Embedded-cluster study of the lithium trapped-hole center in magnesium oxide

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(Received 15 February 1991; revised manuscript received 13 May 1991)

The lithium trapped-hole center in magnesium oxide is studied by using the simulation program package ICECAP (ionic crystal with electronic clusters, automatic program). The defective crystal is simulated as a molecular cluster embedded in a shell-model lattice. The molecular cluster, which contains the trapped-hole center, is treated quantum mechanically by using the unrestricted Hartree-Fock approximation. Correlation correction is also included in the calculations. Different types and sizes of defect cluster are used to determine the equilibrium configurations of the defective lattice. The role of the correlation correction is found to be significant. The results show very consistently that the Li^+ ion and the O^- ion (the O^{2-} ion with the trapped hole) move toward each other and the axial O^{2-} ion moves away from the Li^+ ion.

I. INTRODUCTION

Trapped-hole centers containing alkali metals have long been identified in alkaline-earth oxides. The knowledge on the properties of these defect centers can help us to understand the nature of the alkaline-earth oxides with intrinsic and impurity defects. As a typical ionic crystal, MgO is one of the alkaline-earth oxides. It has the rocksalt structure: each ion in the crystalline lattice has six ions of the opposite charge as its nearest neighbors. Scientifically, MgO is an ideal material for studies on point defects. It also has some industrial usages. Lithium can be easily doped in MgO and its doping has been found quite useful in industry. For example, when MgO is used as an insulator in nuclear reactors, lithium doping can reduce the radiation damage to the MgO crystal. Lithium-doped MgO can also be used as a catalyst. This catalytic property is attributed to the trapped holes which result in effective O^- ions. Therefore, this study is of both academic and industrial interest.

In the past few decades, extensive experimental studies on the alkali-metal trapped-hole centers in alkaline-earth oxides were conducted, including optical studies, ESR (EPR) and ENDOR measurements.[1-7] In 1988, Foot, Colbourn, and Catlow[8] reported computer simulations of some of the alkali metal trapped-hole centers in alkaline-earth oxides with the classical shell model which has somewhat restrictive predictability for the trapped-hole centers. In this study we use an embedded-cluster technique to examine the lithium trapped-hole center in MgO.

II. COMPUTATIONAL MODEL

The defective crystalline lattice is modeled as a molecular cluster embedded in a shell-model lattice. The molecular cluster, which contains the defect center, is treated quantum mechanically by using the Hartree-Fock cluster method developed by Kunz and his co-workers.[9,10] This method is basically an *ab initio* LCAO-UHF-SCF (linear combination of atomic orbitals—unrestricted Hartree-Fock—self-consistent-field) method, in which the behaviors of the electrons are described by wave functions satisfying the Hartree-Fock equation of the system. The embedding lattice is described by the shell model.[11] The ions are considered as dipole polarizable point charge cores harmonically coupled to uniformly charged massless spherical shells. The Buckingham-type potentials are used to account for the short-range interactions among the ions, in addition to the long-range Coulomb interactions. The actual simulations are performed by using the program package ICECAP (Ionic Crystal with Electronic Cluster, Automatic Program).[12] In this program package, the quantum-mechanical molecular cluster and the classical embedding lattice are integrated self-consistently to ensure the consistency between them.[13,14]

Since the Hartree-Fock approximation ignores the correlations among the electrons by definition, corrections based on the second-order many-body perturbation theory (MBPT) are included in the calculations.

The Buckingham potentials between the host ions and between the Li^+ ion and the O^{2-} ion were derived by us

in a previous study using ICECAP.[15] But the parameters of the potentials between the O^- ion and the other ions are not available. Those for the O^{2-} ion are used instead.

Gaussian-type orbitals (GTO's) are used for the UHF calculations. For the O^{2-} ion and the Mg^{2+} ion, the O^{2-} (7,7/4) set and the Mg^{2+} (7,7/4) of Pandey and Vail[13] are used. These basis sets have been used in some previous MgO calculations[13,15,16] and the results are quite satisfactory. The basis set for the Li^+ is the Li(6) set of Seel, Kunz, and Hill[17] in whose work this basis set also yielded reasonably reliable results. The basis set for the O^- ion, denoted by O^- (7,7/4), is developed by reoptimizing the O^{2-} (7,7/4) set of Pandey and Vail with an O^--6 Mg cluster.

III. RESULTS

A. HOLE LOCATION

When an isolated Li^+ ion substitutes an Mg^{2+} ion in MgO, charge neutrality requires that a hole be trapped around the Li^+ ion. First of all, one might ask the question: where is the hole located? It is split evenly (hopping) among the O^{2-} ions around the Li^+ ion or attached to one of these six O^{2-} ions? Energetically, it is favorable for the hole to be located at one of the six O^{2-} ions, instead of hopping around them. Analyses based on experimental observations[1-5] do indicate that the hole is attached to one of the six O^{2-} ions. Here, a simple test is performed to see if the ICECAP calculation can give the correct result. Using the Li^+-centered 7-ion cluster, it is attempted to force an equal "piece" of the hole onto each of the six O^{2-} ions. The lowest total energy obtainable is about 4 eV higher than that of the configuration with the hole located on one of the O^{2-} ions. This means that the even splitting of the hole is energetically unfavorable. Thus, the hole must be located at one of the six nearest-neighbor O^{2-} ions, as indicated by ESR and ENDOR measurements.[1-5]

B. Lattice distortion

Although the lithium trapped-hole center is uncharged, there are effective charges: -1 at the Li^+ ion and $+1$ at the O^- ion. These effective charges form an effective dipole. It is reasonable to expect this effective dipole to polarize the surrounding ions and produce significant distortions in the lattice.

1. The Li^+-centered 7-ion cluster

The relaxed configuration is illustrated in Fig. 1. The numbers and the arrows show the amounts and directions of the displacements from the perfect lattice configuration of MgO. With this cluster, the Li^+ ion is found to have moved toward the O^- ion by about 5% of the lattice constant, which is 2.106 Å for MgO. And the O^- ion moved outward by about 16% of the lattice constant. Thus, the distance between the Li^+ ion and the O^- ion is smaller by about 21% than the lattice constant.
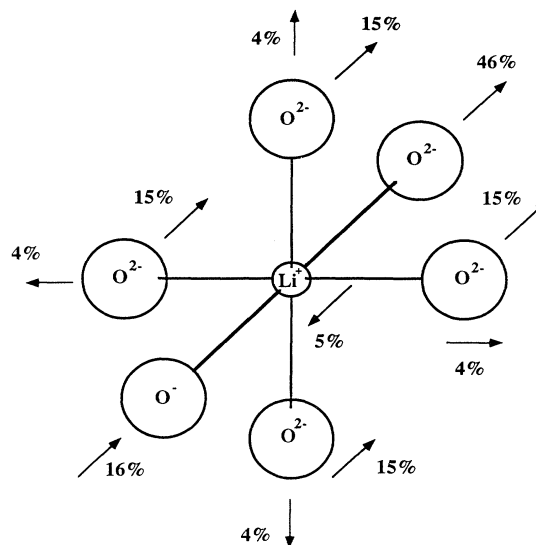

FIG. 1. The equilibrium configuration of Li^+-centered 7-ion cluster.

The axial O^{2-} ion (opposite to the O^- ion) is found to have moved outward by 46% of the lattice constant. The other four O^{2-} ions are relaxed outward, by about 4%, with a shift of about 15% in the [$\bar{1}00$] direction.

In 1970, Schirmer[2] suggested that the Li^+ ion relaxes away from the O^- ion. Later, based on their experiments, Abraham, Unruh, and Chen[7] reported a calculated increase of 21% of the lattice constant in the Li^+-O^- distance. Their results are in contradiction to the result presented above.

Intuitively, the Li^+ ion and the O^- ion should attract each other because they carry opposite effective charges, which is the fundamental principle of electrostatics. It violates this principle if they move away from each other. For the same reason, one may expect the O^{2-} ion opposite to the O^- ion to be repelled away from the Li^+ ion. Also, the other four O^{2-} ions in the cluster have the tendency to move away from the Li^+ ion. But the results of the calculations of Abraham, Unruh, and Chen[7] indicate that the distance between the O^- ion and the axial O^{2-} ion is about 15.8% larger than the lattice constant, while our result above implies a 30% increase. This can be said to be in qualitative agreement.

Note that the axial O^{2-} ion moved outward by 46%, which is a very large distance. This may be attributed to the fact that there is no quantum-mechanical ion beyond that ion. The shell-model ions surrounding the defect cluster do not provide sufficient constraint against this ion (the ion size effect is missing). Thus, this ion moved outward under the repelling force of the effective dipole formed by the Li^+ ion and the O^- ion. To see if adding more quantum-mechanical ions to this 7-ion cluster can improve the result, two Mg^{2+} ions are added to the cluster, one on each side of the x axis. That is the Li^+-centered 9-ion cluster.

2. The Li^+-centered 9-ion cluster

For this cluster, the relaxed configuration is shown in Fig. 2. As indicated in the figure the distance between the Li^+ ion and the O^- ion is 8% smaller than the lattice constant. The distance between the O^- and the axial O^{2-} ion is about 15% larger than the lattice constant. Comparing these results to those from the Li^+-centered 7-ion cluster, the contribution of the two added Mg^{2+} ions is obvious. This shows the importance of the cluster size. For the calculation of the lithium trapped-hole center, since significant lattice polarization is present, a cluster with the first neighbors only is not large enough.

3. The O^--centered 7-ion cluster

The above calculations are done with Li^+-centered clusters. In order to see if consistent results can be obtained, O^--centered clusters are used to do the calculations. With the same basis sets as used in the Li^+-centered cluster calculations, the equilibrium configuration was obtained as shown in Fig. 3. The Li^+–O^- distance is 25% smaller than the lattice constant, which is qualitatively consistent with the previous results obtained with the Li^+-centered clusters.

4. MBPT correction

In order to see the contribution of the electronic correlation interactions, we use the O^--centered 7-ion cluster to do the calculation with the MBPT correction. An O^- (7,7,1,1/4,1) basis set is developed by adding two s-type primitives and one p-type primitive to the minimal O^- (7,7/4) set, with all the three primitives optimized. Before doing the MBPT calculations, we recalculated the equilibrium configuration of the O^--centered 7-ion cluster to see the effect of the three added primitives, which have longer range than the ones in the O^- (7,7/4) set. The total energy of the equilibrium configuration is almost the same as that obtained with the minimal set
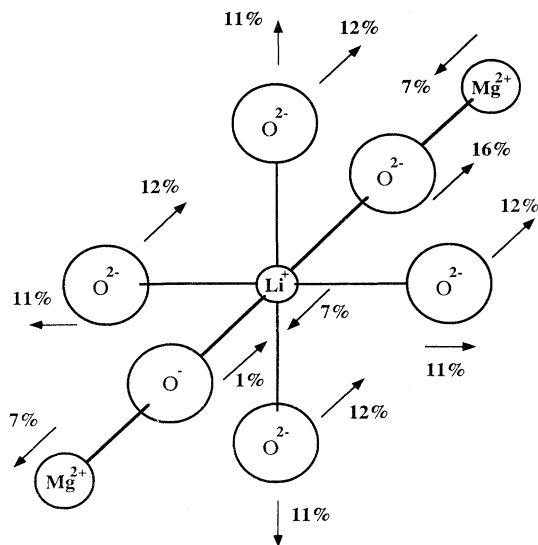

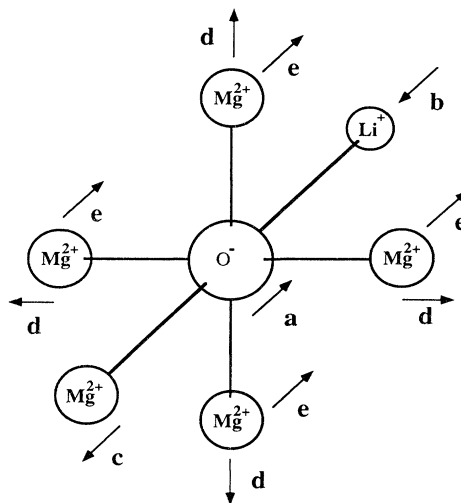FIG. 2. The equilibrium configuration of the Li^+-centered 9-ion cluster.

FIG. 3. The equilibrium configuration of the O^--centered 7-ion cluster. With O^-(7,7/4) set, $a=12\%$, $b=13\%$, $c=6\%$, $d=2\%$, $e=1\%$; with O^-(7,7,1,1/4,1) set, $a=9\%$, $b=8\%$, $c=2\%$, $d=5\%$, $e=1$; with O^-(7,7,1,1/4,1) set and MBPT corrections, $a=6\%$, $n=5\%$, $c=3\%$, $d=5\%$, $e=1\%$.

(difference: 0.041 eV). The position changes are shown in Fig. 3. The Li^+–O^- distance is 17% smaller than the lattice constant and the axial Mg^{2+} ion shifted outward by 2%. Comparing with the corresponding 25% and 6% obtained with the minimal O^- (7,7/4) set, we can see that the three longer-range primitives added to the minimal basis set do have some effects on the equilibrium configuration. This is not unreasonable because the trapped hole on the O^{2-} ion makes its outermost shell open. The electrons in this open shell are more active than those in a closed shell and interact more strongly with the electrons of the other ions. Therefore, the Li^+ ion and the O^- ion cannot move as close as with the minimal set. The added primitives provide a better description of the trapped hole. As shown in Fig. 3, with the expanded basis set and the MBPT corrections, we found that the Li^+–O^- distance is 11% smaller than the lattice constant (6% smaller than the change without the MBPT corrections) and the axial Mg^{2+} ion moved outward by 3% (2% without the MBPT corrections). The contribution of the correlation interactions is obvious and should be considered significant. In ground-state calculations, electronic correlation usually does not play a significant role if the shells are closed. But in this case, correlation interactions do make significant contribution to the lattice relaxation since a shell is open and strong polarization is present. Because of the opposite effective charges on the Li^+ ion and the O^- ion, these two ions tend to move toward each other. The correlation interactions provide additional resistance to excess overlapping of the electron clouds. Note that the changes due to the MBPT corrections are along the axial direction in which the polarization points, while the changes due to the added primitives are everywhere except in the axial shift of the four systematic Mg^{2+} ions. The results of this work and the results of Abraham et al. are compared in Table I.

TABLE I. Ion-ion distances (Å).

Cluster	Li^+-O^-	O^--O^{2-}
Li^+-centered 7-ion cluster	1.664	4.844
Li^+-centered 9-ion cluster	1.938	4.528
O^--centered 7-ion cluster	1.580	
O^--centered 7-ion cluster[a]	1.748	
O^--centered 7-ion cluster[b]	1.874	
Abraham et al.	2.547	4.547

[a]With O^- (7,7,1,1/4,1) set.
[b]With O^- (7,7,1,1/4,1) set and MBPT corrections. The perfect lattice constant of MgO: 2.106 Å.

5. Energies

Table II gives a summary of the total energies and energy gains obtained by relaxing the clusters from the perfect lattice configuration of MgO. Since an isolated lithium trapped-hole center in MgO is unstable at room temperature,[7] the 11.046-eV energy gain for the Li^+-centered 7-ion cluster is too large to believe. For the Li^+-centered 9-ion cluster, adding only two Mg^{2+} ions cuts the energy gain by half. This shows again the importance of the cluster size. Note that the energy gains for the O^--centered clusters are much smaller than those for the Li^+-centered clusters. This is due to the fact that the interactions between an anion and its surrounding ions are much stronger than those between a cation and its sur-

TABLE II. Energies (eV).

Cluster	Perfect lattice configuration	Equilibrium configuration	Energy gain
Li^+-centered 7-ion cluster	-12278.847	-12289.893	11.046
Li^+-centered 9-ion cluster	-23088.841	-23094.294	5.453
O^--centered 7-ion cluster	-29217.596	-29218.736	1.140
O^--centered 7-ion cluster[a]	-29218.082	-29218.695	0.613
O^--centered 7-ion cluster[b]	-29219.186	-29219.816	0.630

[a]With O^- (7,7,1,1/4,1) set.
[b]With O^- (7,7,1,1/4,1) set and MBPT corrections.

rounding ions.

Note that the equilibrium total energy obtained with the O^- (7,7/4) set and the one obtained with the O^- (7,7,1,1/4,1) set are virtually the same while the equilibrium configurations are quite different. This clearly shows the importance of basis sets. One must use basis sets that can give good description of the electrons of the system under study. Although it may give correct total energy of the system, a minimal set may not yield reliable equilibrium configuration when a shell is open and strong lattice polarization is present.

IV. SUMMARY AND CONCLUSION

The Li^+ ion and the O^- ion (the O^{2-} ion with the trapped hole) form an effective dipole which polarizes the surrounding lattice. As expected, this creates significant distortion in the lattice. The Li^+ ion and the O^- ion move toward each other. The axial O^{2-} ion is pushed outward and the other four nearest-neighbor O^{2-} ions surrounding the Li^+ ion are repelled outward with a shift in the direction the axial O^{2-} ion moves. The axial Mg^{2+} ion next to the O^- ion moves away from it and the other four nearest-neighbor Mg^{2+} ions surrounding the O^- ion relax outward. These results fit very well the basic principle of electrostatics and should be considered, at least qualitatively, correct.

The results indicate that larger clusters may be needed for obtaining reliable equilibrium configuration of the defective lattice. This is because the ions beyond the nearest neighbors of the Li^+ ion and the O^- ion, especially those along the axial direction, are also significantly perturbed by the effective dipole. An alternative for a larger cluster is to use localized potentials. One such localized potential is the Kunz-Klein localizing potential (KKLP).[9,10] Also, good basis sets are essential to obtaining reliable results.

The result from the O^--centered 7-ion cluster with the MBPT correction shows the role of correlation correction. With open shells and strong lattice polarization, correlation interactions may contribute significantly to the lattice relaxation.

Although the results obtained in this study are just preliminary, they are very encouraging. As seen in this study, with its capability of long-range lattice relaxations, the flexibility of ICECAP is ideal for studying defects in ionic crystals.

For the lithium trapped-hole center problem, this ICECAP study is just a beginning. Many improvements are to be made. For example, the parameters of the Buckingham potentials among the O^- ion and the other ions need to be derived (it can be done with ICECAP). It is also worth trying to use pseudopotentials rather than enlarging the size of the UHF molecular cluster. Spin densities at various sites may be calculated and compared with available experimental results.

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