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Excitonic states in pure and impurity-doped magnesium oxide

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Excitonic states in pure and anion-impurity-doped MgO are investigated in several well-defined models using unrestricted Hartree-Fock (UHF)/ICECAP (ionic crystal with electronic cluster, automatic program) simulation procedures. The calculated excitation energies in pure MgO are in excellent agreement with the experiment. The results for S^{2-}- or Se^{2-}-doped MgO show quite conclusively that the lattice response needs to be consistently incorporated with the defect electronic structure.

I. INTRODUCTION

Magnesium oxide (MgO) has been considered the prototypical oxide for spectroscopic studies and is a particularly good testbed for both experimental and theoretical studies of the properties of defect-oxide crystals.

The fundamental optical-absorption spectrum of MgO is dominated by the excitation of the oxygen into an excitonic state. This excitonic transition has been interpreted in terms of transitions from the $2p^6$ ground-state configuration to the $2p^5 3s$ excited state.[1] In this paper, we seek to examine such excitonic states in pure MgO as well as MgO with anion impurities substituted for oxygen in the lattice. A recent series of such studies has been made successfully by Goalwin and Kunz[2] for atomic, molecular, and solid-state systems including alkali halides. However, no theoretical attempt has so far been made in MgO.

Our calculations are based on the molecular cluster model[3] assuming that the excitonic states may be described by localized Frenkel excitons. These calculations will not simply be of one-electron energies, nor will spectroscopy by obtained by using Koopman's theorem, but rather by evaluation of total system energies and their differences. Multiplet splittings are included in these calculations. Furthermore, the role of accurate solid-state modeling in describing such excitonic states will be assessed.

In Sec. II we give a brief description of our computational model simulating the excitonic states in MgO. The results are presented and discussed in Sec. III. Finally, in Sec. IV the conclusions are summarized.

II. COMPUTATIONAL MODEL

Since MgO has NaCl structure with octahedral site symmetry, pure and impurity-doped MgO are therefore modeled as a molecular cluster of an oxygen and/or impurity ion surrounded by six nearest-neighbor Mg^{2+} ions, thereby incorporating the details of electronic structure of neighboring ions. The molecular cluster is then embedded in point-ion arrays representing the lattice environment in providing the correct Madelung field and ensuring overall charge neutrality. Lastly, the molecular cluster is embedded in a shell-model lattice using the program package ICECAP (ionic crystal with electronic cluster, automatic program) which treats the cluster electronic structure and the lattice response to the cluster in a self-consistent way. The simulation models considered are therefore (i) the $[X+6Mg^{2+}]$ cluster, where X is O^{2-}, S^{2-}, or Se^{2-}, (ii) the $[X+6Mg^{2+}]$ cluster in a point-ion array, and (iii) the same cluster in a shell-model lattice. We thus show a systematic improvement at each successive step for the simulation of excitonic states in pure and impurity-doped MgO.

The unrestricted Hartree-Fock self-consistent-field (UHF-SCF) approximation is employed to describe the electronic structure of the molecular cluster and has been discussed elsewhere by Kunz and co-workers.[2-5]

ICECAP combines electronic-structure calculations with shell-model treatment of lattice polarization and distortion, the electronic structure and lattice relaxation components themselves being integrated self-consistently. The ICECAP methodology is described in detail in a variety of other papers.[6-8] Recent applications of ICECAP to study *F*-type centers and hydrogen anions in MgO (Ref. 7) and copper in NaF (Ref. 8) have demonstrated its value in understanding the optical processes associated with point defects in ionic crystals.

Our molecular cluster consists of either oxygen or a substitutional anion impurity, namely S^{2-} or Se^{2-} at the cluster center and the six nearest-neighbor Mg^{2+} ions at the sites $(a,0,0)$, where a is the nearest-neighbor spacing. The Gaussian basis set associated with Mg^{2+} ions consists of a (7, 7/4) contraction set and is derived from perfect-lattice cluster calculations in MgO using the procedure of Pandey and Vail.[7] The O^{2-} basis set is based on the (4, 3/4) contraction for O^0 of Huzinaga[9] and is extended by the addition of diffuse *s*- and *p*-type Gaussian primitives to more accurately describe the negative oxygen ion. The exponents of these primitives have been optimized. *s*-type primitives have also been added to describe the excited states. A similar procedure has been used to obtain the basis sets for both S^{2-} and Se^{2-} ions from S^0 and Se^0 sets, respectively, given by Huzinaga.[9]

The nearest-neighbor distance and the parameters for the shell-model and short-range potentials for MgO used in ICECAP calculations are taken from Sangster and Stoneham.[10]

III. RESULTS

The purpose of this investigation has been to study and quantitatively identify local excitonic processes occurring in pure and impurity-doped MgO. The experimental data are available for pure MgO, so this case is used to judge the predictive value of our model.

Excitation energies are obtained by calculating ground- and excited-state configurations separately and then taking the difference in energy of these two configurations. This is referred to as the ΔSCF method. Our molecular cluster involves a closed-shell ground state. An electron-hole pair in either the triplet or the singlet spin state describes low-lying excited states in our calculations.

Excited states are known to cause computational difficulty due to either the variational collapse (that is, if the ground and excited states of the system have the same symmetry, the Hartree-Fock equations will tend to converge to the state of lowest energy), or the nonuniqueness of the Hartree-Fock solutions, which may cause a convergence problem of the Hartree-Fock equation for a desired excited state. We use the technique developed by Kunz to achieve convergence in an excited state. The technique is as follows.

(1) The ground state of the system is obtained consisting of occupied and virtual (unoccupied) orbitals. One of the occupied orbitals is then chosen to be depopulated and a virtual orbital is selected to take its place.

(2) This set of orbitals is then used to construct a new Fock operator, which is selected for a new set of orbitals.

(3) The new set of orbitals is examined to see which orbital has the greatest overlap with the orbital depopulated in step (1). This orbital is now excluded and steps (2) and (3) are repeated to convergence.

It is to be noted here that the triplet state is the ground state for $S_z=1$. In the UHF formalism triplets can therefore be easily obtained. But it is impossible to specify an excited state that is pure singlet. We therefore apply a backprojection technique, obtaining the energy of a pure singlet state from the known energy of the pure triplet state and the known energy and expectation value of S^2 of the triplet-contaminated singlet state. Thus,

$$E_s=\frac{2E_s'-S(S+1)E_t}{2-S(S+1)}\ , \tag{1}$$

where E_s' is the energy of the contaminated state, $S(S+1)$ is the calculated S^2, and E_t is the triplet energy.

The calculated transition energies in three different simulation models, namely the cluster and the cluster embedded in either point-ion arrays or a shell-model lattice, are given in Table I. The calculated values of the spin in the triplet state (1.000–1.002) are found to be very close to the expected values for a pure triplet state. Referring to Table I, we notice that the energies associated with $p^6 \rightarrow p^5s$ excitation reduce substantially as we improve our model chosen to simulate the excitonic states in pure and impurity-doped MgO.

In pure MgO, Roessler and Walker[1] have obtained the room-temperature reflectance spectrum exhibiting a strong peak at 7.60±0.01 eV. At 77 K this peak moved to higher energy, splitting into a doublet with component maxima at 7.69 and 7.76 eV, suggesting that the observed structure is due to an excitonic transition. In comparison, our calculated values associated with excitonic transition in pure MgO are 9.65 and 11.32 eV in the cluster model, 7.37 and 7.39 eV when we embed the cluster in a point-ion array, and 7.73 and 7.77 eV in the ICECAP model, respectively. Thus, ICECAP results are in excellent agreement with the observed energies, showing the importance of accurate solid-state modeling in such a simulation study. The calculated singlet-triplet splitting comes out to be 0.04 eV, as compared to the observed separation of 0.07 eV.

TABLE I. Energies associated with $p^6 \rightarrow p^5s$ excitation in pure and impurity-doped MgO.

	Energy (eV) Triplet	Singlet
MgO		
cluster	9.65	11.32
cluster + point-ion array	7.37	7.39
ICECAP	7.73	7.77
MgO:S^{2-}		
cluster	13.24	13.89
cluster + point-ion array	8.99	9.03
ICECAP	7.09	7.12
MgO:Se^{2-}		
cluster	13.25	13.96
cluster + point-ion array	8.22	8.25
ICECAP	6.68	6.71

We now turn our attention to impurity excitonic states assuming that the excitation is out of a p^6 orbital into a localized p^5s state, with the excited electron and its hole resonating at the impurity site. In our model, impurity sites are sites in which the impurity takes the place of the oxygen in the lattice.

Substitutional S^{2-} and Se^{2-} ions are isovalent impurities in MgO and are therefore considered to possess no effective charge when in the oxide lattice. Both ions, however, are substantially larger than the O^{2-} ion and are therefore expected to produce a significant distortion in the lattice.

It is to be noted here that ICECAP minimizes the total energy of the defect lattice containing the molecular cluster with respect to all lattice positions and simultaneously with respect to variational parameters in the molecular cluster wave function. This minimization is updated while nuclear positions of the cluster are varied to give overall minimization of the energy. For the $[O^{2-}+6\ Mg^{2+}]$ cluster, the nearest-neighbor Mg^{2+} ions have relaxed inward slightly (< 1%), thereby demonstrating the compatibility of the quantum-mechanical cluster with the shell-model description of the embedding lattice in pure MgO. For S^{2-} and Se^{2-} impurities in MgO, larger outward relaxation of the Mg^{2+} ions, of about 6% and 8%, respectively, have been obtained, as expected.

Referring to Table I, we notice that the energies associated with $p^6 \rightarrow p^5 s$ excitation of impurities are predicted to be in the band gap of MgO. The calculated excitation energy comes out to be 7.09 eV for the S^{2-} ion and 6.68 eV for the Se^{2-} ion in MgO. It is interesting to note that ICECAP results do provide a quantitatively sensible picture for the impurity excitonic states in MgO.

We now propose to extend the investigation to compute the relaxed excited states and the frequency for optical emission providing the Stokes shift directly. Finally, we hope that the present work will stimulate the experimental studies to identify anion impurity excitonic states in MgO.

IV. CONCLUSION

It appears that the low-lying excitonic states in MgO can be explained satisfactorily using a localized excitation model. The calculated spectral levels in pure MgO are in excellent agreement with the experiment. The inclusion of lattice response in the defect electronic structure is shown to be significant for the case of isovalent impurities in MgO.

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