

The initial production of defects in alkali halides: F and H centre production by non-radiative decay of the self-trapped exciton

N Itoh[†], A M Stoneham and A H Harker

Theoretical Physics Division, AERE Harwell, Oxfordshire OX11 0RA

Received 1 April 1977, in final form 9 May 1977.

Abstract. Radiation damage in KCl can be produced by the decay of a self-trapped exciton into an F centre and an H centre. We present calculations of the energies of the states involved for various stages in the evolution of the damage. These lead to important conclusions about the very rapid damage process, and support strongly Itoh and Saidoh's suggestion that damage proceeds through an excited hole state. The results also help in understanding the prompt decay of F and H pairs at low temperatures, the thermal annihilation of F and H centres, the effects of optical excitation of the self-trapped exciton, and some of the trends within the alkali halides.

The calculations use a self-consistent semi-empirical molecular-orbital method, here the CNDO method as implemented in our MOSES code. A large cluster of ions is used (either 42 or 57 ions) plus long-range Madelung terms. The ion positions were obtained from separate lattice-relaxation calculations with the HADES code. The choice of CNDO parameters and the adequacy of the method were checked by a number of separate predictions. These include the energy of π luminescence, where the 2.33 eV predicted is very close to the 2.31 eV observed.

1. Introduction

It is now widely accepted that ionic displacements to give F and H centres can be produced by the non-radiative recombination of self-trapped excitons. Much uncertainty remains, however, about the identity of the states from which damage production begins, and about the evolution of F and H centres separated by a distance large enough to prevent rapid recombination.

Damage is produced very rapidly. Experiment shows that F centres can be produced in their ground states in a few picoseconds. The speed of the process puts limits on its study experimentally. Indeed, the main aim of the present work has been to unravel some of the critical early steps. To this end, we have calculated energies for different stages in the evolution of F and H centres from a self-trapped exciton. The same calculations give a number of other energies which can be compared with both experiment and other approaches, so that there are a number of checks on the methods used.

A wide range of methods has been used for estimates of the electronic structure of isolated defects in ionic crystals and for the calculation of total energies for closed-shell systems (e.g. Stoneham 1975). We are very restricted in our choice of method here, since we want total energies for open-shell systems involving a relatively large number of

[†]Permanent address: Dept of Nuclear Engineering, Nagoya University, Nagoya, Japan.

atoms. Following a successful treatment of similar problems for light impurity atoms in metals (Mainwood 1976), we choose to use our code MOSES† based on the so-called CNDO method. This is basically a semi-empirical molecular orbital approach which differs from conventional Hartree–Fock theory in replacing certain matrix elements by suitable approximate forms involving empirical parameters. The choice of parameters is vital. In the next section we shall show that suitable values can be found which satisfy three criteria: they can be used efficiently even in complicated systems, they reproduce observed properties of small molecules better than Hartree–Fock theory, and they give results which agree with those from other methods whenever we can make comparisons.

2. The CNDO method and the choice of parameters

The CNDO method is one of a class of semi-empirical methods which has the advantage of being simple, self-consistent and easily modified, whilst retaining physical sense. It approximates the Hartree–Fock–Roothaan equations by neglecting terms of the order of the overlap between orbitals on different atoms, and by approximating other matrix elements systematically. A basis set of Slater orbitals is used for the outer electrons on each atom: 4s and 4p for K, and 3s and 3p for Cl; an s orbital for the F centre electron was also introduced, but was omitted when found unimportant in the present work.

Standard CNDO parametrisations exist, although, as stressed earlier, these are not adequate for our purposes. The essence of our approach is to make sure that the same parameters predict well the properties of interest for small molecules. Three main parameters are needed:

- (i) Orbital exponents ξ . These enter into expressions for electron–electron and nuclear attraction integrals. The same exponents are used for corresponding s and p orbitals;
- (ii) The ionisation potential (I) and electron affinity (A) which are used in the form $(I + A)/2$ to determine the relative attraction for electrons of different chemical species;
- (iii) Bonding parameters, β , which are essentially resonance integrals. The bonding parameter between two species A and B is taken as $\beta_{AB} = (\beta_{AA} + \beta_{BB})/2$; this relationship is sometimes generalised, but proved adequate in the present work. Given the values of the various parameters, the CNDO program obtains self-consistent solutions analogous to the Hartree–Fock approaches. The solutions list total energies, one-electron energies, wavefunctions and a number of other properties.

2.1. Choice of parameters for alkali and halogen

Two sets of parameters have been derived, each stressing slightly different aspects of the problem. In almost all respects the results we get agree for the two sets of parameters, which is encouraging. Roughly speaking, the sequence in fitting is this. Estimates of the exponents ξ and electronegativities $(I + A)/2$ are made from standard tables. Modest variations in these are then made and the bonding parameters β varied to fit potential energy data for molecular KCl or Cl_2^- . Loosely speaking, the exponents fix the equilibrium spacing, the electronegativities affect the absolute energies and molecular-dipole moments, and the bonding parameters affect the vibrational frequencies. The

† MOSES (molecular orbital semi-empirical system) is a Harwell computer code which incorporates a variety of semi-empirical molecular orbital methods, including CNDO, INDO and MINDO. It differs from the widely-available codes by improved data input and matrix manipulation methods, plus a wide range of extra facilities to improve convergence and flexibility.

Table 1. Values and sources of CNDO parameters.

Species	Model	Exponent $\xi(\text{bohr}^{-1})$	Electronegativity $\frac{1}{2}(I + A)eV$		Bonding parameter βeV
Cl	I	2.197 ^(a)	23.6 ^(e)	10.72	-15.0 ^(g)
	II	1.80 ^(b)	19.1 ^(b)	6.22 ^(b)	-9.5 ^(b)
	Standard ⁽ⁱ⁾	2.197	21.59	8.71	-22.33
K	I	1.03 ^(c)	2.20 ^(c)	1.15 ^(e)	-5.0 ^(g)
	II	1.10 ^(c)	2.30 ^(c)	1.25 ^(e)	-5.0 ^(g)
	Standard ⁽ⁱ⁾	0.874	2.42	1.37	
F centre	I	0.587 ^(d)	8.0 ^(f)	—	+0.8 ^(h)
	II	0.587 ^(d)	6.0 ^(f)	—	+0.4 ^(h)

(a) Clementi and Raimondi (1963).

(b) Fit to Cl_2^- interionic potential (Tasker *et al* 1976).

(c) Fit to KCl interatomic potential with corresponding Cl parameters.

(d) From variational calculation using one Slater orbital and the point-ion model.

(e) Fit to KCl dissociation energy and dipole moment.

(f) To fit optical absorption by F centre.

(g) Partly from band structure for KCl crystal and partly from KCl molecule vibrational data.

(h) Only F-alkali terms treated; see § 2.3.

(i) 'Standard' data refer to (a) for exponents and to Pople and Beveridge (1970) for electronegativities.

results and their sources are summarised in table 1. It can be seen that the exponents and electronegativities are close to the standard values, but that the bonding parameters can be very different.

2.2. Comparison of derived parameters with experimental data

Two types of comparison can be made. One involves those parameters which we have positively tried to fit. Success here merely demonstrates that the model is sufficiently general. The other checks involve predictions of unrelated observables, and these show whether or not our model is realistic. The accuracy of fitting is demonstrated in figures 1 and 2, for example.

2.2.1. Molecular data. For the fitted parameters, essentially exact agreement was achieved. These parameters were the equilibrium spacings for KCl and Cl_2^- , and the dissociation energy of Cl_2^- in model II. Dipole moments for KCl can be predicted with these results:

Model I	9.68 Debye
Model II	9.10 Debye
Experiment	10.24 Debye (Herbert <i>et al</i> 1968).

No allowance has been made in the predictions for zero-point motion, which may well reduce the small discrepancy.

Potential-energy curves can also be compared with other work. Figure 1 compares the Cl_2^- potential for model II with the valence bond calculation of Tasker *et al* (1976), and shows satisfactory agreement. The result of a Morse potential fit to experiment for KCl is compared with the predictions of model I in figure 2. Again the agreement is good, and within the uncertainties one should assume for the 'experimental' curves.

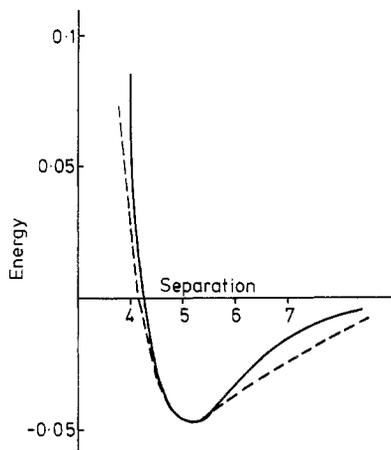


Figure 1. Potential energy curves for Cl_2 . The full line corresponds to our CNDO calculation, and the broken line represents the valence-bond theory of Tasker *et al* (1976). Units are atomic units (27.2 eV and 0.529 Å); the set II of CNDO parameters were used.

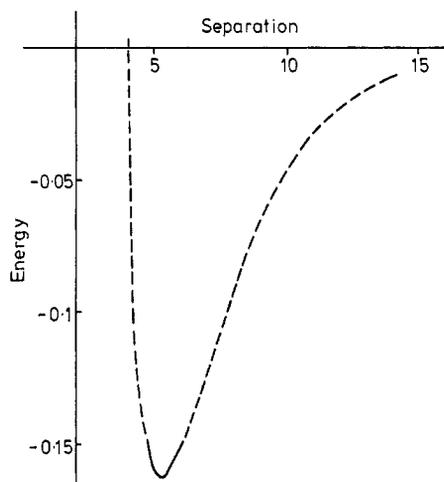


Figure 2. Potential energy curves for KCl molecule. The full line represents our CNDO results and the broken line is a generalised Morse-potential fit to experimental data.

2.2.2. Perfect crystal data. The molecular data concentrated on potential energy curves and related data, i.e. on total energies as a function of geometry. Agreement with experiment suggests that both the charge densities and the redistribution of charge with variation of spacings are reasonably represented. However, this need not ensure that one-electron excitations will be predicted well. The band structure of the crystal, notably through the valence band width and the band gap, is a check of these other aspects. Since there are long-range coulomb interactions with ions outside the cluster, we have included proper Madelung corrections in all our crystal calculations. In these corrections the ions outside the cluster are treated as point charges $\pm |e|$ at the perfect lattice sites.

The results for the valence band width:

Model I 2.32 eV (27 atom cluster), 2.8 eV (42 atom cluster)
 Model II 3.4 eV (27 atom cluster)
 Experiment 2.7 eV

and for the forbidden band gap:

Model I 9.38 eV (27 atom cluster), 8.55 eV (42 atom cluster)
 Model II 8.3 eV (27 atom cluster)
 Experiment 8.4 eV

are in very acceptable agreement with experiment. Some dependence on cluster size remains. For this reason our later calculations on the radiation damage mechanism used either the 42 atom cluster or the still larger 57 atom cluster.

3. Results for crystal defects and their formation

In this section we discuss results for the F centre, the self-trapped exciton, the H centre, and

several of the intermediate stages in the creation of vacancy and interstitial pairs. Results for the 57 atom cluster omit the p orbitals on the cations. Those for the 42 atom cluster include s and p orbitals on both anions and cations.

3.1 Geometry

Here two points of principle are involved. First, the defect cluster used should be large enough that no defect is in immediate contact with the cluster boundaries. This can be achieved in the 42 or 57 atom clusters of figure 3. The larger cluster is most important

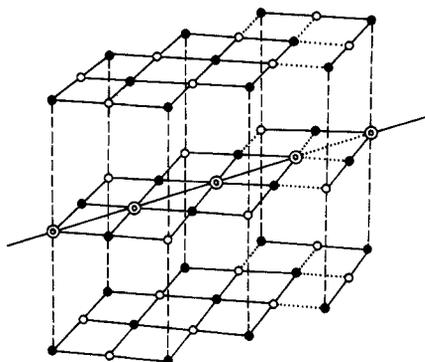


Figure 3. The 57 atom cluster is shown here, with the (110) close-packed row drawn in. The 42 atom cluster is obtained by removing the atoms joined to the rest by dotted lines (.....). The scale is expanded in the (001) direction for clarity. (Cations ●; Anions ○ and ⊙)

when separated F and H centres are considered. Secondly, the energies depend on the detailed local lattice distortions. Strictly, this is a self-consistent electronic and lattice deformation problem. In our work we have used ionic displacements calculated assuming that it is the hole, rather than the relatively-diffuse excited electron, which determines the distortion. The displacements and ionic polarisation were then determined by calculations using the HADES program of Norgett (1974), together with interatomic forces for Cl_2^- and Cl_3^- from Tasker *et al* (1976). Obviously the displacements will differ for the ground and excited hole states. In table 2 the positions of the two Cl ions in the Cl_2^- ion are given for a number of cases.

Table 2. Positions of ions in Cl_2^- . In the perfect crystal the two Cl^- ions are at $\pm(0.5, 0.5)$. The values given here include cases where the Cl_2^- ion has also been moved along the (110) axis. In these cases the coordinates are $(+a, +a)$, $(+b, +b)$, given here as a ; b . Thus the normal self-trapped hole involves ions at $(+0.30, +0.30)$ and $(-0.30, -0.30)$ here, and $(a = 0)$ corresponds to the saddle point of figure 4.

Hole in ground state	Hole in excited state
-0.30 ; +0.30	-0.37; +0.40
-0.204; +0.40	-0.30; +0.44
+0.096; +0.70	-0.2 ; +0.505
+0.192; +0.80	0.0 ; +0.65
	+0.1 ; +0.73

3.2 The H centre

The H centre, or neutral interstitial, consists of a Cl_2^- molecular ion substituting for a Cl^- ion. The important defect energy is that which compares a cluster containing an H centre with a perfect cluster plus a Cl^0 atom at infinity. This gives a defect energy of +4.46 eV for the cluster of 42 atoms, and 2.50 eV for the 57 atom cluster. Both results are larger than results from other calculations. Dienes *et al* (1967) give 1.57 eV for the (110) H centre and 1.40 eV for the (111) centre, even omitting a chemical bonding term of perhaps 1 eV (Stoneham 1975, p 673). Diller (1976) similarly estimates a lower value of 0.41 eV. The discrepancy appears to be associated with states at the edge of the cluster, and only seems to be important when the number of atoms in the cluster is altered. Thus both the F centre and H centre formation energies are sensitive to the edges of the cluster, but the errors largely cancel when we discuss the relative energies of various F–H arrangements.

We have not studied the optical excitations of the H centre in detail. However, the predicted one-electron energy differences of 2.7 eV (57 atom cluster) and 2.2 eV (42 atom cluster) are in acceptable accord with the observed 2.4 eV π transition.

3.3. The F centre

In the radiation damage process, the F centre is formed directly in its ground state. There is thus no need for a description of the F-centre excited-state for present purposes. This eliminates one possible source of complication, namely whether our basis orbitals should contain ones centred on the F centre itself, or whether the ionic basis of the neighbouring atoms suffices.

The main disadvantage of including explicit F-centre orbitals is that it is hard to know how they evolve during the radiation damage process. There is evidence too that they are unnecessary, in that successful LCAO calculations (e.g. Kojima 1957) have been made without such orbitals. In this section we calculate basis orbitals centred on the F centre. We find that their effect on interaction of F centres in their ground state with other defects is negligible, although the extended basis improves estimates of the optical absorption energy to the (irrelevant) excited state.

The three CNDO parameters for the F-centre orbital were estimated as follows. First, the orbital exponent was taken from a separate point-ion calculation using a single Slater orbital giving $\alpha_F = 0.587242$ a.u. for KCl. Secondly, the bonding parameter can be estimated in terms of other known parameters. Only the bonding with the nearest-neighbour cations is important, and we choose β_F to give a satisfactory value of $\beta_{FA} \equiv (\beta_F + \beta_A)/2$ for this bonding. Here the suffix A refers to the alkali. The bonding parameter is defined through the equation:

$$\beta_{FA} \langle \psi_F | \psi_A \rangle = \langle \psi_F | T + V_A + V_F | \psi_A \rangle \quad (3.1)$$

where T is the kinetic energy and V_A and V_F are one-electron core potentials. Since V_F is zero, there being no core associated with the F centre, the right-hand side is simply proportional to ε_A , the eigenvalue of the outermost electron of the alkali:

$$\beta_{FA} \langle \psi_F | \psi_A \rangle = \varepsilon_A \langle \psi_F | \psi_A \rangle \quad (3.2)$$

or, expressing the result in terms of β_F rather than β_{FA} :

$$\beta_F = 2\varepsilon_A - \beta_A. \quad (3.3)$$

Thus the bonding parameter of the F centre can be expressed in terms of the

electronegativity and bonding parameter of the cation. For KCl we find $\beta_F = 0.8$ eV. Thirdly the electronegativity ϵ_F was determined so that the calculated transition energy was close to the observed F-band energy. For KCl we find $\epsilon_F = -8.0$ eV. The observed energy is 2.29 eV; if we omit the F centre orbital we obtain 4.1 eV, whereas the result is 2.2 eV on including the orbital.

The defect formation energy also depends significantly on the presence or absence of an F-centre orbital (+3.06 eV without an orbital and -2.97 eV with one) but, as noted earlier, the influence on defect interaction energies is very slight.

3.4. Binding of F and H centres

The binding energy of the two product defects can be defined by the equation

$$-E_{\text{bind}} = E(\text{F,H pair}) - [E(\text{F}) + E(\text{H})] \quad (3.4)$$

where the formation energies of the various defects are given. The formation energies are the differences between the total energy of the perfect cluster and of the cluster with the defect present. Clearly the binding energy tends to zero at large separations, where the F–H interaction will be primarily elastic. Here we concentrate on the nearest-neighbour and next-nearest-neighbour positions in the (110) row.

The detailed geometry used is important, of course. For nearest-neighbour F and H centres we have used the results of HADES calculation assuming the F centre to be a vacancy, so that the trapped electron did not contribute to the interatomic forces. This may not be adequate at such a small defect–defect spacing, so it is hard to assess the accuracy of the result. For next-nearest-neighbour F and H centres we assumed, in line with HADES calculations, that the only significant distortion came from the H centre, and that this distortion was not affected by the presence of the F centre.

Table 3. Binding energies of the F and H centres in eV

	Without F-centre orbital		With F-centre orbital	
	nn	nnn	nn	nnn
Ground state of H centre				
42 atom cluster	-0.52	+2.62	-0.70	
57 atom cluster	-1.075	+2.15		

The results are shown in table 3. They indicate that it makes little difference whether or not an F-centre orbital is included, and that the broad features do not depend on the cluster size. One particularly striking feature is the repulsive F–H interaction at the nearest-neighbour spacing, compared with the attractive interaction at the larger spacing. This appears to be genuine, not an artefact of our approximations. It ensures the separation of the F and H centre and provides a barrier against F–H recombination.

Recombination of F and H centres has been observed in several experiments, although these may involve different relative positions of the F and H centres from those we discuss here. Behr *et al* (1967) and Saidoh and Itoh (1973) observe two forms of recombination for KCl and for KBr: that of correlated F–H pairs, with 0.04 and 0.055 eV activation energies, and that involving long-range motion of the H centre with 0.088 and 0.12 eV activation energies, respectively. The electron pulse experiments of Hirai *et al* (1971) also exhibit

F–H annihilation. One component of F centre annihilation appears to be associated with electron tunnelling, but decay rates are also enhanced at higher temperatures by a mechanism which has a 0.015 eV activation energy. Presumably tunnelling is important for the short separations in our model.

3.5. Excited states of the F-centre–H-centre system

Whilst there is strong experimental evidence that the F centre is formed directly in its ground state, it is still useful to see what the relative energies of the excited states are, for these can have observable consequences.

Results were obtained for nearest-neighbour F and H centres, and include the ground state and the first two excited states. The ground state proves best described as an $\alpha\text{-(Cl}^-\text{)}_2$ pair, rather than an F–H pair. Electron charge density is removed from the F centre (giving something close to a vacancy, or α centre) to the two neighbouring ions constituting the H centre. In essence, the halogen molecular ion Cl_2^- has a greater electron affinity than the cations around the vacancy. However, we stress that the ion positions chosen are those appropriate for an F–H pair. Thus the energy of the $\alpha\text{-(Cl}^-\text{)}_2$ pair should be regarded as that of the unrelaxed state reached directly through radiative recombination of the F–H pair. The F–H pair, as first intended, corresponds to the first excited state. The second excited state can be described as $\text{F}^*\text{-H}$, in that the electron trapped at the vacancy is in a p-like excited state.

The precise energies depend on whether F-centre orbitals are included or not. However, the ground state ($\alpha\text{-Cl}_2^-$) has sufficient energy to decay into the lowest state of the self-trapped exciton. This accounts for the π -emission seen in F–H recombination (Purdy and Murray 1975, Tanimura *et al* 1976) as the exciton state is formed and recombines radiatively. Both σ and π emission have been seen, but recent experimental results suggest the σ emission is produced indirectly.

3.6. Isolated self-trapped exciton

The combination of new experimental methods (Williams and Kabler 1974) and extensive theoretical calculations by Hartree–Fock (Stoneham 1974) and pseudopotential methods (Song *et al* 1975, Harker *et al* 1977) has led to a fairly complete understanding of the energy levels of the self-trapped exciton. In essence, there are two main types of excitation. The excitations of the electron in its relatively diffuse orbit are readily treated by the pseudopotential method. The hole excitations involve mainly a Cl_2^- ion, and are best treated by Hartree–Fock or similar methods. Neither method gives the recombination energy well. The CNDO approach can do so; indeed, our present approach gives good values for electron–hole recombination as well as for electron and hole excitations.

The results are summarised in table 4, where energies are given relative to the lowest state of the self-trapped exciton. In particular, the predicted recombination energy is 2.33 eV, remarkably close to the observed 2.31 eV.

3.7. Evolution of a self-trapped exciton displaced along the $\langle 110 \rangle$ row

Much of the discussion of the photochemical production of F centres has concerned the state of the self-trapped exciton from which F and H centres evolve. There is evidence that the important state is not the lowest (unrecombined) state of the exciton (e.g. Itoh 1977). This follows from a variety of arguments involving the observed radiative transitions, and

Table 4. Energies for the self-trapped exciton

State	Pseudopotential	CNDO	Expt.
Ground state (recombined but distorted geometry)	not predicted	-2.33	-2.31
Electron excitations:			
lowest state A_{1g} (chosen zero)	0.0	0.0	0.0
B_{3u}	0.70	1.36	not seen
B_{2u}	2.1-2.2	1.9 ± 0.15	1.87
B_{1u}	2.1-2.2	2.2 ± 0.15	2.12
A_{1g}^*	2.5	2.7	not seen
Ionisation limit	not predicted	not predicted	2.6

also from observations of the effects of subsequent excitation on defect production. The excited state or states involved may be ones in which the electron component of the exciton alone is excited (e.g. the proposal of Toyozawa) or ones in which the hole component is also excited (e.g. Itoh and Saidoh 1973). Since the local lattice distortion is strongly affected by the hole state, the distinction is important. Indeed, whereas the equilibrium Cl-Cl spacing is smaller with the hole in the ground state than the value $\sqrt{2}a$ in the perfect crystal the equilibrium Cl-Cl spacing is greater than $\sqrt{2}a$ for the hole in an excited state.

Figure 4 shows the ionic motions involved in the evolution of an F-H pair. The positions are roughly correct for the hole in its lowest state, and show the sequence of self-trapped, saddle-point and F-H configurations. Some of these are reported in figures 5a and 5b, which show the way the total energies evolve for different electronic states.

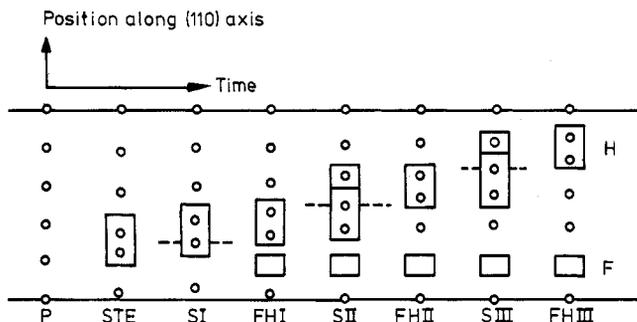


Figure 4. Evolution of the ionic positions with time. Only the critical close-packed row (\odot in figure 3) is shown. The various stages are P: Perfect (110) close-packed row. STE: Self-trapped exciton with the hole in its lowest state. SI, SII: Saddle-points, as ions pass points midway between lattice sites. FHI, FHII, FHIII: F centre and H centre pairs at increasing spacings.

The results for the hole in its lowest state (figure 5a) may be summarised as follows. First, the system is stable against small displacements of the centre of gravity of the self-trapped exciton. This is true at least up to displacements of the centre of mass of half the Cl-Cl distance, and appears to hold for both ground and excited electronic states of the exciton. Secondly, as the displacement increases, the attractive potential of the vacancy left behind becomes more important. For a nearest-neighbour F-H pair the ground state is best described as $(\alpha\text{-Cl}_2^-)$, as mentioned in § 3.5. However, the relative energies of the F-H

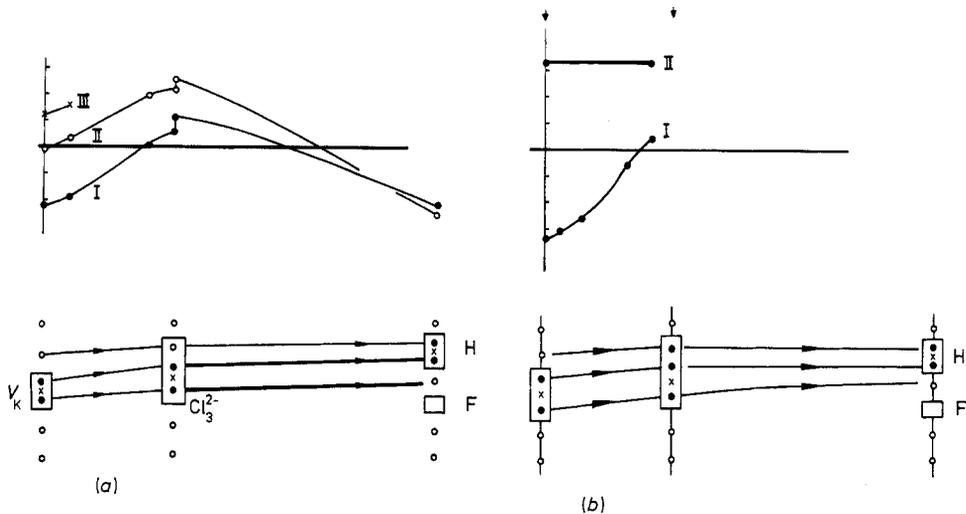


Figure 5. Energy levels in eV of the self-trapped exciton as the lattice evolves to F and H centres. The lower half of each diagram gives ion positions in the same way as figure 4. The zero of energy corresponds to infinitely separated F and H centres. (a) Hole in lowest state. The levels labelled are: I: Recombined electron and hole for some geometry. II: Ground state of self-trapped exciton. III: Electron excited to next lowest state. (b) Hole excited to a π state. The levels labelled are: I: Recombined electron and hole for same geometry. II: Electron in a totally symmetric state (either a_{1g} or a_{1g}^* —see text).

state and the $(\alpha\text{-Cl}_2^{2-})$ states are marginal for the second-neighbour position. The small energy difference may lead to strong configuration admixture. The experimental result (Hirai *et al* 1971) that prompt decay of F–H pairs occurs at liquid helium temperatures may be accounted for by a change from a second-neighbour F–H pair to an $(\alpha\text{-Cl}_2^{2-})$ pair. The $(\alpha\text{-Cl}_2^{2-})$ pair differs from the perfect crystal only through distortion of the Cl^- sublattice, and the pair may be unstable at such a small spacing in a close-packed row against relaxing to the perfect crystal.

It is much harder to calculate the energies when the hole is excited. The problem occurs with any self-consistent method, for it is hard to enforce convergence on the desired state when others of the same symmetry have much the same energy. The excited state we have obtained corresponds to the hole in an excited π state and the electron in a σ state, probably a_{1g}^* . The interesting feature is that the excited state is flat to within our accuracy. There seems to be no barrier against evolution into (F + H). As the ions are displaced towards the saddlepoint the charge density evolves as one would expect: the electronic charge shifts towards the emerging F centre and the hole moves in the opposite direction to the two ions which will constitute the H centre.

We can use symmetry arguments to construct a correlation diagram relating the states of the self-trapped exciton to those of the resulting F and H centres. This is shown in table 5 for the closest F–H spacing. The F centre is known to form in its ground state. If the H centre is also formed in its ground state, and if configuration mixing can be neglected, only the $(b_{3u}; b_{3u})$ state and excited states of the same symmetry evolve into the F–H pair. However, there are several configurations which can lead to excited states of the H centre.

Our estimate of the energy of a nearest-neighbour F–H pair can be compared with two

Table 5. Correlation diagram. This table relates the states of the self-trapped exciton to those of an F and H centre pair at their closest spacing.

Self-trapped exciton		F-H pair	
State		Total wavefunction	
Electron state	$\left\{ \begin{array}{l} a_{1g} \\ b_{3u} \\ b_{1u} \\ b_{2u} \end{array} \right.$	A_{1u}	A_1
Hole in lowest state (b_{1u})		A_{1g}	A_1
		B_{2g}	B_2
		B_{1g}	B_1
Hole state	$\left\{ \begin{array}{l} b_{1g} \\ b_{2g} \\ b_{1u} \\ b_{2u} \\ b_{3g} \end{array} \right.$	B_{1g}	B_1
Electron in lowest state (a_{1g})		B_{2g}	B_2
		B_{1u}	B_2
		B_{2u}	B_1
		B_{3g}	A_2

earlier predictions, although the accuracy of the absolute value of the formation energy may be poorer than the binding energies we predict. Smoluchowski's value of 5.0 eV is apparently much smaller than our value of 8.0 eV, though Smoluchowski's calculation omits the electronic interaction energy, and will underestimate the energy. Elango (1976) predicts a formation energy for F and H centres at infinite separation of 7.0 eV. His approach would presumably give a value closer to ours at short distances. Elango's value may be an overestimate, because the relaxation energy of the ionised I centre to the H centre has not been taken into account. Both Elango's arguments and the work of Schulz and Hardy (1972) indicate that the α -I pair has lower energy at infinite separation. The present result that the nearest α -I pair is lower in energy than the F-H pair appears to be genuine, and consistent with the earlier results, after allowing for differences in terms they omitted. The large F-H repulsion at close separation may come from the overlap of the π electrons of the Cl_2^- with the s electrons on the K^+ ions associated with the F centre.

4. Discussion

The present work gives some insight into both the F-H annihilation process and the production of the F-H pair. We can also comment on trends from one crystal to another.

4.1. Thermal annihilation of F and H centres

There are two important experimental results for annihilation. First, π emission is seen during thermal annihilation of F-H pairs. (Purdy and Murray 1975; Tanimura *et al* 1976). Secondly, prompt decay of pairs is seen after pulsed-electron excitation. There are two stages in the thermal annihilation of F-H pairs: a first-order reaction and a second-order reaction. Thermoluminescence with the same emission spectrum as the π emission is seen following the F centre annihilation curve almost exactly at both stages in KBr and at the second stage in KCl. The quantum yield appears to be much less than unity (K Tanimura, private communication). The present calculation gives a higher energy for a widely separated F-H pair than for the lowest state of the self-trapped exciton, and so predicts

that thermal annihilation with π emission is energetically possible. There is a barrier, for the F–H pair at nearest-neighbour separation is higher in energy by around 2 eV. Since the H centre can rotate easily at these temperatures, the thermal annihilation may take place from different atomic arrangements for which such a strong repulsion does not occur. The large attraction between F and H centres at second-neighbour spacing may indicate a configuration for which annihilation by tunnelling can occur. If this configuration occurs, decay into the perfect lattice could take place by tunnelling and subsequent non-radiative transitions. Even though it is hard to predict the quantum yield, it is easy to see it could be much less than unity.

The prompt decay of F–H pairs after pulsed excitation can be understood in terms of the F–H energies. If an F–H pair evolves to the second-neighbour spacing, it has about 2 eV less energy than at infinite separation. Thus there is a barrier to further motion, and the H centre may stop at this second-neighbour position. The prompt decay would then correspond to annihilation from this position.

4.2. Formation of separated F and H centres

The barrier to further separation of the F–H pair just mentioned can be overcome if the H centre is formed in an excited state (Itoh and Saidoh 1973). This F–H state may still have a higher energy than the distant pair. The critical point is whether the excited hole state has a long enough lifetime for the F–H pair to become sufficiently separated. Presumably the energetic motion of the interstitial will be limited by the lifetime of the excited state. It is not easy to estimate the lifetime. However, it need not be very long, for Bradford and Williams (1975) have observed F centre production in about 10^{-11} s.

Other results of the present work also favour evolution from an excited hole state. When the hole is in its ground state, the self-trapped exciton is stable against translational motion of the Cl_2^- ion. One might expect excitation of the hole from its σ_u state to an excited π state (i.e. an electron is excited from a π state to σ_u) would reduce the repulsive interaction between the halogen π orbitals and cation s orbitals. We have been unable to obtain predictions for the state in which only the hole is excited. However, we do have results for an excited state of the same symmetry, with both hole and electron excited. These show that there is *no barrier against translational motion* of the Cl_2^- ion in this state. If the hole is excited, one can draw a smooth adiabatic potential from the self-trapped exciton configuration to the close F–H pair configuration. It would still be useful to have results for the state in which only the hole is excited, for Williams (1976) has observed that F-centre production is enhanced by exciting self-trapped excitons in their ground state by 1.79 eV light. This can produce either electron or hole excitation, but is too small to give both. Our results suggest that electron excitation is not important (figure 5a), though we have not been able to verify that hole excitation suffices.

4.3. Trends from crystal to crystal

Rabin and Klick (1960; see also Ikezawa *et al* 1968, Townsend 1973) noted that E_x , the x-ray energy needed to create a single F centre, had a systematic dependence through the alkali halides. In essence, E_x decreases along the sequence from iodides to fluorides. Several explanations are possible. Rabin and Klick argue that the collision sequence along the close-packed row is of most importance, so that the trends come from geometric factors. Elango's discussion stresses the initial step more, for he argues that the critical factor is the excess energy from exciton excitation over the amount needed to create

isolated F and H centres. Williams' observation of the enhancement of F centre production by excitation of the self-trapped exciton makes this less likely. Our calculations introduce a third factor, namely the stability of close F-H pairs. This depends on the attraction between F and H centres at the second-neighbour distance, and will probably show the right trend from crystal to crystal.

Acknowledgments

We are especially grateful to Dr M J Norgett and Mr Andrew Ross for their HADES calculations of the ion positions.

References

- Behr A, Peisl H and Waidelich W 1967 *Phys. Lett.* **A24** 379
Bradford J N and Williams R T 1975 *Phys. Rev. Lett.* **35** 300
Clementi E and Raimondi D L 1963 *J. Chem. Phys.* **38** 2686
Diller K 1976 *AERE report* TP642
Dienes G J, Hatcher R D and Smoluchowski R 1967 *Phys. Rev.* **157** 692
Elango M A 1976 *Sov. Phys.-Solid St.* **17** 1555
Harker A H, Lyon S and Wasiela A 1977 *Solid St. Commun.* **21** 1053
Herbert A J, Lovas F J, Melendres C A, Hollowell C D, Story T L and Street K 1968 *J. Phys. Chem.* **48** 2824
Hirai M, Kondo Y, Yoshinari T and Ueta M 1971 *J. Phys. Soc. Japan* **10** 440
Ikezawa M, Shirohata K and Kojima T 1968 *Colour Centre Conf., Rome Abst.* 92
Itoh N 1977, *J. Physique* in press
Itoh N and Saidoh M 1973 *J. Physique* **34** C19 101
Kojima T 1957 *J. Phys. Soc. Japan* **12** 908, 918
Mainwood A 1976 *AERE report* TP684
Norgett M J 1974 *AERE report* R7650
Pople J A and Beveridge D L 1970 *Approximate Molecular Orbital Theory* (New York: McGraw-Hill)
Purdy A T and Murray R B 1975 *Solid St. Commun.* **16** 1293
Rabin H and Klick C 1960 *Phys. Rev.* **117** 1005
Saidoh M and Itoh N 1973 *J. Phys. Chem. Solids* **34** 1165
Schulz P D and Hardy J R 1972 *Phys. Rev.* **B6** 1580
Stoneham A M 1974 *J. Phys. C: Solid St. Phys.* **7** 2476
— 1975 *Theory of Defects in Solids* (London: Oxford UP)
Song K S, Stoneham A M and Harker A H 1975 *J. Phys. C: Solid St. Phys.* **8** 1125
Tanimura K, Fujiwara M, Okada T and Suita T 1976 *Phys. Lett.* **A50** 301
Tasker P, Balint-Kurti G G and Dixon R N 1976 *Molec. Phys.* **32** 1651
Townsend P D 1973 *J. Phys. C: Solid St. Phys.* **6** 961
Williams R T 1976 *Phys. Rev. Lett.* **36** 529
Williams R T and Kabler M N 1974 *Phys. Rev.* **89** 1897