

Electronic structure of the V^- centre in MgO

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Abstract. We have investigated in detail the two models of the V^- centre, where a hole is trapped at a cation vacancy. These are the model of Bartram, Swenberg and Fournier, where optical transitions occur within an O^- ion, and the model of Schirmer, Koidl and Reik, which involves a hole hopping from one oxygen ion to another.

Our calculations show (i) that the hole should be self-trapped on a single oxygen, as observed, (ii) that our predictions of ground-state ionization energy and of elastic and electrical dipole moments (apart from some uncertainties in local-field corrections) agree adequately with measurements, (iii) that the transitions within an O^- ion appear to account for observed structure at around 1.5 eV, both in energy and oscillator strength, and (iv) that the observed 2.3 eV band corresponds to the transition suggested by Schirmer *et al.* Calculations are also given for some centres related to the V^- centre, V^0 , $V_{(A)}$ and $[Na]^0$, again predicting optical absorption in good agreement with experiment.

1. Introduction

Centres in which a hole is trapped by a cation vacancy have been observed in many oxides. The review of Hughes and Henderson (1972) describes data for these V^- centres in the cubic oxides MgO, CaO and SrO, for the wurtzite systems BeO and ZnO, and for alumina. No doubt analogous centres exist in more complex oxides.

Both spin resonance and optical absorption have been detected for some of these systems, including MgO, CaO and Al_2O_3 . The main features of the ground state are fairly clearly understood. The hole is trapped on one of the six oxygen ions neighbouring the cation vacancy, giving an O^- ion instead of O^{2-} . In pure systems, the localization is a result of the lattice distortion produced by the hole, i.e. there is self-trapping, analogous to that seen in V_K centres. Of course, the hole can hop between the oxygen ions adjacent to the vacancy, but this occurs relatively slowly, and can be inhibited by the random strains in the crystal.

Many of the properties of V^- centres can be understood reasonably well on a simple model (Bartram *et al* 1965, with some extensions by Hughes and Henderson 1972). In this model, one concentrates on the energy levels of an O^- ion in a crystal field whose axial component results from the presence of the vacancy. The axial field splits the 2p levels of the oxygen, the p-state along the O^- vacancy axis being raised in energy. In this simple model, the splitting Δ of the 2p levels can be estimated in three ways: from a simple crystal-field theory, from the orbital contribution to the g factor, and from the observed optical absorption.

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Qualitatively, the theory is very successful. However, there remain discrepancies in detail which suggest that a more complicated model is necessary. Two of these problems are qualitative, and so insensitive to many of the details of the model. Thus the observed g_{\parallel} exceeds the free-spin value, whereas the opposite inequality is predicted. Further, the variation of magnetic circular dichroism with field direction is wrong (Izen *et al* 1973). A third problem is quantitative, and appears because there are significant inconsistencies in the detailed values of parameters (like the spin-orbit coupling λ and the axial splitting Δ) which are hard to eliminate. For these and other reasons, Schirmer *et al* (1974) proposed another model. In this, the optical excitation is best regarded as a polaron transition. The hole on one oxygen transfers to an adjacent oxygen in a time so short that the lattice does not relax to its new equilibrium configuration. Thus the transition energy is determined by the self-trapping distortion produced by the hole.

We present here quantitative calculations of both models, and we shall show that a combination of both models agrees well with most observations.

2. Lattice relaxation calculations

Two types of calculation are involved in the present work. One includes the Hartree-Fock calculations of electronic structure for specified lattice geometries. The other requires a variety of estimates of lattice geometries and of the related polarization and distortion energies. In this second class we use a shell model which has already proved successful in dealing with other intrinsic defects in MgO.

2.1. Model for lattice relaxation studies

The lattice relaxation studies used the Harwell program HADES, which is an efficient and general code for evaluating energies and geometries.

HADES requires an interatomic potential which, for an ionic material like MgO, consists of a Coulomb part and a short-range part; it is also necessary to account for ion polarization. Catlow *et al* (1976) have developed suitable potentials based on the shell model. The ions are doubly charged, and the assumed short-range interaction ϕ_{ij}^{SR} has overlap and van der Waals parts:

$$\phi_{ij}^{\text{SR}}(r) = A_{ij} \exp(-r/\rho_{ij}) - C_{ij}/r^6. \quad (2.1)$$

All parameters used are listed in table 1.

The nearest-neighbour interactions were fitted using the lattice constant, combinations of the elastic constants, and the equilibrium condition. The $\text{O}^{2-}-\text{O}^{2-}$ parameters A_{--} and ρ_{--} were taken from Catlow's (1974) *ab initio* Hartree-Fock work. His calculation assumed that, since the extra electron on O^{2-} is not bound in the free ion, the short-range $\text{O}^{-}-\text{O}^{-}$ interaction would be close to the desired potential. The short-range $\text{Mg}^{2+}-\text{Mg}^{2+}$ parameters A_{++} , C_{++} were set to zero, as was C_{+-} . The remaining parameters A_{+-} , ρ_{+-} and C_{--} were obtained from $(c_{11}-c_{12})$, c_{44} and the lattice spacing through the equilibrium condition.

The elastic constants of MgO have $c_{44} > c_{12}$, the fairly large deviation from the Cauchy relation indicating significant non-central or many-body terms in the potential. The most satisfactory model of Catlow *et al* (1976) used a breathing-shell model to describe the non-central terms. Thus the pair-potential was fitted to $c_{11}-c_{12}$ and c_{44} , which have no contribution from symmetric ion deformations. Explicit inclusion of

Table 1. Parameters for interatomic potential

| | |
|--|---|
| (a) Short-range interactions: | |
| Anion-cation potential A_{+-} | $\exp(-r/\rho_{+-})$ |
| $A_{+-} = 1152.0$ eV | $Mg^{2+}-O^{2-}$ interaction in models I and II and |
| $\rho_{+-} = 0.3065$ Å | $Mg^{2+}-O^-$ in model I |
| $A_{+-} = 331.2$ eV | $Mg^{2+}-O^-$ interaction in model II |
| $\rho_{+-} = 0.3632$ Å | |
| Anion-anion potential A_{--} $\exp(-r/\rho_{--}) - C_{--}/r^6$ | |
| $A_{--} = 22760.0$ eV | |
| $\rho_{--} = 0.149$ Å | |
| $C_{--} = 28.96$ eV Å ⁶ | |
| (b) Shell-model parameters | |
| Core charges X_+ | $= 2.0 e $ |
| X_- | $= 0.62 e $ |
| Shell charges Y_+ | $= 0.0 e $ |
| Y_- | $= -2.62 e $ |
| Shell-core force constants k_+ | $= \infty$ |
| k_- | $= 19.01$ eV Å ⁻² |

These parameters (Catlow *et al* 1976) are fitted to $c_{11} - c_{12}$, c_{44} , w_{TO} , ϵ_0 , ϵ_∞ , lattice parameter and Hartree-Fock O-O interactions.

ion deformation had a negligible effect on defect energies, and we have omitted this effect in the present work. The shell parameters for O^{2-} (Mg^{2+} was regarded as unpolarizable) were adjusted to give a best fit to the observed static and optic dielectric constants and to the infrared dispersion frequency.

The model for the perfect lattice is thus well defined. In treating the V^- centre, we need O^- parameters also. The dominant effect is simply the change of the anion charge from $-2|e|$ to $-|e|$. A unit increase in the shell charge leads to a physically reasonable reduction in polarizability. We have verified separately that our results are insensitive to the O^- polarizability. The parameters A and p for the $Mg^{2+}-O^-$ interaction are less simple, and we have used two models. In model I the $Mg^{2+}-O^-$ repulsion was assumed to be the same as the corresponding $Mg^{2+}-O^{2-}$ term. In many cases this is acceptable, for the hole leads to a relaxation of the cations away from the O^- , so that the repulsive term is small. However, we also need to consider hole jumps at fixed lattice configuration, and the results are then quite sensitive to the assumed interaction. Thus we obtained a model II which estimated the $Mg^{2+}-O^-$ interaction directly by a statistical method (see Wedepohl 1967, Gordon and Kim 1972).

2.2. Predictions common to both models of the V^- centre

A useful preliminary check of the shell model involves three features which are common to both the models of Bartram *et al* and of Schirmer *et al*. First, the model should predict correctly that the hole is localized on one of the oxygens, rather than spread over all six. Secondly, it should give the correct ionization energy for the thermal loss of the trapped hole. Thirdly, the reorientation behaviour should be correctly predicted, both the static dipole strengths and the dynamic behaviour.

When the hole is localized onto one, rather than all six, of the oxygens adjacent to the cation vacancy, there is a big gain of polarization energy. On the other hand, the hole can gain in kinetic energy by spreading out on all of the oxygens. The gain in polarization energy is estimated as 2.33 eV, appreciably larger than the kinetic energy term which is around 1 eV using Schirmer *et al*'s estimate of the tunnel matrix element.

We have also confirmed that localization on two sites is unfavourable, the polarization term being around 1.5 eV and the kinetic term a few tenths of an electron volt. Thus self-trapping of the hole onto a single site is favoured, in agreement with observation.

The binding energy of the hole was calculated by comparing the energy of the V^- centre with the energy of an isolated vacancy and a hole trapped on a distant oxygen ion. The prediction, 1.41 eV, agrees well with the measured value of 1.6 ± 0.2 eV (Tench and Duck 1973, 1975). Searle and Glass's (1968) less direct experimental estimate of 1.13 eV is also in the same range. In fact their result is closer to the ionization energy expected for the V_{Al}^- centre, where the (002) Al^{3+} substituting for Mg^{2+} repels the hole slightly and reduces the binding energy by 15–20%.

The energy for reorientation has been calculated by methods analogous to those used by Norgett and Stoneham (1973) for the V_K centre. The energy which is calculated, E_a , is (with certain qualifications) the activation energy which would be observed at high temperatures; for MgO, this would probably be appropriate above about 500°C. At lower temperatures, a much smaller effective activation energy, E_a^{eff} , would be found by fitting an Arrhenius form over a small temperature range. We predict the high temperature value E_a to be 1.36 eV, whereas the E_a^{eff} is only about 0.1 eV in the temperature range where motional effects on spin-resonance spectra are seen. No appropriate analyses of the experimental data are known, although Rius *et al* (1976) have reported studies at very low temperatures. The values of E_a and E_a^{eff} seem plausible, and it would be useful to have higher-temperature data to check them.

2.3. Dipole moments of the V^- centre

The V^- centre can be aligned by either uniaxial stress or by an electric field. Under a (100) pressure, the centre aligns along the stress axis. The energy difference between the parallel and perpendicular orientations can be described by an elastic dipole moment μ where (Rius *et al* 1976)

$$\mu = -(9.6 \pm 0.4)(10^{-3} \text{ K}(\text{kg cm}^{-2})^{-1}) \equiv -0.85 \text{ eV}/(\text{unit strain } 2e_{zz} - e_{xx} - e_{yy}) \dots \quad (2.2)$$

The unit strain needed in the second expression is the value that would occur in a perfect MgO crystal; no effects of altered local force constants are built in. Similarly, the energies of V^- centres in an electric field can be described by a dipole $|e|L$, where

$$\begin{aligned} L &= (3.4 \pm 0.4) \text{ \AA} && \text{(Rose and Cowan 1974)} \\ &= (3.2 \pm 0.1) \text{ \AA} && \text{(Ruis *et al* 1976).} \end{aligned} \quad (2.3)$$

We now calculate the two terms μ and L .

The main problem theoretically concerns the effects of local field corrections, both elastic and electrical, and the very slow convergence of sums appearing in expressions for the elastic dipole. In principle, these local corrections can be calculated directly by calculating energies in a compressed crystal, for example. This works well for silicon and diamond (Larkins and Stoneham 1971), but there are technical problems because of the long-range forces in ionic crystals, and comparable calculations would be too demanding here.

In absence of local corrections, the elastic dipole is given by a sum over all ions i of the form

$$\mu_{\text{theory}} = \frac{1}{3} \sum_i (F_{zi} z_i - \frac{1}{2} [F_{xi} x_i + F_{yi} y_i]) \quad (2.4)$$

where F_i is the force on ion i and $r_i \equiv (x_i, y_i, z_i)$ the (relaxed) position of ion i . Values of μ_{theory} , listed in table 2, are around -2 eV. The sign means that the V^- centre prefers to lie along the compressive stress axis, in agreement with observation. The predicted value is too large by a factor 2.3 which we tentatively associate with the effects of differences between the local and bulk strains.

The simplest picture of the electric dipole simply considers a net charge $+|e|$ (corresponding to O^-) which can move over the vertices of an octahedron[†]. The 'point ion' dipole moment is then $|e|a \equiv 2.10 |e|\text{\AA}$. However, this moment polarizes the lattice, reducing the net dipole moment, and the expression analogous to (2.4) is

$$\mu_z = \sum_i Q_i z_i \quad (2.5)$$

where i labels the various shell and core charges Q_i . Values are given in table 2. The reduction is calculated to be about 24% in this case, giving around $1.6|e|\text{\AA}$. This is still not what

Table 2. Dipole moments

(a) Electrical dipole moment with the sum taken over a sphere of radius Ra centred on the vacancy, with a the nearest-neighbour distance. Values in $|e|\text{\AA}$ are given for (A) no local field correction, for (B) the Onsager correction $3\epsilon_0/(2\epsilon_0 + 1)$ and for (C) the Lorentz-Lorenz correction $(\epsilon_0 + 2)/3$

| Model | A | B | C |
|---|------|---------|------|
| Unpolarizable point ions, rigid lattice | 2.10 | | |
| I $R = 5.0$ | 1.49 | 2.13 | 5.86 |
| $R = 6.0$ | 1.62 | 2.31 | 6.37 |
| $R = 6.5$ | 1.64 | 2.34 | 6.45 |
| II $R = 5.0$ | 1.41 | 2.01 | 5.45 |
| $R = 6.0$ | 1.53 | 2.18 | 6.02 |
| Experiment | | 3.2-3.4 | |

(b) Elastic dipole moment. Values are in eV and without the elastic analogue of a local field correction.

| Model | Moment |
|--------------|--------|
| I $R = 5.0$ | - 2.23 |
| $R = 6.0$ | - 1.87 |
| $R = 6.5$ | - 2.21 |
| II $R = 5.0$ | - 1.69 |
| $R = 6.0$ | - 1.41 |
| $R = 6.5$ | - 1.73 |
| Experiment | - 0.85 |

is measured, for the field must be given a local correction. General discussions are given by Herring (1956), Smith and Dexter (1973) and Stoneham (1975). It is here that ambiguities set in. In the Onsager model, a cavity-field correction of $3\epsilon_0/(2\epsilon_0 + 1)$ is appropriate, giving around $2.3 |e|\text{\AA}$. The Lorentz-Lorenz correction, on the other hand, is $(\epsilon_0 + 2)/3$, giving $6.3 |e|\text{\AA}$. These bracket the experimental value.

[†] One must remember that the cation vacancy does not move in the reorientation. If the centre of charge were fixed instead, the effective dipole moment would be $3/2 ea$.

2.4. Electric field gradients

The quadrupole terms observed (see e.g. Chen and Abraham 1975) in the spin resonance of a related centre, the $[\text{Na}]^0$ centre (basically a V^- centre with an Na^+ ion in the cation vacancy), allow an estimate of the electric field gradient at the Na nucleus. There are some uncertainties, mainly because of the large effect of the Sternheimer antishielding factor.

We can calculate the electric field gradient from a sum over all the charges present (i.e. cores and shells):

$$q = \sum_i \frac{r_i^2 - 3z_i^2}{r_i^5} Q_i. \quad (2.6)$$

Here $r_i \equiv (x_i, y_i, z_i)$ is measured from the Na^+ nucleus, and the z axis is along the join of the hole and the impurity. In a rigid, undisturbed lattice, q is $q_0 = -2|e|/a^3$ with a the nearest-neighbour distance. We find a value significantly less:

$$q = 0.47 q_0. \quad (2.7)$$

Since other calculations have used (q/q_0) as a measure of the Na^+-O^- separation, we note that such arguments suggest a separation of about $1.29 a$, whereas the atomistic model gives about $1.1a$. Whilst the hole dominates in the field gradient, the discrepancy shows that other contributions are important too. This is in line with earlier comments (Stoneham 1975, § 13.7) on the problems of measuring lattice distortions by spin-resonance methods.

3. The Bartram–Swenberg–Fournier model

We start by using the earlier of the two models, and make detailed predictions for V^- centres in MgO . Simple versions of the model have been applied to MgO by Hughes and Henderson (1972). Whilst the results had many of the right features, the anomalies mentioned in § 1 remain. The predicted transition energy was 1.47 eV, significantly less than the 2.3 eV observed, for example, and a very low oscillator strength is indicated, probably lower than the observed 0.1. However, it is not clear whether or not these values are in error only because of simplifying assumptions, rather than for more fundamental reasons. For this reason we have extended the calculations in several respects, whilst maintaining the same basic model.

3.1. Generalizations of the model

The simple version of the model contained several important assumptions to make the calculations easier:

- (i) The O^- ion is assumed to be very compact, so that it experiences an essentially uniform electric field;
- (ii) The O^- orbitals are the same as those of a free O^- ion in Hartree–Fock theory;
- (iii) The electric field is entirely due to the charge missing from the vacancy site, regarded as a point charge;
- (iv) There is no lattice distortion.

We have generalized the model to cover these aspects.

The first generalization is that we have made Hartree–Fock calculations for an O^- ion in an appropriate array of point charges. Thus the main differences between the crystal ion and the free ion have been dealt with, and the inhomogeneity of the crystal field included. Some approximations do remain, however, including overlap terms of various sorts. Their effects are likely to be small in the present case.

The second generalization is that we have calculated the local lattice distortion, using the model described elsewhere in this article. We have not only used this local geometry in our Hartree–Fock calculations, but also we have ensured that the electric field at the O^- is properly calculated, including electronic polarization and long-distance ionic displacement terms. These features are important in both the energies and the transition probabilities for, roughly speaking, the optical transition is from a $2p_x$ or $2p_y$ state to a $(2p_z + 2s$ admixture) axial state, and the $2s$ admixture depends strongly on the applied field.

3.2. Details of geometry and basis functions

In our calculations, the O^- ion was surrounded by six point charges. Five of these were charges $+2|e|$, and corresponded to the neighbouring cations. Their positions were fixed by an independent lattice-relaxation calculation. The sixth, a charge of $-2|e|$ was placed on the axis the other side of the cation vacancy so as to ensure the correct electric field at the O^- ion. The positions are listed in table 3.

Table 3. Local geometry for generalized Bartram–Swenberg–Fournier model

| Ion | Coordinates† | Charge ($ e $) |
|--------------------------------|---|-----------------------|
| Oxygen | (0, 0, 0) | $Z = 8 + 9$ electrons |
| Axial cation | (0, 0, -0.808) | 2 |
| Equatorial cations | ($\pm 0.842, 0, 0.167$), (0, $\pm 0.842, 0.167$) | 2 |
| Charge to ensure correct field | (0, 0, 1.854) | -2 |

† Units are those of the nearest-neighbour distance in the perfect crystal

The atomic basis functions were chosen from the experience of a number of previous workers, including Clementi (1965) and Harker (1974). Five s functions (two $1s$ and three $2s$) and five p functions were used; these are listed in table 4. The energy levels

Table 4. Basis functions for O^- ion

| Type | Exponent (au) |
|------|---------------|
| 1s | 7.6126 |
| 1s | 13.3654 |
| 2s | 3.2045 |
| 2s | 6.2896 |
| 2s | 1.7637 |
| 2p | 1.7424 |
| 2p | 3.4363 |
| 2p | 0.8565 |
| 2p | 0.47 |
| 2p | 7.807 |

and wavefunctions were calculated using the ATMOL program provided by Dr Saunders of the Atlas Laboratory. In all cases we calculated excited states self-consistently, i.e. we did not use Koopmanns' Theorem.

3.3. Results

We have calculated three parameters: the optical transition energy, the oscillator strength, and the orbital reduction factor needed in estimating spin resonance parameters.

The optical transition energy proves to be 1.56 eV. This is almost exactly the same as the simplest calculations (cf Hughes and Henderson 1972), which gave 1.47 eV. Both are significantly less than the main V^- band at 2.3 eV. It is our view that the transitions within O^- are responsible for a separate transition near 1.5 eV, as suggested by Rose and Cowan (1974).

The oscillator strength is estimated to be 0.09. Whilst approximations in the wavefunctions affect this, the effects are probably slight. For example, if the (non-self-consistent) virtual excited state is used instead of the self-consistent one, the oscillator strength is still of order 0.08. Thus the optical transition is a significant fraction of the observed total oscillator strength of about 0.1.

The s-p admixture in the axial $2p\sigma$ state is relatively small, despite its importance in the oscillator strength. There are only slight effects of this admixture and of the modifications of the relative forms of the $2p\sigma$ and $2p\pi$ states from the crystal field on the matrix elements of L , the orbital angular momentum. In particular, the matrix element of L between the $2p\sigma$ and $2p\pi$ state is reduced by only 2% from the value for pure $2p$ functions. Reduction factors are hard to deduce consistently from experiment, but will contain other components which we have not estimated, like covalency effects and, in suitable circumstances, Jahn-Teller terms.

4. The Schirmer-Koidl-Reik model

This model argues that the important optical transition is a small-polaron transition, in which the transition energy is related to the self-trapping distortion of the hole. By self-trapping of the hole we mean that, when the hole is localized on only one of the oxygens neighbouring the cation vacancy, the energy gain from distortion and polarization of the lattice exceeds the kinetic energy advantages of placing the hole symmetrically on all six neighbours. The energetics of self-trapping were discussed in § 2.2.

4.1. Optical transitions of V^-

In the Schirmer-Koidl-Reik model, the optical transitions result from hole transfer from one oxygen to the other oxygen neighbours of the vacancy at constant lattice configuration. In line with most other colour-centre calculations, it is natural to assume the electronic polarization does follow the hole in its transition, although the lattice distortion does not. We have used the shell model of § 2 to calculate the optical transition energy. The main results are given in table 5. These confirm that the Schirmer *et al* (1974) model correctly describes the 2.3 eV band.

We now outline the different contributions to the transition energy. The main contribution is the energy to move a hole from one oxygen (the 'axial' oxygen) to one of the four equivalent 'equatorial' oxygens. The transfer is at constant geometry but with the

electronic polarization following the hole. This part of the transition energy shows a systematic dependence on the model. It is higher for a rigid ion model, where there is no electronic polarization to follow the hole's motion. Further, model I gives a higher energy than model II: the more accurate representation of the smaller O^- ion leads to a further reduction in energy. We note incidentally that it is the size of the O^- ion rather than its polarizability which is important; changes in the polarizability over a wide range produced only insignificant changes (~ 0.04 eV) in the transition energy.

Table 5. Optical transitions of the V^- and related centres

The values listed in eV all refer to the Schirmer–Koidl–Reik polaron model. For reference, one value is also given for the rigid ion model; all others refer to the shell models of § 2. The contributions are the basic transfer energy Δ_0 , the tunnelling correction $4J \equiv \Delta_T$, and the crystal field correction Δ_{CF} ; the final energy is $(\Delta_0 - \Delta_T - \Delta_{CF}) \equiv \Delta E$. Strictly, this is for the lower of two absorption bands; their centroid is higher by $J \approx 0.18$ eV.

| Centre | Model | Δ_0 | Δ_T | Δ_{CF} | ΔE | Experiment |
|-----------|-----------|------------|------------|---------------|------------|------------------------|
| V^- | Rigid Ion | 6.08 | | | | |
| | I | 5.15 | 0.72(a) | -0.14 | 4.57 | |
| | II | 3.49 | 0.72 | 0.62 | 2.15 | 2.3(c) |
| $[Na]^0$ | II | 3.27 | 0.72 | 1.04 | 1.51 | 1.58(d) |
| $V^-(Al)$ | II | 3.78 | (0.72)(b) | 0.52 | 2.54 | 2.32(c) 2.33(e) |
| V^0 | II | 3.77 | (0.72)(b) | 0.89 | 2.16 | ~ 2.3 (c) 2.37(e) |

(a) Schirmer 1975, 1976; (b) estimated from comparison with other centres; (c) Chen and Abraham 1975; (d) Abraham *et al* 1973; (e) Kappers *et al* 1974.

The result just cited assumes the hole is transferred to a single oxygen. In fact, as Schirmer *et al* have noted, the transition is to a final state in which the hole moves among the four equatorial oxygens. The tunnelling term reduces the transition energy by $4J$, or around 0.72 eV in Schirmer's most recent estimate. Provided that the electronic polarization follows the hole in its motion between these four oxygens, just as it does in the main transition, then the polarization energy is not altered.

A second correction comes from the crystal field splitting of § 3. For the O^- ion, there are two p-like orbitals with energy $-\delta$, all doubly occupied, and one higher singly-occupied orbital with energy $+2\delta$. The energy $3\delta \equiv \Delta_{BSF}$ is the transition energy in the Bartram–Swenberg–Fournier model. Now the splitting at the final site, $3\delta_F$ is different from that at the initial one, just because the lattice distortion does not follow the hole. This leads to an extra energy correction in $(E_{final} - E_{initial})$ of $2(\delta_i - \delta_F) = \frac{2}{3}\Delta_{BSF}(1 - \delta_F/\delta_i)$. Estimating δ_F/δ_i from the magnitudes of the shell-core displacements in the two cases allows us to estimate the corrections Δ_{CF} of table 5. Whilst the shell-core displacements are only approximately related to crystal-field splittings, they do reflect correctly both the purely electrical and short-range repulsive terms, and the rough value of the correction should be adequate.

Collecting the results together, we see that the predicted transition energy in model II is 2.15 eV, strikingly close to the observed peak at 2.3 eV. Thus our calculations verify the proposal of Schirmer *et al* that the main V^- transition is a polaron transition. They also show how important it is to have the correct short-range $O^- - Mg^{2+}$ repulsive terms, for the less accurate model I leads to a much higher transition energy.

4.2. Optical transitions of centres related to V^-

We have also calculated transition energies in the Schirmer–Koidl–Reik model for three centres related to V^- . These are (i) a V^- centre with an Na^+ ion in the cation vacancy, the so-called $[\text{Na}]^0$ centre, (ii) a V^0 centre with two holes trapped at opposite oxygens adjacent to a cation vacancy, i.e. a (V^- centre + hole) system and (iii) a V_{Al}^- centre, with an Al^{3+} substituting for the closest axial Mg^{2+} opposite the O^- ion in the V^- centre.

The calculations proceed in much the same way as before. There are some differences in detail. The centres are electrically neutral, so the polarization energies tend to be less. For the two-hole V^0 system, the crystal-field splittings for both O^- ions must be included. Here, as for other centres, we have used the dipole moments from HADES to scale the Hartree–Fock result of §3; this is probably the weakest part of our calculation. Tunnelling parameters J have only been estimated by Schirmer for V^- and for the $[\text{Na}]^0$ centre. In both cases $J \sim 0.18$ eV, so we have retained this value for the V^0 and V^- : Al centres.

The agreement with experiment (table 5) is very good. The low transition energy for $[\text{Na}]^0$ is particularly well reproduced, and we confirm that the V^0 , V^- and V^- (Al) centres all give transitions around 2.3 eV, in agreement with experiment. If V^- and V^- (Al) centres contribute to the observed 2.3 eV band, then our results suggest that the V^- centre should give the major low-energy contribution and the V^- (Al) centre the major part at higher energies.

5. Conclusions

Our atomistic calculations of the properties of trapped-hole centres in MgO have led to a quantitative understanding of their behaviour. We have confirmed that the hole should be localized on one oxygen, as observed, and that the elastic and electric dipole moments of the V^- are in reasonable agreement with those observed. Transition energies have also been calculated, including the ionization energy, and there is very good agreement with experiment. In particular, a recent controversy has been resolved: we have shown that the observed 2.3 eV band of the V^- centre corresponds to the polaron transition proposed by Schirmer *et al* (1974), whereas the intra- O^- transition proposed by Bartram *et al* (1965) appears to be responsible for structure around 1.5 eV. Similar results have been obtained for centres related to the V^- centre, again in very good agreement with experiment:

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