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Geometry and charge distribution of H centres in the fluorite structure

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Abstract. The analysis of experimental optical and spin-resonance data for the H centre gives a consistent picture of the local geometry and one-electron wavefunctions. One of the two ions in the F_2^- molecular in remains very close to the perfect lattice site; the other is at a distance close to that found in other F_2^- centres. This analysis is confirmed by atomistic calculations using the HADES code. The results are used to give a preliminary analysis of the self-trapped exciton data.

1. 'Molecule in a crystal' defects

Some important defects can be described as a 'molecule in a crystal', (see, e.g., Stoneham 1975, Hayes and Stoneham 1974). They behave like a free molecular species, apart from a slight change in dimension because of the surrounding matrix. The most important example is the self-trapped hole in halides, where the V_k centre is essentially an X_2^- molecular ion substituting for two X^- halogen ions. Another important example is the H centre, the neutral anion interstitial in alkali halides, where an X_2^- molecular ion substitutes for a single X^- ion.

In all these cases one can deduce the X–X separation within the X_2^- ion from spectroscopic measurements, both optical and spin resonance (Schoemaker 1973, Jette *et al* 1969, Tasker and Stoneham 1977). For the H centre in the fluorite structure, the situation is less clear, for the geometry is more complicated and the two halogens are not equivalent. This is shown in figure 1. We shall show, nevertheless, that the spectra do define the positions of the two halogens. These deduced positions can be compared with predictions based on atomistic calculations.

The critical experimental results compare the ultraviolet optical absorption of the H and V_k centres. From this we can put bounds on the difference in Madelung potential at the sites of the two components of the interstitial. In calculating the effect of this asymmetric potential, we can predict too the asymmetry in the hyperfine constants, which have also been measured. Quantitatively, however, it is more accurate to start from atomistic calculations of the geometry and to predict spectroscopic quantities. We shall follow this latter approach here.

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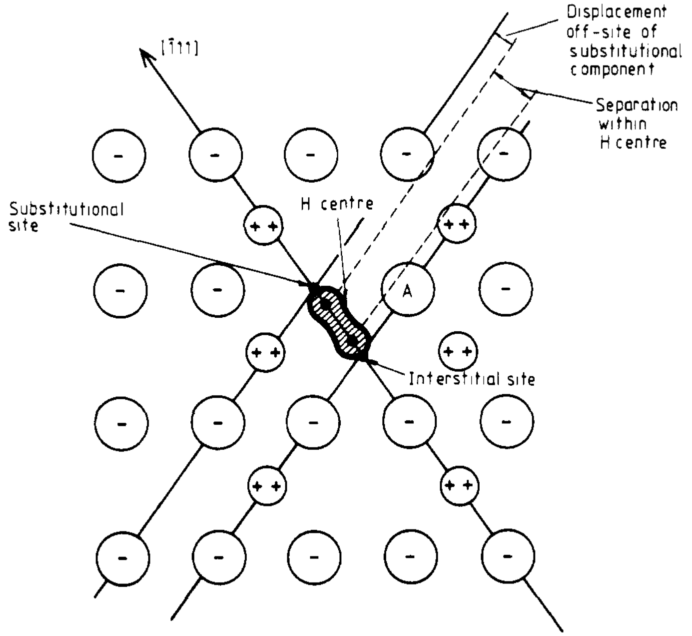

Figure 1. CaF$_2$ interstitial geometry. The diagram shows a (110) plane and defines the distances referred to in the text. The site A is one of the possible vacant sites for the self-trapped exciton.

2. Geometry and observed spectra

The H centre in the fluorite structure lies along a ⟨111⟩ axis, with one ion near the tetrahedral interstitial site and the other close to a substitutional site. There are thus two key distances—the separation within the H centre, and the shift of the ion closest to substitutional from the perfect lattice site. Since it is a rule from all other X_2^- systems that the X_2^- ion has a spacing close to its free-space equilibrium value, it is the shift rather than the separation that needs especial attention.

The main effect of the difference in Madelung potential between the two halogen sites is to mix the σ_u and σ_g molecular orbitals of the X_2^- molecular ion. The ultraviolet absorption band is one in which an electron is excited from the σ_g state to the σ_u state. Consider first a simple model in which the σ_u and σ_g orbitals both derive from non-overlapping atomic p_z orbitals (X_2^- is along the Oz axis):

$$\sigma_u = [p_{z1}(r) + p_{z2}(r)]/\sqrt{2} \tag{2.1}$$

$$\sigma_g = [p_{z1}(r) - p_{z2}(r)]/\sqrt{2} \tag{2.2}$$

or alternatively

$$p_{z1}(r) = [\sigma_u + \sigma_g]/\sqrt{2} \tag{2.3}$$

$$p_{z2}(r) = [\sigma_u - \sigma_g]/\sqrt{2}. \tag{2.4}$$

It is convenient to use the atomic orbitals, not the molecular orbitals, as a basis. When the two sites are equivalent, $\langle p_{z1}|\mathcal{H}|p_{z1}\rangle = \langle p_{z2}|\mathcal{H}|p_{z2}\rangle$ and the energy 2ε of the ultraviolet transition is determined by the off-diagonal matrix element $\langle p_{z1}|\mathcal{H}|p_{z2}\rangle$ (which is just ε in this case). When the sites are not equivalent there are extra terms defined by $2\Delta = \langle p_{z2}|\mathcal{H}|p_{z2}\rangle - \langle p_{z1}|\mathcal{H}|p_{z1}\rangle$. We then note that the transition energy is increased to

$$E_{uv} = 2\varepsilon[1 + (\Delta/\varepsilon)^2]^{1/2}$$

and that the wavefunctions, which determine the hyperfine constants, are now altered by terms which are functions of Δ/ε.

This model is too simple in several respects. First, it is clear that both s and p_z orbitals are involved. This means that we must consider a (4 × 4) secular determinant, involving s and p_z orbitals on the two sites (1) and (2) (site (1) refers to the one near the substitutional site and (2) the interstitial site). Secondly, there are complications in the choice of Δ. Normally one would argue that 2Δ is simply the difference in Madelung potential between the two sites. However, when the asymmetry is at all significant, the net charge on each ion changes, and we must consider the shifts in one-electron energy from intra-atomic effects.

The full (4 × 4) secular determinant within the basis of p_{z1}, p_{z2}, s_1 and s_2 is as follows:

$$\begin{vmatrix} E_p^0 - \Delta - E & \varepsilon & 0 & -V \\ \varepsilon & E_p^0 + \Delta - E & V & 0 \\ 0 & V & E_s^0 - \Delta - E & W \\ -V & 0 & W & E_s^0 + \Delta - E \end{vmatrix} = 0,$$

E_s^0 and E_p^0 are the energies of the 2s and 2p electron states respectively in free F^-. V and W are the off-diagonal energy matrix elements which are introduced with the inclusion of s orbitals. Qualitatively speaking, ε determines the ultraviolet absorption energy as mentioned earlier. V determines the s–p admixture of the hole state, and W describes the splitting of much deeper states which are primarily s-like. The absorption energy, as well as the hole population on the two inequivalent sites, are determined by $E_p^0 - E_s^0$, and not by the absolute values of the levels.

Various approaches may be made in the evaluation of the matrix elements. We decide to fit ε and V empirically to the experimental absorption energy and the s–p fraction of the V_k centre in fluorites. In this fashion ε is determined to be 1.935 eV and 1.845 eV respectively for CaF_2, SrF_2 and BaF_2. V is estimated to be 3.9 eV from the s–p fraction of V_k centre in alkali fluorides (Schoemaker 1966). W is not accessible directly. We therefore estimated its value to be somewhere around −1.0 eV. Indeed we found out that the hole state in the H centre depends very little on the precise values taken for V or W. For a change by a factor as large as 2 or more of these two parameters, the hole population at the two sites with respect to the s and p states varies by about 1%. This is obviously related to the large separation between E_p^0 and E_s^0. $E_p^0 - E_s^0$ is taken as 23.6 eV (the average in the energy difference in F^0 and F^- (Clementi and Roetti 1974)). In view of the large energy difference between s and p sub-bases, it has proved sufficient to handle s and p orbitals separately as (2 × 2) problems and treat the s–p admixture by perturbation. Finally, 2Δ requires some comments. This term represents the sum of the Madelung potential difference on the two sites and the difference in the one-electron energy resulting from the different charge state at the two sites. The first component is obtained from the lattice calculation, and the second has to be determined self-consistently by solving the secular determinant, as it depends on the net charge on the two sites. From the tabulated ionisation potentials (for fluorine the ionisation potential is

0.64 au and the electron affinity is 0.125 au) we can attain a low level of self-consistency by using linear interpolation. Specifically, if Z and $1 - Z$ are the fractional charges on the two ions of the H centre (e.g. with $Z = 0.6$ one has $F^{-0.6}$ near the lattice site and $F^{-0.4}$ near the interstitial site), then the second component in 2Δ is $14.01\,(1 - 2Z)$ eV. As there is only a slight difference, we have used the same value of 2Δ for the s orbitals. We are now in a position to estimate the value of Z, the transition energy and the one-electron wavefunctions. The wavefunctions will be related to the hyperfine constants by requiring the same parameters describe correctly the V_k centre spin-resonance data.

Even at this stage we can comment on the geometry from a comparison (table 1) of the observed V_k centre and H centre optical bands (Beaumont *et al* 1970, Williams *et al* 1976). Suppose that one of the two H centre ions remains exactly at the substitutional site, and that the other lies in a (111) direction at a distance equal to the free F_2^- ion separation. Then, from observed spectra and the known Madelung potentials, we deduce values 1.12 eV (CaF_2), 1.34 eV (SrF_2) and 0.72 eV (BaF_2) for 2Δ. From our model for 2Δ we find this implies Z to be 0.76 (CaF_2), 0.69 (SrF_2) and 0.69 (BaF_2). On the other hand, direct solution of the full secular determinant leads to values 0.65, 0.67 and 0.60 respectively; the slight discrepancy can be corrected by small changes in ion positions. From this simple calculation we learn three things. First, the closeness of the V_k centre and H centre bands itself gives useful geometric information. Secondly, the values of Z will be about 0.6–0.7, a point we confirm later in discussing hyperfine constants. Thirdly, only very modest changes from the assumed geometry are consistent with observation. This is one of several cases (V_k centres being another) where spectroscopic data alone give useful information on defect geometry.

Table 1. Optical transition energies. The experimental data are from Beaumont *et al* (1970), and the theory from the present paper, using the HADES predictions of geometry.

		Energy (eV)	
Host	V_k centre	H centre (experiment)	H centre (theory)
CaF_2	3.87	4.03	3.98
SrF_2	3.80	4.03	3.89
BaF_2	3.69	3.76	3.76

3. Atomistic calculations

We used a generalised Mott–Littleton (1938) approach to calculate the energetics of the H and F centres in the three alkaline earth fluorides. These atomistic simulation methods are coded in the HADES II program (Norgett 1974, Catlow 1980) which may be applied generally to the study of point defects in cubic crystals. The reliability of the methods used by the program has been demonstrated in several studies of point defect energies in ionic materials (Catlow and Norgett 1973, Catlow *et al* 1976, 1977).

Atomistic calculation requires the specification of interatomic potentials both for the host lattice interaction and for the interactions between host and defect ions. Shell model potentials for three alkaline earth fluorides are taken from the work of Catlow and Norgett (1973). For the H centre we took the intramolecular potential calculated using Hartree–Fock methods by Gilbert and Wahl (1971). This numerical potential was fitted to a simple analytical function of the Buckingham form by Norgett and Stoneham (1973). The same analytical function was used in our calculations. Interaction between the host ions and the component atoms of the H centre were taken to be the same as the lattice ion–ion interactions. Calculations were performed on the H centre with both polarisable and unpolarisable component atoms. In the former case the same polarisation parameters (shell charges and spring constants were used as for the lattice F^- ion.

Our calculations investigated a number of charge distributions in the H centre in order to determine whether an asymmetric charge distribution would be stabilised by the surrounding lattice. Thus, in addition to the symmetric case where both component atoms have a charge of 0.5, we examined asymmetric distributions in which we placed partial charges on the component atoms. The intra-atomic potential for F_2^- calculated by Gilbert and Wahl (1971) is only strictly applicable to the case of a symmetric charge distribution. Our calculation thus ignores the effects of the perturbation of the charge distribution on this interaction. However, our results are not strongly dependent on details of this potential, and this approximation should not seriously affect the reliability of our calculations.

The results which emerge confirm the qualitative arguments given in the earlier sections. First, we find the F_2^- spacing close to that (1.885 Å) of the free molecular ion. For $Z = 0.65$, the spacings are 1.90 Å (CaF_2), 1.922 Å (SrF_2) and 1.912 Å (BaF_2); as Z rises, the spacings increase by about 0.01 Å per $0.1|e|$ charge change. Secondly, one of the two fluorines remains close to the substitutional site. The displacements away from the anion site are 0.09 Å (CaF_2), 0.15 Å (SrF_2) and 0.23 Å (BaF_2) for $Z = 0.65$, increasing by about 0.04 Å per $0.1|e|$ increase in Z. The defect energy becomes systematically lower as Z rises. Basically, there is an energy advantage when the hole is near the interstitial site, where the Madelung potential is slightly favourable, rather than at the anion site, where the potential is repulsive. Roughly, the difference in Madelung potential changes by 0.45 eV per $0.1|e|$ change in Z, after allowance for geometry changes. This Madelung term is, of course, balanced by the shifts in one-electron levels discussed in § 2.

As in previous work on V_k centres (Norgett and Stoneham 1973) we find the energy is insensitive to the electronic polarisabilities assumed for the ions in the F_2^- molecular ion. However, the geometries do show some sensitivity: the separations become bigger, and the shifts of the substitutional ion less if there is no electronic polarisation (figure 2). This simply reflects the way the ionic polarisation takes up the response which would otherwise be achieved by the electronic terms.

4. Comparison with experiment for the H centre

We have seen that the broad-band optical data and the HADES calculations agree in their predictions of the H centre geometry. This verification can be seen from table 1. However, a stronger test of the picture comes from hyperfine constants. Using the fractional charge distribution on the two sites or, more exactly, using the eigenvectors obtained from the molecular secular determinant, one can estimate the isotropic and

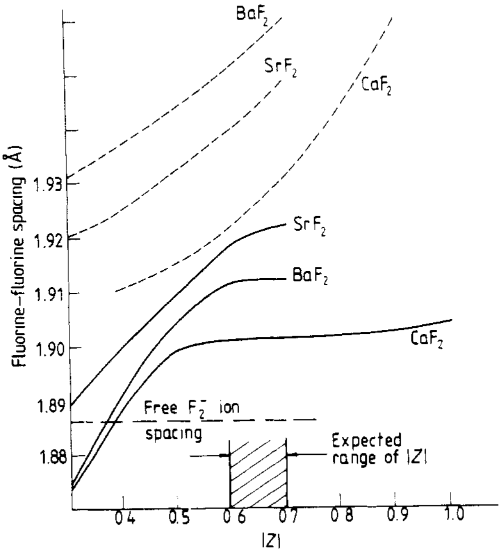

Figure 2. Equilibrium fluorine–fluorine spacings for different charges Z on the fluorine closest to the substitutional site. The broken lines refer to fluorines in the F_2^- ion which are electronically unpolarisable; the full lines assume the same electronic polarisability for these ions as for the other fluorine ions in the lattice.

anisotropic hyperfine constants on the two sites. The hyperfine constants are defined by

$$\begin{aligned}\mathcal{H}_{\mathrm{hf}} &= I_0 \boldsymbol{I} \cdot \boldsymbol{S} + I_1(3I_zS_z - \boldsymbol{I} \cdot \boldsymbol{S}) + I_2(I_xS_x - I_yS_y)\\ &= A_zI_zS_z + A_xI_xS_x + A_yI_yS_y.\end{aligned}$$

It is also possible to derive the A_z and A_x constants on the two sites and compare them directly with the experimental values reviewed by Hayes and Stoneham (1974). Table 2 presents these data. From the various studies the sign of A_x for V_k centres in fluorides is known to be negative. We have assumed the same sign here. Our model reproduces quite reasonable values for both the isotropic and the anisotropic parameters although the agreement is less satisfactory for the isotropic term. It is known that I_1 varies much

Table 2. Hyperfine interaction parameters (in Gauss) for the H centre in CaF_2, SrF_2 and BaF_2. Both (A_z, A_x) and (I_0, I_1) are given. The experimental data are bracketed. The superscripts a and b refer to the substitutional and the interstitial sites respectively.

	V_k		H centre			
Host	I_0	I_1	I_0^a	I_0^b	I_1^a	I_1^b
CaF_2	(267)	(316)	311 (221)	215 (230)	242 (186)	390 (425)
SrF_2	(269)	(315)	310 (230)	222 (258)	248 (188)	382 (406)
BaF_2	(269)	(315)	307 (246)	226 (265)	254 (211)	376 (392)

Host	A_z^a	A_z^b	A_x^a	A_x^b
CaF_2	795 (593)	995 (1079)	69 (|35|)	−175 (|195|)
SrF_2	806 (607)	986 (1071)	62 (|42|)	−160 (|148|)
BaF_2	815 (667)	978 (1048)	53 (|35|)	−150 (|127|)

less from system to system than I_0. We also obtain the general trends among the three fluorites adequately. It is to be noted that from our model the signs of the transverse components of A are opposite on the two sites.

5. Discussion

We have shown that one can construct a consistent 'molecule in a crystal' picture for the H centre in the fluorite structure, despite the low symmetry. The optical data alone give good results for the distortions, and distortions calculated atomistically lead to satisfactory hyperfine constants.

The natural extension of this work would be to treat the self-trapped exciton, in which a neutral vacancy (F centre) as well as a neutral interstitial (H centre) are involved. We have made preliminary calculations which show two main features. First, there are several sites near to the interstitial at which one might find the vacancy. Which site is favoured depends sensitively on how one treats the trapped electron in choosing a suitable interatomic potential. Secondly, if one makes a sensible choice of site the resulting hyperfine constants are not well represented by superposition of F and H centre contributions. Clearly, a fuller treatment is needed, and we defer this to a later paper.

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