

Calculations of Diffusion Energies for Defects in MgO Crystals

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Abstract: This paper describes theoretical investigations into the mechanisms of diffusion of some charged and neutral atomic species in MgO and some electronic defects (F and F⁺ centres) in MgO, using *ab initio*, semi-empirical, and pair-potential techniques.

Pair-potential Calculations: MgO is an important ceramic material with several technological applications including its possible use in fusion reactors [1]. In stoichiometric unirradiated materials with the rock-salt structure Schottky defects usually predominate and this proves to be so also in MgO. Pair-potential (PP) calculations were carried out using the Mott-Littleton (ML) strategy as implemented in the computer code CASCADE due to Leslie [2]. Details of the method, including the evaluation of short-range forces, are given in [3] and references therein. In semi-empirical INDO (intermediate neglect of differential overlap) calculations, two computer codes developed at the University of Riga were used [4, 5]. Defect formation energies for MgO are given in Table 1. All of the results quoted from calculations using the two-region ML method, except those of Mackrodt [6] who used periodic boundary conditions [3].

Table 1. Defect formation energies (in eV) for MgO. S = Schottky, cF = cation Frenkel, aF = anion Frenkel, vp = vacancy pair.

Defect	CFN[7]	MS[8]	SS[9]	M[6]	this work
S	7.7	7.5	7.7	7.66	7.78
cF	12.4	11.9	12.4	-	12.34
aF	12.1	15.2	12.3	-	12.50
vp	5.3	4.95	-	-	5.06

These results display a remarkable concordance, the only exception being the Frenkel defect results of Mackrodt and Stewart [8] which have an asymmetry between anion and cation not seen in the other results. This is due to their different interionic potentials. Calculated migration energies are also rather similar so we give in Table 2 only those of SS[9] to compare with ours. From formation and migration energies one may calculate the Arrhenius energy to be expected if a particular defect

mechanism predominates, and these results are given in Table 3.

Table 2. Calculated migration energies (in eV) for defect motion in MgO. *c* = cation, *a* = anion, *v* = vacancy, *i* = interstitial, *vp* = vacancy pair.

Defect	SS[9]	this work
<i>cv</i>	2.07	1.98
<i>av</i>	2.11	2.09
<i>ci</i>	0.55	0.43
<i>ai</i>	0.65	0.54
<i>cvp</i>	-	3.64
<i>avp</i>	-	3.80

Table 3. Calculated Arrhenius energies (in eV) for diffusion in MgO. The interstitialcy mechanism assumes a majority of vacancy defects, as indicated by formation energies.

Mechanism	SS[9]	this work
<i>cv</i>	5.92	5.87
<i>av</i>	5.96	5.98
<i>ci</i>	9.10	8.90
<i>ai</i>	9.10	9.15
<i>cvp</i>	-	8.70
<i>avp</i>	-	8.86

Experimental results for Mg diffusion in MgO are 2.03 ± 0.17 eV [1], 2.3 ± 0.2 eV [10] and 2.2 eV [11]; and also 2.52 eV [12] for Ca in MgO which should be almost the same as, but perhaps slightly larger than that of Mg in MgO. Our calculated migration energy for *cv* is 1.98 eV, slightly lower than the experimental values, which may include effects from association. Mackrodt's value of 2.11 eV [6] though, agrees well with experiment. Significantly none of the experimental work has disclosed an intrinsic region for cation diffusion. This is consistent with the rather large concentrations (10 - 250 ppm) of trivalent metal impurity generally present in MgO. (Of course, we are comparing calculated *energies* at constant volume at 0 K with *enthalpies* at T up to 2000 K, but this is in fact not an unreasonable thing to do [6, 13].) The most relevant data for anion diffusion are those from molecular beam epitaxy experiments [12] which yield D values some two orders of magnitude less than other reported results. This may be linked to the improved crystal quality of the samples grown by MBE. The Arrhenius energies are 6.91 eV for intrinsic MgO and 2.66 eV for the extrinsic region. These results indicate a vacancy mechanism at low temperatures and a diffusion mechanism at high temperatures that involves both anion vacancies and anion jumps into vacancy pairs and possibly also (depending on the concentration of *cation* impurity) anion interstitials. A knowledge of the formation and migration entropies and of the *cv*-trivalent cation association energy

and entropy would be necessary to perform a theoretical calculation of $D(T)$.

INDO Calculations on MgO Although there have been several first-principles calculations on MgO, only a semi-empirical method is suited to calculations on the large clusters of 1-200 atoms that are necessary for the study of excited states, complex defects, or diffusion of electronic defects such as the F and F^+ centres in MgO. The computer code SYM-SYM written by Kantorovich and Livshicz [16] permits automated geometry optimization and is well-suited to this purpose. Trapped hole and electron centres in Al_2O_3 have been discussed recently elsewhere [17,18]. In calculations on MgO, cubic clusters of O_h symmetry containing 125 atoms were embedded in the electrostatic field simulating the remainder of the infinite lattice. The O atom at the centre was removed and one or two electrons added to the cluster, making no assumptions as to their localization and electron-density distribution. The ions surrounding the vacancy were allowed to relax in order to minimize the total energy and achieve self-consistent electronic and atomic structures for the defect. Absorption and luminescence energies were calculated as the difference between the relaxed atomic SCF ground and excited states. In the ground states of F^+ (F) centres the one (two) trapped electron(s) is (are) well-localized in the O vacancy, but in the excited state of the F^+ centres approximately 0.56e is delocalized over the six nn cations. In the F centre singlet excited state $-0.7e$ is delocalized. These INDO calculations place the ground state of the F centre about 3 eV above the valence band and the excited state about 0.06 eV below the bottom of the conduction band. The INDO method is a semi-empirical one and so the results for each centre must be scaled to one known property, here the absorption energies of the F^+ and F centres. The comparatively good agreement for the luminescence bands then demonstrates that the A_{1g} configuration coordinate curves are well represented by the calculations with just one point in the excited state curves fixed to experimental data. S and T luminescence bands are overlapped and too close to be resolved experimentally.

Table 4. Calculated luminescence energies (in eV) for F^+ and F centres in MgO. Experimental results are from refs. [19]. S = singlet T = triplet.

	F^+	F
Calculated	3.6	2.61 (S), 2.76 (T)
Experiment	3.2	2.3

For the saddle-points for diffusion of F^+ or F centres 224-atom clusters of C_{2v} symmetry were used. Activation energies for diffusion were calculated to be 2.50 eV for av, 2.72 eV for F^+ and 3.13 eV for F. The vacancy value is a little higher than that calculated from PP. The larger values for F^+ and F seem reasonable but have not been determined experimentally. However, in additively coloured MgO the $F^+ + F$ absorption band decays only at about 900°C suggesting a migration activation energy of ~ 3 eV.

Oxygen Atom Interstitials in MgO Irradiation of MgO produces F centres and therefore O atoms [20]. However, little was known about the fate of these O atoms until recently when two parallel,

but independent, investigations [21,22] revealed that an interstitial O atom in MgO combines with a lattice O²⁻ ion to form a symmetrical O⁻ - O⁻ 'dumbbell' centred on a lattice site. However, a fundamental difference in the results was that the former investigation [21] of Brudevoll et al. predicted that the stable position for the dumbbell was along <111> while the latter one [22] of Evarestov et al. gave the most stable configuration along <110>. Brudevoll et al. [21] used a full-potential linear-muffin-tin-orbital method (LMTO-LDA) [23] whereas Evarestov et al. used a periodic Hartree-Fock self-consistent field (HF) large unit cell (LUC) method [24]. A significant difference between the two investigations was that in [21] the LUC or supercell used contained 8 primitive unit cells (S8) whereas in [22] S16 supercells were used. Furthermore, Evarestov et al. [22] used a CNDO method to verify that neither the charge distribution nor the defect levels in the band gap changed significantly as the size of the supercell increased from S16 to S32, S64 and S128. It became a major concern to both groups to resolve this discrepancy and especially whether it arose from a fundamental difference between the LMTO and HF methods or was just an artefact due to the differences in supercell size. Accordingly, the HF calculations were repeated using S8 supercells, paying very careful attention to the lattice relaxation. No automated way currently exists to do this and accordingly the ion positions must be relaxed 'by hand'. Results in Table 5 show the atomic coordinates to be in excellent agreement. Since these calculations were carried out completely independently, it appears that the same energy minima have been located, and that the energy differences in Table 6 are due to the different methods employed. To put these differences in perspective, one should note that the HF energy of vdn in the S8 supercell is -2272.9415 H, so that the worst difference of 8.67 eV amounts to 0.014%! So at this defect concentration one may say that the LMT and HF calculations agree in their predictions and that the differences found formerly [21,22] are due to differences in supercell size.

Table 5. Atomic coordinates of the interstitial ion and its near-neighbours for O_i defects in MgO. v = volume-centred, f = face-centred, d=dumbbell, n denotes the relaxation of all symmetry-related near-neighbour ions that lie completely within the supercell.

Defect	Atom	Atomic Coordinates					
		HF			LMTO		
vn	O _i	0.0	0.0	0.0	0.0	0.0	0.0
	O ₁	-0.283	-0.283	-0.283	-0.283	-0.283	-0.283
	Mg ₁	0.256	-0.256	-0.256	0.259	-0.259	-0.259
fn	O _i	0.0	0.0	0.0	0.0	0.0	0.0
	O ₁	-0.295	-0.295	0.0	-0.293	-0.293	0.0
	Mg ₁	-0.286	0.286	0.0	-0.289	0.289	0.0
fdn	O _i	0.116	0.116	0.0	0.116	0.116	0.0
	Mg ₁	0.536	0.001	0.0	0.532	0.003	0.0
	Mg ₂	0.0	0.0	0.498	0.0	0.0	0.464
vdn	O _i	0.096	0.096	0.096	0.094	0.094	0.094
	Mg ₁	0.517	0.002	0.002	0.518	0.005	0.005

Table 6 Energy (in eV) of the oxygen atom interstitial in MgO in various configurations: D is the distance between the centres of the two atoms in a dumbbell in Å. Defect energies are given with respect to the ground state, vdn.

Defect	E/eV		D/Å	
	HF	LMTO-LDA	HF	LMTO-LDA
vn	12.25	3.57		
fn	2.30	1.45		
fd	1.96		1.328	
vd	1.08		1.364	
fdn	0.09	0.15	1.380	1.375
vdn	0	0	1.390	1.364

Atomic mechanisms for the diffusion of O_i atoms and O_i^{2-} ions are shown in Figure 1.

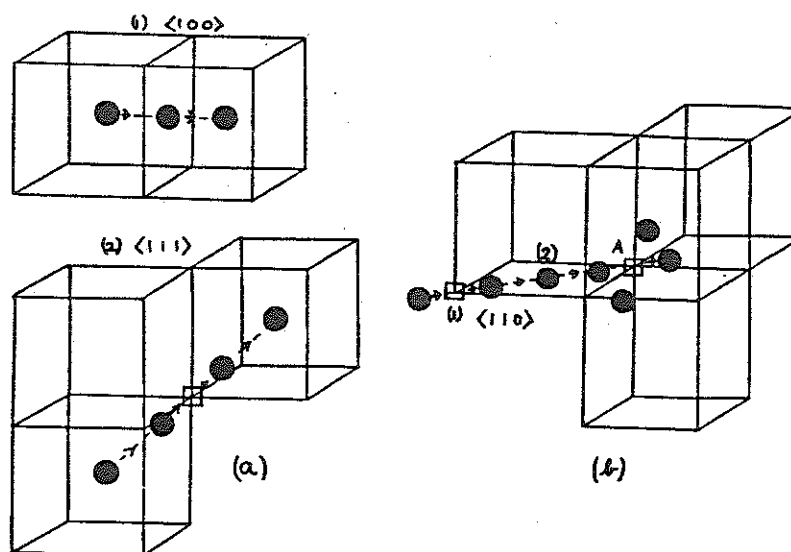


Figure 1. Diffusion mechanisms in MgO crystals for (a) charged interstitials (Mg_i^{2+} , O_i^{2-}): 1 and 2 denote the saddle points for direct and collinear interstitial jumps, respectively; and (b) for interstitial oxygen atoms O_i . In the latter case the equilibrium configuration is a dumbbell (1) and the saddle point is a face-centred interstitial (2). 3 D diffusion occurs via occasional rotation of the dumbbell at lattice sites like A.

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