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SHELL MODEL CALCULATIONS OF POINT DEFECT FORMATION ENERGIES IN FLUORITE CRYSTALS

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Résumé. — Les énergies de formation des défauts de Frenkel dans CaF_2 , SrF_2 , BaF_2 et UO_2 , sont calculées théoriquement. Ces valeurs sont comparées aux déterminations expérimentales. L'accord est bon dans le cas de CaF_2 et BaF_2 . Le mauvais accord dans le cas de UO_2 conduit à suggérer le réexamen de l'interprétation des résultats expérimentaux.

Abstract. — Shell model potentials are derived for CaF_2 , SrF_2 , BaF_2 and UO_2 , by fitting to bulk crystal data. The anion-anion interactions, in which there are large or even dominant attractive terms, are treated by combining the results of *ab initio* Hartree-Fock calculations with the empirical fitting procedure. The potentials are then used in computer simulations, using the HADES program, of a variety of point defects in all four crystals. Good agreement with experimental anion Frenkel energies is obtained for CaF_2 and BaF_2 ; while disagreements for SrF_2 and UO_2 suggest incorrect interpretations of the experimental data. Re-analysis of this data gives revised Frenkel formation energies in much better agreement with our calculations; the revised value for UO_2 of 5.1 eV is considerably higher than previous estimates. The anion Frenkel pair in UO_2 is also shown to comprise doubly and not singly charged interstitials and vacancies; and unlike the F^- interstitial in the fluoride crystals, the O^{2-} interstitial in UO_2 , it is suggested, is distorted along the $\langle 110 \rangle$ direction from the body centre position of the cubic interstitial site.

1. Introduction. — Several calculations of defect formation energies in fluorite crystals have been reported in recent years. The work of Franklin (1968) on CaF_2 was followed by that of Norgett (1971 a, b) on CaF_2 , SrF_2 and BaF_2 ; while Tharmalingam (1971) attempted the more difficult problem of point defect energies in UO_2 . All these calculations use the Born model of the ionic solid to obtain the defect formation energy; the lattice is simulated by point polarisable ions to which are added short range interactions, for which parameters are obtained by fitting the model to bulk crystal data.

However, there are known to be serious inadequacies in the point polarisable ion (PPI) model. Firstly, if short range repulsive forces are obtained by the usual procedure of fitting to elastic constants, the static dielectric constant is overestimated. This leads to a consequent error in the calculated energy of relaxation around a defect with non-zero effective charge.

The second major problem with PPI calculations is their susceptibility to the polarisation catastrophe.

This instability — discussed in detail by Faux (1971) — occurs in the calculation when two dipoles increase without bound, owing to their mutual dipole-dipole interaction energy outweighing the self energy of polarisation. Faux showed that the instability was inherent to certain PPI calculations.

These difficulties are largely removed on replacing the PPI by the shell model of Dick and Overhauser (1958). Ionic polarisation is described in this model by the displacement of a shell relative to a core, the shell being connected to the core by an isotropic harmonic spring constant. Since short range interionic forces are taken to act between the shells, the model includes a description of the interdependence of these interactions and ionic polarisation — the feature whose omission leads to the failures of the PPI model.

In the calculations reported in this paper, we have therefore simulated the lattice using the shell model. We have obtained parameters for this model for the three alkaline earth fluoride crystals and for UO_2 ; which we have then used in computer simulations of a variety of point defects in these crystals.

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2. The Model. — Parameters for the model are obtained by fitting to the lattice parameter (r_0).

elastic and dielectric constants (C_{11} , C_{12} , C_{44} , ϵ_0 , ϵ_∞), Raman and transverse optic vibrational frequencies (ω_{TO} , ω_R); and for the three fluoride crystals the ionic polarisabilities (α_+ , α_-) were also included.

Short range interactions are described by the Born-Mayer potential :

$$V_{ij} = A e^{-r_{ij}/\rho} \quad (2.1)$$

which is supplemented for the second neighbour (anion-anion) interaction by an attractive r^{-6} term. The inclusion of the apparent attraction — an order of magnitude too large for conventional Van der Waal's forces — is required if correct elastic constants are to be calculated by the model. But its presence leads to difficulties. For the term is certainly appreciable at the anion-anion lattice separation in CaF_2 and SrF_2 , while it is dominant at these separations in BaF_2 and UO_2 . Meaningful information about the repulsive component of the second neighbour interaction cannot therefore be obtained by fitting to crystal data. Thus we calculated the component using *ab initio* MO techniques, for both the $\text{F}^- \dots \text{F}^-$ interaction (Catlow and Hayns, 1972) and the $\text{O}^- \dots \text{O}^-$ interaction (Catlow and Hayns — to be published). Calculations of the $\text{O}^{2-} \dots \text{O}^{2-}$ potential were not feasible owing to the unbound nature of the O^{2-} ion; and we will assume that the screening provided by the unbound electrons will have only a small effect on the $\text{O}^- \dots \text{O}^-$ interaction at close separations.

The oxygen-oxygen potential calculated by the *ab initio* techniques includes an attractive term — O_2^{2-} is isoelectronic with F_2 . Thus for UO_2 two potentials were employed: the first in which anion-anion parameters were obtained directly from the fit of the calculated interaction to the form:

$$V(r) = A e^{-r/\rho} - Cr^{-6} \quad (2.2)$$

and the second in which only the Born-Mayer parameters obtained from the above fit were included in the crystal potential, with the coefficient of the r^{-6} term being obtained from the empirical fit. The latter potential, which should give an accurate description of the anion-anion interaction for interionic distances close to the lattice separation, was used in calculations in which no anion-anion separation was very much smaller than this value; while the former potential, which gives a more reasonable description of the anion-anion interaction over a wider range of separations was employed for calculations — e. g. these for anion interstitial migration saddle points — in which there are small anion-anion separations.

The $\text{F}^- \dots \text{F}^-$ potential is found to be purely repulsive, fitting accurately to the Born-Mayer form of the interaction. This component is therefore fixed from the calculation, with the attractive term again being obtained from the empirical fit.

Besides obtaining satisfactory values for all crystal data used in the fit, the potentials also predicted

acceptable values for third order elastic constants of the fluoride crystals. The inadequacies of the PPI model, in which elastic and dielectric constants may not both be correctly described, are therefore removed. The principle remaining problem is in the treatment of the second neighbour attractive interaction. For the origin of this term is unclear; and further work on potentials will require knowledge of whether the attraction is genuine — arising possibly from covalence — or apparent — arising from deficiencies in the model.

3. Calculations. — The basic method of the calculation follows the approach of Boswarva and Lidiard (1967): the lattice is divided into two regions — region 1, surrounding the defect, in which all ions are explicitly relaxed to zero force; with the relaxation of more distant regions (region 2) being calculated on the basis of the macroscopic dielectric constant using the method of Mott and Littleton (1938). Minimisation techniques for the relaxation in region 1 are discussed by Norgett and Fletcher (1970); and more detailed discussions of the method are given by Norgett (1971 a) and Lidiard and Norgett (1972).

The calculations were performed using a general program for defect calculations — HADES (*), written by Norgett. For all four crystals, the energies of formation of cation and anion interstitials and vacancies were obtained for a variety of sizes of region 1. Calculations were also performed on saddle point configurations for defect migration mechanisms.

4. Results. — The superiority of shell over PPI models is most strikingly shown by the stability of our calculations using the former model to the expansion of region 1. For both fluoride and oxide crystals, variations on expansion are small after the inclusion of two shells in region 1; and stability has certainly been reached by at most eight shells. In contrast, the PPI calculations of Norgett (1971 a) and Tharmalingam (1971) showed considerable decreases in calculated defect energies on increasing the size of region 1. This effect follows directly from the incorrect representation of dielectric properties by the PPI model; for as the region of lattice simulated by this model expands, the underestimation of the defect formation energies increases. The effect is more marked for UO_2 owing to the much higher dielectric constant of this crystal; and the necessity of simulating this lattice by the shell model is correspondingly greater.

Indeed, the use of the PPI model led to the loss of even qualitative significance in Tharmalingam's work on UO_2 . His calculations predicted Schottky disorder for the crystal, while both diffusion studies (Auskerne and Belle, 1961) and neutron diffraction work (Willis, 1964, Cheetham *et al.*, 1970) find anion interstitials in the oxidised crystals, indicating that, as with the fluo-

(*) Harwell Automatic Defect Evaluation System.

ride crystals, the intrinsic disorder of UO_2 is of the anion Frenkel type.

In contrast to Tharmalingam's work, our calculations confirm the anion Frenkel model. The calculated Schottky energy is 10.3 eV; and Frenkel energies for UO_2 and for the fluoride crystals are given in table I,

TABLE I
Frenkel formation energies in fluorite crystals

Crystal	Calculated value (eV)	Experimental value (eV)
CaF_2	2.6	2.7 ^(a)
SrF_2	2.4	1.7 ^(a) (*)
BaF_2	1.9	1.9 ^(b)
UO_2	5.0	3.3 ^(c) (**)

^(a) Bollmann *et al.*, 1970.

^(b) Barsis and Taylor, 1968 b.

^(c) Auskerne and Belle, 1961.

(*) Revised value 2.5 eV.

(**) Revised value 5.1 eV.

where they are compared with experimental values. Apart from the obvious improvement for UO_2 , the use of the shell model has also led to an improvement in the calculated Frenkel energy for CaF_2 . The overestimation of relaxation energies inherent to the PPI model resulted in a low value for the calculated Frenkel formation energy — 2.1 eV (Norgett, 1971 a), compared with the experimental value of 2.7 eV (Bollman *et al.*, 1970). This latter figure is however, in good agreement with our calculated value of 2.6 eV.

For BaF_2 , we see that the calculated value is again satisfactory. But for SrF_2 and UO_2 there appear to be discrepancies. These we believe are due not to inadequacies in our calculations, but to incorrect interpretation of experimental work. Thus the Frenkel energy for SrF_2 reported by Bollman *et al.* was derived using a vacancy migration activation energy obtained from measurements on Na^+ doped crystals. But conductivity studies of Barsis and Taylor (1966) indicated that in BaF_2 , the dopant enters at interstitial sites, and the fact that Bollmann *et al.* for SrF_2 find similar activation energies in the dissociation regions of trivalent doped (interstitial excess) as in monovalent doped crystals, suggests that in the latter case the charge compensating defect is also the anion interstitial; that is, the monovalent dopant enters at an interstitial site.

The investigation of vacancy motion in SrF_2 will thus require dopants other than Na^+ ; but from the values for CaF_2 and BaF_2 , we may estimate the vacancy activation energy in SrF_2 as 0.55 eV. Thus a re-analysis of the data of Bollman *et al.* using this figure gives a revised estimate of the Frenkel energy of 2.5 eV — in reasonable agreement with our calculated value.

For UO_2 , Auskerne and Belle (1961) assume that the activation energy obtained from their diffusion

studies on the *oxidised* crystals may be used in deducing a Frenkel formation energy from data on the stoichiometric crystal. But in the oxidised crystal, diffusion must take place by an interstitial mechanism; while in the stoichiometric crystal, analogy with other fluorite crystals would suggest a vacancy mechanism. We may again re-analyse the experimental data — in this instance using our calculated vacancy activation energy — and obtain a revised value for the Frenkel energy of 5.1 eV.

Our calculations show that in CaF_2 , the F^- interstitial has a symmetric structure; the ion occupies the body centre position of the cubic interstitial site. Thus the detection of interstitials distorted from these sites in work on Y^{3+} doped CaF_2 (Cheetham *et al.*, 1970, 1971) must be attributed to some clustering mechanism involving interstitials and substitutionals; and such a mechanism has indeed been suggested as a result of computer simulation work using HADES (Catlow, 1973). For UO_2 , however, distorted structures are predicted for the isolated interstitial. The energy minimum occurs at a displacement of $\sim 0.2 \text{ \AA}$ along the $\langle 110 \rangle$ direction. The feature follows from the very short range nature of our oxygen-oxygen potential. This in turn may be attributed to our assumption of a negligible screening effect of the unbound electrons on this potential. Experimental verification of distorted structures for the *isolated* interstitial would therefore clearly be of importance in testing this qualitative feature of our oxygen-oxygen interaction.

A final feature of work on the interstitial in UO_2 is the demonstration of the lower formation energy of doubly compared with singly charged anion Frenkel pairs. Calculation of the latter value required energies for the O^- interstitial and the F^+ centre. The latter was obtained by combining calculations using HADES with point ion calculations by Harker (private communication) following the method of Gourary and Adrian (1957). The energy of formation of the singly charged Frenkel pair was calculated as 8.9 eV — considerably higher than the 5.3 eV obtained for the doubly charged species.

Finally, we report the results of calculations of activation energies for anion diffusion in the crystals. For anion vacancy migration the mechanism is obvious — a $\langle 100 \rangle$ migration of a lattice anion to the adjacent vacancy. But for interstitial migration the problem is less simple. Two processes may be envisaged: the first a direct $\langle 110 \rangle$ migration of the interstitial to a neighbouring vacant interstitial site; and the second a concerted or *interstitialcy* mechanism in which a lattice ion is displaced by the migrating interstitial into a neighbouring interstitial site. Calculations by Chakravorty (1971) had suggested that the interstitialcy mechanism was favoured in CaF_2 . Our results given in table II support Chakravorty's conclusion, and show the interstitialcy mechanism to be general to anion interstitial migration in the fluorite lattice.

TABLE II
Anion diffusion activation energies

Crystal	Vacancy		Activation Energy		Experimental
	Calculated	Experimental	Direct	Interstitial	
CaF ₂	0.20	0.55 ^(a)	3.30	0.69	1.0 ^(a)
SrF ₂	0.30	—	3.23	0.69	0.94 ^(b)
BaF ₂	0.37	0.56 ^(b)	2.88	0.69	0.79 ^(c)
UO ₂	0.25	—	2.11	0.57	1.3 ^(d)

^(a) Bollmann *et al.*, 1970.

^(b) Barsis and Taylor, 1968 a.

^(c) Barsis and Taylor, 1968 b.

^(d) Auskerne and Belle, 1961.

Discrepancies, however, are found between our calculated and experimental migration activation energies. Our calculations indicate rather lower values than those obtained from conductivity and diffusion studies; although some support is provided for our results by the lower measured activation energies found in nmr studies of Lysiak and Mahendroo (1966) and Miller and Mahendroo (1968). We are not sure, therefore, whether these disagreements result from inadequacies in our calculations, or from oversimplified interpretations of the experimental data.

5. Conclusions. — More detailed discussions of the work reported here are given for the fluoride crystals by Catlow and Norgett (1973) and for UO₂ by Catlow (1973, to be published). However, the features of the work that we wish to emphasise are, firstly, the demonstration of the superiority of the shell over the PPI model — principally the removal by this model of the deficiencies arising from the failure of the PPI model

to simulate the dielectric properties of the crystal. Secondly, we have aimed to show how computer simulation techniques — in particular the HADES program — may be used not only for calculating accurate defect formation energies, but also for investigating structural and mechanistic problems in defect studies. Finally, we would like to point specifically to the work on UO₂. Here, we have corrected the errors of previous theoretical treatments — in particular, we have shown that the intrinsic disorder is of the anion Frenkel type; we have confirmed that the anion interstitial is doubly charged; and we have suggested that, in contrast to the fluoride crystals, distortions of this interstitial from the body centre position of the cubic interstitial site, may occur.

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