

The Formation Energy of Point Defects in Ionic Crystals

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Abstract

Simple calculations have been made of the formation energy of different types of defect centres such as those formed by hexavalent uranium introduced into lithium fluoride in an oxygen atmosphere. The Coulomb energies are compared for different configurations of the same defects. The method of calculation is described and results quoted for configurations including, in addition to oxygen ions, (a) a uranium ion and a divalent positive ion, (b) a uranium ion and a negative-ion vacancy and (c) two uranium ions.

1. Introduction

Some time ago one of us (Runciman 1955) discussed atomic configurations in luminescent centres in which small clusters of defects formed charge-compensated centres. A particular study was then made of uranium-activated sodium fluoride and models were proposed for the observed luminescent centres (Runciman 1956). No firm identifications were made and progress has been slow for all centres other than the principal centres which have been ascribed to UO_5 groups (Feofilov 1959). Similar centres occur in lithium fluoride (Runciman and Wong 1979). When single crystals are available the symmetry of the centres can be established by means of polarized luminescence (Runciman *et al.* 1981), uniaxial stress (Kaplyanskii and Moskvin 1962) and electric field measurements (Kaplyanskii *et al.* 1970). The symmetry of the principal centres is C_{4v} and, even in this case, an alternative to the UO_5 model has been proposed comprising a $\text{UO}_6\Box_{\text{F}}$ group with the fluorine vacancy in a crystal-axis direction relative to the uranium ion (Bleijenberg and Timmermans 1978). Symmetry considerations do not distinguish between the alternatives. Hence it is attractive to consider whether energy calculations can assist in the task of assigning atomic models to observed centres. In the present paper we restrict ourselves to comparisons of centres containing different configurations of the same defects, as the energy differences found in our calculations are likely to be more reliable in such cases.

Calculations were made for many other centres, such as those containing trivalent and tetravalent ions in addition to the uranium ion, but they are not reported as they do not illustrate any novel features. Since negative ion vacancies predominate in defect studies of the alkali halides, results for centres with positive ion vacancies are also omitted.

Simpler calculations were also made in which the Coulomb energies were estimated on the basis of the *excess* charges compared with the perfect lattice, when it is assumed that the defect ions replace lattice ions of similar sign of charge. The hexavalent uranium and the divalent oxygen ions have excess charges of +5 and -1 respectively. These calculations were useful in (i) clarifying thoughts on the number of possible atomic configurations, (ii) forming simple physical ideas of the terms responsible for the energy differences between configurations, and (iii) checking the more rigorous, but relatively complex, computer calculations. Comparison of the total Coulomb energies between configurations is meaningless, but there is good agreement with the relative energies of the rigorous Coulomb calculations performed according to the procedure described in the next section and in Appendix 1. A justification of the excess charge model is given in Appendix 2.

2. Procedure

We have based our calculations of defect energies on several assumptions. We have assumed that the effect of crystal relaxation, both displacement and polarization, is negligible within a class of defect structures. We feel that this is probably not usually true when comparing different classes, although each case should be considered specifically.

It is possible to perform detailed displacement relaxation calculations (Norgett 1974; Richardson 1982) although these are very complex and consume computer resources. Polarization relaxation can also be accounted for, by shell model calculations or otherwise (Richardson and Mahanty 1983), and is likewise very involved, properly requiring a detailed study of electronic structure. Fortunately, polarization effects are smaller for lithium fluoride (LiF) than for other alkali halides.

In order to perform more detailed estimates, it is necessary to account for both short-range and Coulomb potentials in describing the interactions between ions in the system. For our particular problem short-range potentials are not available for the defect clusters in LiF, although potentials for LiF itself are well known (Catlow *et al.* 1977). Approximations could be made based on iso-electronic analogues. For example, the short-range interaction of O^{2-} with other ions has been treated as equivalent to that of F^- (Catlow 1977). The situation for hexavalent uranium is more complicated, however, and we know of no suitable substitute.

The relative contribution of short-range and Coulomb potentials to defect and lattice energies is of interest. In estimating lattice energies, the short-range potential is typically only 10% of the total. In the case of point defects this contribution to the energy can be even smaller (Richardson 1982), although short-range potentials can dramatically affect displacement relaxations (Hardy and Karo 1979).

Because of these problems and the desire to keep our calculations simple, we have assumed that both relaxation and short-range effects are unimportant for studying the relative stability of uranium oxide complexes in LiF, but that Coulomb effects arising from changes to the ionic charges at the defect sites are the major contributors to stability. We discuss below, on the basis of our results, the validity of this assumption.

We present the method for calculating the Coulomb contribution to unrelaxed defect energies in Appendix 1. The method used is very simple and gives accurate results. Accuracy is important with such large defect clusters, as total energies are large in magnitude while energy differences between structures may be only a few per cent (and of order 1 eV).

Our calculations are performed by using Madelung constants for alkali halide crystals, and account for the changes of some terms in the lattice sums due to the presence of vacancies or substitutional ions. The accuracy depends only on the accuracy of the Madelung constants and on the lattice parameter. With this technique, clusters of large size can be studied. We have considered clusters of up to 12 ions.

3. Results

Coulomb energies are inversely proportional to the lattice parameter which is twice the nearest neighbour distance between positive and negative ions in the lattice. The lattice parameters for LiF and NaF, extrapolated to 0 K, are 3.992 and 4.590 Å respectively (Catlow *et al.* 1977). Previous work by one of us (Srinivasan 1982) gave results for a lattice parameter of 3.97 Å for LiF.

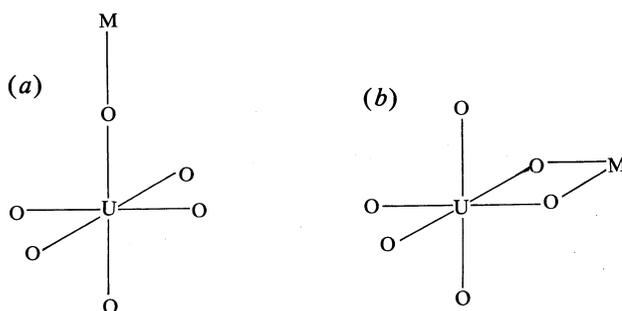


Fig. 1. Atomic configurations of UO_6M centres showing (a) tetragonal and (b) orthorhombic structures.

Table 1. Total Coulomb energy and relative energy (in eV) of defect centres calculated both rigorously and using the excess charge approximation

Centre	Symmetry	Energy		Relative energy	
		Rig. calc.		Rig. calc.	Excess charge
UO_6M	Tetragonal	-300.15		0.00	0.00
	Orthorhombic	-299.37		0.78	0.78
$\text{UO}_6\Box_{\text{F}}$	Trigonal	-273.77		0.00	0.00
	Monoclinic	-273.75		0.02	-0.01
	Tetragonal	-272.97		0.80	0.79
U_2O_{10}	Tetragonal A	-522.43		0.00	0.00
	Monoclinic	-521.72		0.71	0.70
	Orthorhombic	-516.99		5.44	5.38
	Tetragonal B	-511.46		10.97	10.88

(a) UO_6M Centres

The UO_6 complex has an excess charge relative to the lattice of -1 and this can be compensated by a divalent ion M replacing a monovalent lithium ion. The two likely centres are shown in Fig. 1, and the energies (and energies relative to the lowest energy found) of these centres calculated by both the rigorous and excess

charge methods are listed in Table 1. The relevant experimental information has been described elsewhere (Runciman *et al.* 1984).

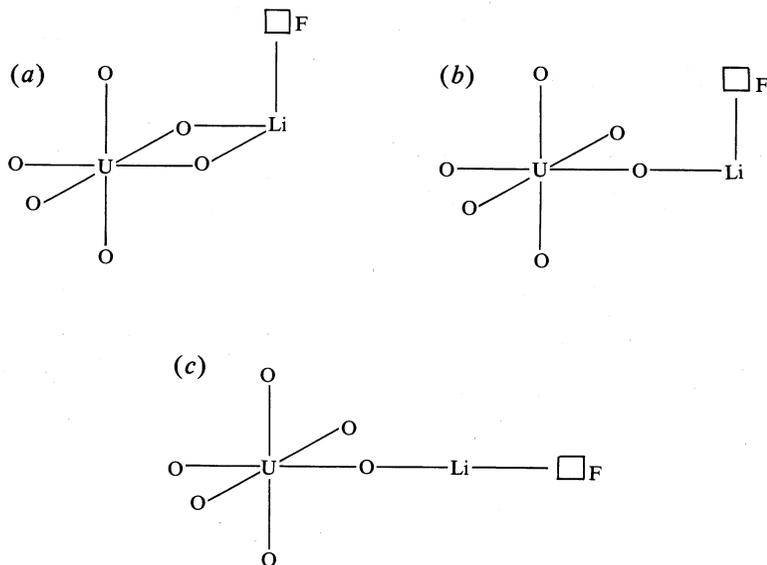


Fig. 2. Atomic configurations of $\text{UO}_6\Box\text{F}$ centres showing (a) trigonal, (b) monoclinic and (c) tetragonal structures.

(b) $\text{UO}_6\Box\text{F}$ Centres

The UO_6 complex can also be charge-compensated by a fluorine vacancy yielding a $\text{UO}_6\Box\text{F}$ centre. Three possible atomic configurations are shown in Fig. 2. The rigorous Coulomb calculations given in Table 1 suggest that the trigonal centre is at slightly lower energy than the monoclinic centre. The tetragonal centre has a higher energy. Many fluorescent centres have been detected and seven have fluorescent line pairs of electric and magnetic dipole character (Runciman and Wong 1979). However, none of these centres have trigonal symmetry and there is no firm experimental evidence for any $\text{UO}_6\Box\text{F}$ centres.

(c) U_2O_{10} Centres

It is tempting to think that the UO_5 centres might pair to form U_2O_{10} dimers. However, it may be noted that it appears impossible to get more than 0.03 at.% U into LiF and 0.2 at.% U into NaF. Hence it is possible that the formation of uranium ion pairs is not favoured. Four possible configurations are shown in Fig. 3, and the relative energies are listed in Table 1. There is no experimental evidence for these centres, although calculations favour the formation of the tetragonal A configuration of all the U_2O_{10} dimers considered.

4. Conclusions

Simple Coulomb calculations are a useful first step in listing likely defect centres and in giving an indication of relative energies of different configurations of centres

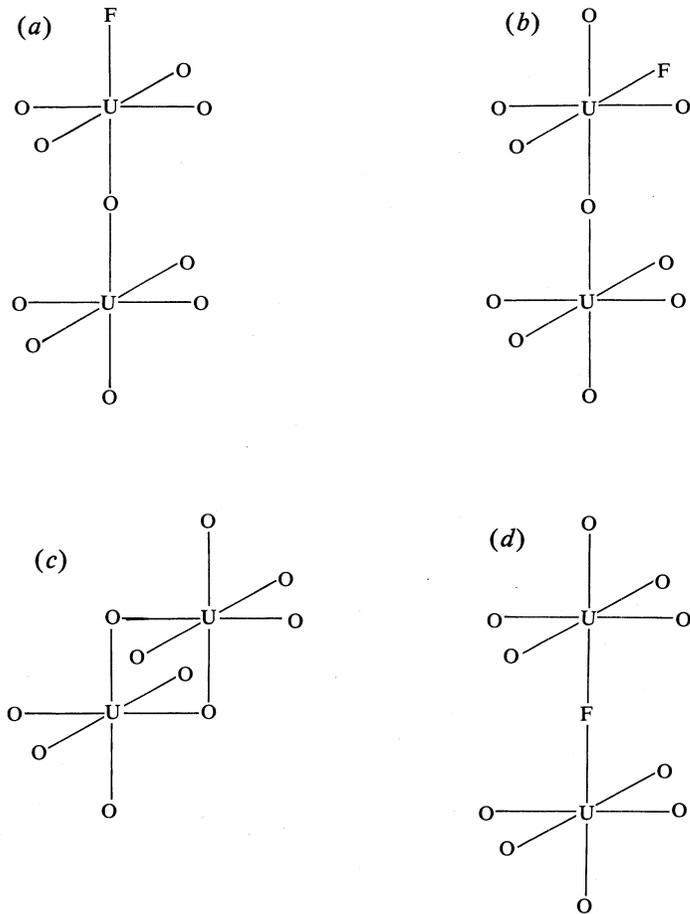


Fig. 3. Atomic configurations of U_2O_{10} centres showing (a) tetragonal A, (b) monoclinic, (c) orthorhombic and (d) tetragonal B structures.

with the same composition of defects. The excess charge approximation works surprisingly well in providing relative energies. Few experimental results are available for comparison with theory. However, LiF containing uranium, magnesium and oxygen provides the best example to date for more detailed investigation. A complete theoretical study would require all the relevant pair potentials and would include both polarization and lattice relaxation effects. In view of the small energy differences which have been found, it would appear to be necessary to develop such a program if the precise structures of these complex defects are to be determined. The work would be along similar lines to that formulated for simpler defect structures (Norgett 1974; Richardson 1982).

Acknowledgments

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Appendix 1. Unrelaxed Coulomb-potential Defect Calculations

The Coulomb energy of a single (point) defect in a crystal can be estimated by the Madelung constant, as is well known. The resultant energy is for a crystal with a single defect and is unrelaxed: no account is taken of either displacement of ions around the defect, or the changes in the state of polarization of the crystal.

We have extended this concept to encompass charge-compensated defects which are composed of many ions situated substitutionally in an otherwise perfect crystal. Such calculations have been considered indirectly elsewhere (Norgett 1974; Richardson 1982) in studies of the energies of defects in relaxed crystals with shell-model potentials. We present here a description of a simplified calculation suitable for the defect clusters discussed in this paper. Our nomenclature follows that of Norgett (1974) and Richardson (1982).

The calculation can be divided into two parts—a contribution to the defect energy as a result of the interaction of defect ions with the host lattice ions, and a contribution arising from the interactions between defect ions. We consider each part in turn.

The interaction of defect ions with the host crystal is given by the sum of all Madelung energies for each individual defect ion i , less the Madelung energy for the ideal crystal,

$$E_{\text{Mad}} = \sum_i \alpha_i q_i - \sum_v \alpha_v q_v^0, \quad (\text{A1})$$

where the sum i is over all defect ions and the sum v over all defect sites (including vacancies), α_i is the Madelung constant for site i , and q_i is the defect (substitutional ion) ion charge at site i , while q_v^0 is the original ionic charge at site v . As is always the convention in calculations of this nature, the reference state from which defect ions are drawn, and to which removed ions are taken, is a state of ionic dispersal at infinity. The sums are only over the same sites if the final defect crystal has no vacancies.

For the contribution arising from the interactions between defect ions there are terms arising from vacancies, E_{vac} , and terms from the substitutional ions, E_{int} . By

terms arising from vacancies we mean those terms which were there before the ions were removed, but which will now be absent.

The total energy term arising from vacancy effects is derived as follows. We need to include the interaction energies of all vacancies introduced with all the substitutional ions, and at the same time remove from the Madelung sum those terms arising from the interaction of ions which have been removed from the lattice to be replaced either by vacancies or foreign ions. This gives us the vacancy contribution to the defect energy as

$$E_{\text{vac}} = k \sum_v \sum_{i \neq v} \frac{q_v^0 q_i}{r_{vi}} - \frac{1}{2} \sum_v \sum_{v' \neq v} \frac{q_v^0 q_{v'}^0}{r_{vv'}}, \quad (\text{A2})$$

where the sums are over defect sites, as for (A1). The separation of sites is represented by r_{vi} and $r_{vv'}$. The constant k is unity if site v has no substitutional ion and is one-half if v is a substitutional site.

The contribution from substitutional defects is similar. We need to add in the interactions between the defect ions themselves and subtract from the Madelung sum the spurious terms arising from the interactions of the defect (substitutional) ions with host lattice ions which have been removed, to be replaced by defects. The result is the interstitial contribution

$$E_{\text{int}} = \frac{1}{2} \sum_i \sum_{i' \neq i} \frac{q_i q_{i'}}{r_{ii'}} - k \sum_i \sum_{v \neq i} \frac{q_i q_v^0}{r_{iv}}. \quad (\text{A3})$$

Therefore the energy of the entire defect cluster is obtained from equations (A1)–(A3) as

$$E_{\text{def}} = E_{\text{Mad}} + E_{\text{int}} - E_{\text{vac}}. \quad (\text{A4})$$

If the charges of ions are given in e.s.u. and the distances are in multiples of the lattice parameter, then all energies can be converted to eV by multiplying by 14.399 and dividing by the lattice parameter in Å (10^{-10} m).

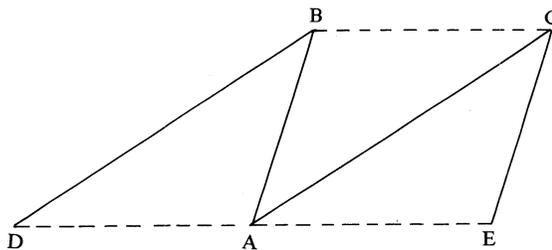


Fig. 4. Calculation of pair interactions.

Appendix 2. Justification for Excess Charge Calculations

We consider the change in Coulomb energy when a pair of ions in a configuration 1 with charges q' and Q' respectively on sites AB changes to a configuration 2 with the ions on sites AC (see Fig. 4). The normal charges of the ions in the perfect lattice

are q and Q respectively. Consider the pair interaction of ions A, B, C, D and E, where D and E are located as indicated in Fig. 4:

$$\begin{aligned}\Delta E &= E_1 - E_2 \\ &= (E_{BA} + E_{BD} + E_{CA} + E_{CE})_1 - (E_{BA} + E_{BD} + E_{CA} + E_{CE})_2 \\ &= \frac{q'Q'}{r_1} + \frac{qQ'}{r_2} + \frac{q'Q}{r_2} + \frac{qQ}{r_1} - \frac{q'Q}{r_1} - \frac{qQ}{r_2} - \frac{q'Q'}{r_2} - \frac{qQ'}{r_1} \\ &= \frac{(q' - q)(Q' - Q)}{r_1} - \frac{(q' - q)(Q' - Q)}{r_2}.\end{aligned}$$

This is the predicted difference on the excess charge model, which has been shown to be exact in this simple case. When only one ion is moved in more complex configurations, the excess charge calculation of the change in Coulomb energy may still be exact, for example the configurations of UO_6M in Fig. 1. This result is obtained by summing interactions for the mobile ion with each of the fixed ions. In other cases the excess charge method is a good approximation.

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