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Self-trapping holes and excitons in the bulk and on the (100) surfaces of MgO

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Abstract. Self-trapping of holes and excitons in the bulk and on the surface of MgO has been simulated using the self-consistent semi-empirical intermediate neglect of differential overlap method within an embedded molecular cluster model. Our results suggest that, while holes are not self-trapped in the bulk of MgO, they probably are on the surface. It is likely that excitons in both the bulk material and on the (100) surface are self-trapped but that they are highly mobile. The 'on-centre' model of bulk exciton self-trapping yields a Stokes shift of 0.65 eV which is in agreement with experiment. Similarly, the calculated peak energy of 6.4 eV for the excitonic excitation spectrum of the (100) surface agrees with the experimental reflectance peak value of 6.6 eV. The emission energy of the self-trapped exciton on the surface is determined to be 5.7 eV. The results of our calculations show that a single excitonic excitation cannot lead to surface disintegration. However, with high-density irradiation, excitation of an $F^+ - O^-$ metastable state, derived from an exciton, may cause surface disintegration and oxygen atom emission.

1. Introduction

Self-trapping of holes and excitons in insulating solids is a topic of considerable current interest. However, although the self-trapping of excitons in halide crystals [1, 2] has been considered in great detail, significantly less attention has been given to the problem of exciton self-trapping in oxides. Nevertheless, it has been established both experimentally [3, 4] and theoretically [5, 6] that excitons in crystalline SiO_2 are self-trapped, while holes are not. Self-trapping of excitons in Li_2O has also been suggested theoretically [7]. In NaCl-type cubic oxides such as ZnO [8] and MgO [9] sharp edge emission bands have only been observed at low temperatures, suggesting the absence of exciton self-trapping. In other alkaline-earth oxide crystals, specifically CaO and SrO, no edge luminescence has been detected; however, at liquid nitrogen temperatures wider luminescence bands have been observed at lower energies [10]. Rachko and Valbis [11] have observed a decrease in the edge luminescence in MgO above liquid nitrogen temperature accompanied by a build-up of a broad Stokes-shifted emission

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band at 6.9 eV. This broad luminescence has been attributed to a recombination of self-trapped excitons. It has also been shown that the intensity change of both of these luminescences exhibits the same activation energy of about 0.04 eV [11].

A theoretical analysis of the electronic and atomic structures of self-trapped excitons in SiO_2 and Li_2O has been presented in previous papers [7, 12, 13]. These studies suggested that the lattice free volume for anion displacement into an interstitial position is an important factor governing the self-trapping process. Thus, it is of interest to compare the self-trapping of excitons in SiO_2 and Li_2O with that in NaCl-type oxides which have a more compact crystalline structure. Furthermore, if the free volume is really an important factor, the self-trapping of excitons should be more favourable on surfaces where it is possible for the anion to be displaced outward from the surface. Recently Tench and Pott [14] and also Coluccia *et al* [15], observed emission and excitation spectra in powdered cubic oxides that were different from those in the bulk crystals. This was attributed to the excitation and recombination of excitons in the surface region.

Through a comparative theoretical study we have attempted to clarify some of the features associated with hole and exciton self-trapping in the bulk and on the surface of oxides. MgO is a particularly appropriate material for such a study since there are a significant number of experimental and theoretical results concerning defects. Thus, in this article we have simulated the self-trapping of holes and triplet excitons in the bulk and on the (100) surface of MgO. In addition, we have studied the optical absorption and luminescence of the excitons trapped near a surface cation vacancy. Finally, we investigated a possible mode for surface decomposition which is induced by further excitation of an exciton-induced metastable state.

2. Method of calculation

The semi-empirical self-consistent intermediate neglect of differential overlap (INDO) [16, 18] method was used in all the calculations. Our general approach is based on the embedded molecular cluster model [19]. The parameters used in the semi-empirical INDO calculations are the same as those used in previous work [7, 12, 17, 18]. The basis set includes 3s functions on magnesium ions and 2s and 2p functions on oxygen ions. When simulating exciton self-trapping in the bulk and on the surface, the basis set was extended by including several sets of 1s floating Slater-type orbitals. The INDO parameters were optimized with reference to a series of molecular species [17, 18] including all the different bonding possibilities that will be important in our study of exciton formation.

Using these parameters we determine the electronic structure and lattice constant of the bulk material using a periodic large unit cell (LUC) method [18, 20]. The bulk band-gap energy determined from these LUC calculations using the restricted configuration interaction (RCI) method was 7.6 eV; the valence band width was 6 eV and the inter-ionic distance was 3.976 au ($\equiv a_0$). All are in good agreement with previous experimental and theoretical results [10, 21, 22]. Lowdin population analysis was used to calculate the effective ion charges; the values for oxygen and magnesium ions in the perfect lattice were -1.8 and 1.8 respectively. This is consistent with the very ionic character of MgO predicted in *ab initio* calculations [22].

The surface was simulated by a periodic slab model a few layers in thickness but of infinite extension. The LUC method was also used to calculate the surface electronic

structure and rumpling. Investigations of the electronic structure and surface layer rumpling of the (100) perfect structure were performed on slabs containing three, five and seven layers. Electronic structure and surface layer rumpling have been found to settle down for slabs of thickness greater than five layers [18, 23]. According to our calculations, cations on the surface are displaced inward from their ideal positions in the lattice by $0.02 a_0$. This is in good agreement with the result of *ab initio* calculation and experimental data [24, 25]. Conversely, anions are predicted to remain at lattice positions to within $0.01 a_0$. In addition, good agreement was found between the surface dispersion curve calculated with the present method [18] and that calculated using an *ab initio* Hartree-Fock method [22, 24]. Further details of the method and results of calculations of the electronic structure of the surface have been presented elsewhere [18].

Following the perfect lattice simulations we calculated the electronic structure and relaxed configurations of holes and excitons in the bulk by using a quantum cluster in a three-dimensional lattice of non-point ions [19]. Similarly, a cluster embedded in an infinite slab was used to investigate hole and exciton stability on the (100) surface.

The frozen electronic density distribution of the embedding non-point ions in both the bulk and the surface cluster calculations were determined from the LUC calculations and were used to calculate the matrix elements of the Madelung potential of the crystal. These data constituted the embedding potential of the crystal and were used in the cluster calculations. To simulate the self-trapping of a hole and an exciton in the bulk, the polarization of the remaining crystal, not included in the quantum cluster, is accounted for in a self-consistent manner [19]. This self-consistency means that the potential of the electric field generated as a consequence of the response of the lattice to the charged defect is incorporated directly into the Fock matrix on each iteration of the procedure.

3. Hole and exciton self-trapping in the bulk of MgO

3.1. Hole self-trapping

To simulate the self-trapping of the hole in MgO we used the molecular cluster $Mg_{24}O_{24}$ embedded in an infinite lattice of non-point polarized ions. We first investigated the possibility of relaxation within the ions of a non-defective cluster simulating the perfect lattice. Displacements not larger than $0.01 a_0$ were determined even on the border of the cluster. This result shows that the cluster model is appropriate for our calculations.

The first ionization potential of the $Mg_{24}O_{24}$ perfect cluster was calculated to be 8.3 eV, which is slightly higher than the band-gap energy of 7.6 eV determined with the RCI method. The hole in the perfect cluster is spread equivalently over several symmetrical oxygen ions.

To investigate the possibility of hole self-trapping we chose, as an initial configuration, a perfect lattice geometry in which the hole was localized on one oxygen ion only. Several different modes of lattice ion relaxation were investigated. These included the displacement of one of the oxygen ions towards an interstitial position, the relaxation of cations around an oxygen ion and finally the displacement of two oxygen ions to form an oxygen molecular ion (V_k -centre-type self-trapping). We found that the total energy was lowered only by the second model of cation relaxation. Minimization of

the total energy of the crystal through this distortion, which includes lattice polarization, was accompanied by hole localization or trapping on the central oxygen ion. Around this, the nearest-neighbour cations were displaced outwards by $0.06 a_0$ and the next-nearest anions inwards by $0.02 a_0$. A small off-centre distortion of about $0.01 a_0$ of the centre oxygen was also found. The total energy gain due to relaxation from the initial state, where the hole was localized on one oxygen ion in the perfect lattice, and when only the electronic part of lattice polarization was included into the final completely relaxed configuration was 2.4 eV. The polarization contribution to the relaxation energy from all the crystal was 1.9 eV. Our relaxation energy is slightly larger than the value obtained in the HADES calculation (1.73 eV) [26]. When the embedding polarization was not included in the calculation we obtained the same displacements of the cluster ions, but the total relaxation energy was 2.1 eV.

We must now consider if this seemingly large relaxation energy means that the holes in MgO are self-trapped. In order to answer this question we must estimate the energy necessary to localize a hole in the cluster. The conventional way to do this is to take half of the valence band width [27, 28], which according to our calculation is 3.0 eV. This estimation of the localization energy is appropriate only for one-site localization [28] and therefore valid in our case. In general, however, one has to evaluate the energy necessary to localize a hole in a given small cluster. A comparison of the relaxation energy with the half band width suggests that the energy lost in localizing the hole is greater than, or close to, that gained by lattice relaxation. Thus, hole self-trapping would seem to be unlikely. This has, in fact, been shown experimentally [29].

3.2. Exciton self-trapping

As described in previous work, exciton self-trapping in SiO_2 and Li_2O [7, 12], is accompanied by localization of the hole component to an oxygen ion which is displaced towards a lattice interstitial position. The associated electron is then trapped on cation orbitals adjacent to the vacancy formed by the displaced oxygen ion. In this exciton model, the large lattice relaxation resulting from the unscreened hole usually leads to a large Stokes shift of the excitonic luminescence.

The model usually used to explain the experimentally observed excitonic-type excitation spectra of MgO is the on-centre oxygen 2p–3s excitation [21, 30]. Accordingly self-trapped excitons in MgO, if formed, may exhibit an on-centre symmetric relaxation which is different from the relaxation apparent in other oxides [11]. In order to determine whether the on-centre or off-centre model can best explain the experimentally observed Stokes shift (about 0.75 eV [11]†), we simulated exciton-self-trapping using the $\text{Mg}_{24}\text{O}_{24}$ molecular cluster. The cluster was embedded in an infinite lattice of non-point polarizable ions and calculations were carried out for a number of different basis sets. In all of our calculations the lowest triplet state of the exciton was simulated by a triplet state of the cluster, in a similar manner to previous studies [5, 7, 12]. We minimized the total energy of the crystal with respect to ion displacements in an embedded cluster, and polarization of the remaining crystal was included self-consistently in the relaxation calculation. The energy of the triplet luminescence was calculated from the difference between the total energy of the triplet and singlet states

† It is not clear yet whether the experimentally observed luminescence has a singlet or triplet character. We presume that the exchange energy is not as large as it is in the case of free excitons in alkali halides [2].

of the crystal in the ion configuration corresponding to the minimum for the triplet state. This is the so-called Franck-Condon vertical transition. The Stokes shift was determined from the difference between the exciton excitation energy in the perfect lattice configuration and the triplet luminescence energy.

The first calculations employed atomic basis sets of cations and anions but no additional floating functions. In this case the excitation energy necessary to form the exciton was 7.1 eV. The total energy of the crystal in the triplet state was lowered through a T_d -type Jahn-Teller (JT) distortion of the nearest-neighbour cations surrounding a central oxygen ion. In addition, the central oxygen ion off-centres in the $\langle 001 \rangle$ direction along the axis of the JT distortion. Thus, the total minimum energy occurs at the following configuration of the nearest ions: the four cations in the plane perpendicular to the fourfold axis are displaced outward by $0.06 a_0$, the two cations on the axis are displaced outward by $0.07 a_0$ and the oxygen ion displaced along the JT axis by $0.04 a_0$. In this configuration the exciton hole component was completely localized on the oxygen ion while the electron occupied a less well localized state composed from the atomic orbitals of surrounding cations. The total energy gain from the lattice relaxation was about 1 eV, which includes a polarization contribution from the remaining crystal of 0.3 eV. The polarization energy is significantly lower than that determined in the calculation of hole self-trapping because at large distances from the exciton the hole charge is screened by the exciton electron. The Stokes shift of the triplet luminescence was 2.8 eV. This is much larger than the experimental value of 0.75 eV.

The large Stokes shift predicted in this calculation may be the consequence of an inadequate provision for the delocalization of the electron component of the exciton since we have used a fairly restricted basis set. The relaxation of the system would then tend to compensate for the incorrect description of the delocalized electron and result in a relaxed configuration of too low an energy relative to the unrelaxed state.

In order to investigate this possibility we have repeated the calculations using a much wider basis set which includes floating 1s Slater-type atomic orbitals, centred at all cubic interstitial points in the cluster. The floating function Slater exponents were optimized so that the calculated exciton excitation energy is in agreement with the experimental value of 7.6 eV. With this basis set, the one-electron wavefunction of the exciton electron was distributed over both the cations and the floating orbitals. As in the previous calculation, the total energy of the crystal was lowered by a JT distortion. The corresponding ion displacements and the Stokes shift of the triplet luminescence determined with this larger basis set are very similar to those obtained with the previous less flexible basis set. As a consequence, the Stokes shift is still predicted to be much too large. This suggests that the previous poor representation of the exciton electron as a delocalized state is not the cause of the large Stokes shift.

An alternative explanation for the large calculated Stokes shift may be that the basis does not provide for an adequate description of the density of the electron in the space between the central oxygen and its nearest-neighbour cations. This inadequacy would manifest itself in an overestimation of the nearest-neighbour relaxation since the hole charge would be significantly less well screened and the lattice distortion would consequently result in a large Stokes shift.

To simulate the situation in which the exciton electron is localized inside the first sphere of cations, the so-called on-centre model, we have extended the basis set to include 1s Slater-type orbitals centred in twelve equivalent face-centred $(0.5, 0.5, 0) a_0$ -type positions around the central oxygen ion. These functions were orthogonalized to

the other atomic orbitals and their exponents were optimized so that the calculated singlet-triplet excitation energy agreed with experimental value of 7.6 eV. These calculations predict the electron to be localized on the floating functions rather than the nearest-neighbour ions. In this state, the distortions of the nearest-neighbour cations and anions, which minimize the total energy of the crystal, are no larger than 1% of the interatomic distance, considerably smaller than those of the previous two models. The corresponding relaxation energy and the Stokes shift were 0.3 and 0.65 eV, respectively, again much smaller than the previous estimates. We note the excellent agreement between the calculated (0.65 eV) and experimental (0.75 eV) Stokes shifts and also, between the calculated exciton luminescence energy, 6.95 eV and the experimental value, 6.9 eV [11]. Thus, the on-centre model of the exciton is able to offer a significantly better fit to the available experimental data.

The activation energy for self-trapped exciton motion is usually less than the lattice relaxation energy [31]. Since our calculations would suggest that the lattice relaxation energy is small, we would expect excitons in MgO to be mobile even at low temperatures. Since all the anion sites between which excitons can jump are equivalent, we can consider the free exciton as a specific case of the one-centre exciton, corresponding to the situation when exciton hopping is so fast that the lattice relaxation cannot follow the exciton motion. Under such circumstances, the relaxation energy comes only from electronic polarization and as such may be much smaller than the total relaxation energy that we calculated. To change from a free to self-trapped exciton, a small energy barrier must be overcome [11]. The origin of the barrier has been discussed in several previous articles (see, for example, [32] and references therein). If excitons are free to move through the lattice, they may become trapped by defects. However, since the exciton is of a one-centre type this should not unduly affect the luminescence properties of this centre. Although we have not investigated this hypothesis for the bulk, later in this study we do consider perturbations to the luminescence properties of a surface exciton adjacent to a surface cation vacancy.

The on-centre model for free and self-trapped excitons in MgO is in marked contrast with models for SiO₂ and Li₂O where the cation atomic orbitals provide a major contribution to the exciton electron wavefunction. According to Kuusmann *et al* [10] the intrinsic luminescence in CaO and SrO is observed at photon energies separated from the band-edge to a greater extent than in MgO. In addition, since band-gap energies in these crystals are smaller than that in MgO, we expect the role of cation orbitals in describing the exciton electron in CaO and SrO to be more significant. This suggests that the self-trapped excitons in these crystals, if they exist, are somewhat more like those in Li₂O and SiO₂. Consequently, the Stokes shift of the exciton luminescence in these crystals should be larger than it is in MgO. As such, the luminescence observed by Kuusmann *et al* may conceivably be due to the recombination of self-trapped excitons.

4. Hole and exciton self-trapping on the (100) surface

4.1. Hole self-trapping

An investigation of hole self-trapping on the (100) surface was carried out using the same quantum cluster as was used for the bulk but now it is embedded in a five-layer

slab. The surface rumpling calculated using the cluster model was the same as that obtained with the periodical LUC method.

In our calculation, even on a perfect surface, the hole appears to be trapped by several surface anions. The energy of the crystal is minimized by the following ion displacements: the oxygen that has trapped the hole is moved in the direction of the bulk by $0.03 a_0$, the nearest-neighbour five cations are shifted outwards by $0.06 a_0$ and the eight next-neighbour anions were moved inwards by $0.02 a_0$. The energy gain due to this relaxation even without lattice polarization is 2 eV. In order to determine if a surface hole is self-trapped, we must compare the relaxation energy with the energy necessary to localize the hole to one surface anion. Since the hole is localized even on the perfect surface, the localization energy can be equated to half the band width of the valence surface states. The width of this band, calculated using the LUC method, is 1.1 eV, which compares well with the results of the previous *ab initio* calculation [24]. Thus, we believe that the holes on the (100) surface of MgO will be self-trapped to a depth equivalent to about 1 eV.

4.2. Exciton self-trapping

To study the stability of surface on-centre excitons we used the same surface model as for the hole self-trapping simulation but with the basis set augmented by 12 floating Slater functions of the type used to investigate excitons in the bulk. The exciton excitation energy was calculated to be 6.4 eV which is close to the peak energy, 6.6 eV, of the excitation spectrum for powdered MgO [15, 33]. Relaxation of the ions surrounding the excited oxygen resulted in the five nearest-neighbour cations being displaced outward by $0.03 a_0$, which was slightly higher than in the bulk. The inward displacements of the eight next-nearest oxygen ions was about $0.01 a_0$, and the oxygen ion that trapped the hole was displaced towards the bulk by $0.05 a_0$. The calculated energy gain due to relaxation was about 0.45 eV, slightly larger than that for the bulk exciton. The triplet luminescence energy was 5.7 eV which corresponds to exciton luminescence at the surface. We also observed that the electron population of the floating orbitals located outside the surface plane was larger than those located inside, indicating the exciton polarization by the surface.

We consider that the same type of arguments as those used in discussing bulk excitons can be applied to the surface case, as such self-trapped excitons are highly mobile on the surface. Thus, it may be that luminescence arises from the interaction of excitons with defects. We investigated this possibility by calculating the atomic and electronic structure of the exciton near a cation vacancy on the surface. The cation vacancy itself produces a large lattice distortion: the nearest anions are displaced outward by $0.13 a_0$, while the next-nearest-neighbour cations are displaced inward by $0.05 a_0$. Forming an exciton on one of the surface oxygen ions neighbouring the vacancy requires 6.7 eV. The major influence on the exciton relaxation, due to the presence of the cation vacancy, is that the oxygen ion trapping the hole is displaced towards the vacancy by $0.06 a_0$. The calculated triplet luminescence energy was 5.6 eV, very close to the previous value for the exciton on the undefective surface. The small influence of the cation vacancy on both the exciton excitation and luminescence is a consequence of the one-centre nature of the exciton.

5. Surface decomposition induced by electronic excitation

In principle, it is possible that the energy possessed by a surface exciton could be utilized in a surface decomposition reaction. This has previously been discussed with respect to halide crystals [34]. As we have already suggested, excitons which are self-trapped on the surface of MgO may be mobile at high temperatures. Consequently, surface decomposition and atomic desorption at high temperatures may take place adjacent to surface defects and impurities since these can act as trap sites for excitons.

We have used simulation calculations to investigate exciton-induced decomposition from a perfect surface and from a previously excited state. We calculated the change in the total energy of the crystal by displacing an exciton anion outwards from the surface. As the exciton anion was moved, we found that it assumed a charge state of O^- and an F^+ centre remains on the surface. Our results show that the adiabatic potential energy surface for oxygen displacement has a shallow local minimum when the O^- ion is above one of the nearest-neighbour ions of the F^+ centre (the energy needed for O^-F^+ recombination is only 0.02 eV). There is a barrier of about 0.3 eV between the exciton state and the F^+ and O^- minimum. Further separation increases the total energy and indicates that the O^- ion is bound to the surface. Two effects occur as the anion is displaced: the polarization of the crystal by the O^-F^+ dipole which lowers the total energy, and the decrease in the Coulomb attraction between the O^-F^+ pair which acts to increase the total energy. The configuration at the minimum is a result of the competition between the two effects at small displacements. The result that O^- is displaced rather than O^0 is analogous to the formation of the α -I centre pair in the bulk of alkali halides [1, 2]. In this case, the two charged centres are attracted by their Coulomb interaction and the energy is lower than that for the F-H pair of neutral defects. Similarly the formation of an F^0O^0 pair on the MgO surface would require electron transfer from O^- to F^+ .

It is possible that the metastable O^-F^+ state described earlier can be re-excited under dense electronic excitation. We have calculated the transition energy from the O^-F^+ pair to the F^0O^0 pair to be 5.5 eV. From a relaxed configuration of the F^0O^0 pair, the back charge transfer de-excitation occurred by emitting 3.5 eV photons. We also found that the binding energy of the pair after relaxation is only 0.5 eV. The binding energy arises from the fact that the second electron of the now neutral F centre does not completely screen the vacancy charge since the F^0O^0 distance is small. With such a low energy barrier some of O^0 atoms may be desorbed, but the majority of the oxygen will recombine with F centres emitting 3.5 eV photons. The luminescence observed around 3.2 eV by Coluccia *et al* [15, 33] in powdered MgO may be a consequence of this type of luminescence.

6. Summary

We find that holes are not self-trapped in the bulk of MgO, although they may be on the surface plane. The result that the holes are not self-trapped in the bulk is consistent with the experimentally observed high hole mobility [29].

Both free and self-trapped excitons in MgO are best described by a one-centre-type model. This is quite different to the situation in Li_2O and SiO_2 . The configuration for a self-trapped exciton on the perfect surface is very similar to that in the bulk,

although they are slightly more stable on the surface due to the availability of oxygen relaxation perpendicular to the surface. We predict the emission energy from the surface triplet self-trapped excitons to be 5.7 eV.

Finally, we found that surface decomposition accompanied by oxygen atom emission is unlikely to arise from single electron excitation, as it does in halide crystals. However, decomposition can be achieved through a second excitation from a metastable O^-F^+ state to an F^0-O^0 configuration. The metastable state is itself derived from the self-trapped surface exciton.

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