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Density-functional study of the NiO_6^{10-} cluster

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The electronic structure of NiO is investigated by means of a series of calculations for a NiO_6^{10-} cluster with use of the local-spin-density-functional theory. Energies of transitions relevant to photoemission and optical excitation are obtained with use of the transition-state method. Ionization potentials and electron affinities are obtained and used to evaluate the Hubbard electron interaction parameter U, which is found to be in the range of 1.5—3.3 eV depending on the manner of its definition.

I. INTRODUCTION

The electronic structure of the insulating antiferromagnet NiO has been of concern for many years because it is a typical member of a class of materials which would be expected to be conducting according to elementary band theory, but which are in fact insulators. Early investigations of its properties are summarized in a review by Adler and Feinleib.[1] Recently, work of Williams and coworkers,[2–5] who have proposed an interpretation of the properties of this material based on energy bands calculated according to local-spin-density-functional theory, in which antiferromagnetic order plays a key role, has aroused much interest and controversy.[2–5] The essential question as to what model furnishes a reasonable starting point for describing the properties of NiO remains open: Is a conventional band description of NiO inadequate or not? Is NiO a Mott-Hubbard insulator?[6] Or, is some other description, such as a periodic Anderson model[7] more appropriate?

We will study these questions using a cluster approach. In this method, which has been applied to transition-metal compounds for more than 20 years since its introduction by Sugano and Shulman[8] in regard to $KNiF_3$, one considers instead of the entire bulk crystal, a cluster consisting of a central nickel atom and its six nearest oxygens, and containing enough electrons so that the oxygen atoms are doubly charged ions. This is the NiO_6^{10-} cluster. The fundamental physical assumption underlying study of this cluster is that many of the electronic processes in bulk NiO are local; i.e., that they take place either on a single nickel atom or within a single cluster. This point of view receives support from observations[9] in optical absorption, of low-energy transitions that are closely related to those observed for isolated nickel atoms in MgO, and which can be described as transitions of an isolated Ni^{2+} ion in a crystalline field. Further, the fundamental absorption edge at 3.8 eV (Refs. 9 and 10) is most easily described as a transition from an occupied oxygen $2p$ state to a vacant nickel d state. (There is still some controversy on this point, with an alternative view being that the transition involves two nickel atoms in a $d^8+d^8 \rightarrow d^9+d^7$ process;[11] but this picture of charge transfer from oxygen to nickel is supported by the high observed value of the optical absorption measured; nearly 10^6 cm^{-1}.)[12]

A rigorous theoretical basis in many-body theory for a cluster approach does not yet exist. If extended in the most straightforward way, i.e., by adjoining clusters to form a periodic crystal, the techniques of this paper would give a standard energy band calculation, which ought to agree under suitable assumptions about the magnetic order with the calculations of the IBM group. Hence one may question the value of cluster calculations given the existence of high-quality band calculations. However, we are not convinced that band calculations necessarily supercede cluster calculations for a material such as nickel oxide. The fundamental question is whether the excited states of interest are localized or extended. If localized, the cluster approach is relevant. Localization can, however, be produced by electronic and (or) lattice relaxation around the site at which excitation occurs. (The importance of electronic relaxation has been emphasized by Kunz.[13]) This point of view regards the excited states as Frenkel excitons. Then the cluster approach enables one to include electronic relaxation in the calculation via the transition-state method.[14] We find that the transition-state results for ionization potentials and electron affinities are significantly different from values based on ground-state eigenvalue differences.

We note here several recent cluster calculations for NiO, including two briefly described local-density supercell computations, one by Kübler and Williams (who considered $NiMg_7O_8$),[12] the other by Norman and Freeman,[15] and calculations based on the Hartree-Fock approximation by Fujimori *et al.*[16] and van der Laan *et al.*[17] (the latter authors consider other approaches as well). The calculations of Refs. 16 and 17 are of a semiempirical type, in that parameters are chosen which allow results of some experiments (for example, photoemission) to be reproduced approximately. We believe that, possibly to avoid undesirable proliferation of empirical parameters, some significant approximations have been introduced within their cluster framework. The most important is probably neglect of the splitting of the oxygen $2p$ levels. The wave functions of these states are extended and even neglecting hybridization between Ni($3d$) and O($2p$), there is a rather broad manifold of states from which a $2p$ electron can be drawn in a charge-transfer process. In other words, there is not a single $|d^9\underline{L}\rangle$ state [$\underline{L}$ denotes hole in O(2p)] but several $|d^9\underline{L}_i\rangle$, where i denotes a specific symmetry. Moreover, no account has been taken of the repulsion of electrons in O(2p) states, which will change when an electron is transferred to nickel.

Ab initio Hartree-Fock calculations for the $\mathrm{NiO_6}^{10-}$ cluster have been reported by Surrat and Kunz[18] and by Bagus and Wahlgren,[19] the latter including some configuration interaction. These calculations lead to a strongly ionic picture of the electron distribution in which the d orbitals are strongly localized on the metal ion with little covalent bonding.

The present calculation emphasizes the role of hybridization. All of the wave functions available to the d electrons on the nickel atom hybridize with oxygen p functions, and considerable effort involving fairly large basis sets has been devoted to describing this hybridization adequately. However, there are symmetrized combinations of oxygen p functions in this cluster which do not mix with any nickel function: representations t_{1g} and t_{2u} in particular. These may be considered as pure oxygen states. Other representations have weak hybridization between oxygen s and p and nickel p (t_{1u}) or nickel s (a_{1g}): but a population analysis shows many of these states to be almost pure oxygen p.

It is a consequence of hybridization that for this cluster there are no pure nickel atomic d states: the relevant d states extend through the cluster. Nonetheless, a population analysis (discussed in detail in Sec. III), easily identifies "mostly d" states. These states, which belong to the e_g and t_{2g} representations, will be (loosely) called nickel d states and when we refer to a particular nickel configuration (d^7, d^8, or d^9), it is done in reference to these mostly d states. For example, in d^8, the $e_{g\uparrow}$ state which defines the Fermi energy is doubly occupied; in d^7 it is singly occupied, whereas in d^9 the down spin member of the exchange split pair is singly occupied. But note that if the nickel d states are extended throughout the cluster by hybridization, the Coulomb repulsion of electrons in these states (the Hubbard U) will be considerably reduced from the free atom value, as is discussed in Sec. III. In fact, density functional theory constructs its basic quantities, the charge and spin densities by occupying these (hybridized) single-particle states, and therefore enables one to calculate rather readily the energies associated with configurational changes. In contrast, it is not easy to describe atomic multiplet structure within the density functional approach, and we will not expect to obtain accurate results for the energy separation of such states.

We speculate that a full theory of bulk NiO is likely to resemble a periodic Anderson model in which a primary element is the oxygen p—nickel d hybridization. The oxygen p band is quite broad but in contrast, the direct nickel d-d interactions are likely to be weak. Effective nickel d bands will be formed, probably mostly through hybridization. We think it will be useful to solve the hybridization problem first in a cluster context, which is the task partially accomplished here. A more complete approach can then consider the formation of extended states, involving a single cluster Coulomb interaction with an interaction parameter U which is of significant size (a few eV) but much reduced in comparison to its free-Ni-atom value. Interactions within the effective d band should then lead to magnetic order, as in Anderson's theory,[20] which our point of view resembles. However, it is doubtful that theories of magnetic order which assume one is in the large-U limit will apply, since—as will be seen in Sec. III—it is probable that U is at most a few eV.

II. METHOD

The method used to perform these calculations has been described in detail in previous papers[21] and will only be briefly summarized here. The linear combination of Gaussian orbitals (LCGO) method and a local-density exchange correlation potential were employed to perform self-consistent all-electron calculations of the electronic structure of the $\mathrm{NiO_6}^{10-}$ cluster. We used the von Barth-Hedin[22] form of the exchange-correlation potential, as parametrized by Rajagopal *et al.*[23] The matrix elements of the exchange-correlation potential were evaluated numerically using a three-dimensional "doubling" grid in $\frac{1}{48}$ of the cubic cluster. In the doubling grid, the number of grid points is doubled each time a step is taken closer to the nuclei, producing a very dense grid of points near the nuclei where the exchange-correlation potential varies most rapidly. The regions farther away from the nuclei contain a less dense grid of points. The total number of grid points used for the $\mathrm{NiO_6}^{10-}$ cluster was 3263. Numerical tests indicated that integrals performed on the grid are accurate within about 2%.

Our model assumes that a Ni atom gives up two electrons to an O atom, as in the case of solid NiO, so that a Ni^{2+} ion and six O^{2-} ions form the cluster. This gives a net charge of -10 for the seven-atom cluster. In order to obtain convergence of the self-consistent-field (SCF) calculation, it was necessary to make the cluster electrically neutral. This was done by adding 12-point charges, each having a charge of $+\frac{5}{6}$, at the positions of the 12 second-nearest neighbors of crystalline NiO. This technique of employing fractional point charges has been used previously by Shashkin and Goddard.[24] By placing the point charges at the positions of the second-nearest neighbors, we maintain cubic symmetry which greatly simplifies the calculation. Figure 1 shows the $\mathrm{NiO_6}^{10-}$ cluster with the 12-point charges added. We can regard the addition of point charges as a sort of embedding procedure in which we try to force a free cluster into something approximating a crystal.

After the point charges were included, we were able to converge the SCF calculation to any desired degree of accuracy. The actual convergence criterion used was 10^{-4} Ry in the total energy. With a small SCF mixing factor of 0.03, approximately 250 SCF iterations were required to achieve this level of convergence.

In addition to SCF convergence, we also obtained a high degree of convergence with respect to the choice of the nickel d and oxygen p basis sets. In the case of the nickel d basis set, we started with that given by Wachters,[25] which has five basis functions and a smallest orbital exponent of 0.4864. No contractions were em-

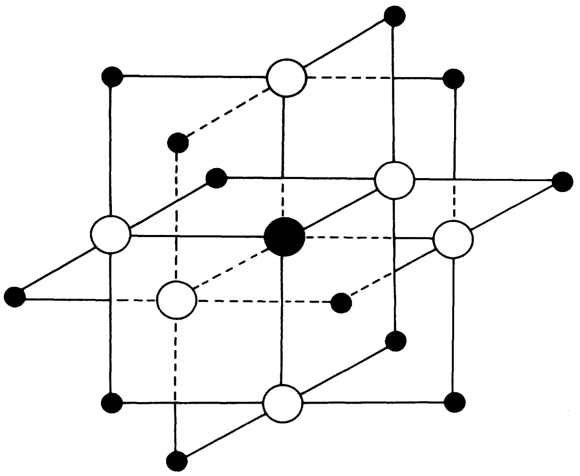

FIG. 1. NiO_6 cluster with surrounding point charges in second neighbor positions.

ployed. We extended this set by successive addition of other *d* functions obtained by repeated division of the smallest exponent by a factor of 1.5. We added eight *d* functions obtained in this way, as shown in Table I. The addition of the eight *d* functions decreased the energies of predominately *d* levels by up to 0.9 eV with respect to the original Wachters basis, but the energies obtained using the 13-member *d* basis set differed from those obtained with 12-*d* functions by at most 0.01 eV. We considered this to be adequate indication of convergence.

In the same way, we started with an oxygen *p* basis set given by van Duijneveldt[26] and added additional small exponents, in the manner described above for the nickel *d* basis set, to obtain the 11-member oxygen *p* basis set shown in Table II. This oxygen *p* basis set is also converged to 0.01 eV (i.e., the oxygen *p* and nickel *d* levels are converged to 0.01 eV when this basis set is used). The addition of the three smaller oxygen *p* exponents, 0.092, 0.066, and 0.047, produced significant changes in the oxygen *p* levels, lowering them by up to 0.2 eV, and also lowered the nickel *d* levels due to nickel *d*—oxygen *p* hybridization. A few *d* basis functions were added to the oxygen basis set but these had little effect on the energy levels of interest. The entire oxygen basis set is given in Table II.

Our program requires basis functions to be placed on all sites, including the point charges mentioned above. We put 2 *s* and 1 *p* relatively tightly bound functions on these sites. Our intention was to inhibit the flow of charge on to these sites.

A significant localization of charge on these sites would, of course, be unphysical in the NiO_6^{10-} cluster. The purpose of the point charges in this calculation is only to achieve electrical neutrality of the cluster so that SCF convergence can be obtained. During the SCF iterations, it was found that the most diffuse nickel *s* basis function from the Wachters basis set (the one with an exponent of 0.0464) was causing nickel *s* charge to localize on the fractional point charges and thereby producing an artificially low Ni(4*s*) state. In order to prevent this unphysical flow of nickel *s* charge out to the point charges, it was necessary to remove this small *s* exponent from the nickel basis set, as shown in Table I. Since the Ni(4*s*) state plays an insignificant role in the fundamental types of NiO excitations considered here, the removal of the diffuse nickel *s* basis function has very little effect on the results of these calculations. Thus if point charges are used to embed or neutralize a cluster, it may be necessary to limit the diffusiveness of the basic functions in order to prevent the unphysical localization of electronic charge on these point charges. The principal unfavorable consequence of this embedding procedure is therefore that we do not obtain accurate results for the energy of the nickel 4*s* state.

All of our calculations were made with uncontracted bases of independent orbitals. Since there are three types of *p* orbitals for each orbital exponent and five types of *d* orbitals per exponent, there is a total of 111 basis functions on the Ni ion, 56 basis functions on each O ion, and 5 basis functions on each fractional point charge. Thus the total number of basis functions in the cluster is 507. Cubic symmetry was used to block diagonalize the Hamiltonian so that the largest matrix that was actually diagonalized was of order 55 (for the t_{1u} irreducible representation). Because of the large number of basis functions in the cluster, it would be very time consuming to compute all of the two-electron integrals needed for the matrix ele-

TABLE I. Ni basis set.

s	*p*	*d*
284 878	1774.18	48.9403
41 997.9	423.403	13.7169
9627.67	138.311	4.639 51
2761.96	53.1703	1.574 33
920.488	22.3874	0.486 409
341.805	9.928 48	0.324
138.023	4.116 25	0.216
59.2587	1.710 31	0.144
20.3712	0.672 528	0.096
8.594 00	0.146 588	0.064
2.394 17	0.044 447	0.043
0.918 169		0.028
0.130 176		0.019

TABLE II. O basis set.

s	*p*	*d*
105 374.9	200.00	1.292
15 679.24	46.5334	0.4
3534.545	14.6218	
987.365	5.313 06	
315.979	2.102 53	
111.654	0.850 223	
42.6995	0.337 597	
17.3967	0.128 892	
7.438 31	0.092	
3.222 87	0.066	
1.253 88	0.047	
0.495 155		
0.191 665		

ments of the Coulomb or Hartree potential. Therefore the charge density was fitted to symmetrized combinations of s and r^2 type Gaussians, which enabled the Coulomb matrix elements to be more easily evaluated. The s and r^2 fitting basis sets for each type of atom were obtained from the regular basis sets for that atom (given in Tables I and II) by doubling the s and p orbital exponents, respectively. The fitted charge density was compared to the exact charge density and found on the average to be accurate to 0.1%. The lattice constant used in this cluster calculation was 4.1684 Å, which is the value of the lattice constant in crystalline NiO.[27]

After the SCF calculation was completed for the cluster, excitation energies, ionization potentials, and electron affinities were calculated using the Slater transition-state method.[14] In the transition-state calculation of the excitation energies, half an electron is removed from an occupied state and placed in an empty state, while the rest of the occupation numbers of the electronic states are kept at the values they had (either 0 or 1) at the end of the SCF calculation. The system is then maintained in this new configuration (all of the occupation numbers, including the two half-integer ones, are held fixed) until a new self-consistency is achieved. The excitation energy is then given by the difference of the eigenvalues of the two states with the half-integer occupation numbers. This procedure eliminates quadratic terms in the dependence of the total energies on occupation numbers in regard to the calculation of energy differences. This contrasts with the procedure used by Norman and Freeman[15] which assumes a linear dependence of the eigenvalues on occupation numbers.[28] The ability to set or control occupation numbers seems to be a significant advantage of our method.

As in the case of the SCF calculation, the transition-state calculations were made self-consistent to an accuracy of 10^{-4} Ry. In the case of double excitations (the excitation of two electrons from a degenerate occupied state to a degenerate empty state), a whole electron is removed from the occupied state and placed in the empty state. After self-consistency is reached, the excitation energy is given by twice the difference of the eigenvalues of the two states.

In a similar manner, ionization potentials were calculated by removing half an electron from an occupied state, maintaining the other occupation numbers at their SCF values, and making the system self-consistent. The ionization potential is then given by the negative of the eigenvalue of the state with the half-integer occupation number. Similarly, electron affinities were computed by adding half an electron to an empty state and making the system self-consistent while holding the other occupation numbers at their SCF values. The electron affinity is then given by the negative of the eigenvalue of the state with the half-integer occupation number.

III. RESULTS

A. Cluster ground state

We begin with the ground-state eigenvalues. The core-state eigenvalues are listed in Tables III (nickel) and IV (oxygen); those of the oxygen valence bands and the nickel occupied $3d$ states are given in Table V, together with the results of a Mulliken population analysis. Our eigenvalue distribution has many qualitative resemblances to that determined in early $X\alpha$ calculations[29,30] but ours is somewhat more compact in energy and there are some differences in the outer of levels. Table VI lists the lower seven unoccupied states. For several of these levels the population anslysis does not give meaningful quantitative results, but the levels can be characterized as primarily nickel d or oxygen p. The results are summarized graphically in the energy level diagram of Fig. 2. The population analysis yields a total nickel d state occupancy of 8.76 with a local magnetic moment of 2.24.

TABLE III. Energies of nickel core levels (in rydbergs) according to spin (majority ↑ and minority ↓).

	Majority	Minority
$1s$	−595.021	−595.021
$2s$	−70.204	−70.144
$2p$	−61.301	−61.256
$3s$	−7.570	−7.466
$3p$	−4.857	−4.757

In general, these results appear to be consistent with the band calculations and super cell cluster of the IBM group[2–5,12] (but numerical values are not given in their papers). The nickel d levels all of which are hybridized to some extent with the oxygen p lie above a set p levels (only some of which have appreciable d admixture) that we will call the oxygen p bands. The Fermi energy coincides with a nickel d level ($4e_{g\uparrow}$). An unoccupied nickel d level ($4e_{g\downarrow}$) lies only 0.62 eV above it. The occurrence of an unoccupied nickel $3d$ state just above E_F is seen to be quite natural; the separation is just the Ni exchange splitting. This exchange splitting does not imply that we have a ferromagnetic model. A cluster with a nickel atom on another spin sublattice will have "up" and "down" interchanged but, the same magnitude of exchange splitting. The splitting is a local effect which would be found in a free Ni ion and is consequence of the existence of a magnetic moment on the nickel atom which should be nearly independent of the type of magnetic order, or of the existence of magnetic order in the crystal. This feature does not by itself imply that NiO is an insulator, because for an extended system, levels at different parts of the zone could overlap in energy.

TABLE IV. Energies of oxygen core levels (in rydbergs). The $2s$ level is slightly split by bonding and hybridization: (a) a_{1g}, (b) t_{1u}, (c) e_g.

		Majority	Minority
$1s$		−37.0526	−37.0491
$2s$	(a)	−1.493	−1.487
	(b)	−1.455	−1.449
	(c)	−1.444	−1.437

TABLE V. Occupied oxygen $2p$ and nickel $3p$ levels (in rydbergs). Results of a Mulliken population analysis are shown. Percentages do not always add to 1 because of rounding and inaccuracies of the Mulliken analysis.

	Energy	Ni s	Ni p	Ni d	O s	O p
			Mostly oxygen $2p$			
$1t_{2g\uparrow}$	−0.5681			0.02		0.97
$1t_{2g\downarrow}$	−0.5595					1.00
$6a_{1g\uparrow}$	−0.5427	0.14			0.01	0.85
$6a_{1g\downarrow}$	−0.5343	0.14			0.01	0.85
$5t_{1u\uparrow}$	−0.5133		0.13			0.87
$5t_{1u\downarrow}$	−0.5087		0.13			0.87
$1t_{2u\uparrow}$	−0.4476					1.00
$1t_{2u\downarrow}$	−0.4431					1.00
$6t_{1u\uparrow}$	−0.4220		0.19			0.83
$6t_{1u\downarrow}$	−0.4130		0.18			0.83
$1t_{1g\uparrow}$	−0.3749					1.00
$1t_{1g\downarrow}$	−0.3707					1.00
			Hybridized nickel $3d$—oxygen $2p$			
$3e_{g\uparrow}$	−0.5194			0.53	0.01	0.46
$3e_{g\downarrow}$	−0.4706			0.37	0.01	0.62
$2t_{2g\uparrow}$	−0.3398			0.82		0.18
$2t_{2g\downarrow}$	−0.2826			0.84		0.16
$4e_{g\uparrow}$	−0.2339	(E_F)		0.96	(−0.08)	0.12

B. Charge transfer transitions

We will now report the calculated energies of some transitions important in describing the properties of NiO, beginning with the transfer of an electron from the oxygen p levels to the nickel d states. As mentioned in the introduction, all these calculations are made according to the transition state method and therefore take account of rearrangement of the electron distribution. We have calculated the transition energies from the p band complex to $4e_{g\downarrow}$; the result is to produce a d^9 configuration on the Ni atom with a p hole on the oxygen. It must be observed that there is not a single transition, but seven of them, depending on which p level has the final hole. The transition-state approximation to the transfer energy from a state $|n_{i\downarrow}\rangle$ (i denotes one of the symmetry types of Fig. 2) to $4e_{g\downarrow}$ is the following:

$$\Delta_i = \bar{\varepsilon}(4e_{g\downarrow}) - \bar{\varepsilon}(n_{i\downarrow}) ,$$

where the $\bar{\varepsilon}$ are not the eigenvalues of Tables III–VI but are obtained in a separate self-consistent calculation in which the occupancy of $4e_{g\downarrow}$ is constrained to be $\frac{1}{2}$ and that of i has been reduced by $\frac{1}{2}$ from that found in the ground state. Our results for the transition energies are

TABLE VI. Eigenvalues (in rydbergs) of the lowest seven unoccupied levels.

$4e_{g\downarrow}$	−0.1881	(mostly nickel $3d$)
$5e_{g\uparrow}$	−0.1731	(mostly nickel $3d$)
$7t_{1u\uparrow}$	−0.1722	(oxygen and nickel p)
$7t_{1u\downarrow}$	−0.1661	(oxygen and nickel p)
$5e_{g\downarrow}$	−0.1245	(mostly nickel $3d$)
$3t_{2g\uparrow}$	−0.1133	(mostly oxygen p)
$3t_{2g\downarrow}$	−0.1055	(mostly oxygen p)

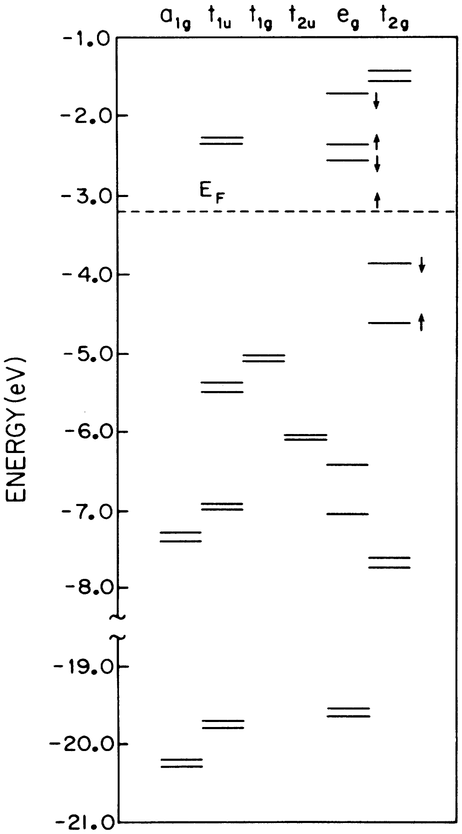

FIG. 2. Energy level diagram. E_F indicates the Fermi energy. Arrows adjacent to some levels near E_F indicate spin. Spatial symmetry classifications are shown.

contained in Table VII. We have considered only transitions from spin-down states; i.e., those which do not change the magnetic moment of the cluster.

The transition of lowest energy originates on the unhybridized state $1t_{1g\downarrow}$ and has an energy of 2.44 eV. Optically allowed transitions are marked by A in Table VII. The weighted average energy of all the transitions (weights are simply degeneracies) is 3.72 eV; similarly the average of the optically allowed transition energies is 3.61 eV.

The transition-state energies given in Table VII are not much different from the ground-state eigenvalue separations; the latter being slightly larger. The largest difference occurs in regard to state $3e_{g\downarrow}$ which is fairly strongly hybridized, but amounts to only 0.08 eV; in the case of the unhybridized levels the differences do not exceed 0.05 eV. We believe this implies that electronic rearrangement effects are relatively small.

Experimentally, NiO begins to absorb radiation at a photon energy of about 3.8 eV.[11] This is significantly larger than our calculated threshold of 3.0 eV. While it is possible that dispersion and matrix element effects could shift the apparent threshold, we are inclined to attribute the smaller than experimental value obtained here to basic difficulties in local-density functional theory well known to be manifest in the calculation of energies of transitions between empty and occupied states in semiconductors.[31]

C. Ionization potentials and electron affinities

We have calculated ionization energies of the oxygen p and nickel $3d$ levels using the transition-state method. Our results are contained in Table VIII. In contrast to the charge-transfer calculations, we find here that the differences between the transition-state results and the eigenvalue differences is rather substantial, ranging from 0.56 eV for $4e_{g\uparrow}$ to 0.69 eV for $5t_{1u\uparrow}$ (the transition state results are always larger). Rearrangement of the electronic structure is quite important in the case of ionization.

We note from Table VIII that the d electron photoemission spans a range of 1.6 eV below E_F. This is our estimate of the d band width relevant to photoemission measurements and is probably an underestimate; i.e., a lower bound, because the interaction of d electron states on different atoms—the formation of Bloch waves—will lead to a broadening of the bands. (The result of the IBM group for the d bandwidth seems from graphical data to be about 2.7 eV.) Photoemission from the oxygen $2p$ bands would begin in 2.0 eV below the Fermi energy and extends for 2.7 eV (our cluster estimate of the p bandwidth) down to an energy of 4.7 eV below E_F. These results are in fair agreement with the photoemission measurements of McKay and Heinrich.[32] Their estimate of the $2p$ bandwidth is about 1 eV larger than ours, however. This may be explainable in terms of our neglect of k-space dispersion (the IBM result appears to be about 4 eV). Resolution effects may also play some role. Our interpretation of the measurements in regard to the d bandwidth differs from that of McKay and Heinrich, but we believe that ours is also consistent with the observations.

In addition, we have calculated the electron affinities of certain levels above the Fermi energy. These results are also included in Table VIII. The transition-state results are larger than the eigenvalues by amounts ranging from 0.35 eV in the case of the level closest to the Fermi energy ($4e_{g\downarrow}$) to 0.07 eV in the case of a level well removed from E_F ($3t_{2g\downarrow}$). However, there may be some reason for concern as to whether the transition-state method is accurate in the case of the electron affinity.[33]

These results enable an estimate of the Hubbard U parameter for nickel. For this purpose, we take the point of view that U should be the difference between the ionization potential and the electron affinity, or in other terms $E(d^7)+E(d^9)-2E(d^8)=U$. In regard to the affinity it is natural to choose the lowest unoccupied d level $4e_{g\downarrow}$. If we then take the ionization potential of the highest occupied d state ($4e_{g\uparrow}$) we get a rather small U, 1.45 eV. But the usual simple definitions of U do not take into account

TABLE VII. Charge-transfer energies (in eV) for O($2p$) to Ni($3d$). Optically allowed transitions are designated by an A.

Initial state		Transition energy
$1t_{1g\downarrow}$		2.44
$6t_{1u\downarrow}$	A	3.01
$1t_{2u\downarrow}$	A	3.45
$3e_{g\downarrow}$		3.75
$5t_{1u\downarrow}$	A	4.36
$6a_{1g\downarrow}$		4.66
$1t_{2g\downarrow}$		5.03

TABLE VIII. Ionization potentials and electron affinities (in eV).

Level	Ionization potential	Electron affinity
$3t_{2g\downarrow}$		1.36
$3t_{2g\uparrow}$		1.46
$5e_{g\uparrow}$		2.02
$7t_{1u\downarrow}$		2.04
$7t_{1u\uparrow}$		2.13
$5e_{g\downarrow}$		1.54
$4e_{g\downarrow}$		2.28
$4e_{g\uparrow}$	3.73	
$2t_{2g\downarrow}$	4.66	
$2t_{2g\uparrow}$	5.32	
$1t_{1g\downarrow}$	5.69	
$1t_{1g\uparrow}$	5.77	
$6t_{1u\downarrow}$	6.16	
$6t_{1u\uparrow}$	6.32	
$1t_{2u\downarrow}$	6.67	
$1t_{2u\uparrow}$	6.74	
$3e_{g\downarrow}$	6.91	
$5t_{1u\downarrow}$	7.60	
$5t_{1u\uparrow}$	7.67	
$3e_{g\uparrow}$	7.73	
$6a_{1g\downarrow}$	7.87	
$6a_{1g\uparrow}$	8.03	
$1t_{2g\downarrow}$	8.27	
$1t_{2g\uparrow}$	8.40	

the splitting of the atomic d state due to crystal field and hybridization effects. To do this roughly, we take a degeneracy weighted average of the ionization potentials of the mostly d states $4e_{g\uparrow}, 2t_{2g\uparrow}, 2t_{g\downarrow}$, which gives $U=2.40$ eV. If one extends the average to include the strongly hybridized pair $3e_{g\uparrow}, 3e_{g\downarrow}$ which are in the p band complex, U rises to 3.28 eV, which is about as large a value as can be forced from this argument.

We note that Kübler and Williams[12] estimated U to be about 4 eV on the basis of a density functional supercell calculation, but the brief account of this work does not give details as to the manner in which this value was obtained.

The values of U obtained here are significantly smaller than the currently accepted value (7–9 eV). This probably results from the greater spatial extent of the levels we have chosen to call d states here than occurs with atomic d states. However, the expansion of the d states in the cluster is an inevitable consequence of the strong hybridization with oxygen p functions. We have reported a cluster U, and not an atomic U. If one attempts to follow Anderson's program[20] in regard to a subsequent study of magnetic order, according to which one should take all hybridization effects into account first, then subsequently solve a Hubbard problem within an effective d band with p bands inert, the cluster U will probably be more relevant than the atomic U. Then the relatively small value of U obtained here implies that one cannot expect the large U limit of the Hubbard model to apply: the cluster U is not going to be enormously larger than the d bandwidth (perhaps a factor of 2 at most). It should be noted that McKay and Heinrich obtain a value of U (2.7 eV) which is consistent with our estimates. (But there is a question as to whether the quantity they interpret as U is the same as that defined here.)

It is certainly possible that density-functional theory could overestimate the degree of hybridization of p and d wave functions and hence underestimate U. *Ab initio* Hartree-Fock calculations[18,19] would almost certainly yield larger U's since they support an ionic model. Furthermore, there is not an adequate theory of photoemission (direct and inverse) for NiO so that the relation of the present estimates to experiment is not clear. Possibly the experiments are better described in terms of unhybridized states.

D. Transitions within the 3*d* states

We have calculated energies for rearrangements of the $3d$ electrons without change of the total occupancy. With references to the energy band diagram of Fig. 2 the lowest energy transitions of this type are (a) $4e_{g\uparrow}\rightarrow 4e_{g\downarrow}$ and (b) $2t_{2g}\rightarrow 4e_{g\downarrow}$. There should be transitions to $5e_{g\uparrow}$, including (c) $4e_{g\uparrow}\rightarrow 5e_{g\uparrow}$, (d) $2t_{2g}\rightarrow 5e_{g\uparrow}$. Energies are listed in Table IX. None of these transitions is allowed optically. Moreover, a, $b2$, and $d1$ are additionally forbidden because spin reversal is involved.

Transition (a) is a simple spin-flip transition in which the moment of the nickel ion changes to zero. The energy measures the spin splitting of the upper nickel d states. It is interesting that the transition-state result, 0.44 eV, is substantially smaller than the eigenvalue difference (0.62 eV). In three other cases ($b2$, $d1$, and $d2$) as well, the transition-state result differs by 0.1 eV or more from the eigenvalue difference.

TABLE IX. Energies of d rearrangement transitions (in eV).

Transition		Energy
a	$4e_{g\uparrow}\rightarrow 4e_{g\downarrow}$	0.44
b 1	$2t_{2g\downarrow}\rightarrow 4e_{g\downarrow}$	1.29
2	$2t_{2g\uparrow}\rightarrow 4e_{g\downarrow}$	1.78
c	$4e_{g\uparrow}\rightarrow 5e_{g\uparrow}$	0.85
d 1	$2t_{2g\downarrow}\rightarrow 5e_{e\uparrow}$	1.69
2	$2t_{2g\uparrow}\rightarrow 5e_{g\uparrow}$	2.37

NiO is known experimentally to have several weak optical absorption lines below the onset of the main absorption edge at about 3.8 eV.[9] The energies of the major peaks are, in eV: 1.13, 1.75, 1.95, 2.15, 2.75, 2.95, 3.25, and 3.52 eV. These energies are also close to those peaks observed in the absorption of Ni in MgO. The 1.1-eV experimental peak has been interpreted as measuring the t_{2g}-e_g splitting;[27] our value of 1.3 eV is reasonably close (probably as close as one can expect to get in view of the simplicity of the model cluster). We have no explanation for the other peaks. However, these presumably involve the multiplet structure of individual Ni^{2+} ions; and local-density-functional theory is hard pressed to describe atomic multiplets.[34]

E. Transitions involving the nickel core

X-ray photoemission (XPS) and x-ray photoabsorption (XAS) measurements on several nickel compounds (including NiO) have been reported by van der Laan *et al.*[17] In both the XPS and XAS measurements, an electron is excited from a nickel $2p$ state. In XPS, the electron leaves the crystal, and various rearrangements follow, whereas in XAS the electron is caught in an excited state and again rearrangements occur. We have calculated energies for several of the processes using the transition-state method.

The energies of the transitions are listed in Table X using a notation consistent with Ref. 17. Our calculations do not include spin-orbit coupling, so in the comparison with experiment, we have approximately removed spin-orbit coupling from the experimental results by forming a weighted average ($\frac{2}{3}$ times the energy of transition from the $2p_{3/2}$ state plus $\frac{1}{3}$ of that from the $2p_{1/2}$). In regard to Table X, the notation $\underline{c}$ means that a nickel $2p$ hole is present, while $\underline{L}$ means that there is a hole in the oxygen $2p$. As we have seen, there are several oxygen $2p$ levels in which a hole could be present. As the calculations are fairly lengthy, we have considered only the case in which the hole (or holes) are in the upper level $1t_{1g}$. The notation d^8 means that the ground-state occupancies are used, d^9 means that an additional electron is present in $4e_{g\downarrow}$. For the transition-state calculation of the energy difference between $\underline{c}d^{10}\underline{L}_2$ and the ground state, the occupancies in the transition state differ from those in the ground

TABLE X. Energies of transition (in eV) from the Ni($2p$) core states. Experimental result from Ref. 7 with spin-orbit coupling removed.

Final state	Present	Expt.
	Transitions relevant to XPS	
$\underline{c}\uparrow d^8$	853.52	
$\underline{c}\downarrow d^8$	852.97	
$\underline{c}\uparrow d^9\underline{L}$	855.39	
$\underline{c}\downarrow d^9\underline{L}$	855.01	
$\underline{c}\uparrow d^{10}\underline{L}_2$	857.58	
$\underline{c}\downarrow d^{10}\underline{L}_2$	857.33	
	Transitions relevant to XAS	
$\underline{c}\uparrow d^9$	849.73	858.9
$\underline{c}\downarrow d^9$	849.36	

state by $-\frac{1}{2}$ for the nickel $2p$, $+1$ for $4e_{g\downarrow}$, and -1 for $1t_{1g\downarrow}$. The energy difference is then approximated by

$$E(\underline{c}d^{10}\underline{L}_2)-E_G=2\bar{\varepsilon}(4e_{g\downarrow})-2\bar{\varepsilon}(1t_{1g\downarrow})-\bar{\varepsilon}(2p) ,$$

where the $\bar{\varepsilon}$ are the self-consistently calculated eigenvalues with the constrained occupancy. This result will be correct up to but not including third derivatives of the energy with respect to the occupation number.

It will be seen from Table X that the magnitudes of the excitation energies agree with experiment within an error of roughly 10 V in 850, whereas if the calculations are made using the ground-state eigenvalues the errors are nearly three times larger.

The following results emerge from the calculation. The energy required to transfer an electron from the upper oxygen $2p$ level to a nickel atom containing a $2p$ hole is roughly 1.95 eV, about 0.5 eV less than what it is with no core hole present. The additional energy required to transfer a second electron is roughly 2.25 eV, which is about 0.3 eV larger than that required to transfer the first electron.

F. Transitions from O($2s$)

Powell and Spicer[11] observed a strong maximum in the optical absorption of NiO at a photon energy of 17.6 eV. We predict that there are several transitions in the energy range of 17—18 eV that are optically allowed. The initial state is oxygen $2s$; the final state is an unoccupied oxygen p state, some of which hybridize with nickel (these states should presumably be regarded as conduction-band states). The energies of the transitions are listed in Table XI. The transition-state energies are in excellent agreement with the ground-state eigenvalue differences (largest difference is 0.07 eV). Although we have not calculated the matrix elements, the Mulliken population analysis suggests that the transitions should be strong. Therefore, we propose that the 17.6-eV peak in the optical absorption is due to transitions between oxygen $2s$ states and p-like states in the conduction band.

TABLE XI. Energies (in eV) of some optically allowed transitions with an O($2s$) initial state.

Transition	energy
$5a_{1g\uparrow}-7t_{1u\uparrow}$	18.04
$5a_{1g\downarrow}-7t_{1u\downarrow}$	17.95
$4t_{1u\downarrow}-5e_{g\downarrow}$	18.02
$4t_{1u\uparrow}-5e_{g\uparrow}$	17.45
$4t_{1u\downarrow}-4e_{g\downarrow}$	17.15
$2e_{g\uparrow}-7t_{1u\uparrow}$	17.34
$2e_{g\downarrow}-7t_{1u\downarrow}$	17.28
$4t_{1u\uparrow}-3t_{2g\uparrow}$	18.31
$4t_{1u\downarrow}-3t_{2g\downarrow}$	18.29

IV. CONCLUSIONS

We have performed self-consistent calculations of the electronic structure of a NiO_6^{10-} cluster using local-spin-density-functional theory. Slater's transition-state approach has been applied to determine (1) the energies of transitions between the oxygen $2p$ levels and the nickel d states, (2) the ionization potential and electron affinities of p and d states, (3) the energies of some rearrangement transitions of $3d$ electrons on nickel, and (4) the energies of transitions from the nickel $2p$ core states to the $3d$ level. In addition, (5) a prominent feature in the optical absorption at a photon energy of 17.6 eV has been identified as involving transition from oxygen $2s$ states. Electronic rearrangement affects ionization energy and electron affinity calculations significantly.

A major conclusion which results from this investigation is that the electron interaction parameter U representing repulsion of electrons of opposite spin in nickel d orbitals is rather small, in the range of 1.5—3.3 eV depending on the states involved in its definition. The relatively small values result from hybridization of nickel d with oxygen p functions, which creates rather extended mixed p-d wave functions. Since we find that occupied d states span a range of about 1.6 eV, it follows that a Hubbard model calculation of magnetic order in NiO should not assume that the electron interaction is much larger than the bandwidth.

In a general way, the comparison with experimental results is fairly good, indicating local-density-functional theory is reasonably adequate in the description of this cluster. The major discrepancies seem to be (1) underestimate of the apparent band gap measured by optical absorption [assuming it to be due to charge transfer from oxygen ($2p$) to nickel ($3d$) states] by 20—30 % and (2) inability to describe specific multiplet structure of the nickel ion. In addition to the remarks made previously concerning electron interactions, it is also apparent that other theories do not treat the level structure of a cluster adequately, i.e., there is not a single oxygen $2p$ level for the cluster but a distribution. A more comprehensive theoretical formulation involving more adequate inclusion of the electronic structure of a cluster would seem to be required for further progress.

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[1] D. Adler and J. Feinleib, Phys. Rev. B **2**, 3112 (1970).

[2] T. Oguchi, K. Terakura, and A. R. Williams, Phys. Rev. B **28**, 6443 (1983).

[3] K. Terakura, A. R. Williams, T. Oguchi, and J. Kübler, Phys. Rev. Lett. **52**, 1830 (1984).

[4] K. Terakura, T. Oguchi, A. R. Williams, and J. Kübler, Phys. Rev. B **30**, 4734 (1984).

[5] A. R. Williams, J. Kübler, and K. Terakura, Phys. Rev. Lett. **54**, 2728 (1985).

[6] B. H. Brandow, Adv. Phys. **26**, 651 (1977).

[7] J. W. Allen, J. Mang. Magn. Mater. **47-48**, 168 (1985).

[8] S. Sugano and R. G. Shulman, Phys. Rev. **130**, 517 (1963).

[9] R. Newman and R. M. Chrenko, Phys. Rev. **114**, 1507 (1959).

[10] R. J. Powell and W. E. Spicer, Phys. Rev. B **2**, 2182 (1970).

[11] R. Merlin, Phys. Rev. Lett. **54**, 2727 (1985).

[12] J. Kübler and A. R. Williams, J. Magn. Magn. Mater. **54-57**, 603 (1986).

[13] A. B. Kunz, in *Excited States in Quantum Chemistry*, edited by C. A. Nicolaides and D. R. Beck (Reidel, Dordrecht, 1978), p. 471.

[14] J. C. Slater, *The Self Consistent Field for Molecule and Solids* (McGraw-Hill, New York, 1974).

[15] M. R. Norman and A. J. Freeman, Phys. Rev. B **33**, 8896 (1986).

[16] A. Fujimori, F. Minami, and S. Sugano, Phys. Rev. B **29**, 5225 (1984).

[17] G. van der Laan, J. Zaamen, G. A. Sawatzky, R. Karnatak, and J. M. Esteva, Phys. Rev. B **33**, 4253 (1986).

[18] G. T. Surrat and A. B. Kunz, Solid State Commun. **23**, 555 (1977).

[19] P. S. Bagus and U. Wahlgren, Mol. Phys. **33**, 641 (1977).

[20] P. W. Anderson, in *Magnetism*, edited by G. T. Rado and H. Shul (Academic, New York, 1963), Vol. 1, p. 25.

[21] K. Lee, J. Callaway, and S. Dhar, Phys. Rev. B **30**, 1724 (1984); K. Lee, Ph.D. thesis, Louisiana State University, 1984 (available from University Microfilms International, Ann Arbor, MI 48106).

[22] U. von Barth and L. Hedin, J. Phys. C **5** 1629 (1972).

[23] A. K. Rajagopal, S. Singhal, and J. Kimball (unpublished) as quoted by A. K. Rajagopal, in *Advances in Chemical Physics*, edited by G. I. Prigogine and S. A. Rice (Wiley, New York, 1979), Vol. 41, p. 59.

[24] S. Y. Shashkin and W. A. Goddard III, Phys. Rev. B **33**, 1353 (1986).

[25] A. J. H. Wachters, J. Chem. Phys. **52**, 1033 (1970).

[26] F. B. van Duijneveldt, IBM Research Report No. RJ945, 1971 (unpublished).

[27] R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1965), Vol. 1.

[28] M. R. Norman, D. D. Koelling, A. J. Freemen, H. J. F. Jansen, B. I. Min, T. Oguchi, and Ling Ye, Phys. Rev. Lett. **53**, 1673 (1984).

[29] K. H. Johnson, R. P. Messmer, and J. W. D. Connolloy, Solid State Commun. **12**, 313 (1973).

[30] R. P. Messmer, C. W. Tucker, and K. H. Johnson, Surf. Sci. **42**, 341 (1974).

[31] J. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983); L. J. Sham and M. Schlüter, *ibid.* **51**, 1888 (1983).

[32] J. M. McKay and V. E. Heinrich, Phys. Rev. Lett. **53**, 2343 (1984).

[33] R. Tang and J. Callaway, J. Chem. Phys. **84**, 6854 (1986).

[34] J. Callaway and N. H. March, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1984), Vol. 38, p. 135.