A Born model calculation of the energies of vacancies, ion interstitials and inert gas atoms in calcium fluoride

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Abstract. We have used the Born model to calculate the energy of vacancies and ion interstitials in calcium fluoride. We have calculated the energy of inert gas interstitials and the activation energy for gas diffusion. Values for the binding energy of the gas into vacancies suggest that there may be a slight modification of the diffusion due to gas trapping. All the calculations were performed by minimizing the energy with respect to the displacements and dipoles of ions in a relatively large region (15–20 shells) surrounding the defect. A new numerical method used in the calculation of the relaxation is ten or twenty times faster than conventional minimization methods.

1. Introduction

Norgett and Lidiard (1968) successfully calculated the activation energies for the migration of inert gas atoms in the alkali halides by using the Born model for the ionic crystal and by postulating reasonable forms for the unknown ion–inert gas interaction. Their interpretation emphasized the importance of the trapping of the inert gas into vacancies. At low temperature, the occurrence of these vacancies is a consequence of the neutron irradiation used to generate the inert gas. At higher temperatures, the concentration of Schottky vacancies in the alkali halides at thermal equilibrium is sufficient to modify the observed diffusion. The importance of trapping means that it is possible to make certain definite predictions about the effect of doping the crystal with divalent cations, which alters the vacancy concentration. These predictions have been confirmed by recent experiments of Felix and Müller (1970, private communication) who also demonstrated that doping the crystal has related effects on the electrical conductivity and rare gas diffusion in certain alkali halides.

In part, the motivation for both the experimental and theoretical study of inert gas diffusion in ionic solids is the technological importance of the release of fission gas from ceramic nuclear fuels. The alkali halides are studied as models of the uranium carbide system while the alkali earth fluorides are perhaps more realistic models for uranium dioxide.

Norgett and Lidiard (1969) have previously reported preliminary calculations for the alkaline earth–inert gas systems CaF_2/Ar, SrF_2/Kr and BaF_2/Xe. Unfortunately, these were based on an incorrect potential for the ionic crystals contained in unpublished work of Birtwistle (1967). Even if these errors are corrected, it seems that there is no straightforward way of deriving a satisfactory interaction potential of the simple Born–Mayer type for this class of materials. Thus, while Benson and Dempsey (1962) have used the properties of all the alkaline earth fluorides to obtain a set of ionic radii for use in a simple exponential repulsive potential, Franklin (1968) has found that a more rigorous attempt to fit parameters to the elastic constants of each fluoride separately leads to certain difficulties. In particular, the fluoride–fluoride interactions, which should, in the spirit of the Born model, be equal, in fact vary considerably and are even attractive for BaF_2. We have confirmed Franklin's observations and extended his work by including Van der Waals interactions between the ions but the same difficulties remain.

However, for CaF_2 there is a reasonably convincing description of the ionic interactions in terms of a Born model. Also, Franklin (1968) has calculated the energies of vacancies

and interstitial defects for this substance with considerable success, even though the calcu-
lations employ only restricted explicit relaxations of ions about the defect. In consequence,
we report a set of results calculated for CaF$_2$ alone. We have calculated the various energies
of the argon interstitial needed to predict the diffusion of the inert gas atom. We have
calculated the energy of the anion and cation vacancy allowing extensive relaxation of the
crystal about the defect. In addition, we have computed the binding energies of the inert
gas into each vacancy. Finally, in order to estimate the energies of the intrinsic Schottky
and Frenkel defects, we have calculated the energies of the interstitial ions of both types.

The calculation of the relaxation and polarization about the defect is a lengthy computa-
tion if normal minimization procedures are applied to calculate the configuration of the
crystal corresponding to the lowest energy. We have developed a method based on the
use of a restricted response matrix for the crystal. This is used as a starting point for an
iterative minimization procedure which employs the principle of the variable metric
algorithm developed by Fletcher and Powell (1963). In this way the computation time
for these relaxation calculations is reduced by a factor of between ten and twenty compared
to more usual methods. The calculated activation energies for inert gas migration agree
reasonably well with the results of Felix (1970). Also the Schottky and Frenkel energies
are similar to the values calculated by Franklin (1968) and both results agree reasonably
well with the experimental value of the Frenkel energy measured by Ure (1957).

2. Calculation

In all these calculations, the approach is to consider explicitly some limited region about
the defect. The ions interact by Coulomb forces and in addition at short distances, repel
each other because of the overlap of their electronic charge clouds. Van der Waals interac-
tions are also included. In addition, a point dipole is associated with each ion. The dis-
placements and dipoles of each ion in the region are treated as independent variables in
the minimization scheme. The lattice symmetry about the defect is preserved.

If the defect has no net charge (e.g. the inert gas interstitial) then the distorted region
(region I) is surrounded by an infinite region of perfect crystal. The fact that the defect is
an elastic singularity which causes distortions of the crystal which fall off only slowly
away from the defect is ignored. The repulsive interactions, being short range, are calclated
explicitly as a function of the displacements and the formation energy of the defects only
involves ions in region I and its immediate environment. The long range Coulomb inter-
actions are best expressed as a contribution arising from the interaction of each displaced
ion in region I with a perfect lattice, calculated by Ewald's method, and the interactions
of ions and compensating charges of opposite sign in the distorted region.

For the charged defects, the region outside the immediate neighbourhood of the defect
is treated in the approximation of Mott and Littleton (1938) using a method of calculation
due to Boswarva and Lidiard (1967). Boswarva and Lidiard divided the crystal into two
regions, as we do. Then they expressed the energy in four parts, the formation energy of
the defect in a rigid lattice, the relaxation energy of region I, the interaction of the two
regions and the relaxation of the outer region II. Using X and M to denote coordinates
and dipoles in region I and ξ and μ to apply in the same way to the outer region, then

$$W = W_1 + W_2(X, M) + W_3(X, M, \xi, \mu) + W_4(\xi, \mu). \tag{2.1}$$

If the outer region is treated only in second order, then at equilibrium

$$\left. \frac{\partial W}{\partial \xi_i} \right|_{\xi_i = \bar{\xi}_i} = \left. \frac{\partial W_3}{\partial \xi_i} \right|_{\xi_i = \bar{\xi}_i} + \sum_j \left. \frac{\partial^2 W_4}{\partial \xi_i \partial \xi_j} \right|_{\xi_i, \xi_j = 0} \bar{\xi}_j + \sum_j \left. \frac{\partial^2 W_4}{\partial \xi_i \partial \mu_j} \right|_{\xi_i, \mu_j = 0} \bar{\mu}_j$$

$$\left. \frac{\partial W}{\partial \mu_i} \right|_{\mu_i = \bar{\mu}_i} = \left. \frac{\partial W_3}{\partial \mu_i} \right|_{\mu_i = \bar{\mu}_i} + \sum_j \left. \frac{\partial^2 W_4}{\partial \mu_i \partial \xi_j} \right|_{\mu_i, \xi_j = 0} \bar{\xi}_j + \sum_j \left. \frac{\partial^2 W_4}{\partial \mu_i \partial \mu_j} \right|_{\mu_i, \mu_j = 0} \bar{\mu}_j. \tag{2.2}$$

Then the energy can be written

$$W = W_1 + W_2(X, M) + W_3(X, M, \bar{\xi}, \bar{\mu}) - \tfrac{1}{2}\sum_i \frac{\partial W_3}{\partial \xi_i}\bigg|_{\xi_i=\bar{\xi}_i} \bar{\xi}_i - \tfrac{1}{2}\sum_i \frac{\partial W_3}{\partial \mu_i}\bigg|_{\mu_i=\bar{\mu}_i} \bar{\mu}_i \quad (2.3)$$

This expression involves only interactions in which at least one ion is in region I, but the summations still extend over all ions in region II. These summations are treated in two ways. The sum corresponding to the Coulomb interaction of the defect with the displacements and dipoles in region II, calculated in the Mott–Littleton approximation, converges only slowly (as $1/r^4$). For these terms, the appropriate summations calculated analytically by Jones and Ingham (1925) and quoted by Mott and Littleton, are used. The repulsive interactions, on the other hand, and also the interactions of region II with the displaced ions and dipoles close to the defect, are negligible except for those ions bordering region I. These contributions to the energy can thus be calculated explicitly. Thus we have calculated these interactions for a group of ions, region II', in close proximity to region I, which is treated explicitly. In all the calculations we have varied the size of both regions and computed the defect energy to observe how it depends on the sizes of the regions chosen.

We make a slightly different approximation to that used by Boswarva and Lidiard (1967) in minimizing the energy. Now the last two terms in equation (2.3) involve X and M, the displacements and dipoles in region I, through the derivatives of W_3. Boswarva and Lidiard include these in the energy function which is used in the calculation of the optimum displacements and dipoles in region I. However, these latter terms are in fact equal to $W_4(\xi, \mu)$, which does not depend explicitly on X and M, so we exclude them from the minimization. There is no difference in the methods if the Mott–Littleton description of region II is completely accurate. In fact we find that the two methods do give essentially identical results. Our choice allows a considerable simplification in the computation when we use our particular minimization method.

The two succeeding sections deal with the choice of the potential describing the ionic interactions and the method of minimization.

2.1 *The potentials*

Table 1 contains the values of various dielectric and elastic constants for CaF_2. The dielectric constant is required for calculating the displacements in the region described by the Mott–Littleton formulae.

Table 1. Properties of calcium fluoride

Anion–anion distance $r_0 = 2.718\,\text{Å}$
—(Batchelder and Simmons (1964) at 6 K)
Anion electronic polarizability $\alpha_- = 0.759\,\text{Å}^3$
—(Tessman *et al.* (1953))
Cation electronic polarizability $\alpha_+ = 0.979\,\text{Å}^3$
—(calculated from α_- and ε_∞)
Static dielectric constant $\epsilon_0 = 6.7$
High frequency dielectric constant $\epsilon_\infty = 2.045$
—(Kaiser *et al.* (1962))
Elastic constants $C_{11} = 17.4 \times 10^{11}\ \text{dyn cm}^{-2}$
$C_{12} = 5.6 \times 10^{11}\ \text{dyn cm}^{-2}$
$C_{44} = 3.59 \times 10^{11}\ \text{dyn cm}^{-2}$
—(Hoffman and Norwood (1960)).

The repulsive interactions are deduced using the equilibrium equation, the value of the compressibility and the difference in C_{11} and C_{12}. The repulsive and Van der Waals interactions are considered to act only between nearest anion–cation and next nearest anion–anion neighbours. This restriction is also imposed in the calculation of the energies

of the various defects. The Van der Waals constants used are those calculated by Benson and Dempsey (1962). They appear, together with the repulsive parameters employed, in table 2.

Of various expressions for the elastic constants found in the literature, those of Srinivasen (1958) contain an error in the formula for C_{12}. This was corrected by Rajagopal (1962).

Table 2. Repulsive and Van der Waals parameters for CaF_2/Ar

1. Repulsive parameters
   $A_{++} = 10460 \cdot 0 \text{ eV}$
   $A_{+-} = 2914 \cdot 0 \text{ eV}$
   $A_{--} = 721 \cdot 3 \text{ eV}$
   $\rho_{++} = \rho_{+-} = \rho_{--} = 0 \cdot 2705 \text{ Å}$

Abrahamson	Fumi–Tosi
$A_{+0} = 8534 \cdot 0 \text{ eV}$	$A_{+0} = 4213 \cdot 0 \text{ eV}$
$A_{-0} = 2241 \cdot 0 \text{ eV}$	$A_{-0} = 1106 \cdot 0 \text{ eV}$
$\rho_{+0} = \rho_{-0} = 0 \cdot 2731 \text{ Å}$	$\rho_{+0} = \rho_{-0} = 0 \cdot 3011 \text{ Å}$

2. Van der Waals parameters

$C_{++} = 44 \cdot 23 \times 10^{-12} \text{ erg Å}^6$	$D_{++} = 94 \cdot 5 \times 10^{-12} \text{ erg Å}^8$
$C_{+-} = 18 \cdot 06 \times 10^{-12} \text{ erg Å}^6$	$D_{+-} = 24 \cdot 6 \times 10^{-12} \text{ erg Å}^8$
$C_{--} = 9 \cdot 51 \times 10^{-12} \text{ erg Å}^6$	$D_{--} = 5 \cdot 63 \times 10^{-12} \text{ erg Å}^8$
$C_{+0} = 43 \cdot 59 \times 10^{-12} \text{ erg Å}^6$	$D_{+0} = 78 \cdot 74 \times 10^{-12} \text{ erg Å}^8$
$C_{-0} = 21 \cdot 10 \times 10^{-12} \text{ erg Å}^6$	$D_{-0} = 21 \cdot 81 \times 10^{-12} \text{ erg Å}^8$

The expressions of Reitz *et al.* (1961) for C_{11} and C_{12} are essentially correct but we have used the expressions given by Axe (1965) which employ more accurate values of the Coulomb sums. The three equations are solved to obtain values of the parameters A_{+-}, A_{--} and ρ. These are used in the normal Born–Mayer exponential form of the interionic repulsive potential

$$\phi_{ij} = A_{ij} \exp \left(\frac{-r}{\rho_{ij}} \right). \tag{2.1.1}$$

Franklin (1968) has collected various values of the parameters for the repulsive interactions in CaF_2 and our results are quite consistent with the other values from various sources.

In estimating the ion–gas interaction we have followed our previous approach used successfully for the alkali halides. We have estimated the gas–gas interaction in two ways. Firstly we have used the potentials of Abrahamson (1964) based on his Thomas–Fermi–Dirac calculations. Abrahamson (1969) has recently expressed the results of these calculations in an exponential Born–Mayer form. Alternatively we have used a potential based on an analysis by Fumi and Tosi (1964) of repulsive interactions for the alkali halides. Their expression for the interaction between ions i and j is

$$\phi_{ij} = 0 \cdot 159 \, C_{ij} \exp \left\{ \frac{(r_i + r_j - r)}{\rho} \right\} \text{eV}. \tag{2.1.2}$$

Here r_i is the ionic radius and C_{ij} the Pauling factor which takes into account the dependence of the potential on the charge Z_i and number of electrons n_i in the outer shell of the ith ion

$$C_{ij} = 1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j} . \tag{2.1.3}$$

For the Ar–Ar interaction, we have used this expression taking the mean of the radii of the isoelectronic ions K^+ and Cl^- as the appropriate radius for Ar.

The gas–ion interaction is taken as the geometric mean of the appropriate ion–ion and

gas–gas interactions so that if the exponential form (equation (2.1.1)) is used for ϕ_{ii} and ϕ_{jj}, then ϕ_{ij} has the same exponential dependence on r and

$$A_{ij} = (A_{ii}A_{jj})^{1/2}$$

$$\frac{1}{\rho_{ij}} = \tfrac{1}{2}\left(\frac{1}{\rho_{ii}} + \frac{1}{\rho_{jj}}\right). \tag{2.1.4}$$

To find the gas–cation potential, we need to know the cation–cation interaction which cannot reasonably be obtained from an analysis of the elastic properties of the crystal. A value of A_{++} was therefore deduced from A_{+-} and A_{--}, again by use of the geometric mean rule but with a small modification to take account of the Pauling factors

$$A_{++} = C_{++}\left(\frac{A_{+-}}{C_{+-}}\right)^2 \bigg/ \left(\frac{A_{--}}{C_{--}}\right). \tag{2.1.5}$$

2.2. The numerical minimization method

The calculation of the energy of even a limited region of a distorted and polarized crystal is a lengthy computation involving a summation over all pairs of ions. The usual minimization procedures, requiring repeated linear searches, involve repeated calculation of the energy and are very inefficient.

We have developed a method which markedly shortens the calculation. When minimizing the energy of a lattice of interacting ions, it is advantageous to use methods employing both first and second derivatives of the energy. Thus if the energy of N ions is expressed in terms of a potential $\phi(r_i - r_j)$ acting between pairs of ions at r_i and r_j then

$$E = \sum_{i,j}^{N} \phi(r_i - r_j). \tag{2.2.1}$$

The gradient involves only a single summation

$$g_i = \sum_j^{N} \frac{\partial \phi}{\partial x_i}(r_i - r_j) \tag{2.2.2}$$

and the second derivatives only one interaction if $i \neq j$

$$W_{ij} = \frac{\partial^2 \phi(r_i - r_j)}{\partial x_i \,\partial x_j}. \tag{2.2.3}$$

All the derivatives g_i and second derivatives W_{ij} may be calculated in a summation that ranges only once over each ion pair.

We now denote the vector containing the derivatives of the energy with respect to each independent coordinate by g and let $\mathbf{W}$ be the approximate matrix of second derivatives. If E is expanded to second order in the displacement vector δ, then

$$E(\delta) = E_0 + g.\delta + \tfrac{1}{2}\delta^{\mathrm{T}}.\mathbf{W}.\delta \tag{2.3.4}$$

and the obvious step to reduce the value of E is

$$\delta = -\mathbf{W}^{-1}.g. \tag{2.3.5}$$

The usual procedure would be to calculate $\mathbf{W}^{-1}$ and g at some initial estimate of the minimum r_0, obtain δ and recalculate $\mathbf{W}^{-1}$ and g at the improved estimate of the minimum. An alternative approach is to use a technique of improving the current value of $\mathbf{H} = \mathbf{W}^{-1}$ using only the values of the gradient. This technique has been discussed in a slightly different context by Fletcher (1969) who considers a number of formulae which may be used to update $\mathbf{H}$ at each iteration. We employ the most usual expression, equation (2.3.6). Then the sequence of the iteration is (i), calculate g_1 and $\mathbf{H}_1$ at some initial estimate of the

minimum r_1; (ii), calculate $\boldsymbol{\delta}_1 = -\mathbf{H}_1 \cdot \boldsymbol{g}_1$ and $\boldsymbol{r}_2 = \boldsymbol{r}_1 + \boldsymbol{\delta}_1$; (iii), recalculate $\boldsymbol{g}_2$ at the new coordinates $\boldsymbol{r}_2$; (iv), update the current version of $\mathbf{H}$

$$\mathbf{H}_2 = \mathbf{H}_1 + \frac{\boldsymbol{\delta}_1 \boldsymbol{\delta}_1^{\mathsf{T}}}{\boldsymbol{\delta}_1 \cdot (\boldsymbol{g}_2 - \boldsymbol{g}_1)} - \frac{\{\mathbf{H}_1 \cdot (\boldsymbol{g}_2 - \boldsymbol{g}_1)\} \{(\boldsymbol{g}_2 - \boldsymbol{g}_1)^{\mathsf{T}} \cdot \mathbf{H}_1\}}{(\boldsymbol{g}_2 - \boldsymbol{g}_1)^{\mathsf{T}} \cdot \mathbf{H}_1 \cdot (\boldsymbol{g}_2 - \boldsymbol{g}_1)} \tag{2.3.6}$$

(v), recalculate $\boldsymbol{\delta}_2 = -\mathbf{H}_2 \cdot \boldsymbol{g}_2$, etc.

This method of calculation is particularly suited to our type of relaxation calculation. The obvious initial estimate for the coordinates has each ion at its lattice site and each dipole zero. Then the matrix $\mathbf{W}$ of second derivatives is easily calculated and the inverse is the quadratic response function for a limited region of the crystal about the defect. The forces arise only from the defects in the crystal.

The calculation of the matrix $\mathbf{H}$ for any other configuration of the crystal is very tedious but this step is eliminated if the gradients of the energy, that is the forces, are used to correct the matrix after each iteration.

One difficulty can arise in the treatment of charged defects, when the initial iteration may give spurious results due to a polarization catastrophe. The energy of the defect system may be divided into the relaxation energy of the distorted crystal about the defect together with the interaction energy of the defect and the surrounding ions. If the energy of the crystal is expanded about the undistorted configuration, all the first derivatives of the first term are zero while the inverse of the matrix of the second derivatives is positive definite. The first derivatives of the interaction with the defect correspond to the forces acting on the undisplaced ions. However a consistent use of Newton's method requires that we include the second derivatives of the defect–lattice interaction in calculating the response function $\mathbf{W}^{-1}$. However, large Coulomb contributions to this term may cause the matrix $\mathbf{W}^{-1}$ to become negative definite. Physically this corresponds to the immediate neighbours of the defect relaxing inwards towards the vacancy, attracted because of the unlimited and unphysical increase in polarization energy that is allowed in the model. This problem is avoided by simply omitting these dangerous contributions to $\mathbf{W}$ in the initial iteration. Essentially, the first relaxation step is performed assuming that the defect exerts constant forces on the surrounding ions.

The method normally converges to a minimum in between four and twelve iterations. Essentially, we have a minimization method which requires only about a dozen calculations of the energy, which is very much less than the number of computations required in a minimization method employing a search procedure. We have carried out comparisons of the two methods only in a few relatively simple cases which are basically quite favourable to search procedures. However, this new method is still between ten and twenty times faster. In particular, the method is very satisfactorily applied to problems involving many variables, up to about fifty independent coordinates and fifty dipoles. Search procedures become relatively less efficient as the number of variables increases but the convergence of the new method is not seriously affected. The only effective limitation is imposed by the computer storage required for the matrix $\mathbf{H}$. However, this is not frequently referenced and it could easily be stored on a device with a slow access time without hindering the speed of computation.

3. Conclusions

The results of our calculations are collected in tables 3.1 to 3.7. The results in tables 3.1 and 3.2 are the energies of the inert gas held at an interstitial site and at the saddle point during diffusion. Results are given for various sizes of the relaxed regions. The best estimates of the activation energy are contained in table 3.3.

The results are generally insensitive to the choice of potential and this is true especially for the activation energy. Felix 1970 has investigated the CaF$_2$/Ar system experimentally and finds that the behaviour is similar to that for the alkali halides (see, for example Felix

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Table 3. Numerical results for CaF_2/Ar

Table 3.1. Energy of inert gas interstitial

Potential	Number of shells relaxed	Energy
A	2	3·52 eV
	8	3·03 eV
	16	2·96 eV
FT	2	4·31 eV
	8	3·70 eV
	16	3·61 eV

Table 3.2. Energy of inert gas at saddle point along diffusion path

Potential	Number of shells relaxed	Energy
A	2	9·67 eV
	10	6·17 eV
	22	5·43 eV
FT	2	9·92 eV
	10	6·57 eV
	22	5·83 eV

Table 3.3. Energy of gas interstitial and gas atom at saddle point along diffusion path with activation energy for interstitial diffusion (Δh_i)

Potential	E_{Int}	E_{SP}	Δh_i
A	2·96 eV	5·43 eV	2·47 eV
FT	3·61 eV	5·83 eV	2·22 eV

Table 3.4. Vacancy formation energies

Vacancy	Number of shells in region I	Number of shells in region II'	E_f
Anion	2	41	4·82 eV
	8	35	4·55 eV
	15	28	4·52 eV
Cation	2	22	23·30 eV
	8	16	23·02 eV
	16	8	22·94 eV

Table 3.5. Interstitial ion formation energies

Interstitials	Number of shells in region I	Number of shells in region II'	E_f
Anion	2	22	−2·18 eV
	8	16	−2·35 eV
	16	8	−2·41 eV
Cation	2	22	−15·63 eV
	8	16	−16·38 eV
	16	8	−16·56 eV

(1967) and (1968)). The Arrhenius plot shows two regions. At high temperatures, we associate the observed process with an interstitial diffusion mechanism. The observed value of the activation energy is $3\cdot0$ eV which is in reasonable agreement with our value of $2\cdot2$–$2\cdot5$ eV. However, we will discuss whether the process is modified by trapping into vacancies after a discussion of our results for the formation energies of the intrinsic defects in CaF_2. The low temperature region, with an observed activation energy of $6\cdot0$ eV, is presumably characterized by trapping into vacancy aggregates or other extrinsic defects. Our values for the solubility energy and interstitial activation energy suggest an activation energy for such a process of about 5–6 eV.

Tables 3.4 and 3·5 give the formation energies of ion vacancies and interstitials respectively. Results are given for various sizes of the two regions whose significance in the calculation is discussed in § 2. It is found that extending the region of explicit relaxation (region I) slightly reduces the calculated formation energy. But there is no dramatic effect, suggesting that the use of the Mott–Littleton approximation to describe the distortion and polarization of the crystal outside a very limited relaxed region is a remarkably successful expedient in calculating the energy of formation of a charged defect.

The results do not differ substantially from the values quoted by Franklin (1968). The anion Frenkel energy (g_{F_A}) is 2·1 eV, the cation Frenkel energy (g_{F_C}) 6·4 eV. These are slightly lower than Franklin's results (2·7 eV and 7·1 eV respectively) and the anion Frenkel energy is not in such good agreement with the experimental value of 2·8 eV given by Ure (1957). However, the experience with similar calculations on the alkali halides (see, for example, Boswarva and Lidiard (1967) and Scholz (1968)) would lead us to expect that the calculated value should be too small. Using the calculated lattice energy, 27·55 eV, the energy of formation of a Schottky trio (g_S) is 4·4 eV, again less than Franklin's value.

Table 3.6. Energy to remove ion and introduce gas atom into vacancy

Vacancy	Potential	Number of shells in region I	Number of shells in region II'	E_f
Anion	A	15	28	6·40 eV
	FT	15	28	6·84 eV
Cation	A	16	8	23·72 eV
	FT	16	8	23·92 eV

Table 3.6 gives values of the energy required to remove an ion to infinity and insert an interstitial Ar atom into the resulting vacancy. The trend in the results as the extent of the relaxation about the defect is altered exactly parallels that found for the simple vacancies. Results are therefore given only for the largest relaxed regions.

Table 3.7.

Potential	B_A	$B_A - \frac{1}{2}g_F$	B_C	$B_C - (g_S - g_F)$	$\Delta h_i'$
A	1·08 eV	−0·0 eV	2·18 eV	−0·1 eV	2·5 eV
FT	1·29 eV	0·2 eV	2·63 eV	0·3 eV	2·5 eV

Table 3.7 gives the binding energies into the vacancies. Norgett and Lidiard (1969) have shown that the diffusion coefficient for the gas is given by

$$D = \frac{\gamma_i D_0 \exp(-\Delta h_i / kT)}{\gamma_i + \sum_T \gamma_T C_T \exp(B_T / kT)} \tag{3.1}$$

where Δh_i is the activation energy for interstitial diffusion, γ_i and γ_T are the entropy factors

for the interstitial and trapped gas atom, C_T is the trap concentration and B_T is the binding energy into the trap. In an intrinsic region, where the trap concentration is given by an expression of the form $C_T \propto \exp(-g_T/kT)$, trapping of the gas atom is important if $\exp\{(B_T - g_T)/kT\} > 1$, if $B_T > g_T$. In this case the observed activation energy for gas diffusion is $\Delta h_i' = \Delta h_i - B_T + g_T$.

In table 3.7, binding energies are compared with the thermal factors for each vacancy ($g_T = \frac{1}{2} g_{F_A}$ for the anion vacancy and $g_T = g_S - g_F$ for the cation vacancy). The binding energies are in all cases rather similar in value to the appropriate trapping energies g_T. Our calculation employing the Fumi–Tosi gas–ion potential suggests that there is some trapping of gas atoms into cation vacancies. However, the effect is not large and our results are not sufficiently precise to show whether the gas is actually trapped into either type of vacancy at high temperature. The predicted activation energy $\Delta h_i'$, modified where appropriate to take account of trapping, is given in the last column of table 3.7.

The experimental results of Lagerwall (1965) show that the diffusion is not affected by doping CaF_2 with Na^+ or Y^{3+} ions. This result does not bear directly on any interpretation of diffusion in the intrinsic region which was the region studied by Lagerwall. The behaviour at low temperatures was obscured by a gas migration process with very low activation energy which is probably due to diffusion along dislocations. The effect of doping, as shown by Felix and Muller (1970, private communication) for the alkali halides, is to move the temperature of the boundary between the high and low temperature regions.

Thus it seems that within the limits imposed by the large uncertainties in the calculations and the difficult nature of the experiments, there is no fundamental discrepancy between the calculated and experimental results for argon diffusion in calcium fluoride.

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