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The self trapped hole in alkaline earth fluorides: I. Static properties

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Abstract. Optical and spin resonance properties have been calculated for the self trapped hole (V_k centre) in CaF_2, SrF_2 and BaF_2. The electronic properties are regarded as those of an F_2^- molecular ion whose internuclear spacing has been changed by the crystalline environment, and evidence is given that this is a good approximation. The spacing is obtained from a detailed lattice relaxation calculation allowing motion of many neighbours to the defect. The results are not sensitive to the different interatomic potentials used. Good agreement with experiment is obtained for optical transition energies and linewidths and for spin resonance parameters.

1. Introduction

The hole in alkali halides and alkaline earth fluorides is self trapped. Thus the polarization and distortion of the host lattice it produces make it very immobile, so that in many respects the hole centre (V_k centre) resembles a defect. Spin resonance and optical data are available for V_k centres in alkaline earth fluorides (Hayes and Twidell 1962, Marzke and Mieher 1969, Beaumont *et al* 1970), and show that the centres have [100] orientation. The model is shown schematically in figure 1.

The major approximation in the theory can be described as the 'molecule in a crystal' hypothesis. The spin resonance data show that the hole is concentrated on two of the fluorine ions. We shall assume that the electronic properties of the V_k centre are those of an F_2^- molecular ion, and that the crystal environment merely changes the interatomic spacing. The accuracy of the assumption can be tested in three ways. First, Jette *et al* (1969) give expressions for the hyperfine constants and excited states of the F_2^- ion, based on the Hartree–Fock calculations of Gilbert and Wahl (1971). If the hypothesis is valid, the observed spin resonance and optical data should define a unique separation. As can be seen from figure 2, the data agree quite well. It is not certain whether the deviations occur because the wavefunctions of the free molecular ion are not good enough, or because the crystal has a significant effect apart from changing the equilibrium spacing. A second test of the hypothesis concerns the hole charge density on ions neighbouring the F_2^- group. Hyperfine structure from the neighbouring axial ions has been detected. It is small for CaF_2, less in SrF_2 and undetectable in BaF_2. Thus the hole is almost completely concentrated on the F_2^- group. The third test of the 'molecule in a crystal' hypothesis concerns the effect of crystal fields on the molecular ion. Unlike the F_2^- ion, the V_k centre does not have axial symmetry so that there should be two

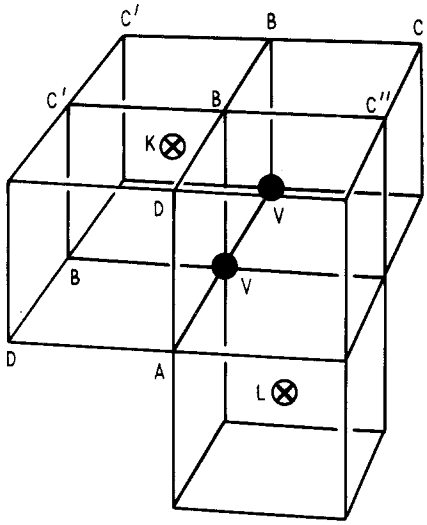

Figure 1. Geometry of the V_k centre in the fluorite lattice. The anions lie at the vertices of the simple cubic lattice shown. The two V_k ions are labelled V, and the two cations ⊗ labelled K and L. Anion notation follows that of Marzke and Mieher. Jette and Das include explicitly only the ions V, A, K and L, together with others related by symmetry; our work treats all labelled sites and their equivalents explicitly.

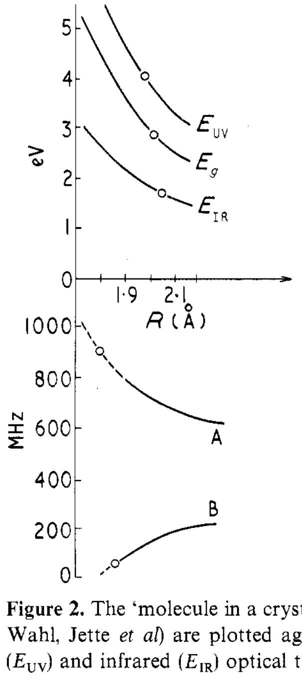

Figure 2. The 'molecule in a crystal' model. Properties of the F_2^- molecular ion (Gilbert and Wahl, Jette *et al*) are plotted against internuclear separation, R. These are the ultraviolet (E_{UV}) and infrared (E_{IR}) optical transition energies, the energy E_g derived from the g factor, and the hyperfine parameters A and B. Experimental values for the V_k centre do not differ significantly from CaF_2 to SrF_2 and BaF_2, and are plotted at the correct ordinate. All points should lie on the same vertical line if the hypothesis and calculations are exact. Present calculations estimate $R \sim 1{\cdot}9$ Å.

distinct g factors for magnetic fields normal to the axis, and certain optical transitions may be split. However, these effects are not seen; there are no observable deviations from axial symmetry.

In this paper we shall be primarily concerned with the lattice configuration near the V_k centre in alkaline earth fluorides. Lattice relaxation energies are also found. They are useful both in indicating stability and in studies of the motion of the V_k centre. The motion of the hole is considered in the following paper. Previous work on the lattice configurations of V_k centres has been given by Das *et al* (1964) and Jette *et al* (1969) for the alkali halides and by Jette and Das (1969) for CaF_2. The general approach here follows closely that of the earlier work. The main differences lie in our inclusion of work on SrF_2 and BaF_2, and in improvements in the lattice relaxation calculations. Thus many more ions are allowed to relax, and the interatomic potentials used are considerably better. The lattice distortion is substantial, so it is necessary to go beyond the simple harmonic motion of a small number of neighbours.

2. The model

In this section, we discuss the models used in our calculations. We describe in separate subsections the potential for the ions of the perfect lattice, a representation of the calculated potential for the F_2^- molecule and the interaction of the molecule and lattice. Our calculations use a much better crystal potential than that used by Jette and Das (1969) in earlier work on the V_k centre in CaF_2. The greatest uncertainty is in describing the lattice defect interaction; and here we use alternative potentials and show that our results are insensitive to the choice made.

2.1. Lattice potential

Jette and Das (1969) used a potential for the ionic interactions due to Reitz *et al* (1961). In addition, they employed the point-polarizable ion model to account for the polarization of ions close to the defect, treating the remainder of the crystal in the approximation of Mott and Littleton (1938). It is now clear that this type of calculation can encounter serious difficulties (see eg Lidiard and Norgett 1972) which arise because the point polarizable ion model represents a lattice which is too polarizable. In particular, there is a discontinuity in dielectric properties between the inner region of the crystal where the ions are relaxed explicitly and the outer Mott–Littleton region where the ions are displaced so as to give the proper continuum behaviour.

These difficulties are resolved by using a shell model which permits a realistic description of both elastic and dielectric properties. Catlow and Norgett (to be published) have recently made a detailed analysis of possible models for CaF_2, SrF_2 and BaF_2 with particular attention to the interionic potentials. They have shown that, using a common F^-–F^- interaction in all three crystals, it is possible to fit the elastic constants of all three fluorides and also obtain realistic values of the third order elastic constants. Catlow and Norgett have developed several variations of such a model. As a rule, we shall use a form with the interionic potentials fitted to the elastic properties of all three fluorides and shell parameters calculated from the transverse optic frequency, dielectric constants and ionic polarizabilities for each material separately. The potential parameters are collected in Appendix 1.

2.2. The F_2^- molecule potential

This potential has been computed by Gilbert and Wahl (1971) using a selfconsistent-field molecular orbital method. We have fitted their results at six points with interatomic separation between 1·4 Å and 2·6 Å using a three parameter potential

$$V(r) = A\exp(-r/\rho) - C/r^6. \tag{2.1}$$

This arbitrary choice of functional form was adopted because this type of potential was conveniently available in a general modular program HADES (Harwell Automatic Defect Evaluation System) for calculating relaxation about defects in ionic materials. The exponential form should give a reasonable description of overlap repulsion at small interatomic distances. The attractive inverse sixth term is invoked to describe bonding and the mutual polarization of the ions in the molecule.

2.3. The lattice-defect interaction

The dominant interaction is the monopole interaction due to the localized hole. In our calculation, the hole is spread equally between the two fluorine ions of the molecule. A less important interaction arises from the polarization of the defect ions by electric fields due to the lattice ions. As there is no way to specify how the lattice fields effect the bonding of the F_2^- molecule, we have considered two models. In the first, model I, the ions at which the hole is localized are unpolarizable. Alternatively, we assume that these ions can be represented as a charged shell and core coupled harmonically. In the second model, model II*a*, the shell parameters are the same as for the lattice fluoride ions. The polarization affects the bonding because the molecular potential is calculated as a function of the separation of the shells rather than the ionic cores.

The other problem is to specify the short range overlap interaction between lattice and defect. Our first two models regard the defect ions as normal F^- lattice ions in this respect. Our results for the single V_k centre do not seem to depend critically on this assumption, but in the following paper we show that such interactions dominate the calculated hopping behaviour of the V_k centre. At this point we present without comment results for a third model, model II*b*, which is the same as model II*a* except that the repulsive interaction between the ions of the V_k centre and the nearest lattice F^- ions on the defect axis are reduced by a half. The reasoning that leads us to consider such an anomalous model is given in the succeeding paper.

3. Calculation and results

We have calculated the equilibrium configuration and relaxation energy of the V_k centre. Following Mott and Littleton (1938), ions in an inner region are relaxed explicitly until they experienced no resulting force, while ions in the remainder of the lattice are displaced so that the polarization of the crystal is the same as that of the material regarded as a dielectric continuum.

Jette and Das (1969) employed the same approximation but limited the inner region to a very small region about the V_k centre and restricted the relaxation to be radial with respect to the centre of the defect. Using the HADES program, which employs fast relaxation methods (see eg Lidiard and Norgett 1972), we can readily carry out calculations involving the explicit relaxation of many more ions. Using our shell models, chosen so that the dielectric properties of the explicit lattice match the continuum dielectric behaviour enforced in the outer region, we find that the sequence of defect energies calculated as the inner region is expanded converges rapidly. We found no appreciable decrease in defect energy after including in the relaxation all ions that are third neighbour to any defect ion.

The calculation of the defect energy involves summing explicit interactions between pairs of ions in the inner region and also interactions between the explicit region and the continuum region. These latter terms involve infinite summations over contributions from all lattice points. The most important of these terms are the Madelung energy of each ion in the inner region and the leading polarization term due to the polarization of the lattice by the monopole field of the effective charge of the localized hole. These energy terms are computed using a rapidly converging summation method over the direct and reciprocal lattices. Smaller contributions to the interaction of the two regions are computed by explicitly summing the interaction of ions in region I with a finite number of ions in the adjoining continuum region. We find that these summations can be restricted to include only a few further shells surrounding the inner region and we have tested the convergence by demonstrating that the defect energies do not change significantly as the summations are extended.

Table 1. Energies of V_k centre (in eV)

	Model I	Model II*a*	Model II*b*
CaF_2	5·04	4·99	4·89
SrF_2	4·75	4·70	4·65
BaF_2	4·35	4·26	4·25

The results of our relaxation calculations are contained in tables 1 to 3. In all cases the numerical results are accurate to at least the number of figures quoted. Table 1 contains the defect formation energies. The formation energy is the energy required to remove two F^- ions separately to infinity and then to introduce an F_2^- molecule, originally with the atoms separated, into the crystal. The defect energies are very similar for all three potential models. Table 2 contains the interionic separations of the two ions of the $F_2{}^-$ molecule. Again there is very little variation between the results obtained with different potentials but it is more significant that the interionic separations are effectively the same in all three crystals.

Table 2. Atomic separation of V_k centre (in Å)

	Model I	Model II*a*	Model II*b*
CaF_2	1·93	1·87	1·89
SrF_2	1·95	1·90	1·91
BaF_2	1·96	1·84	1·84

Our relaxation calculations also give displacements and dipole moments of the neighbouring ions in the crystal. The pattern of results is similar for all three substances so, rather than give many values, we include in table 3 the displacements calculated for CaF_2 using the three different models. These can be compared directly with the results of Jette and Das (1969).

Table 3. Displacements and dipole moment axis for CaF_2

Undisplaced site(a)	Displaced site(b)			Dipole axis(c)
V ($\frac{1}{2}$, 0, 0)	0·3549	0	0	(1, 0, 0)
	0·3500	0	0	
	0·3464	0	0	
	0·369	0	0	
K (0, $\frac{1}{2}$, $\frac{1}{2}$)	0	0·5741	0·5741	(0, 0·71, 0·71)
	0	0·5786	0·5786	
	0	0·5774	0·5774	
	0	0·5919	0·5919	
B* ($\frac{1}{2}$, 1, 0)	0·5007	0·9799	0·0141	(0·02, 0·11, −0·99)
	0·4994	0·9798	0·0159	
	0·4988	0·9811	0·0155	
	—	—	—	
L (1, $\frac{1}{2}$, $-\frac{1}{2}$)	1·0137	0·5199	−0·5199	(0·74, 0·48, −0·48)
	1·0127	0·5177	−0·5177	
	1·0106	0·5182	−0·5182	
	1·0192	0·5096	−0·5096	
A ($\frac{3}{2}$, 0, 0)	1·4377	0	0	(1, 0, 0)
	1·4412	0	0	
	1·4096	0	0	
	1·419	0	0	
C′* ($\frac{1}{2}$, 1, 1)	0·5089	1·0200	1·0200	−(0·88, 0·47, 0·47)
	0·5098	1·0220	1·0220	
	0·5096	1·0214	1·0214	
	—	—	—	

(a) Units of length: F–F separation in the undistorted lattice. Ions labelled * were displaced by Jette and Das in the Mott–Littleton approximation.

(b) Order: (i) Model I, this paper; (ii) Model II*a*, this paper; (iii) Model II*b*, this paper; (iv) Jette and Das radial relaxation to the geometric centre of the V_k centre is assumed. C″ and D displace by less than 1% of the F–F separation.

(c) Dipole axes for model II*a*; others much the same.

4. Discussion

The most important parameter predicted is the separation of the two ions constituting the V_k centre. Experiment, together with the 'molecule in a crystal' hypothesis, suggests separations of about 2·01 Å from optical data and about 1·85 Å from spin resonance results. Our predicted separations of the ion cores lie between 1·84 Å and 1·96 Å, depending on the model and host lattice.

None of the results are sensitive to the model chosen, so that the polarization of the V_k centre is unimportant. In addition, the separations vary little from CaF_2 to SrF_2 to

BaF_2, and for certain models there are no simple trends. This occurs because the shell model parameters we have used do not vary systematically through the sequence of fluorides. These results show that the F_2^- molecule is only slightly distorted in the crystal, since Gilbert and Wahl (1971) give a free molecule separation of 1·90 Å. Any differences are only of the order of the error in our parameterization of the molecular potential which has a true minimum at 1·95 Å. In the same way, there is no essential difference between our results and those of Jette and Das (1969) who find the separation to be 2·01 Å for CaF_2.

The displacement of the ions adjacent to the defect are basically similar for all three materials. The results in table 3 for CaF_2 show also that the displacements do not vary for the three different potentials. Moreover, we see that the more restricted calculations of Jette and Das agree with ours in general, although there are differences in detail. Thus the displacement magnitudes are often different, as shown clearly by the A, V and K sites, whose direction of displacement is fixed by symmetry. The directions of displacement are different in other cases, notably for the L cations which move more nearly parallel to the V_k axis than in the earlier work. We give calculated displacements for some ions (eg B and C′) which Jette and Das included in the Mott–Littleton region only and have not published explicit values of the relaxation.

No experimental estimates of atomic positions are available. In principle, some idea of the displacements could be obtained from the ENDOR work of Marzke and Mieher (1969), but detailed calculations have not been published. One would expect, however, that the orientation of the dipole moments of the fluorine ions in our work would bear some simple relation to the principal axes of the hyperfine tensor. There are indeed similar trends, although not apparently agreement in detail.

Our calculated energies of the V_k centre can be used to estimate the stability of the self trapped hole relative to a hole in its lowest energy state in the valence band of an undistorted crystal. The two energies can be estimated by taking two cycles of operations, starting from the same configuration in each case. Similar cycles have been described by Jette *et al* (1969) and Fowler (1968). We find that the self trapped configuration is more stable, as observed, if the energy

$$E_s = E_{vk} + \tfrac{1}{2}E_v - E_m \tag{4.1}$$

is negative. Here E_{vk} is our calculated defect energy, E_v is the width of the valence band in the undistorted crystal, and E_m is the anion Madelung energy. The result assumes the repulsive parameters of F^0 and F^- are the same, a result which is probably adequate and is consistent with our models. Values of E_s for model I are:

CaF_2: $\tfrac{1}{2}E_v - 5{\cdot}72\,\text{eV}$

SrF_2: $\tfrac{1}{2}E_v - 5{\cdot}39\,\text{eV}$

BaF_2: $\tfrac{1}{2}E_v - 5{\cdot}14\,\text{eV}$.

For all plausible estimates of E_v, these are negative, confirming that self trapping should occur.

We have also estimated the effective force constants κ and effective masses ϕ for relative motion of the V_k ions in which the other ions follow adiabatically. This is an oversimplification, since the other ions, especially the heavy cations, will not follow so rapidly. In consequence, ϕ is probably too large and κ too small. The product, $\phi\kappa$, needed later, may be reasonably accurate. The results are summarized in table 4. The force constants are best compared directly with the free molecule value, since it is not possible

Table 4. Linewidths, effective force constants, masses and frequencies

Model	Force constant κ ($\mathrm{eV\,Å^{-2}}$)	Mass ϕ ($\frac{1}{2}$ fluorine mass)	Linewidth W (eV)	Phonon energies ($\mathrm{cm^{-1}}$)†		
				(A)	(B)	(C)
CaF_2I	12·15	1·66	0·99	474	265	475
CaF_2II*b*	8·23	1·88	1·05	367	265	475
SrF_2I	11·55	2·10	0·94	411	191	382
SrF_2II*b*	9·16	2·52	0·95	334	191	382
BaF_2I	11·06	3·35	0·85	319	133	335
BaF_2II*b*	5·66	3·00	1·03	241	133	335
Free molecule	12·36	1·00	—	616	—	—

† (A) From (4.4) using κ from this table; (B) from the temperature dependence of observed hyperfine constants; (C) longitudinal optical phonon energy. The frequencies (A), (B), (C) need not be related.

to get a really accurate fit to the curvature near the minimum of the F_2^- potential. Indeed, Gilbert and Wahl quote values which correspond to a value of κ some 30% smaller than from (2.1).

The linewidths of the optical bands can be predicted in terms of ϕ and κ, assuming that the higher electronic energies are linear in the separation of the V_k ions near the minimum (Das *et al* 1964). If κ is in $\mathrm{eV\,Å^{-2}}$ and ϕ in units such that $\phi = 1$ for the free molecular ion, then the width of the ultraviolet band is given by:

$$W = 2{\cdot}09/(\phi\kappa)^{1/4}\ \mathrm{eV}. \tag{4.3}$$

The infrared band should be about 25% narrower. The predictions are shown in table 4, and are in excellent agreement with the observed values of about 1 eV (Beaumont *et al* 1970).

Another question concerns the temperature dependence of the V_k hyperfine constants (Assmus and Dreybrodt 1969), which involves a characteristic frequency. We have verified, in agreement with Assmus and Dreybrodt, that this characteristic frequency is always much less than that associated with the relative motion of the V_k ions:

$$\hbar\omega = 175{\cdot}32\sqrt{\kappa/\phi}\ \mathrm{cm^{-1}}. \tag{4.4}$$

Even using the lower Gilbert–Wahl value for the free ion κ and assuming adiabatic motion of the neighbours, $\hbar\omega$ is too large. Assmus and Dreybrodt attribute the temperature dependence of the hyperfine constants to modes involving only cation motion.

5. Conclusion

We have carried out detailed calculations on the V_k centre in CaF_2, SrF_2 and BaF_2 using the 'molecule in a crystal' hypothesis. Results for optical transition energies, linewidths, and hyperfine constants are in good agreement with experiment. Thus the static properties of the centre verify the model, and are not sensitive to the detailed interatomic potentials chosen. In the following paper we treat the V_k hopping motion by the same methods.

Acknowledgments

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Appendix 1. Interionic potentials

A1.1. Lattice potential

Cation–Anion potential	$V(r) = A_{+-} \exp(-r/\rho_{+-})$
Fluorine–fluorine potential	$V(r) = A_{--} \exp(-r/\rho_{--}) - C_{--}/r^6$
Shell charges	$Y_+ \quad Y_-$
Spring constants	$k_+ \quad k_-$

	CaF_2	SrF_2	BaF_2
A_{+-} (eV)	1329·6	2001·6	3212·1
A_{--} (eV)	1808·0	1808·0	1808·0
ρ_{+-} (Å)	0·2979	0·2979	0·2979
ρ_{--} (Å)	0·293	0·293	0·293
C_{--} (eV Å^6)	109·1	109·1	109·1
Y_+ ($\lvert e \rvert$)	5·24	7·53	−16·99
Y_- ($\lvert e \rvert$)	−2·38	−3·70	−1·59
k_+ (eV Å^{-2})	320·9	530·3	1709·1
k_- (eV Å^{-2})	101·2	252·4	43·5

A1.2. F_2^- molecule potential

$$V(r) = A \exp(-r/\rho) - C/r^6$$
$$A = 17279{\cdot}0 \text{ eV}$$
$$\rho = 0{\cdot}2366 \text{ Å}$$
$$C = 343{\cdot}2 \text{ eV Å}^6$$

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