Simulation of F, F_2^+, and $(F_2^+)^*$ centres in NaF:Mg

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Abstract. The object of this work is to determine the atomistic and electronic configuration of the (F$_2^+$)* centre in NaF. This centre combines an F$_2^+$ centre with an impurity dipole consisting of an Mg^{2+} substitutional ion and an Na vacancy. There are many conceivable configurations for such a combination, and our calculations lead us to propose a particular one. Our result agrees with an earlier experimental conclusion that, in its ground state, this centre has the excess electron localized in a single vacancy, more like an F centre than an F$_2^+$ centre. Our method uses effective potentials derived for interaction of the excess electron with host and impurity ions. We also present a detailed analysis of the F- and F$_2^+$-centre ground states, including isotropic hyperfine constants. The F$_2^+$-centre results support the picture of substantial localization about this defect's centre.

1. Introduction

The (F$_2^+$)* centre has been identified as an F$_2^+$ centre modified by a divalent cation (Mollenauer 1980). In the present work we consider Mg^{2+}. The impurity has the effect of increasing the thermal stability of the defect in laser operations (Mollenauer 1980; Eisele *et al* 1982). In 1985, spin resonance results led to a proposed model of the (F$_2^+$)* centre (Hofmann *et al* 1985). These results strongly suggested that the centre's ground state was like a perturbed F centre, with the excess electron localized in a single anion vacancy, rather than an F$_2^+$ centre with the electron shared between two vacancies.

The Mg^{2+} substitutional impurity is associated with a charge-compensating Na vacancy, denoted V$'_{Na}$. These two defects together constitute an electric dipole in the crystal, oriented from V$'_{Na}$ to Mg^{2+}. The crystal also contains F^{2+} centres, consisting of a pair of F$^-$ vacancies at nearest anion sites, sharing a single electron. Since the F$_2^+$ centre has a net positive charge, it seems intuitively that the impurity dipole will associate with it so as to point away; that is, the V$'_{Na}$ will be nearer the centre of the F$_2^+$ than will the Mg^{2+}. If the two F$^-$ vacancies of the F$_2^+$ centre lie symmetrically relative to the impurity dipole (see, e.g., figure 1), the combined defect would be a perturbed F$_2^+$ centre. Since, experimentally, this is not so, the two F$^-$ vacancies must be asymmetrical, either through spontaneous symmetry breaking by the electronic configuration combined with elastic relaxation, or in an asymmetrical combination with the dipole. Hofmann *et al* (1985) illustrated the latter case as in figure 2, with the dipole 'split', i.e. with the V$'_{Na}$ and Mg^{2+} in second-nearest positions. Even if we restrict V$'_{Na}$ to one of the three inequivalent nearest-neighbour positions relative to the F$_2^+$ centre, there is a large number of unsplit dipole configurations, and many additional split ones. In fact, we count 23 unsplit and 16 split configurations. In principle, if one can calculate the total energies of all these cases, the lowest one will correspond to the most probable configuration. That has been the main object of this work.
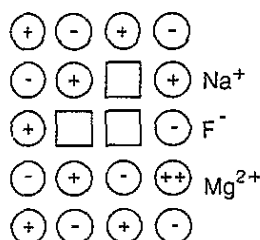
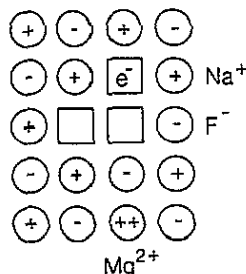**Figure 1.** $(F_2^+)^*$ centre in NaF: symmetrical configuration.

Figure 2. $(F_2^+)^*$ centre in NaF: configuration proposed by Hofmann *et al* (1985).

In section 2, a procedure wil be outlined to render this a practical undertaking. In section 3, subsidiary results on the ordinary F centre (a single excess electron in an F^- vacancy) are presented, including isotropic hyperfine constants for nearest cation and anion neighbours. In section 4, similar results, limited to cation neighbours, are presented for the ordinary F_2^+ centre, in the most detailed simulation of this defect to date. In section 5, our results for the $(F_2^+)^*$ centre are presented and discussed in detail. In particular, we present two configurations with significantly lower energy than that conjectured by Hofmann *et al* (1985).

2. Method

The method of choice for electronic defects in ionic crystals is embodied in a computer program with the acronym ICECAP (Harding *et al* 1985). The method, and many results derived using it, have recently been reviewed (Vail 1990, Vail *et al* 1991). Briefly, a point defect is simulated by a quantum-molecular cluster which includes some neighbouring ions. The rest of the infinite crystal is simulated by the shell model. The embedding shell-model crystal is coupled to the cluster by short-range forces, and by Coulomb interaction with a set of point charges that simulate the charge distribution within the quantum cluster. The quantum cluster is determined so that it is consistent with the harmonic displacements and polarizations of the embedding shell-model ions. In this way, lattice distortion and polarization due to the defect are included self-consistently with the quantum-mechanical solution for the defect cluster. This solution is obtained by the unrestricted Hartree–Fock approximation including the self-consistent field. A number of refinements of this basic approach are described in the reviews (Vail, 1990, Vail *et al* 1991).

Now consider the $(F_2^+)^*$ centre. This is a point defect that involves four atomic sites. In the Hofmann configuration, figure 2, these sites have 18 nearest neighbours (nine Na^+

and nine F^- ions), and the defect has very low symmetry. Thus, even with a minimal basis set, and limited to a nearest-neighbour cluster, such a defect leads to quite a large quantum-chemistry calculation. Furthermore, in minimizing the total energy self-consistently between quantum cluster and shell-model embedding lattice, the ICECAP program varies the positions of ions in the cluster, and at each step of this variation, the quantum-chemistry calculation is repeated. Thus to analyse the Hofmann configuration alone is bordering on the prohibitive, in terms of computer space and time. To also analyse several dozens of other configurations is truly prohibitive.

In order to render our study practicable, we have devised a two-stage process. Briefly, we derive effective classical short-range potentials for the interaction of an excess electron with the ions of the crystal. This then enable us to perform ICECAP calculations with a one-electron quantum cluster consisting solely of the excess electron. Such calculations take very little time, and therefore many different configurations can be considered. We now discuss this approach in detail, because its implementation is far from straightforward.

First, what potentials are needed? Well, we shall consider two classes of configuration, one in which excess electron is localized in a single F^- vacancy, the other whose symmetry allows it to be equally shared between the two such vacancies. These two cases correspond respectively to F-type and F_2^+-type defects. We begin with the F centre. Its interactions with first-neighbour Na^+ ions and second-neighbour F^- ions need to be considered. For this, we use a quantum cluster consisting of an F centre with its six nearest and twelve second-nearest neighbours. By dilating and contracting one set of neighbours with the other kept fixed, we obtain a total-energy curve. Next, the F centre is represented by a single quantum-mechanical electron, with all the ions represented by the shell model. Short-range interaction of the F centre with a given set of ions is represented by a Buckingham-type classical potential. We then evaluate the total energy again, requiring that the short-range potential yield the same shape of energy curve as given by the second-neighbour quantum cluster. In the quantum-cluster calculations, the atomic orbital(s) for the F centre are optimized. The *same* orbitals are used in the one-electron calculations, so that the fitted potentials may represent the quantum-mechanical effect of the F centre's environment.

Next consider the F_2^+ centre. Since the excess electron is shared equally between the two F^- vacancies, we first simply scaled the F-centre potentials by 0.5. However, this did not produce good agreement with the equilibrium configuration derived from a nearest-neighbour cluster. We therefore derived a potential for F_2^+-centre–Na^+ interactions as we had done for the F centre, using the nearest-neighbour cluster of ten Na^+ ions with optimized excess-electron orbitals. The scaled F-centre–F^- potential was maintained in this analysis.

In addition to the above, an Mg^{2+}-F^- potential was derived, and also an F-centre–Mg^{2+} potential from nearest-neighbour clusters.

In applying the F-centre potentials to various $(F_2^+)^*$ configurations, the F-centre orbital was held fixed as discussed above, but the orbital's position was varied to minimize the total energy. We remark that the method that we have described retains the quantum-mechanical energy of the excess electron, including interaction with the ions approximately, and accuately reflects the significant polarization effect of the charged defect on the embedding crystal.

3. The F centre

In order to derive potentials for F-centre interaction with host-crystal ions, as discussed in section 2, basis sets are required for the F centre, and for Na^+ and F^- ions. For Na^+

and F^- the (43/4) free-ion contractions of Huzinaga (1984) were used. For the F centre, a 1s Gaussian $\sim \exp(-\alpha r^2)$ was used, with optimized exponential coefficient $\alpha = 0.09a_0^{-2}$, where a_0 is the Bohr radius. Adding a second 1s orbital, optimized, only lowered the energy by 0.03 eV, and this was not continued. For the embedding shell-model crystal, short-range potentials for NaF were taken from Catlow *et al* (1977). To test whether the excess electron would localize to some extent on the nearest-neighbour Na^+ ions, the 3s orbital from the (433/4) free Na basis set of Huzinaga (1984) was added to the calculation. Mulliken population analysis shows only about 0.02 electrons per ion for each of the six Na^+ 3s orbitals, which we take to be negligible.

The F-centre potentials will be given in section 5. In deriving them from second-neighbour quantum clusters, the ground state was determined. The excess electron is almost completely localized in the vacancy with a Gaussian 1s exponential coefficient $\alpha = 0.09a_0^{-2}$ corresponding to a localization radius $R = (2\alpha)^{1/2} = 2.36a_0$ compared to nearest-neighbour spacing $a = 4.34a_0$ for NaF. The nearest neighbours were undisplaced from perfect-crystal positions, while second-neighbour F^- ions relaxed inward by $0.01a$, under the influence of the defect. The unrestricted Hartree–Fock solution enables us to calculate the spin densities at Na and F nuclei in the cluster. From these, the isotropic hyperfine constants can be evaluated and compared with experiment (Seidel and Wolf 1968). The results are given in table 1. Although agreement to within about 25% for Na^+ is encouraging, the factor of three disagreement for F^- suggests that our treatment of the problem does not allow for enough spin polarization and/or charge transfer for the second-neighbour F^- ions.

Table 1. F-centre ground state in NaF: calculated spin densities S (units $\hbar/(2a_0^3)$), and calculated and experimental isotropic hyperfine constants A (units MHz), for nearest-neighbour Na^+ and second-neighbour F^- ions.

$S(Na^+)$	$S(F^-)$	A(Na^+)		A(F^-)	
		Calculated	Experimental[a]	Calculated	Experimental[a]
0.0674	0.0076	80	107	32	97

[a] Seidel and Wolf (1968).

4. The F_2^+ centre

The F_2^+ centre was analysed with a nearest-neighbour cluster containing ten Na^+ ions. The excess electron basis set was found to contain s and p atomic orbitals in each vacancy, of even parity for the ground state. Their exponential coefficients were $0.09a_0^{-2}$ and $0.11a_0^{-2}$ respectively. The orbital centres were separated by $1.33a$, compared to $1.41a$ between vacancy centres; i.e. they relaxed toward the defect's centre of symmetry. The p-type orbitals were oriented along the defect's axis, with very weak transverse components. The total Mulliken populations in s- and p-type orbitals were 0.47 and 0.07 respectively in each vacancy, indicating some slight charge transfer into the defect ($\sim 9\%$). A model of the F_2^+ centre with excess-electron basis orbitals s and d at the defect centre, optimized, had a higher energy by 0.8 eV. In a coordinate system where the two F^- vacancies are at $(\pm 0.5, \pm 0.5, 0)$, representatives of the three sets of inequivalent nearest neighbours were found to have relaxed positions at $(0.55, -0.55, 0)$, $(0.49, 1.55, 0)$, and $(0.49, 0.49, 1.05)$, indicating 5% dilation due to the positive charge of the defect. We calculated the corresponding spin

densities and anisotropic hyperfine constants for these displaced ions. The results are given in table 2. Experimental values have not been resolved (Hofmann *et al* 1985). The fact that the spin densities at the two Na^+ nuclei nearest the defect centre are an order of magnitude greater than those at the other nearest-neighbour sites agrees with the observation of Hofmann *et al* (1985) that the excess electron is concentrated toward the defect centre. When relaxation due to the defect is ignored, the calculated of A is 249 MHz, 25% higher than after relaxation. The data presented above constitute the first detailed picture of the F_2^+ centre.

Table 2. F_2^+ centre ground state in NaF: calculated spin densities S (units $\hbar/(2a_0^3)$) and isotropic hyperfine constants A (units MHz), for nearest-neighbour Na^+ ions.

Coordinates	S	A
(0.55, −0.55, 0)	0.1595	189
(0.49, 1.55, 0)	0.0102	12
(0.49, 0.49, 1.05)	0.0260	31

5. The $(F_2^+)^*$ centre

Following the procedure described in section 2, potentials have been derived of the Buckingham type:

$$V(r) = [B \exp(-r/\rho) - C/r^6] \tag{1}$$

for interaction of an F centre with host Na^+ and F^- ions, of an F_2^+ centre with Na^+ ions, and for an Mg^{2+} ion with F^- ions and with an F centre. F_2^+ interaction with an F^- ion was scaled by 0.5 from F-centre interaction with an F^- ion. It was assumed that Mg^{2+}-Na^+ interaction is negligible. Fitted values of the parameters B, ρ and C and are given in table 3. It is instructive to compare the potentials of table 3 with those derived by other workers for perfect crystals. Catlow *et al* (1977) have derived and applied shell-model parameters for NaF, and Mackrodt and Stewart (1979) have derived them for MgF_2. These values are given in table 4. We have adopted the NaF values of Catlow *et al* in the present work. For NaF, comparing entries in tables 3 and 4, we see that F centre–Na^+ and F^-–Na^+ are qualitatively distinct, as one would expect. The same is true of F centre–F^- compared to F^-–F^-. Again, comparing Mg^{2+}-F^- interaction in NaF and MgF_2, the difference, due to different lattice structure, is striking.

Table 3. Buckingham-potential parameters B, ρ, and C (1) derived for short-range interactions in NaF.

Species	B (eV)	ρ (Å)	C (eV Å^6)
F centre–Na^+	4493.82	0.27484	212.199
F centre–F^-	7272.47	0.37117	2073.114
F_2^+ centre–Na^+	914.36	0.27494	12.476
F_2^+ centre–F^-	3636.24	0.37117	1036.552
Mg^{2+}–F^-	2246.91	0.18559	1036.557
Mg^{2+}–F centre	16.07	1.2201	0.0

Table 4. Buckingham-potential parameters B, ρ, and C (1) for perfect crystals.

Crystal	Species	B (eV)	ρ (Å)	C (eV Å^6)
NaF[a]	Na^+–F^-	1594.2	0.2555	0.0
	Na^+–Na^+	7895.4	0.1709	11.68
	F^-–F^-	1127.7	0.2753	11.68
MgF$_2$[b]	Mg^{2+}–F^-	4378.43	0.226 14	0.4393

[a] Catlow *et al* (1977).
[b] Mackrodt and Stewart (1979).

Applying the potentials listed in table 3, along with those of Catlow *et al* (1977), table 4, and single excess-electron F- or F_2^+-centre wave functions derived in large-cluster calculations as described in section 3 and 4, we have examined all 39 configurations of the $(F_2^+)^*$ centre having the V'_{Na} at a nearest-neighbour site of the F_2^+ centre, including both split and unsplit dipoles. The single quantum-mechanical electron's wave function was kept rigid: only the position of its centre was optimized, as discussed in section 2. In applying the ICECAP program to this problem we encountered a difficulty that significantly limits the conclusions we can deduce. Because of the low symmetry and extended structure of some of the configurations, we had to limit the size of the so-called Region I of the defect, that is, the region within which ionic positions are varied independently without applying the harmonic approximation. It was found that some configurations allowed a large Region I, and that, at that level, the total energy was sensitive (to ~ 0.1 eV) to the Region-I size. Furthermore, the same origin could not be used for all configurations, and again the total energy was sensitive (to ~ 0.4 eV) to the choice of origin. We restrict our attention to two origins that permit comparisons amongst several configurations, namely an origin at one vacancy of the F_2^+ centre, and an origin at the V'_{Na} site of figure 2. If we list configurations in order of total energy (lowest energy first) for both origins, we find quite a few configurations (14) with lower energies than that conjectured by Hofmann *et al* (1985) (figure 2). Unfortunately, the latter can only be calculated from one origin, the V'_{Na} site. Of the four configurations that can be calculated from both origins, only one has both energies (differing by 0.3 eV) lower than that of Hofmann *et al* . This configuration, denoted 22b, is shown in figure 3. The overall lowest energy is for configuration 6b, shown in figure 4, calculated only from the V'_{Na} origin. Their relative energies, all from the same origin are: 6b, -15.438 eV; 22b, -15.258 eV; Hofmann *et al*, -14.953 eV. There is no significance to the notations 6b and 22b referred to above; they are simply labels that we used to distinguish different configurations.
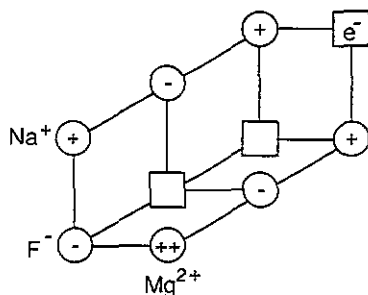
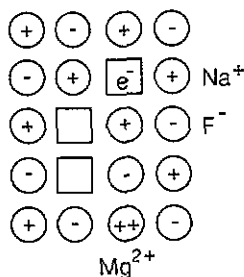**Figure 3.** $(F_2^+)^*$ centre in NaF: configuration 22b (see section 5).

Figure 4. (F$_2^+$)* centre in NaF: proposed ground-state configuration, denoted 6b (see section 5).

We verified that configurations with the Mg^{2+} impurity at a nearest-neighbour site of the F$_2^+$ centre had energies significantly higher than those with the V$'_{Na}$ at such sites. There is only one configuration symmetrical relative to the two F$^-$ vacancies, and even this undergoes symmetry breaking, with a lower energy when the excess electron is in one F$^-$ vacancy rather than equally shared between the two. Thus our model gives agreement with the experimental observation of Hofmann *et al* (1985) that this centre in its ground state is like a modified F centre (single-centred excess electron). Our calculated results, described above, lead us to favour configurations 6b and 22b (figures 3 and 4) over the Hofmann *et al* conjecture (figure 2). Intuitive reasoning supports this view. In figure 2, the vacancy V$'_{Na}$ tends to drive the excess electron to unstable equilibrium shared equally between the two F$^-$ vacancies, and only the distance Mg^{2+} impurity of the split dipole causes localization in a single vacancy. In figures 3 and 4 however, the V$'_{Na}$ keeps the excess electron out of the F$^-$ vacancy nearest to it, with maximum effect when the impurity dipole points away from the negatively charged V$'_{Na}$ in such a way that the Coulomb attraction between Mg^{2+} and the excess electron plays a small role in further stabilizing the latter. Of course, such intuitive arguments would not be contemplated in the absence of explicit calculated results, because there are several mutually dependent contributions to the energy, not simply coulombic ones.

Quantitatively, we note energy differences calculated amongst figures 4, 3 and 2 to be 0.3 eV and 0.2 eV respectively. Although these represent substantial thermal stability, of the order of 2000–3000 K, they are comparable to the uncertainty of the one-electron simulations. Nevertheless, because of the way we have cross-checked between sets of consistent calculations at different origins, we believe that figures 3 and 4 represent the most stable configurations of the (F$_2^+$)* centre's ground state. This could be further tested by much larger calculations on clusters representing these two configurations, containing several quantum-mechanical ions and many electrons. If their energy ordering and difference agree substantially with those obtained here, we could be confident of the result. The identification of the configuration of figure 4 as the ground state would then open the way for a simulation of the optical excitation and emission processes. Such calculations are presently beyond our capacity.

The method developed here could be useful in the analysis of other complicated point defects, particularly once the ICECAP program is modified to allow more classes of ions in Region I. The main use of the method is to identify one or more low-energy configurations from a large number of possibilities. Detailed electronic properties require that such an analysis be followed by larger-cluster calculations.

Acknowledgments

References

Catlow C R A, Diller K M and Norgett M J 1977 *J. Phys. C: Solid State Phys.* **10** 1395

Eisele H, Paus H J and Wagner J 1982 *IEEE J. Quantum Electron* **QE-18** 155

Harding J H, Harker A H, Keegstra P B, Pandey R, Vail J M and Woodward C 1985 *Physica* B **131** 151

Hofmann D M, Lohse F, Paus H J, Smith D Y and Spaeth J-M 1985 *J. Phys. C: Solid State Phys.* **18** 443

Huzinaga S (ed) 1984 *Gaussian Basis Sets for Molecular Calculations* (New York: Elsevier)

Mackrodt W C and Stewart R F 1979 *J. Phys. C: Solid State Phys.* **12** 431

Mollenauer L F 1980 *Opt. Lett.* **5** 188

Seidel H and Wolf H C 1968 *Physics of Color Centers* ed W B Fowler (New York: Academic) ch 8

Vail J M 1990 *J. Phys. Chem. Solids* **51** 589

Vail J M, Pandey R and Kunz A B 1991 *Rev. Solid State Sci.* **5** 241