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Hole trapping in $\text{Li}_x\text{Ni}_{1-x}\text{O}$

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Abstract. Calculations are reported for a hole associated with a lithium impurity in NiO. The method is based on Hartree–Fock molecular clusters embedded in a classical shell-model lattice, with consistent treatment of distortion and polarization. It is shown that the hole is trapped in oxygen 2p states rather than in nickel 3d states, in agreement with experimental x-ray absorption spectroscopy results. In the static lattice approximation the hole localizes on a single oxygen nearest neighbour of the lithium ion, rather than in an O_h -symmetric distribution among all such neighbours.

1. Introduction

The search for the mechanism for high- T_c superconductivity in ceramic oxides has led to numerous studies of the electronic structure of these systems. Many of these investigations are aimed at probing the charge and spin state of the transition metal atom. These studies have rekindled a general interest in the magnetic properties of transition metal oxides, for some of the understanding developed here could be directly applicable to high- T_c materials. A particular example in this regard is the determination of the valence structure of Ni in substituted $\text{Li}_x\text{Ni}_{1-x}\text{O}$. In NiO, it is commonly understood that Ni exists in a Ni^{2+} state. With a Li^+ ion substituting for a Ni^{2+} ion, the extra hole would be free to transfer to a Ni ion making a Ni^{3+} state, thus transforming the system to a mixed-valence one. However, if instead the hole was trapped by the oxygen 2p state, the valence state of the Ni atom would remain unchanged.

A decisive answer to these problems was given recently by Kuiper *et al* [1]. These authors deduced, from x-ray absorption spectroscopy, that the hole associated with lithium substituted in NiO is associated with the oxygen 2p states, rather than with nickel 3d states. They pointed out that this is characteristic of a large number of transition metal oxides, and has great significance for the understanding of their electrical, optical, and particularly their magnetic properties. However, the authors were uncertain about the precise nature of the hole; specifically, whether it has O_h symmetry about the impurity Li^+ , or lower symmetry.

In this paper we provide the first theoretical verification that the added hole is indeed associated with the oxygen 2p state. We further show that the symmetry of the hole is

C_{dv} rather than O_h . Our results are based on total energy calculations using an embedded cluster model.

2. Method

In our method [2] the impurity ion and its near neighbours are treated as a molecular cluster, using the unrestricted Hartree–Fock self-consistent field approximation. This cluster is embedded in an infinite classical shell-model lattice [3], whose parameters are derived from the experimental bulk properties of the material. These parameters define the pairwise short-range potentials between ions, and the ionic polarizabilities in terms of shell charges and shell–core force constants. Thus the cluster is subject to the Madelung potential of the ionic crystal. The total energy of the crystal containing the defect cluster is minimized with respect to the positions of all the point charges: the bare nuclei of the cluster, and the shell-model cores and shells. The distortion and polarization of the embedding lattice are a response to two kinds of force exerted by the cluster, namely Coulomb forces and short-range forces of quantum mechanical origin. To determine the Coulomb forces, the cluster is simulated by an array of point charges that represent the nuclei and the electronic charge distribution. The short-range forces are simulated in terms of the corresponding shell-model potentials.

The cluster Hartree–Fock analysis is based on molecular orbitals that are linear combinations of atomic-like basis orbitals constructed from Gaussian primitive functions [4]. For the Li^+ ion we have used Huzinaga's contraction [5] of four s-type primitives, and for Ni^{2+} ions his (3F, $3d^84s^2$) basis set of (533/53/5) contractions. Our experience with cation impurities in other ionic crystals, including copper and silver in alkali halides [6, 7] and copper and Ni in MgO [8], indicates that such basis sets are appropriate. Further work for Li^+ in MgO [9] supports this view. For O^{2-} ions we have used a (53/5) basis set which we derived [8] for MgO by optimizing the oxygen 2p orbital contraction of Huzinaga's neutral oxygen (53/5) set [5] in a $(Mg^{2+})_6 \cdot O^{2-}$ cluster embedded in MgO. By optimizing the O^{2-} basis set in the rocksalt structure we have described its main feature, although the explicit effect of the cation species (nickel rather than magnesium) should be covered in future work. The effect of the crystal's Madelung field is to reduce the range of the most diffuse 2p primitive basis function [8]. It is known [10] that for the F^+ centre in MgO the relative ordering of oxygen 2p and F^+ centre ground-state levels is sensitive to the O^{2-} basis set, but the F^+ centre wavefunction has a radius more than twice that of any of the ions in the present study. In particular, the Ni^{2+} ion, whose levels are of interest here, is highly localized. We believe that the effect reported is principally due to Coulomb rather than overlap effects, and is therefore relatively insensitive to the O^{2-} basis set.

Our shell-model parameters for NiO were adapted from those of Sangster and Stoneham [11], which had been fitted to the low- and high-frequency dielectric constants, the lattice spacing, and the transverse optical frequency. For the lithium–oxygen interaction, one might think that shell-model parameters are not needed, since this interaction is embodied in the Hartree–Fock treatment of the cluster. While this is true, the dipole moments, induced by the defect in the nearest-neighbour oxygens, act on the embedding lattice through both short-range and Coulomb forces that are not simulated in our present treatment of the cluster. In such a case, it is necessary to begin by subjecting the embedding lattice to shell-model ions representing the cluster. For this purpose, we have used the lithium shell-model parameters derived by Chadwick *et al* [12] for Li_2O ,

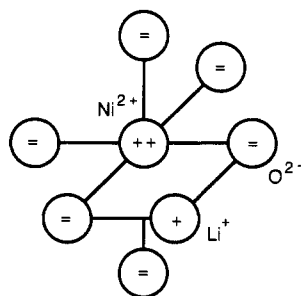


Figure 1. $\text{Li}^+ \cdot \text{Ni}^{2+} \cdot (\text{O}^{2-})_6$ cluster in NiO, centred on Ni^{2+} .

namely $Y = 1.267e$, and $K = 36.64 \text{ eV } \text{Å}^{-2}$, where Y and K are shell-charge and shell-core force constants respectively. The short-range lithium–oxygen Born–Mayer interaction $B \exp(-r/\rho)$ from [12] has $B = 383.72 \text{ eV}$ and $\rho = 0.32415 \text{ Å}$. We note that these values are derived for Li_2O , whose anti-fluorite structure is quite different from the rocksalt structure geometry of the lithium–oxygen system of the present work. On the other hand, shell-model Born–Mayer parameters have been derived [13] for BeO , which has the rocksalt structure: their values are $B = 846 \text{ eV}$ and $\rho = 0.28 \text{ Å}$. We have therefore adopted a stronger value of B than that given by Li_2O , namely in what follows we used $B = 840 \text{ eV}$.

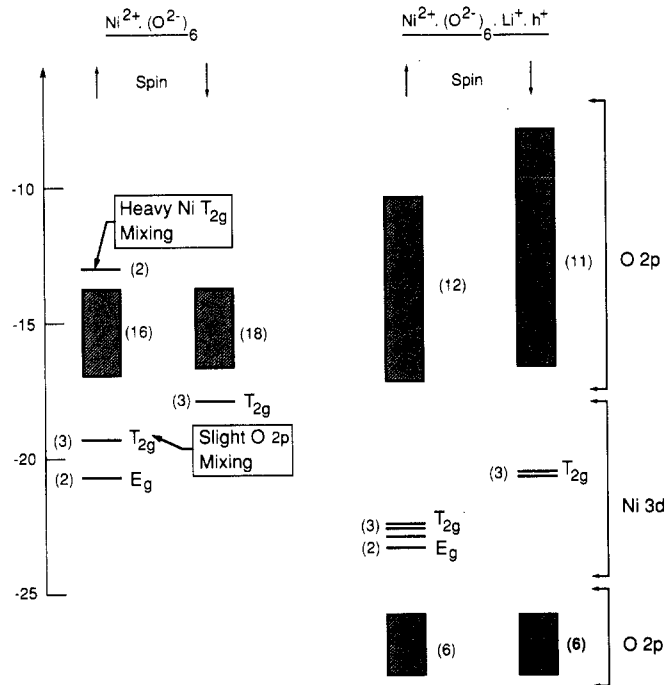
3. Calculations

Our first calculation addresses the question of where an electron hole will go in $\text{NiO}:\text{Li}$. For this, we consider an embedded cluster containing lithium, nickel and oxygen. Now Li^+ has two electrons, Ni^{2+} has 26, and O^{2-} has 10. Because of limited computer capacity, we must limit our all-electron quantum mechanical calculation to a small cluster, yet we want to allow fully for hybridization of nickel 3d and oxygen 2p orbitals. We therefore consider a $\text{Li}^+ \cdot \text{Ni}^{2+} \cdot (\text{O}^{2-})_6 \cdot h^+$ cluster (where h^+ is an electron hole) embedded in an infinite NiO lattice. This Ni^{2+} -centred cluster with a Li^+ ion on a second-neighbour site is illustrated in figure 1. We introduce an electron hole into the cluster by assigning only 87 electrons to the latter, instead of the nominal 88 electrons of $\text{Li}^+ \cdot \text{Ni}^{2+} \cdot (\text{O}^{2-})_6$. In this calculation the cluster ions are fixed on perfect lattice sites, so although the cluster geometry is not optimized the polarization of the embedding lattice is. To induce the polarization field in the embedding lattice, the lithium ion is simulated by a charge $+e$. This prejudices the result, favouring the exclusion of the hole from lithium. We deal with this point in another calculation below. In earlier work, with the same basis set as is used here, the Hartree–Fock ground state of the free Ni^{3+} ion and in $\text{MgO}:\text{Ni}^{3+}$ was found to have spin 1.5, so in this calculation we have taken 45 electrons of spin up and 42 of spin down. The resulting calculated value of the total spin is 1.500 078.

Mulliken populations are a useful guide to the number of electrons associated with a given ion and will be discussed here. For the $\text{Li}^+ \cdot \text{Ni}^{2+} \cdot (\text{O}^{2-})_6 \cdot h^+$ cluster described above, we obtain the values shown in table 1. From these results it is clear that the nickel ion is very much like spin-1 Ni^{2+} , with a total of 26 electrons rather than the 25 that it would have had it trapped the hole to become Ni^{3+} . Correspondingly, the six O^{2-} ions have a hole in the spin down set, with a total Mulliken population just under 59, rather than the 60 that they would otherwise have. Not surprisingly, the Li^+ ion is essentially in a $1s^2$ configuration.

Table 1. Mulliken populations for a $\text{Li}^+ \cdot \text{Ni}^{2+} \cdot (\text{O}^{2-})_6 \cdot \text{h}^+$ embedded cluster in NiO.

	Spin up	Spin down	Total
Li^+	1.0	1.0	2.0
Ni^{2+}	14.0	12.1	26.1
$(\text{O}^{2-})_6$	30.0	28.9	58.9

**Figure 2.** Single-electron Fock eigenvalues (eV) for $\text{Ni}^{2+} \cdot (\text{O}^{2-})_6$ and $\text{Ni}^{2+} \cdot (\text{O}^{2-})_6 \cdot \text{Li}^+ \cdot \text{h}^+$ embedded clusters in NiO, showing predominant atomic character oxygen 2p or nickel 3d, the former indicated by shaded bands, with the number of states in brackets.

It would be interesting to compare the energy level structure of NiO in its pure state with that associated with a Li^+ impurity and a trapped hole. In terms of our embedded cluster method, a perfect lattice NiO cluster should be compared with the cluster of figure 1. The comparable embedded cluster is clearly $\text{Ni}^{2+} \cdot (\text{O}^{2-})_6$. In figure 2 we show the single-electron Fock eigenvalues for these two clusters, along with their predominant atomic characters. For $\text{Ni}^{2+} \cdot (\text{O}^{2-})_6$ we note that there is strong mixing of Ni 3d(T_{2g}) states with the two spin-unpaired oxygen 2p states at the top of the valence band. When the Li^+ ion and its compensating hole are added to this cluster, two strong effects are noticed. First, the nickel 3d levels are forced down slightly, and their strong mixing at the top of the valence band is suppressed. Second, the oxygen 2p band is split and spread out, with much greater energy changes than occurred for the nickel levels. This is understandable, since the hole is much less effective in screening the oxygens than in

screening the nickel ion from the charged Li^+ impurity. Furthermore, O^{2-} is much more polarizable than Ni^{2+} .

Summarizing, our calculated results show, from table 1, that the hole compensating for Li^+ in NiO is localized on neighbouring oxygen rather than nickel ions. From figure 2, we see strong effects, induced by the Li^+ ion plus a hole, on the relationship between nickel 3d and oxygen 2p levels.

Experimentally [14–16], it has been determined that at the top of the NiO valence band there is a nickel 3d peak strongly overlapping a lower-lying oxygen 2p peak. The respective experimental techniques were frequency-dependent photoemission [14], angle-resolved ultraviolet photoemission [15], and combined x-ray photoemission and bremsstrahlung isochromat analysis [16]. Our calculations for $\text{Ni}^{2+} \cdot (\text{O}^{2-})_6$ (figure 2) do not reproduce this structure in detail. This is not surprising, given our limited basis set, small cluster size, and lack of correlation correction, which is known to be important. By way of contrast, a thorough band structure calculation for NiO has been performed by Kunz [17, 18]. His method was based on the Hartree–Fock self-consistent field approximation, as is ours. However, he included the correlation effect and symmetry projection. Furthermore, he determined the energy bands from ionization energies and electron affinities calculated from total energies, rather than from one-electron Fock eigenvalues. His resultant valence band density of states is in striking agreement with the experimental photoemission intensities of Eastman and Freeouf [14].

For localized features such as core levels, our simple NiO_6 cluster gives good semiquantitative results. We refer to core-level x-ray photoemission data of Rao *et al* [19] for NiO. They find energies of 861 eV and 529 eV for the nickel 2p level and the oxygen 1s level. Our calculated values of 895 eV and 557 eV agree with experiment to within 5%. Furthermore, our cluster method is well suited to represent the hole localization that will be produced by the net negative charge of a Li^+ ion at a Ni^{2+} site.

Having determined that the hole associates with the oxygen ions, we now turn to the question implicitly raised by Kuiper *et al* [1] in a footnote of whether the hole has O_h symmetry about the impurity Li^+ , or lower symmetry. For the latter case we consider C_{4v} symmetry, where the hole would localize on a single oxygen ion. For this question we consider an embedded cluster of the form $\text{Li}^+ \cdot (\text{O}^{2-})_6 \cdot \text{h}^+$. There are a number of other low-symmetry configurations that the hole could adopt that still involve only oxygen nearest neighbours of the Li^+ impurity. One of the most interesting would be the case where it binds two oxygens into an O_2^{3-} molecular ion.

First we discuss the case where the hole localizes on a single oxygen ion, a nearest neighbour to the Li^+ impurity (see figure 3). We seek the configuration with C_{4v} symmetry that has minimum total energy. The distortion and polarization of the embedding lattice as seen by the Hartree–Fock cluster are induced by point charges of -1 on one oxygen ion on the positive x axis, and of -2 on the other five. We used the shell-model potentials described earlier to determine the cluster configuration, as well as that of the embedding lattice. The results of this calculation are given in table 2, and include the equilibrium Cartesian coordinates and Mulliken populations of the cluster ions. The oxygen ion that traps the hole is taken to lie on the positive x axis; there are then four equivalent oxygen ions in a plane parallel to the yz plane. We note from the table that the C_{4v} symmetry of the embedding lattice's polarization field does localize the hole on the corresponding oxygen ion, giving it a Mulliken population of 9, compared with 10 for all the others. Detailed examination of the eigenvectors reveals that the hole occurs in a 2p-like oxygen state. We also note the 3% outward displacement of this oxygen ion, forming an electric

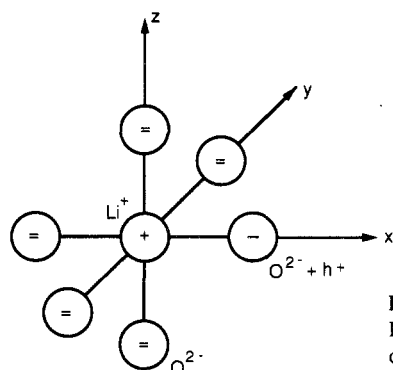


Figure 3. $\text{Li}^+(\text{O}^{2-})_6 \cdot \text{h}^+$ cluster in NiO, centred on Li^+ , with the hole h^+ localized on one oxygen, denoted by single minus sign.

Table 2. Cartesian coordinates (x, y, z) in units of lattice nearest-neighbour spacing, and Mulliken populations of ions in a $\text{Li}^+(\text{O}^{2-})_6 \cdot \text{h}^+$ embedded cluster of C_{4v} symmetry in NiO. ($\times 4$) indicates four equivalent ions. See figure 3.

Ion type	Coordinates	Mulliken population
Li	(-0.06, 0, 0)	2.0
O	(1.03, 0, 0)	9.0
O ($\times 4$)	(0.01, 1.07, 0)	10.0
O	(-1.09, 0, 0)	10.0

dipole with the Li^+ ion which is displaced 6% in the opposite direction. All the other oxygens are rather strongly displaced outward: by 7% for the four equivalent ones and 9% for the other. The total energy of this system is -12292.62 eV, which will be compared below with that of the O_h -symmetric case.

We have done two calculations relating to the O_h -symmetric cluster $\text{Li}^+(\text{O}^{2-})_6 \cdot \text{h}^+$. First we simulated the charge distribution of the cluster with lithium charge +2 and oxygen charges -2 , so as not to pre-judge the question of hole localization. As expected the resultant Mulliken populations were 2.0 for the lithium ion and a total of 59.0 for the six oxygen ions. The lithium–oxygen equilibrium distance in this case was $1.117a$, where a is the lattice nearest-neighbour distance. In the second calculation, the lithium charge was taken to be +1 and the oxygen charges -1.8333 , adding up to -11 for the six oxygens, thus anticipating the uniform distribution of the hole among them. The lithium–oxygen equilibrium distance turned out to be $1.067a$, and the lithium and total oxygen Mulliken populations were found to be 2.0 and 59.0 respectively. Again, the oxygen hole came exclusively from a 2p-like state. The total energy was -12289.55 eV.

4. Discussion and conclusion

We believe that the C_{4v} configuration will be found to be stable. One can think of an O_h -symmetric configuration based on a linear combination of six C_{4v} -symmetric electronic states, each of which has the hole localized on a different nearest-neighbour O^{2-} ion. Such states have been studied, since the work of Bagus and Schaefer [20] on hole states

in O_h^+ , and have been very clearly described by Kunz [17] (pp 493, 494). Since this goes beyond the single-determinant Hartree–Fock approximation, it represents a correlation correction. In this case, the total energy would have to be compared with that of a correlation-corrected C_{4v} -symmetric state. In the present work, the energy associated with relaxation of nearest-neighbour O^{2-} ion positions in O_h symmetry is 1.45 eV, while a further 3.07 eV is gained in the transition to full C_{4v} symmetry. The difference in correlation energies between O_h and C_{4v} symmetric states is unlikely to be this large.

To summarize, we have found that when both electronic energy and lattice distortion and polarization effects are taken into account self-consistently, the C_{4v} -symmetric case with the hole localized on a single oxygen ion is stabilized by 3 eV relative to the O_h -symmetric case with the hole distributed uniformly among the lithium impurity's six nearest-neighbour oxygen ions.

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