ions. The energy function of the solid is minimised explicitly with respect to the displacements and polarisation parameters of the ions in this inner region. The displacements and the polarisation of ions in the other region II are assumed to have the limiting forms corresponding to continuum behaviour. These limiting forms are, for the polarisation, those obtained in H. L. § 3.2 and, for the elastic component of the displacement, that appropriate to a point defect of strength $G$. Unfortunately, for a cubic solid there is, in general, no simple expression for this second term, although for an elastically isotropic solid the well known expression

$$\boldsymbol{\xi}_{\text{elas}} = \frac{G}{4\pi c_{11}} \frac{\boldsymbol{R}}{R^3} \tag{9}$$

may be used. In general the method of LIE and KOEHLER[16] could be applied. We can now evidently proceed to a self-consistent Mott-Littleton calculation using the M. L. forms, including $\boldsymbol{\xi}_{\text{elas}}$, in the expression for $G$. This then gives $G$ in terms of the region I displacement and moments and certain lattice sums over region II. The resulting $\boldsymbol{\xi}_{\text{elas}}$ is then used in the energy function (for the I – II interaction terms) when it is minimised w.r.t. the region I parameters.

In practice the major contributions to $G$ come from the electrical terms in (5). This can be seen from the terms $G^{(1)}$ in (5). Firstly the electrical component of displacement, $\boldsymbol{\xi}_{\text{elec}}$, and the dipole moment, $\boldsymbol{\mu}$, fall off rather slowly as $R^{-2}$ and, although $\boldsymbol{\xi}_{\text{elec}}$ alternates in sign as we go from positive to negative ion so does $\Phi_C''$, with the result that the displacement dipole term $\boldsymbol{R} \cdot \boldsymbol{\xi}_{\text{elec}} \, \Phi_C''$ is of exactly the same form as the electronic dipole term. Both make negative contributions to $G$ proportional to the lattice sum $\Sigma\, R^{-4}$ taken over both positive and negative ions. By contrast $\boldsymbol{R} \cdot \boldsymbol{\xi}_{\text{elas}} \, \Phi_C''$ gives terms of alternating sign so that this contribution is much less. Although far from accurate for the alkali halides we have therefore used (9) to express $\boldsymbol{\xi}_{\text{elas}}$ in terms of $G$ and $R$. In practice, it makes little difference to $G$ if we omit $\boldsymbol{\xi}_{\text{elas}}$ altogether.

## § 3. The Model and Method of Computation

We have used both a polarisable point-dipole model and a simple shell model (anions only polarisable) fitted to empirical room temperature data. For both, the detailed calculations have been carried out in the static lattice approximation, although as we show below the correction for thermal motion is easily incorporated in the quasi-harmonic approximation. For the polarisable point-dipole model we have fitted to the lattice parameter (nearest neighbour separation, $r_0$) and the compressibility $\varkappa$ in the usual way. (The data we used was that compiled by FUMI and TOSI[17], the first set in their Table 1.) As in other Mott-Littleton calculations (e. g. TOSI and DOYAMA[18] and BOSWARVA and LIDIARD[11] the ions are assumed to interact through (i) Coulomb forces, (ii) closed-shell overlap repulsions and (iii) dipole-dipole and dipole-quadrupole Van der Waals terms. For (ii) we have taken the expression

$$b\, c_{ij} \cdot \exp\{r_i + r_j - r)/\varrho\} \tag{10}$$

where $c_{ij}$ is the conventional Pauling factor and $r_{\text{i}}$ is the radius of ion i. For ionic radii we use the values given by TOSI and FUMI[19] in their Table 4 ("generalised Huggins-Mayer form"). The parameters $b$ and $\varrho$ are determined by using the lattice stability condition at $r_0$ and fitting the compressibility, $\varkappa$. The coefficients of the Van der Waals interactions are those given by MAYER[20]. To represent the electronic polarisation of the ions we have used the polarisabilities determined by TESSMAN, KAHN and SHOCKLEY[21] and to evaluate the Mott-Littleton polarisation and displacement coefficients we have additionally used the (room temperature) dielectric constants given by HAUSSÜHL[22].

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For the shell model we assumed that the non-Coulombic interactions between different ions were via shell-shell interactions only and in addition to first-neighbour (cation-anion) interactions we assumed second neighbour interactions between the anions (but not between cations). Both these interactions were assumed to have the simple Born-Mayer form, $A_{+-} \exp\{-r/\varrho\}$ and $A_{--} \exp\{-r/\varrho\}$ respectively. The ions were assumed to have the full net ionic charge of $(\pm e)$, but, in addition, the anions were allowed to be polarisable by assigning them a shell charge, and an internal core-shell spring constant. The cation polarisability was neglected. These five parameters $A_{+-}$, $A_{--}$, $\varrho$ the shell charge and the core-shell spring constant were obtained by fitting the model to $r_0$ (Ref. [17]), the static dielectric constant, $\varepsilon_0$ (Ref. [22]), the limiting high frequency dielectric constant $\varepsilon_\infty$ (Ref. [21]) and the elastic constants $c_{11}$ and $c_{12}$ (Ref. [23], Table VI). Although this is a rather simplified shell model, it should be noted that SZIGETI effective charges [24] calculated from it are in most cases *** in good agreement ($\sim 2\%$) with empirical values obtained from $\varepsilon_0$, $\varepsilon_\infty$ and the Restrahlen frequency $\omega_0$.

The equilibrium distortion of the lattice around the vacancy was determined by minimising the appropriate energy function. For the polarisable point-dipole model we used the general expression (2.3) of BOSWARVA and LIDIARD [11] which gives the energy as a function of the displacements, $\boldsymbol{x}$, of the inner region I – the electronic moments, $\boldsymbol{m}$, in region I and the moments, $\boldsymbol{\mu}$, and displacements, $\boldsymbol{\xi}$, in the outer region II having been determined (for each $x$). Of course, for region II $\boldsymbol{\mu}$ and $\boldsymbol{\xi}$ are taken from the generalised Mott-Littleton approach proposed in § 2. We note that the energy function thereby depends on the elastic strength, $G$, of the defect through the polarisation energy of region II [term 4 on the r.h.s. of Eq. (2.3) of BOSWARVA and LIDIARD [11]] and through the non-Coulombic interaction energy between regions I and II (terms 5 and 6). In addition the moments $\boldsymbol{m}$ on the region I ions are very slightly dependent on $G$ through the field which the region II displacements generate. The computational procedure is therefore as follows. For specified region I displacements $\boldsymbol{x}$, we first find $\boldsymbol{m}$ by solving the field equations (except for the small perturbation of $\boldsymbol{m}$ by $G$ which we evaluate separately). Having obtained $\boldsymbol{m}$ and knowing $\boldsymbol{\mu}$ and $\boldsymbol{\xi}$ in region II we evaluate $G$ by (5) and hence the remaining terms in the energy. The minimisation of the energy, $W$, with respect to $\boldsymbol{x}$ was carried out by a direct search procedure due to POWELL [25]. $W$ is minimised along directions which are progressively updated until they form a set of mutually orthogonal directions with respect to the matrix of second derivatives of $W$.

The program used in this work can be simply modified so as to evaluate defect energies in the usual Mott-Littleton approach ($\boldsymbol{\xi}_{\text{elas}} = 0$) and was, in fact, so applied in order to check it against another program developed by NORGETT [26] in another connection. In Norgett's program the energy function is minimised with respect to the region I parameters $\boldsymbol{x}$ and $\boldsymbol{m}$ before the (presumed) equilibrium values of $\boldsymbol{\xi}$ and $\boldsymbol{\mu}$ are inserted, but the two procedures are exactly equivalent when $\boldsymbol{\xi}$ and $\boldsymbol{\mu}$ are known accurately. In addition, the minimisation is obtained by a modified Newton-Raphson technique which is faster ($\sim 10$ times faster) but requires more core storage and is thus not suitable for smaller computers. For the sizes of region I investigated [all ions out to $(3, 0, 0)\, r_0$] the two predicted Schottky energies were always within 0.05 eV of one another. This good agreement thus supplies an independent check on the program.

For the shell model the expressions for the energy function [Eq. (2.3) of BOSWARVA and LIDIARD] and the elastic strength [Eq. (5) et seq] are modified but as these generalisations are fairly obvious we shall not give them explicitly here. In this case we took an analogous approach and minimised the energy function with respect to core displacements, $\boldsymbol{x}$, and shell displacements, $\boldsymbol{y}$, again using Powell's method.

## § 4. Results

Tables 1 – 4 gives the results obtained for both the Schottky formation energies $W_{\text{S}}$ and the corresponding volumes of relaxation $\Delta V$ on formation of

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[23] H. B. HUNTINGTON, Solid State Physics **7**, 213 [1958].

[24] B. SZIGETI, Proc. Roy. Soc. London A **204**, 51 [1950].

*** Excepting NaF, KF and Rb halides where since the polarisabilities $\alpha$ are such that $\alpha_+ > \alpha_-$, it is obviously wrong to set $\alpha_+ = 0$.

[25] M. J. D. POWELL, Computer Journal **7**, 155 [1964].

[26] M. J. NORGETT, A.E.R.E. Report TP. 412 [1970]; J. Phys. C. (in press); also M. J. NORGETT and R. FLETCHER, J. Phys. C. **3**, L 190 [1970].

Table 1. Values of the Schottky formation energy, $W_S$, and vacancy relaxation volumes (both separately, $\Delta V_+$ and $\Delta V_-$, and together $\Delta V_S$) for four alkali halides as calculated from the polarisable point-dipole model using a region I containing only the nearest neighbours of the vacancies. Corresponding experimental values are obtained from the references given.

| Substance | $W_S$(eV) | $W_S$(expt) (eV) | $\Delta V^+/v_m$ | $\Delta V^-/v_m$ | $\Delta V_S/v_m$ | $\Delta V_S$(expt)$/v_m$ |
|---|---|---|---|---|---|---|
| NaCl | 1.560 | 2.18 – 2.50 (Ref. [1, 28]) | – 0.526 | – 0.423 | – 0.949 | 0.45 – 0.8 (Ref. [5, 7, 8]) |
| NaBr | 1.368 | 1.72 (Ref. [1]) | – 0.555 | – 0.432 | – 0.987 | 0.2 (Ref. [1]) |
| KCl | 1.869 | 2.26 – 2.59 (Ref. [1, 28, 29]) | – 0.404 | – 0.297 | – 0.701 | 0.5 – 0.6 (Ref. [5, 8]) |
| KBr | 1.757 | 2.30 – 2.53–(Ref. [1]) | – 0.399 | – 0.275 | – 0.674 | 0.1 (Ref. [1]) |

Table 2. Values of the Schottky formation energy, $W_S$, and of relaxation volumes for a polarisable point-dipole model of NaCl, showing the effect on the calculated values of enlarging region I to include successively more shells of neighbours of the vacancy.

| Shells included in region I | $W_S$(eV) | $\Delta V^+/v_m$ | $\Delta V^-/v_m$ | $\Delta V_S/v_m$ |
|---|---|---|---|---|
| (100) | 1.560 | – 0.526 | – 0.423 | – 0.949 |
| (100), (110) | 1.651 | – 0.538 | – 0.449 | – 0.987 |
| (100), (110), (111) | 1.640 | – 0.542 | – 0.448 | – 0.990 |
| (100), (110), (200) | 1.393 | – 0.634 | – 0.401 | – 1.035 |
| (100), (110), (200) (300) | 1.189 | – 0.675 | – 0.394 | – 1.069 |
| (100), (110), (200) (300), (400) | 1.082 | – 0.694 | – 0.395 | – 1.089 |

Table 3. Values of the Schottky formation energy, $W_S$, and vacancy relaxation volumes for four alkali halides as calculated from the simple shell model described in § 3. We note the good agreement between calculated and observed values of $W_S$. Only the nearest neighbours of the vacancy are included in region I but for this model the results are very insensitive to the size of this region (Table 4).

| Substance | $W_S$(eV) | $W_S$(expt) (eV) | $\Delta V^+/v_m$ | $\Delta V^-/v_m$ | $\Delta V_S/v_m$ | $\Delta V_S$(expt)$/v_m$ |
|---|---|---|---|---|---|---|
| NaCl | 2.227 | 2.18 – 2.50 (Ref. [1, 27]) | – 0.382 | – 0.304 | – 0.686 | 0.45 – 0.8 (Ref. [5, 7, 8]) |
| NaBr | 2.001 | 1.72 (Ref. [1]) | – 0.429 | – 0.300 | – 0.729 | 0.2 (Ref. [8]) |
| KCl | 2.341 | 2.26 – 2.59 (Ref. [1, 28, 29]) | – 0.344 | – 0.176 | –0.520 | 0.5 – 0.6 (Ref. [5, 8]) |
| KBr | 2.247 | 2.30 – 2.53 (Ref. [1]) | – 0.324 | – 0.181 | – 0.505 | 0.1 (Ref. [8]) |

Table 4. Values of the Schottky formation energy, $W_S$, and of relaxation volumes for the simple shell model of NaCl, showing the insensitivity of the predictions to the size of region I.

| Shells included in region I | $W_S$(eV) | $\Delta V^+/v_m$ | $\Delta V^-/v_m$ | $\Delta V^-/v_m$ |
|---|---|---|---|---|
| (100) | 2.227 | – 0.382 | – 0.304 | – 0.686 |
| (100), (110) | 2.254 | – 0.399 | – 0.312 | – 0.711 |
| (100), (110), (111) | 2.259 | – 0.397 | – 0.316 | – 0.713 |
| (100), (110), (200) | 2.270 | – 0.391 | – 0.283 | – 0.674 |
| (100), (110), (200) (300) | 2.236 | – 0.396 | – 0.277 | – 0.673 |
| (100), (110), (200) (300), (400) | 2.235 | – 0.391 | – 0.277 | – 0.668 |

the vacancies. The volume of formation of Schottky defects is obtained by adding $v_m$ to the values of $\Delta V_S$ given, corresponding to putting the extracted ions back on the surface of the crystal. Table 1 gives results for the polarisable point-dipole model of NaCl, NaBr, KCl and KBr when region I includes only the nearest neighbours of the vacancies. All the calculated $W_S$ are $\sim 25\%$ lower than the experimental values – a feature which has been noted in previous calculations with this model [1]. However this error in $W_S$ becomes even larger when region I is expanded as shown by the results in Table 2 for NaCl. The reason seems fairly obvious. The polarisable point-dipole model predicts too large a static dielectric constant [1, 24] and thus too large a polarisation in region I. (In the Mott-Littleton region II, $\varepsilon_0$ is, of course, given its empirical value.) Thus, as region I increases in size, the calculated energy falls towards a limit which corresponds to a crystal with a much higher dielectric constant than the real substance. We would thus not expect the volumes predicted by this model to have more than a qualitative significance.

However, when we turn to the shell model the picture is rather different. Firstly, not only are the values of $W_S$ calculated for a region I containing just first neighbours in quite fair agreement with experiment (Table 3) but, secondly, these values appear to be quite stable against the enlargement of region I (Table 4). This second feature is, of course, what we would expect since the shell model is fitted to the dielectric constant – as long as our method of calculation is accurate. Which it thus appears to be. Thus we believe that the values of $\Delta V_S$ predicted by this model are physically significant.

## § 5. Discussion

As we have previously commented the negative values of $G$ and thus $\Delta V_S$ result from the long range of the Coulomb field of the vacancy acting on the ions of the lattice, coupled with the equally slow decrease in induced moments (both $q\xi$ and $\mu$) with distance. Thus the negative values of $\Delta V_S$ appear to be a rather general consequence of all models of ionic vacancies. (The same conclusion would not follow for interstitials since for them the lattice stability condition does not lead to the cancellation of the zero order terms, $G^0$, which in that case would be large and positive.) Although this conclusion is in agreement with some experimental results [2–4] it disagrees with the, in principle, more direct determinations of $\Delta V_S$ obtained from measuring the effect of pressure upon ionic conductivity, as is shown in Tables 1 and 2. We are puzzled by this conflict, especially since, in the case of the shell model, all the other indications are that the calculations and the model describe the defect solid well. The gap between the theoretical and experimental values of $\Delta V_S$ is narrowed a little if we correct the static lattice values given above for thermal motion using the Grüneisen approximation. This leads to the additional term in $\Delta V_S/v_m$ of $12\gamma k T/v_m$ or, since we have fitted our static model to room temperature, data, $12\gamma k(T-T_{\text{r.t.}})/v_m$. For $T-T_{\text{r.t.}}=700$ °K we then get additional *positive* terms in $\Delta V_S/v_m$ as follows: NaCl, 0.154; NaBr, 0.169; KCl, 0.143 and KBr, 0.156. It is possible, though perhaps not very likely that the quasi-harmonic approximation substantially underestimates this temperature term. However, if this were the case it might remove some of the conflict between the positive relaxation volumes inferred from high temperature conductivity measurements [6–8] and the negative relaxation volumes inferred from room temperature measurements on irradiated and annealed LiF[2] and MgO[3]. It is clearly necessary to make further calculations of other defect volumes by the present methods in order to test the validity of the models further.

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