Quantum chemical simulations of the optical properties and diffusion of electron centres in MgO crystals

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Abstract

Semiempirical quantum chemical simulations have been undertaken to obtain the self-consistent atomic and electronic structure of the two basic electron defects in MgO crystals: F^+ and F centres (one and two electrons trapped by an O vacancy, V_a). The calculated absorption and luminescence energies agree well with the experimental data; the excited states of both defects are found to be essentially delocalised over nearest-neighbour cations. The activation energy for diffusion is found to increase monotonically in a series $V_a \rightarrow F^+ \rightarrow F$ centre (2.50 eV, 2.72 eV and 3.13 eV, respectively).

Keywords: Quantum chemical simulations; Diffusion; Magnesium oxide; Optical properties

Oxide materials in general, and MgO in particular, are important as catalysts and ceramics and because of their relevance to microelectronics and geophysical problem [1–3]. Point defects arise in oxides naturally, under irradiation and by design, considerably affecting their optical properties. Several kinds of point defects have been identified and studied in the alkali earth oxide materials such as MgO; the two basic electron defects are called F^+ and F centres [1]. They are one and two electrons respectively trapped by an O vacancy (V_a). In particular, a substantial amount of theoretical attention has been paid to these centres in recent years, when a number of careful first-principles calculations have been performed [4]. However, such calculations are unavoidably restricted to quite small quantum clusters or supercells, thus not allowing the study of excited states of these centres. Another technologically important characteristic of the electron centres in oxide crystals which cannot be practically handled by ab initio methods is defect diffusion. At the present moment there is not a single theoretical attempt to calculate the activation energy for F^+ and/or F center diffusion in MgO crystals.

This demonstrates that a simpler theoretical

approach is of great need, allowing us to study big quantum clusters (about 100–200 atoms) and complex defects (such as dimer F_2 centres). Furthermore, it should be able to optimize the defect geometry (in both the ground and excited states) through a minimization of the total energy, and to calculate reliably the excited states and the relevant absorption and luminescence energies. Such an approach to large-scale simulations of static and dynamic properties of defects in ionic solids has been elaborated in recent years on the basis of the semiempirical quantum chemical method of the intermediate neglect of the differential overlap (INDO) [5], which since then has been applied very successfully to the defects in many oxide materials, including MgO, SiO_2, Li_2O, ZrO_2 and α-Al_2O_3 [5–7].

In the work reported in this paper we performed INDO calculations of the optical properties and diffusion of F^+ and F centres in MgO. 125-atom clusters of a cubic shape having high (O_h) point symmetry and modelling nine spheres of atoms around the coordinate origin were used to calculate optical properties. These clusters were embedded into the electrostatic field of non-point infinite crystalline lattice. In the F type centre simulations, the O atom in its centre has been removed and one or two electrons have been added to the cluster making no a priori assumptions about their

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Table 1
Effect charges (in units of e) on atoms surrounding the V_a, F^+ and F centres in both their ground state and excited state (basis set of F^+ and F centres included 1s and 2p atomic orbitals centred on the O vacancy)

Ground state					Excited state			
Atom or centre	V_a	F^+	F	Perfect MgO	Atom or centre	F^+ centre	F centre[a]	
							S	T
Mg (1, 0, 0)	1.808	1.823	1.838	1.831	Mg (1, 0, 0)	1.715	1.701	1.674
O (1, 1, 0)	−1.835	−1.826	−1.819	−1.829	O (1, 1, 0)	−1.824	−1.817	−1.816
Mg (1, 1, 1)	1.823	1.828	1.832	1.831	Mg (1, 1, 1)	1.828	1.832	1.831
Vacancy	−0.002	−1.002	−2.002	—	Vacancy	−0.476	−1.268	−1.127

[a] S and T denote the singlet and triplet states respectively.

localization and the electron density distribution. Then the ions surrounding the O vacancy were allowed to relax in order to obtain a minimum of the total energy, as well as the self-consistent electronic and atomic structures of the defect. The relevant INDO computer code SYM-SYM [8] is perfectly suited for such computer simulations, being based on a complete treatment of the point symmetry and the automated defect geometry optimization. The absorption and luminescence energies were calculated as the difference of total energies for the relaxed atomic self-consistent field (SCF) ground and excited states, known as the ΔSCF method [6].

The optimized geometry of a bare O vacancy, and that which trapped one and two electrons, shows that mainly the six nearest-neighbour (NN) cations are displaced in the direction outwards the vacancy. Naturally, for double-charged V_a the surrounding atomic relaxation is the largest (6.5% of the Mg–O spacing for the nearest Mg ions), but it is reduced to less than 2% for the neutral F centre. Atoms of three spheres surrounding an O vacancy are found to be relaxed noticeably even in the ground state of these F-type centres.

The charge distribution analysis (Table 1) demonstrates clearly that one (two) electron(s) is (are) well localized by an O vacancy in the ground state of the F^+ (F) centre with a very moderate change of the effective charges on atoms surrounding the O vacancy. This is no longer true, however, for their excited states; $0.5e$ is delocalized from the O vacancy over the cations surrounding the F^+ centre, which results in the reduction of their effective charges (by about $0.1e$ on each atom). For the singlet excited state of the F centre $0.7e$ is delocalized. An analysis of the spin density distribution for the ground state of the F^+ centre shows that 90% or more of the unpaired electron lies inside the O vacancy but only 44% in its excited state.

Our calculations put both of the ground levels, of F^+ and F centres, at ca. 3 eV above the top of the valence band, similarly to results recently obtained using much more refined supercell multiple-scattering theory [4a].

The potential energy curves as a function of the full-symmetry A_{1g} relaxation for the F^+ and F centres are shown in Fig. 1. They confirm that the excited states lie very close to the conduction band, in agreement with the experimental data [9] placing the F excited state only 0.06 eV below the bottom of the conduction band. The calculated absorption energies of F^+ and F given in Table 2 practically coincide. The luminescence energy for F^+ exceeds the experimental energy (3.2 eV) by 0.4 eV.

Calculations of the excited F centre predict the singlet luminescence peak at 2.61 eV and the triplet peak at 2.76 eV. The only observed experimentally band is so
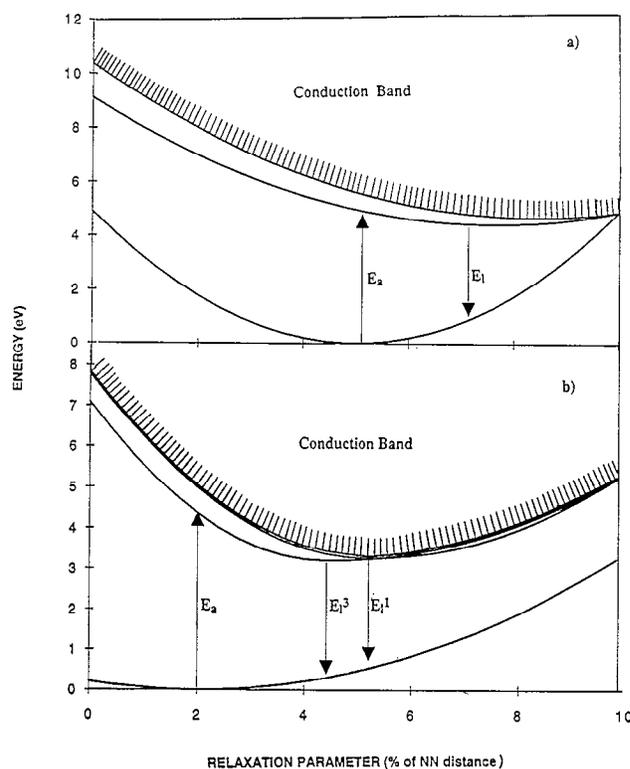

Fig. 1. A_{1g} configuration coordinate curves for (a) F^+ and (b) F centres in MgO (effect of only the symmetric relaxation of NN cations is shown). E_a is the absorption energy and E_l is the luminescence energy of F^+ centre whereas E_l^1 and E_l^3 are luminescence triplet and singlet energies respectively for the F centre.

Table 2
Calculated absorption and luminescence energy (in electronvolts)

Defect	F^+	F
Absorption		
Theory	4.97[a]	4.98[a]
Experiment [1]	4.95	5.02
Luminescence		
Theory[b]	3.6	2.61 (S); 2.76 (T)
Experiment [1]	3.2	2.3

[a] Fitted to the experimental value.

[b] S and T denote theory for the singlet and triplet bands respectively of the F centre.

far at 2.3 eV; probably singlet and triplet energies are too close to be resolved (the width of the experimental emission band is about 0.6 eV). The calculated energies at the minimum of the relaxed singlet and triplet states differ by 0.04 eV only; this probably explains why the optically detected magnetic resonance experiments indicate that "the emitting state is not predominantly an orbital triplet" [10].

In the simulation of defect diffusion, 224-atom clusters of C_{2v} symmetry were employed. They include several spheres of atoms around both a vacancy and its NN O atom with which it exchanges positions. Use of such a big cluster allows us to avoid any potential complications due to boundary effects. The effective charge of an O atom in the saddle-point (half the distance between two regular O sites along the (110) axis) which is at the top of the energy barrier is found to remain practically the same as at the lattice site.

The activation energies for defect diffusion were calculated as the difference between total energies of relaxed atomic configurations corresponding to V_a in its initial (equilibrium) state (the regular lattice site) and the O atom in the saddle-point as defined above.

The relevant diffusion energies E_a are found to be 2.50 eV (V_a), 2.72 eV (F^+) and 3.13 eV (F centre). The first energy is very close to the experimental value of 2.4 eV [11]. The other two energies are not well established experimentally. However, it has been observed experimentally that in additively coloured MgO crystals the complex $F^+ + F$ absorption band begins to decay only at 900 °C. Using the standard expression for a hop frequency $v = v_0 \exp(-E_a/kT)$ with the prefactor of the order longitudinal optical phonons ($v_0 \approx 10^{13}$ s^{-1}) one can estimate that $E_a \approx 3$ eV. This is again in qualitative agreement with the calculated values.

Acknowledgements

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