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Quantum Chemical Calculations of the Electron Center Diffusion in MgO Crystals

By

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Large-scale quantum chemical simulations of the diffusion hops of empty cation and anion vacancies, as well as F^+ and F centers in MgO crystals have been done. The atomic configurations for 224-site cluster and charge density distribution are analyzed for the equilibrium and saddle-point configurations during the defect hops. The relevant activation energy for diffusion increases monotonically in the series $V_a \rightarrow F^+ \rightarrow F$ center.

1. Introduction

Oxide materials are of great importance as high- T_c superconductors, as well as for applications in ceramics, coatings, catalysts, and in gas sensors [1 to 3]. Investigations of mass transport in such oxide ceramics are very important for their fabrication, functional properties, and long-term stability. During the fabrication mass transport controls the rates of sintering, solid-state reactions, and grain growth. The time period for which oxide materials can resist degradation through radiation damage or chemical reaction is also determined by the diffusion-controlled processes [1, 2]. Very often this diffusion is associated with *point defects*. Information about such defect mobility in non-metals derives from the two main sources: mass diffusivity measurements and defect aggregation kinetics [1, 2, 4].

MgO has been extensively studied in the last decades, partly because of both its considerable technological importance and the simple NaCl-type crystalline structure which is characteristic of many ionic solids. The latter allows to extend the understanding of defects and relevant processes achieved already for the well-investigated alkali halides to oxides. Data on the activation energy of diffusion for the major lattice defects – bare anion and cation vacancies (V_a and V_c , respectively) – are summarized in Table 1.

From Table 1 the conclusion could be drawn that different estimates of the diffusion energy E_a for V_a derived from mass-diffusivity measurements all are ranging in the interval 2.4 to 2.7 eV [10 to 13]. On the other hand, the migration energies estimated from the growth rate of dislocation loops and reported to be between 1.90 and 2.03 eV

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Table 1

A summary of experimental and theoretical studies of the activation energy for diffusion (in eV) of the two types of vacancies in MgO crystals

anion vacancy		cation vacancy		anion vacancy		cation vacancy	
experiments				theory			
1.90	[5]	1.56	[14]	2.02	2.06	[18]	
1.95	[6]	2.20	[15]	2.10	2.10	[19]	
2.03	[7, 8]	2.28	[16]	2.11	2.07	[20, 21]	
2.22	[9]	2.76	[17]	2.38	2.16	[22]	
2.42	[10]			2.40	2.10	[23]	
2.61	[11, 12]			2.40	2.20	[24]	
2.71	[13]			2.48	2.39	[25]	
				3.00	2.60	[26]	

[5 to 8] are very likely underestimates due to the use of heavily-irradiated materials where the enhancement of ionic self-diffusion occurs as a consequence of transport along highly distorted paths of the crystals, including dislocations.

The estimated activation energies E_a for V_c diffusion are more scattered. The lowest value of 1.56 eV [14] is in fact presumably associated with the diffusion of some small impurity ions since, according to Wuensch et al. [17], the small ions tend to diffuse faster than large ions (for example, Be^{2+} has $E_a = 1.60$ eV [27]). The largest value of 2.76 eV [17] may contain uncertain contributions from the defect formation enthalpy, dislocation pipe diffusion, and competing diffusion mechanisms [2]. Two recent estimates for V_c are very similar, 2.20 eV [15] and 2.28 eV [16]: they are approximately by 0.3 eV smaller than the *average energy* for V_a characterized by $E_a = 2.5$ eV. This trend is well reproduced in theoretical calculations also collected in Table 1.

We would like to stress that diffusion of electron centers called F^+ and F (one and two electrons trapped by V_a , respectively) is practically not studied. At the same time, the extensive data on F ($V_a + e^-$) center diffusion in alkali halides is based on the mobility measurements under electrolytic coloration. The studies of anion vacancy diffusion are based on the ionic conductivity and radioactive tracer diffusion measurements. A significant effect is found here: charged bare anion vacancies have activation enthalpies typically about half of those of the vacancy with trapped electron (neutral F centers) [2].

Although no comparable data exist for oxides, we could expect that appreciable changes in defect mobility in different charge states ($V_a \rightarrow F^+ \rightarrow F$) could also occur in MgO crystals. We tried to estimate E_a for F centers using the experimental data for additively colored MgO crystals [28]. It has been observed experimentally that in such crystals absorption of the superimposed (F^+ and F) band begins to decay at about 900 °C due to diffusion-controlled aggregation and/or recombination. It is generally accepted to assume that additively colored crystals contain predominantly F centers [29]. (The absence of any step structure on the annealing curves argues that the contribution of F^+ centers is indeed very small, *or* they have the same mobility.) To estimate the activation energy for F center diffusion, one can use the standard expression for the hopping frequency, $\nu = \nu_0 \exp(-E_a/kT)$. Assuming that the pre-factor is of the order of the LO phonon frequency (which is known to be the case in alkali halides),

$\nu_0 = 10^{13} \text{ s}^{-1}$, and that the F center during annealing for 10 min makes at least ten hops, one gets the value of $E_a \approx 3 \text{ eV}$, twice that reported for F centers in neutron-, electron-, or ion-irradiated MgO crystals [30]. In such irradiated MgO crystals, the complex (F^+ , F) band begins to decay already near $500 \text{ }^\circ\text{C}$ [28, 30]. It has been proposed that this is due to oxygen interstitials (O_i) recombining with the immobile vacancies (F-type centers) [29, 30].

2. Theoretical Method

The semi-empirical quantum chemical method of the Intermediate Neglect of Differential Overlap (INDO) was used here. This formalism being a simplified version of the ab initio unrestricted Hartree-Fock method [31] allows calculations of very big molecules and has been widely used earlier, first in organic chemistry and later for cluster calculations of perfect semiconductors and those with defects [32, 33]. However, its direct application to ionic solids does not give good results. It follows from the recent attempt [34] to calculate the activation energy for anion vacancy diffusion which turned out to be an order of magnitude larger than the experimentally observed. This problem has been discovered more than a decade ago [35] and since then an essentially modified INDO-type scheme has been developed being suited for the study of ionic solids and defects therein. We do not discuss these modifications here since they are described in detail in [35 to 38]. The more so, this method has been applied successfully to defect and exciton studies in oxide crystals (see [37 to 45] and references therein) including MgO [46]. Our calculations are performed using the INDO computer code SYM-SYM which is based on a complete treatment of the symmetry of the system and automated search of the optimal defect geometry via total energy minimization [45, 47]. This allows calculations of rather large quantum clusters which are embedded in our approach into the electrostatic field of non-point charges of the rest of the crystal. Since use of a small (30-atom) cluster could be potentially one of the reasons of the failure in previous quantum chemical calculations of V_a diffusion [34], we have employed here big, compact 224-atom clusters of C_{2v} symmetry including several shells of atoms around a vacancy and the nearest O atom along the [110] axis with which it exchanges its position. The use of such a big cluster allows us to avoid any complications due to boundary effects. In defect calculations the O atom in the cluster center was removed and, in the case of F^+ and F centers, one or two electrons are added to the cluster, respectively. We assume no a priori model of the electronic density distribution in the vicinity of the defect and about atomic relaxation of surrounding atoms, they are coming out as a result of the self-consistent field calculations and the total energy minimization with respect to the atomic configuration. The subtle point is the choice of the basis set to be used in F^+ (F) center calculations. It has been shown [38] that optical properties of F-type centers are reproduced better if additional 1s-, 2p-type atomic orbitals (AOs) are centered on the vacancy thus extending the basis set. However, this procedure causes serious problems in the diffusion studies because in the equilibrium state one has one set of AOs whereas there are *two* sets in the saddle point. In its turn, the use of such two different basis sets would not allow to compare directly the total energies for the relaxed equilibrium and saddle-point configurations and to get their difference sought for (i.e. the activation energy for diffusion, E_a). In the present calculations we have used only the standard valence basis set: 2s, 2p orbitals on O atoms and 3s on Mg atoms. Their parameters are presented in [37, 45].

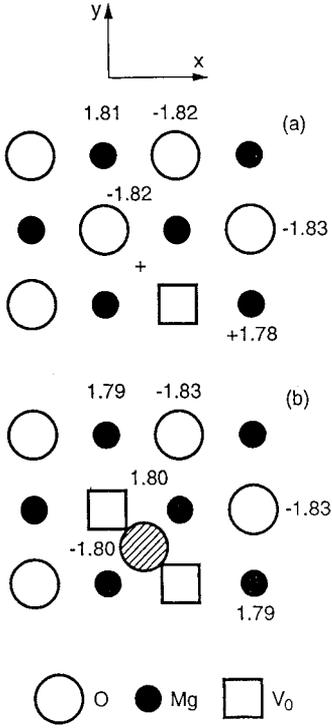


Fig. 1. Diffusion hop of anion vacancy in MgO. a) Initial (equilibrium) atomic configuration. b) Saddle-point (activated) configuration, the moving atom is shaded. The effective charges (in e) of atoms close to a vacancy are given. The coordinate origin is marked by a cross (+). Symbols are explained at the bottom of the figure

3. Results and Discussion

The Mg–O distance (half the lattice constant) obtained in the $\text{Mg}_{108}\text{--O}_{108}$ supercell calculations is $a_0 = 2.02 \text{ \AA}$, which is only 4% less than the experimental one. The optical gap calculated by means of the restricted configuration interaction is 7.6 eV [45], very close to the experimental value of 7.8 eV. The effective charges calculated in terms of Löwdin population analysis are $\pm 1.82e$ on all atoms of the cluster. They demonstrate a predominantly ionic character of the chemical bonding in MgO, in good agreement with previous *ab initio* Hartree-Fock calculations [48]. As we have found, relaxation of only three shells of nearest neighbors around each vacancy contributes predominantly to the total energy

minimization. However, direct use of such quantum clusters leads to a considerably different atomic configuration and total energy of the defect. That is why the use of big (224-site) clusters allows us also to avoid any boundary effects due to broken bonds on the cluster boundary which usually leads to the non-uniform charge distribution between the cluster center and its boundary area [32].

The optimized atomic configurations for a *cation vacancy* in its equilibrium state and the saddle-point show that the nearest O atoms are displaced from their equilibrium positions outwards from V_c by $0.065a_0$. The activation energy for vacancy diffusion hop equals the difference of the total energies for these two configurations (equilibrium and saddle-point) as schematically sketched in Fig. 1. Its magnitude is found to be $E_a = 2.43 \text{ eV}$, in good agreement with the above-discussed experimental data.

In the calculations of an *anion vacancy* we found the activation hop energy to be $E_a = 2.50 \text{ eV}$. This figure confirms the experimentally-observed trend (Table 1) that the diffusion energy for the anion vacancy slightly exceeds that for the cation vacancy. The analysis of the effective charges shows that creation of both types of vacancies, V_c and V_a , does not result in essential charge density redistribution around them. Moreover, the effective charge of the cation and anion in the saddle-point configuration is practically the same as in the regular lattice site which justifies the use of atom–atom potentials in the vacancy hop simulations [49].

In the calculation of the F^+ and F^- centers (one and two electrons trapped by V_a , respectively), as we mentioned above, no AOs were centered on anion vacancies. However, most of the electron density is well localized on several Mg atoms nearest to V_a .

For F^+ and F centers it constitutes $0.84e$ and $1.7e$, respectively. The same is true for the saddle-point configurations of F^+ (F) centers thus demonstrating that here electron(s) is (are) well localized by the two semi-vacancies rather is (are) in the conduction band.

As in the case of bare vacancies, the effective charge of the O atom at the saddle-point configuration coincides practically with that in the regular lattice site. The activation energies are obtained to be 2.72 and 3.13 eV for the F^+ and F center, respectively. The latter estimate is quite close to the value of 3 eV found in Section 2 from the analysis of annealing of additively colored MgO crystals. We know no experimental data for F^+ centers to compare with our predicted energy of 2.72 eV.

4. Conclusion

Large-scale quantum chemical simulations of the diffusion hops of empty cation vacancy, V_c , anion vacancy, V_a , and that which trapped one and two electrons (F^+ and F centers, respectively) in MgO have been performed for the first time employing the same calculation method. The activation energy for diffusion is found to increase monotonically in the series $V_a \rightarrow F^+ \rightarrow F$ center (2.50, 2.72, and 3.13 eV, respectively). This conclusion is important for the quantitative analysis of the possible secondary reactions in irradiated MgO, including metal colloid formation and the radiation-induced degradation effects observed in ceramics [50 to 52]. The bottleneck of our calculations is the basis set at the vacancy. This problem could be solved (and thus our findings could be checked) using the method based on the plane-wave basis set [53]. Such calculations could be of great interest.

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