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Band gap in NiO: A cluster study

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The Mott-Hubbard gap U and the charge-transfer gap Δ of solid NiO are estimated from *ab initio* calculations on the NiO_6^{10-} cluster. Covalency in the essentially localized d^n states and localization for the spatially extended O($2p$) hole states are introduced by means of a limited configuration-interaction calculation. The localized states induce a large polarization effect in the bulk, accounted for in a semiempirical way. The values obtained for U and Δ are quite similar and in the range of 4.4–5.2 eV, in good agreement with the observed gap.

I. INTRODUCTION

The nature and the magnitude of the band gap in NiO have been the subject of many studies. The insulating behavior of NiO and similar antiferromagnetic oxides has led to the introduction of the concept of the Mott-Hubbard insulator.[1] In the Mott-Hubbard theory the band gap is determined by the energy required for charge fluctuations of the type $2d^n \rightarrow d^{n-1}+d^{n+1}$. Because of the large d-d Coulomb interactions this energy is very large, 8–10 eV according to several authors.[2,3] This model, however, fails to explain why NiS and CuS, for which similar Coulomb interactions must be expected, are metallic. Nor does it explain why NiO shows only p-type conduction.[4]

These observations have motivated several recent experimental and theoretical investigations. Spin-polarized band calculations[5] predict a very small gap (0.3 eV), but from "direct" measurements, i.e., photoelectron spectroscopy (PES) and bremsstrahlung isochromat spectroscopy (BIS), a gap of 4.3 eV is estimated,[6,7] slightly larger than the optical-absorption edge at 3.8 eV.[8] There is still some discussion as to the nature of this gap and more specifically to the interpretation of the photoemission spectrum.

Sawatzky *et al.*[6] claim that the band gap results from the energy difference between two localized states. The ionized state is of $|d^8L^{-1}\rangle$ character, the first state in the inverse-photoemission spectrum of d^9 character. In their interpretation a $|d^8L^{-1}\rangle$ state is a d hole strongly screened by an oxygen electron to make the character of the hole state O($2p$) rather than Ni($3d$). It is not quite clear, however, why this state is localized and how it can be distinct from what are called the O($2p$)-band hole states.

The optical gap is usually associated with an O($2p$)-band–Ni($3d$) transition. In fact, Hüfner *et al.* suggest that this gap can be inferred from PES and BIS data. The optical gap is identified with the energy between the onset of the O($2p$) ionization, assumed to be near the Fermi level, and the first $|d^9\rangle$ state. They, and other authors, reject the possibility that two Ni sites are involved in the optical transition.

Previous interpretations of the NiO photoemission spectrum assigned the first peaks to Ni(d^7) states, split by crystal-field effects.[9,10] In the more recent interpretations these d^7 states are associated with a satellite at 7 eV for which in previous interpretations no satisfactory explanation has been given.

The present interpretations, however, are based mainly on model calculations; Zaanen *et al.*[6,11] performed impurity calculations with an Anderson-Haldane Hamiltonian on Ni^{2+} in an O($2p$) band. As a result of interactions between Ni and O levels, two bound states emerge, at the lower and upper end of the band. The lower state has primarily O($2p$) character, the upper Ni($3d$) character. Model calculations by Fujimori on the NiO_6^{9-} cluster,[2] including configurational mixing (d^n, $d^{n+1}L^{-1}$, $d^{n+2}L^{-2}$) also indicate that the lowest ionized state has primarily $|d^8L^{-1}\rangle$ character. The results of these model calculations, however, are very much dependent on the values of parameters such as the d-d Coulomb repulsion U and the charge-transfer energy.

The model calculations indicate that from a localized approach a correct value for the band gap can be obtained. Band calculations, on the contrary, invariably give too small a gap. Recently, Brener and Callaway[12] presented a density-functional study of the NiO_6^{10-} cluster. They obtain overly small values for the Mott-Hubbard gap and for the optical excitation gap. As these authors point out, this is probably a result of the approximations made in the local-density (LD) model.

Here we will present an *ab initio* cluster study which treats the exchange in an exact way. The advantages with respect to the LD approach are that the d^n multiplet structure can be described and that extensions beyond the effective one-electron model can be made in a systematic way.

The bulk crystal is modeled by a NiO_6^{10-} cluster stabilized by point charges. In doing this, it is assumed that an ionic starting point is appropriate. Some covalent interactions, however, can be included, i.e., the Ni–nearest-O interaction and some O-O interaction.

It is expected that in the bulk solid the Ni-Ni interactions are almost negligible. On both experimental and theoretical grounds, a very small Ni($3d$) bandwidth

(<0.5 eV) is expected,[5] and it has been observed that the low-energy optical spectrum of MgO:Ni closely resembles that of NiO.[13] In previous calculations very little effect on the Ni(3*d*) states was found from inclusion of another shell of O ions.[14]

The description of O states may present greater difficulties, as many next-nearest-neighbor O-O interactions are neglected. Therefore, a different modeling of the O(2*p*) band was additionally adopted. Calculations were carried out on O_n clusters. In this model Ni^{2+} ions are represented by point charges only.

State of the art quantum-chemical methods can be used to calculate the electronic structure of the cluster. Previous work has shown that it is of crucial importance to go beyond the effective one-electron model (Hartree-Fock) to obtain a correct description of $3d^n$-like states and of hole states in the O valence band.[14,15]

In the case of $3d^n$ states Hartree-Fock (HF) calculations predict highly localized 3*d* orbitals and correspondingly an overly small value for the effective crystal-field splitting. Configurational mixing with appropriately relaxed $|d^{n+1}L^{-1}\rangle$ charge-transfer (CT) states introduces a substantial amount of delocalization and yields a much improved *d*-*d* spectrum.

The inclusion of CT states is most elegantly carried out in a so-called first-order configuration-interaction calculation (FOCI).[16] This type of calculation allows for the (large) relaxation effects in the CT states. The correlation effects included are of a molecular, nondynamical nature and typical for open-shell systems.

From FOCI calculations on the $NiO_6{}^{10-}$ cluster it was found that the ground state has primarily $|d^8\rangle$ character but with considerable $|d^9L^{-1}\rangle$ mixing, in accordance with the view held by other authors.[2,11]

The open-shell correlation effects also improve the description of the O(2*p*) hole states. Here, they account for localization and polarization effects in the O(2*p*) band. In HF calculations these are only obtained in a broken-symmetry calculation,[15] at the expense of neglecting O-O interactions. A FOCI calculation enables a more balanced treatment of localization and delocalization effects. The energy gain expected in NiO_6 clusters is 3–4 eV compared to symmetry-restricted HF calculations.

In the following we shall study, both by HF and CI calculations, the ionization and electron-addition spectra of $NiO_6{}^{10-}$, as well as direct $O(2p)\rightarrow Ni(3d)$ and $(3d\rightarrow 4s)$-like transitions. Results for the ground state will only be given in relation to these spectra; for a detailed discussion of the electronic structure of the ground state, the reader is referred to Ref. 16.

The present calculations should give some insight into the nature of the states involved in the band-gap transition. Quantitatively correct results for charge-fluctuation energies or transition energies can only be given when dielectric, extra-cluster, effects are accounted for. These effects will be very large in electron-loss or electron-addition processes. They will be discussed in Sec. IV.

II. METHOD

Most calculations were carried out on a NiO_6 cluster with octahedral symmetry. The Ni-O distance was kept fixed at the experimental value of 2.08 Å.[17] Four layers of point charges at lattice sites were used to represent the external Coulomb potential. The charges are obtained by a least-squares fit of the potential they generate in the cluster region to the actual Madelung potential in this region.[16]

The O_n clusters ($n=13$ or 19) also have octahedral symmetry. There is one, central, O^{2-} ion surrounded by one layer of 12 ions (O_{13}) or by two layers of 12 and 6 ions, respectively (O_{19}). The Ni^{2+} ions at internal sites (6 in O_{13}, 14 in O_{19}) were represented by $+2e$ point charges. The external potential was again represented by a finite set of point charges obtained in a similar procedure as for the NiO_6 cluster.

For Ni a large, contracted, Gaussian basis set[18] was employed, which gives near-HF results for the *d*-*d* spectrum, ionization energy, and electron affinity of the free Ni^{2+} ion. For O an optimized O^- set was used.[18] For the O_n clusters a more contracted set was used, derived from the set optimized by Huzinaga.[19] Exponents and contraction coefficients are listed in Refs. 14 and 16.

The electronic-structure calculation for each state starts with a spin-restricted HF-SCF (self-consistent-field) calculation which yields a set of one-electron molecular orbitals. Such a SCF calculation may be performed for a distinct, one-configurational state or for a weighted average of states, e.g., all states in the cluster arising from the d^n manifold. For the SCF calculations the MOLECULE/ALCHEMY package was used.[20]

The orbitals obtained in a SCF calculation are usually divided in two classes: the internal orbitals and the external or virtual orbitals. The former are occupied in the state under consideration, the latter are empty. The internal orbitals can be subdivided into core orbitals, corresponding to deep levels, and valence orbitals, slightly below the Fermi level. In NiO_6 orbitals with predominant Ni(1*s*) through Ni(3*p*) and O(1*s*) through O(2*s*) character are ranked among the core orbitals. Ni(3*d*)- and O(2*p*)-like orbitals are valence orbitals.

Inspection of the atomic experimental and Hartree-Fock ionization energies and electron affinities listed in Table I shows that the removal or addition of an electron is accompanied by a large change in the electronic correlation energy. Inclusion of these correlation effects gives rise to higher ionization energies ($+2.4$ eV for the ionization of a *d* electron from Ni^{2+}) and smaller electron affinities (-3.0 eV for addition of a *d* electron to Ni^{2+}).

A similar estimate for the correlation-energy effect upon ionization of a *p* electron from O^{2-} is not possible, as the free O^{2-} ion is unstable and hence no experimental and numerical Hartree-Fock (NHF) data are available. From HF and configuration-interaction calculations on oxygen ions surrounded by a set of point charges representing the NiO field, and using a large basis set, the correlation effect is estimated to be 0.4 eV for ionization of a 2*p* electron from O^{2-}.

Correlation-energy effects of comparable magnitude will occur upon ionization or addition of an electron in a cluster. In addition, there are also several correlation effects which differentiate between states with the same number of electrons. For *d*-*d* transitions between d^n

TABLE I. Energy levels of nickel ions. Comparison of experimental and theoretical [numerical Hartree-Fock (NHF)] transition energies. All transition energies are given with respect to the ground state of the ions; values in square brackets are with respect to the $^3A_{2g}$ ground state of Ni^{2+}. Determination of CEC (in units of eV).

	State	Expt.[a]	NHF	ΔE_{CEC}[b]
Ni^{3+}	^4F (d^7)	[35.34]	[32.93]	[2.41]
	^4P	2.13	2.67	−0.54
	^2G	2.38	2.70	−0.32
	^2P	2.83	3.58	−0.75
	^2H	3.22	3.58	−0.36
	$a\,^2D$	3.30	3.90	−0.60
	^2F	5.27	6.24	−0.97
	$b\,^2D$	8.26	9.82	−1.56
Ni^{+}	^2D (d^9)	[−18.22]	[−15.25]	[−2.97]
	^4F (d^8s)	0.89	−0.63	1.52
Ni^{2+}	^5F (d^7s)	6.80	5.66	1.14

[a] From Reference 21.

[b] $\Delta E_{\mathrm{CEC}} = \Delta E_{\mathrm{expt}} - \Delta E_{\mathrm{NHF}}$.

states, three types of correlation energy are important.

First, there is $3d$ correlation, which results from symmetry reduction by the crystal field with respect to the free-ion spherical symmetry. This effect is incorporated in a small configuration-interaction calculation. For each spatial symmetry representation Γ and spin S, a number of many-electron functions can be constructed by distributing the n electrons in all possible ways over the five $3d$-like orbitals. These functions are called configuration state functions (CSF's) and correlated wave functions are obtained as independent linear combinations of these CSF's from diagonalization of the Hamilton matrix in this basis. This procedure is called ligand-field CI (LF-CI) and is formally equivalent to the intermediate crystal-field model.

Second, we have the differential d-d correlations between the free-ion states. Like the ionization and electron-addition energy correction, these can be obtained semiempirically and then incorporated in the cluster energies by the method described by Pueyo and Richardson.[22] For each atomic state of spin S and angular momentum L a differential correlation-energy correction (CEC) with respect to the ground state is defined:

$$\Delta E^{SL}_{\mathrm{CEC}} = \Delta E^{SL}_{\mathrm{obs}} - \Delta E^{SL}_{\mathrm{HF}} \ . \tag{1}$$

ΔE_{obs} and ΔE_{HF} are the observed and Hartree-Fock transition energies with respect to the ground state (S_0L_0). The CEC is represented in the $|SL\rangle$ basis by a diagonal matrix:

$$V_{S_0L_0,S_0L_0} = 0 \ , \tag{2}$$

$$V_{SL,S'L'} = \Delta E^{SL}_{\mathrm{CEC}}\delta SS'\delta LL' \ . \tag{3}$$

The $\Delta E^{SL}_{\mathrm{CEC}}$ values of Ni^{3+} are listed in Table I. This matrix is transformed to the strong-field basis $|S\Gamma\rangle$ of the crystal-field symmetry and added to the LF-CI matrix of CSF's. The fact that this basis is not exactly equal to the strong-field basis, but also contains contributions from anion-p–metal-d overlap, is usually neglected. LF-CI plus CEC calculations were carried out with the program CI-CEC.[23]

The third type of correlation is the specific open-shell correlation, which in the case of the d^n states introduces additional Ni($3d$)-O($2p$) covalency. Ideally, incorporation of this effect would require a full-valence FOCI. This involves all CSF's that can be obtained by distributing all valence electrons in all possible ways over the valence orbitals, plus all CSF's that are obtained when one electron is transferred from the valence set to the virtual set.

For d^n states other than d^9, the FOCI list of CSF's tends to become very large due to the large number of spin couplings. This is partly caused by the low (Abelian) symmetry that must be used in the CI calculations (D_{2h}). This does not result in a physical symmetry lowering as O_h-symmetry-adapted integrals can be used. There are several ways to reduce the number of CSF's:[14,16] by deleting all CSF's that differ more than a double electron transfer from all d^n states, by numerical selection based on perturbation theory, or by reducing the number of virtual orbitals.

In the present work an approximation to the FOCI method itself is used: the so-called multireference singles CI (MRS-CI). A large reference set is constructed which consists of all d^n CSF's of a given spin and spatial symmetry $(S\Gamma)$ and all *singly* excited CT [O($2p$)-Ni($3d$)] CSF's of the same symmetry. The full list of CSF's includes these CSF's and all CSF's that are obtained by a single valence–to–virtual electron transfer with respect to a reference CSF. These single-electron transfers are responsible for the relaxation in the CT part of the wave function. As a simplified example, consider a one-determinantal d^1 CSF of symmetry λ:

$$|\, i_\mu \bar{i}_\mu l_\lambda \bar{l}_\lambda d_\lambda \,| \ . \tag{4}$$

i is a valence orbital, l a ligand valence orbital, and μ some symmetry representation. A CT CSF is then

$$|\, i_\mu \bar{i}_\mu l_\lambda d_\lambda \bar{d}_\lambda \,| \ . \tag{5}$$

Examples of (spin-adapted) relaxation CSF's for the CT states are

$$(\,|\,\bar{i}_\mu l_\lambda d_\lambda \bar{d}_\lambda u_\mu\,| - |\,i_\mu \bar{l}_\lambda d_\lambda \bar{d}_\lambda u_\mu\,|\,)/\sqrt{2} \tag{6a}$$

and

$$(2\,|\,i_\mu l_\lambda d_\lambda \bar{d}_\lambda \bar{u}_\mu\,| - |\,\bar{i}_\mu l_\lambda d_\lambda \bar{d}_\lambda u_\mu\,| - |\,i_\mu \bar{l}_\lambda d_\lambda \bar{d}_\lambda u_\mu)\,|\,/\sqrt{2} \ , \tag{6b}$$

with a virtual orbital u_μ.

The present procedure ensures that each CSF differs at most by two electron transfers from a d^n state of symmetry $S\Gamma$.

For the $^3A_{2g}$ ground state of NiO_6^{10-} a MRS-CI can be carried out with 78 virtual orbitals. The quartet states of Ni(d^7)$O_6{}^{9-}$ are calculated with the same set, but for the doublet state a further reduction to 35 virtual orbitals is necessary. For the d^9 states of $NiO_6{}^{11-}$ a full FOCI calculation can be carried out with the large virtual set.

The LF-CI list of CSF's is a subset of the MRS-CI list. For technical reasons the differential atomic correlation effects are not as easily incorporated into the MRS-CI list as into the LF-CI list. Therefore a "molecular" CEC is defined for each state $iS\Gamma$:

$$\Delta E_{\text{CEC}}^{iS\Gamma} = \Delta E_{\text{LF-CI+CEC}}^{is\Gamma} - \Delta E_{\text{LF-CI}}^{iS\Gamma} \; . \tag{7}$$

ΔE is with respect to the d^n ground state of the cluster. This ΔE_{CEC} is added to $\Delta E_{\text{MRS-CI}}$, scaled by λ^2, λ^2 being the sum of the squared coefficients of the d^n CSF's in the MRS-CI wave function.

The calculations of wave functions for the CT states themselves also require inclusion of open-shell correlation effects. In this case, they are responsible for localization effects. In the same simplified model as used above for d^n states, a CT-state wave function looks like

$$|\, i_\mu \bar{i}_\mu l_\sigma \bar{l}_\sigma l_\lambda \,| \quad (\text{"SCF state"}) \; , \tag{8a}$$

with correlation and/or relaxation contributions:

$$\begin{gathered} |\, \bar{i}_\mu l_\sigma l_\lambda \bar{l}_\lambda u_\tau \,| - |\, i_\mu \bar{l}_\sigma l_\lambda \bar{l}_\lambda u_\tau \,| \,)\sqrt{2} \; , \\ (2\,|\, i_\mu l_\sigma l_\lambda \bar{l}_\lambda \bar{u}_\tau \,| - |\, \bar{i}_\mu l_\sigma l_\lambda \bar{l}_\lambda u_\tau \,| - |\, i_\mu \bar{l}_\sigma l_\lambda \bar{l}_\lambda u_\tau \,| \,)\sqrt{6} \; . \end{gathered} \tag{8b}$$

σ and λ are subspecies of the same representation, and μ and τ chosen such that $\mu \times \sigma \times \tau$ contains λ. Here the following approximation to FOCI will be made. First, we distribute the appropriate number of electrons over all orbitals which are *open* in the dominating CSF. Then all single and double electron transfers are made with the restriction of, at most, one external electron. Subsequently, a numerical selection of CSF's based on second-order perturbation theory is carried out.[16]

All CI calculations were carried out with the CI package developed by Hegarty.[24]

III. RESULTS

A. Ground state: Ni(d^8)$O_6{}^{10-}$

The total energy and wave function of the ${}^3A_{2g}$ state were calculated in both the LF-CI and MRS-CI models, using orbitals optimized for the d^8 average of states (Table II). The Ni(3d) orbitals and O(2p) orbitals are well separated. Because of overlap of diffuse functions in the basis set, the formal charge on Ni is not 2e but only 1.3e (Table III). The MRS-CI calculation introduces a delocalization of the hole by mixing in CT states. The $|d^8\rangle$ term is still the dominating term in the wave function, with coefficient 0.98. The energy lowering is only 0.6 eV.

TABLE II. Total energy and wave function of the $NiO_6{}^{10-}$ cluster ground state (${}^3A_{2g}$).

	E^{a}	Configurational compositions
LF-CI	−1968.0274	100% $e_g^2 t_g^2 (d^8)$
MR-SCI	−1968.0512	96% $e_g^2 t_g^2 (d^8)$

[a] Total energies calculated with d^8-average-of-state optimized orbitals in a.u.

B. Charge-transfer transitions

The lowest CT states will be the triplets arising from $(e_g^3 t_{2g}^6 t_{1g}^5)$. This configuration contains a ${}^3T_{1g}$ and a ${}^3T_{2g}$ state, which are not separable on a SCF level. Their energies were calculated with an orbital set optimized in a SCF calculation on the average of these two states. Large reorganization effects with respect to the $|d^8\rangle\,{}^3A_{2g}$ state are observed (Table III). Although the localized, open 3d orbitals show an increase in occupancy of 1.0e, the total charge on Ni is only increased by 0.4e. The closed-shell orbitals adapt themselves to the new situation, such that negative charge flows back to the oxygen sites. The admixture of the diffuse Ni basis functions in the O(2p) orbitals becomes less.

The effects of FOCI with respect to the (symmetry-restricted) SCF are drastic (Table IV). The ${}^3A_{2g}$-${}^3T_{1g}$ transition energy is reduced by ~3 eV. This is of the same order as the localization energy found for O(2p) ionizations in $CrO_4{}^{2-}$.[15]

As the number of electrons stays the same in CT excitations, the differential correlation effects are smaller than in the calculation of ionization energies or electron affinities. However, the localized 3d states and the spatially extended O(2p) states are sufficiently different to cause a differential correlation-energy effect for an O(2p)→Ni(3d) excitation. This may be estimated from the correlation-energy change in the process $Ni^+(d^8s)$-$Ni^+(d^9)$. Applying this correction (Table I) brings the CT state at about 6.2 eV above the $|d^8\rangle$ states, in good agreement with the value found for MgO:Ni.[25] Bulk polarization (Sec. IV) and band-broadening contributions will reduce this value in NiO.

C. $|d^8\rangle$-$|d^7 4s\rangle$-like transitions

The difference between the independently calculated SCF energies (ΔSCF) for the excitation ${}^3A_{2g}$-${}^5T_{1g}$ in $NiO_6{}^{10-}$ is 8.1 eV. The correlation-energy correction, derived from the ${}^3F(d^8)$-${}^5F(d^7 4s)$ transition (Table I), would increase the value to 9.2 eV (Table IV). From open-shell correlation, only a very small differential energy effect is expected and, therefore, it seems safe to put the onset of these excitations 2–3 eV above the onset of the CT excitations.

D. 3d ionizations: $NiO_6{}^{9-}$

The basis of the calculations of the energies of the Ni(d^7)$O_6{}^{9-}$ states is a SCF on the average of $|d^7\rangle$ states ($\overline{d^7}$). Subsequently, a LF-CI calculation gives the energies of all states in this configuration. The Mulliken charge analysis of the $\overline{d^7}$ optimized orbitals shows large reorganization effects with respect to the ${}^3A_{2g}$ state (Table III). The loss of one electron from the 3d orbitals is overcompensated, resulting in a Ni charge of 1.2e.

TABLE III. Mulliken charge populations, given for open shells and summed over all orbitals (total).

State		Ni s	Ni p	Ni d	O s	O p
			NiO_6^{10-}			
$^3A_{2g}$	e_g			1.92	0.00	0.08
	Total	5.95	12.42	8.34	24.01	35.27
$^3T_{1g}+^3T_{2g}$	e_g			2.95	0.02	0.03
	t_{1g}					5.00
	Total	5.81	12.23	9.11	24.06	34.79
			NiO_6^{9-}			
$\overline{d^7}$	e_g			2.42	0.02	0.37
	t_{2g}			4.09		0.11
	Total	6.20	12.80	7.79	23.99	34.21

This reorganization occurs mainly in the closed orbitals, which show an increased admixture of diffuse Ni s, p, and d functions.

The LF-CI energies of the d^7 states cover a range of 10 eV (Table V). The range is reduced to 8 eV when atomic-energy corrections (CEC's) are included.

The results of the MRS-CI calculations on the d^7 states are presented in Table VI. It is clear that the reduction of the number of virtual orbitals increases the total energies, but the differential effects are acceptable.

There are significant differences between the LF-CI and MRS-CI spectra, resulting from configurational mixing with (relaxed) CT states in the latter. The energy changes in the spectrum are connected with a change in the effective crystal-field splitting $[\Delta E(^4T_{2g}\text{-}^4A_{2g})]$, which increases from 1.1 eV in the LF-CI model to 1.6 eV in the MRS-CI model. This means that the effective crystal-field splitting in Ni^{3+} is larger than the Ni^{2+} splitting by a factor of 1.5.

Compared to the results for the $^3A_{2g}$ ground state, the ionized states show an enhanced admixture of the CT states. The $|d^7\rangle$ states, however, are still the predominant terms in the wave function, with coefficients ≥ 0.93. This implies that both the orbital relaxation and enhanced CT mixing are important in increasing the covalency in the ionized state. The energy lowering for the ionized state is now 1.6 eV with respect to LF-CI compared to 0.6 eV in the ground state.

The cluster $3d$ ionization energy (V_{IP}) as calculated from the MRS-CI energies of the $^3A_{2g}$ and $^4T_{1g}$ states is 9.6 eV. Dynamical correlation effects will increase this value by 2.4 eV, resulting in $V_{\mathrm{IP}}(d)=12.0$ eV, with respect to vacuum. Note that all states which arise from a single electron ionization, i.e., $^2E_g(e_g^1t_{2g}^6)$, $^4T_{1g}(e_g^2t_{2g}^5)$, and $^2T_{1g}(e_g^2t_{1g}^5)$, are in the lower part of the spectrum.

TABLE IV. Excitation energies in NiO_6^{10-}. Values in eV.

State	ΔSCF[a]	FOCI[b]
$^3T_{1g}$ (CT)	10.7	7.8
$^3T_{2g}$ (CT)	10.8	7.9
$^5T_{1g}$ $(d\rightarrow s)$	8.1	9.2[c]

[a] With respect to E_{SCF} of $^3A_{2g}$ (d^8).

[b] With respect to $E_{\mathrm{MRS\text{-}CI}}$ of $^3A_{2g}$ (d^8).

[c] With CEC.

E. 2p ionizations

The lowest $2p$ ionized state in NiO_6^{9-} is the $^4T_{2g}$ state from the $(e_g^2t_{2g}^6t_{1g}^5)$ configuration. In the ΔSCF spectrum this state is 2.5 eV above the $^4T_{1g}(d^7)$ LF-CI state (Table VII).

The CI calculation on this $^4T_{2g}$ state shows a further energy lowering of 3.5 eV, of the same order as was found for CT excitations in the NiO_6^{10-} cluster. At the CI level its position is therefore only 0.7 eV above the $^4T_{1g}(d^7)$ state and well below that of most of the other d^7 states (Table VI). The SCF state is the predominant term in the wave function; the other contributions are CSF's with one electron in the virtual set [type (8b), Sec. II]. There is very little admixture from the $^4T_{2g}(d^7)$ state, although their energies seem to be almost the same. In the present calculations a large mixing is not expected. Because of major truncations with respect to the full FOCI CSF space made in the calculation of the wave function for either state, the states will not be degenerate within *one* calculation. Even if a CSF space could be used which comprises both present CI spaces, a large mixing can only accidentally occur if the states are truly degenerate. In other cases the effect will be small, as the direct coupling between the states is zero and only higher-order coupling occurs. The ionization energy with respect to vacuum for a $2p$ ionization from NiO_6^{10-} is, on the basis of FOCI results, 10.3 eV. Dynamical correlation effects (Sec. II) will raise this value by 0.4 eV to 10.7 eV.

It is assumed that the relaxation and localization effects are about equal for all O($2p$) ionized states. Hence, the theoretical bandwidth of the O($2p$) ionization is set equal to the range of O($2p$) orbital energies in NiO_6^{10-}: 3.5 eV.

An alternative approach is to consider an O_{13} or O_{19} cluster. In both clusters a hole in a t_{1u} orbital can localize on the central atom. A Mulliken analysis of the $^2T_{1u}$ state shows that this localization does occur and is complete, despite the possibility of delocalization over neigh-

TABLE V. LF-CI spectrum without and with CEC of d^7 states of $\mathrm{NiO_9}^{9-}$. Energies in eV. Configurational composition of states given in percentages.

State	ΔE	$\Delta E+\Delta E_{\mathrm{CEC}}$	$e_g^4 t_{2g}^3$	$e_g^3 t_{2g}^4$	$e_g^2 t_{2g}^5$	$e_g^1 t_{2g}^6$
$^4T_{1g}$	0.0	0.0		11	89	
$^4T_{2g}$	0.86	0.87		100		
^2E_g	1.69	1.19	1	6		93
$^4A_{2g}$	1.98	1.99	100			
$^2T_{2g}$	2.41	2.01	1	13	86	
$^2T_{1g}$	2.51	2.01	2	4	94	
$^4T_{1g}$	3.03	2.52		89	11	
$^2T_{1g}$	3.16	2.41	0	23	77	
$^2A_{1g}$	3.34	3.03		100		
$^2T_{2g}$	3.57	3.95	1	74	25	
$^2T_{1g}$	3.91	3.26	2	93	5	
^2E_g	4.24	3.57	5	95		0
$^2T_{2g}$	4.66	4.02	34	54	12	
$^2T_{1g}$	4.76	4.07	56	35	9	
^2E_g	4.89	4.41	84	13		3
$^2T_{2g}$	5.99	4.98	6	43	51	
$^2T_{1g}$	6.29	5.37	40	45	15	
$^2A_{2g}$	6.40	5.44		100		
$^2T_{2g}$	9.53	8.06	58	16	26	
^2E_g	9.65	8.11	10	86		4

boring atoms. Formally, such a localized state would be at the center of the O(2p) band. The bandwidth of the O(2p) states is 3.5 eV (both experimental[10] and theoretical) and, therefore, an ionization energy of 10.1 eV with respect to vacuum is expected, in good agreement with the value obtained for the $\mathrm{NiO_6}$ cluster (Table VII).

F. Electron affinity

SCF calculations (Table VIII) on separate $|d^9\rangle$ and $|d^{10}L^{-1}\rangle$ states show that in $\mathrm{NiO_6}^{11-}$ the $|d^9\rangle$ state are far below the $|d^{10}L^{-1}\rangle$ (CT) states. The FOCI calculation (Table VIII) increases the effective crystal-field splitting by only 20%. The CT energies, on the other hand, are lowered by ~3.5 eV, as in the $\mathrm{NiO_6}^{10-}$ and $\mathrm{NiO_6}^{9-}$ clusters. The first $|d^{10}L^{-1}\rangle$ state is found at about 10 eV above the $^2E_g\,|d^9\rangle$ state, in agreement with the assignment made by Hüfner.[7]

From the total FOCI energies a FOCI electron affinity of 2.6 eV is calculated. Correlation-energy effects (Table II) will decrease this value to ~ −0.4 eV.

IV. ESTIMATION OF THE CRYSTAL BAND GAP

A. Mott-Hubbard and charge-transfer gaps

In the following, U is defined as the minimum energy required to remove an electron of mainly d character from one site in the crystal and add it to another site, infinitely far away. By this definition U is the Mott-Hubbard gap, the sum of the smallest d ionization and the smallest d-electron affinity.

In addition, the charge-transfer gap Δ is defined as the sum of the smallest O(2p) ionization energy and the smallest d-electron affinity.

In Table IX a summary is given of the ionization ener-

TABLE VI. LF-CI, MR-SCI, and FOCI spectra of $\mathrm{NiO_6}^{9-}$ (d^7). Calculations were carried out with d^7-average-of-configuration orbitals. All transition energies are given by eV. Ground-state total energies given in a.u.

State	LF-CI	MR-SCI[a]	MR-SCI[b]	MR-SCI+CEC[b]
$^4T_{1g}$	(−1967.6309)	(−1967.6984)	(−1967.6776)	0.0
^2E_g	1.69		0.83	0.39
$^4T_{2g}$	0.86	1.27	1.26	1.27
$^2T_{2g}$	2.41			
$^2T_{1g}$	2.51		2.12	1.71
$^2T_{1g}$	3.16		2.66	2.00
$^4T_{1g}$	3.03	2.84	3.05	2.59
$^4A_{2g}$	1.98	2.83	2.62	2.63

[a] 78 virtual orbitals.

[b] 35 virtual orbitals.

TABLE VII. Relative energies of O(2p) ionized states (eV).

State	ΔSCF	FOCI
$\mathrm{NiO}_6{}^{9-}$ $^4T_{2g}$[a]	13.2	10.3
$\mathrm{O}_{13}{}^{25-}$ $^2T_{1u}$[b]	11.8	
$\mathrm{O}_{19}{}^{37-}$ $^2T_{1u}$[c]	11.8	

[a] With respect to $\mathrm{NiO}_6{}^{10-}$ ($^3A_{2g}$).
[b] With respect to $\mathrm{O}_{13}{}^{25-}$ ($^1A_{1g}$).
[c] With respect to $\mathrm{O}_{19}{}^{37-}$ ($^1A_{1g}$).

gies and electron affinities obtained with the cluster calculations. Using these values we find $U = 12.2$ eV. The contribution of the empirical correlation energy is very small, only 0.6 eV.

For Δ we obtain 10.3 eV from $\mathrm{NiO}_6{}^{9-}$ calculations and 10.0 eV from O_n calculations. Here the correlation contribution is larger, 2.6 eV, as there is no near cancellation for the ionization and addition processes.

The values of U and Δ are still much too large compared to the experimental band gap of 4.3 eV. This is clearly a consequence of the cluster approach, which neglects polarization effects in rest of the crystal.

B. Bulk polarization

The total polarization in the crystal upon ionization or electron addition can be divided into an intracluster and an extracluster contribution. The first are included in SCF and FOCI calculations. The extracluster contribution comprises the polarization from bands and ions outside the cluster. The most efficient way to calculate this contribution is to estimate the polarization of the whole crystal and then subtract the cluster contribution.

To this end, the crystal is assumed to consist of a set of dipole polarizabilities located at the oxygen sites. The size of the polarizabilities is obtained from the Clausius-Mossotti relation:

$$\frac{\epsilon-1}{\epsilon+2}=\frac{4\pi}{3}\frac{4}{8a^3}\alpha\ , \tag{9}$$

where ϵ is the optical dielectric constant and $2a$ the lattice constant. When the empirical value of 5.76 is used,[8] $\alpha = 2.64$ Å^3 results. This polarizability is much larger than that obtained in a finite-field calculation on an O^{2-} ion, with one of the basis sets used in the present work. In such a calculation, $\alpha = 0.80$ Å^3 is found.[14] Test calculations have shown that the presence of diffuse functions on Ni greatly increases the polarizability.

TABLE VIII. Energy levels of $\mathrm{NiO}_6{}^{11-}$. Transition energies from ^2E_g are given in eV, total energies in a.u.

State	ΔSCF	FOCI
^2E_g $(e_g^3 t_{2g}^6)$	(−1967.9426)	(−1967.9556)[a]
$^2T_{2g}$ $(e_g^4 t_{2g}^5)$	0.74	0.89[a]
$^2T_{1g}$ $(e_g^4 t_{2g}^6 t_{1g}^5)$	14.24	10.85[b]
$^4A_{2g}$ $(e_g^2 t_{2g}^6 a_{1g}^1)$	−0.84	

[a] Calculated using d^9-average-of-configuration orbitals.
[b] Calculated using $^2T_{1g}$ SCF orbitals.

TABLE IX. Summary of cluster-ionization energies, electron affinities, and charge-fluctuation energies (in eV).

	ΔSCF	MRS-CI with FOCI	$+\Delta E_{\mathrm{CEC}}$	$+\Delta E_{\mathrm{pol}}$[c]
$V_{\mathrm{IP}}(d)$	10.8	9.6	12.0	8.5
$V_{\mathrm{IP}}(p)$[a]	13.2	10.3	10.7	9.1
$V_{\mathrm{IP}}(p)$[b]	11.8	(10.0)	10.4	8.3
$E_A(d)$	2.3	2.6	−0.4	−3.9
U	13.1	12.2	11.6	4.6
Δ	15.5−14.1	12.9−12.7	10.3−10.0	5.2−4.4

[a] NiO_6 cluster.
[b] O_n cluster. Second column contains ΔSCF value minus $\frac{1}{2}W$ [O(2p) bandwidth].
[c] Including polarization corrections; see text.

The polarization energy for an added point charge in the crystal has been calculated with classical models. Both take account of the interaction between the induced dipoles. The Mott-Littleton (ML) method[26] uses an approximate formula for the induced moment at each site (except for the nearest-neighbor states in the so-called first-order Mott-Littleton theory). The direct-reaction-field (DRF) method[27] solves the self-consistency problem for a limited set of polarizabilities. The results obtained with either method are displayed in Table X, and are quite similar.

For the correction of U, twice the extracluster contribution for the removal of a point charge $|e|$ is needed. From a separate SCF calculation on the $\mathrm{O}_6{}^{12-}$ cluster, the intracluster contribution is found to be 1.5 eV, corresponding to an effective polarizability on each ion of 0.77 Å^3. The bulk polarization is about 5.0 eV (Table X) and hence $U = (11.6 - 2\times 3.5) = 4.6$ eV.

A similar procedure is adopted to correct Δ. First, 3.5 eV is subtracted for polarization upon electron addition. The FOCI ionization energy is corrected as follows. The localization energy includes the polarization energy of five oxygen ions and the nickel ion induced by a hole on a sixth oxygen ion. This polarization energy is 1.2 eV. The bulk polarization is 2.8 eV and hence we must subtract another 1.6 eV from Δ, resulting in $\Delta = (10.3 - 3.5 - 1.6) = 5.2$ eV.

TABLE X. Polarization energy in NiO (eV) when an excess charge is placed at a lattice site (effective polarizability of 2.64 Å^3 at all oxygen sites).

Method	Ni site	O site
Mott-Littleton (ML)	4.6	2.9
First-order ML[a]	5.4	
Direct reaction field[b]	4.8	2.8

[a] The first layer of (six) oxygen ions is treated exactly.
[b] All oxygen sites within a radius of 30 a.u. taken into account: 344 for the Ni site, 488 for the O site.

When the O_n V_{IP} is used, 2.1 eV must be subtracted, as now the intracluster oxygen atoms only contribute 0.7 eV in the SCF polarization energy. So we obtain $\Delta=(10.0-3.5-2.1)=4.4$ eV.

V. DISCUSSION

The present results have been obtained from quantum-chemical calculations with additional semiempirical corrections. This procedure is warranted only if the various contributions can be well defined and mutually separated. In the present study we have chosen a localized starting point and treated a small cluster quantum mechanically and the remaining long-range interactions classically, using empirical information. Empirical data have also been used in the cluster calculation to deal with the dynamic correlation energies which are mainly atomic. The "molecular" effects of intracluster binding, polarization, relaxation, and correlation resulting from near degeneracy of the valence levels on the metal ion and the anions have been accounted for in *ab initio* calculations.

In these calculations we employ a stabilizing Madelung field simulating the electrostatic influence of the rest of the crystal. The main effect of this field is a virtually uniform shift of the energy states belonging to a cluster with a given net charge. Its inclusion is necessary in order to obtain ionization and affinity energies that can be compared with experiment. The influence of the field on the self-consistently determined charge distributions and CI coefficients turned out to be small. This holds *a fortiori* for the electronic polarization fields induced by local ionization and charge-transfer processes. It may be noted that in this type of calculation, where a fixed number of electrons is assigned to a cluster, the external field must be generated by a charge distribution that integrates to a total charge exactly compensating the excess charge on the cluster. Given the structure of the crystal, this means that the only consistent point-charge representation is that given by the Madelung procedure. The resulting field in the cluster region may, of course, be approximated by any computationally convenient model of sufficient accuracy.

Of course, a fully-quantum-mechanical calculation including all three effects—molecular binding, dynamic correlation, and long-range polarization—would be more satisfying. It would also deal with higher-order couplings between these effects. At the moment such a calculation is not quite feasible, but we believe that the adopted method is sensible and enables (cautious) comparison with experiment.

As stated in the Introduction, the cluster model was chosen to allow a more sophisticated treatment of electron correlation effects than is possible in band calculations. The cluster model is a first approximation to a model in which Ni^{2+} is considered an isolated impurity in an extended $O(2p)$ band. Previous calculations[14] have shown that at the Hartree-Fock level the Ni-O interactions are negligible beyond the nearest neighbors. For the CI calculation as well only small contributions are expected from the inclusion of $O(2p)$ levels which are not at nearest-neighbor sites, as the interaction matrix element is expected to decrease exponentially with increasing distance. In fact, cluster and impurity calculations for NiO with an Anderson-Haldane–model Hamiltonian indicate that the cluster model is a very good approximation.[11,28]

The small Ni-Ni interactions are included when a resymmetrization to periodic symmetry is carried out for a set of localized cluster solutions. It is still impossible to carry out this calculation, but previous work on CuCl indicates that only a small effect on the energy is to be expected.[14,29]

The experimental photoemission spectrum shows two distinct peaks near the Fermi level, separated by 1.6 eV. On the basis of our results we suggest that these correspond to ${}^4T_{1g}+{}^2E_g$ and ${}^2T_{1g}\,|d^7\rangle$ final states, respectively. These states are the only ones that can result from the emission of a single d electron.

These peaks are superimposed on a broad band of $O(2p)$ ionized states. The width observed in experimental spectra (3.5 eV) agrees with the width inferred from cluster calculations.

From our calculations, the estimates for the lowest ionization energies are 8.5 eV for Ni($3d$) and 8.3 eV for $O(2p)$, with respect to vacuum. As these values include large and *different* polarization and correlation energies, the difference between these V_{IP} values can only give a crude estimate of their relative position in the photoemission spectrum. The difference is so small and the corrections so large that no definite conclusion concerning the nature of the lowest ionized state can be drawn.

We find that the character of the final states after emission of a d electron is 90% or more $|d^7\rangle$, without any spectacularly enhanced $|d^8L^{-1}\rangle$ admixture. Such an enhanced mixing would have lead to a much larger value for the effective crystal-field splitting than was found in our calculations, and which is necessary to explain the observed peaks near the Fermi level.

In model calculations[2] the $|d^8L^{-1}\rangle$ and $|d^7\rangle$ states are greatly mixed. The degree of mixing, however, is strongly dependent on the relative position of the unperturbed Ni and O levels. In the analysis of the results of these model calculations,[6] the lower state which results from the Ni(d)-O(p) interactions is called "screened," and the upper is called "unscreened." In our calculations, where there are many more degrees of freedom, such distinctly "screened" and "unscreened" states do not occur. In fact, all $|d^7\rangle$ states, whether arising from an e_g or a t_{2g} ionization, or from a more-electron process, show about the same amount of relaxation, i.e., charge reorganization takes place in the same way for all states.

Considering this, it seems likely that the satellite observed at about 7 eV below the first peak is due to d^7 final states which are in the upper part of the crystal-field spectrum (Table V). This would explain why they are enhanced in resonance spectra.[10] Formerly this satellite has been associated with "unscreened" final states.[6]

The estimated charge-fluctuation energies U and Δ are in the range of 4.4–5.2 eV and therefore it seems that the hopping model for conduction is supported by the present results. Which quantity Δ or U determines the band gap cannot be predicted on the basis of our results, due to the large uncertainty in the relative positions of the first ionization energies. As the effective mass of the O(2p) holes is much smaller, it is expected that in either case p-hole conductivity will be predominant.

The results presented in Table IX show clearly the importance of going beyond Hartree-Fock calculations, especially in case of the calculation of Δ, where open-shell and dynamic correlation effects reduce this parameter by ~ 5 eV. The value of U obtained in our calculations is smaller than previous theoretical estimates of 7–9 eV.[30] In these calculations the covalent Ni-O interactions were not explicitly considered.

Our U value is larger than the value recently found in a LD cluster study.[12] The difference is even larger when we consider the fact that in the LD calculations extracluster effects were not taken into account. This large difference may be an artifact of the approximate treatment of the exchange in the LD method, which introduces an unphysical self-repulsion for the electrons. This interaction is particularly large for localized electrons; hence orbitals optimized in the LD model tend to become quite delocalized, as was found by Brener and Callaway. This results in an overly small effective d-d repulsion U and in quite similar p and d states, which again results in an overly small CT gap.

When the calculated value for U in the NiO crystal is compared to the free-ion (Ni^{2+}) value of 17.1 eV,[21] it must be concluded that more than 50% of the reduction results from extracluster polarization, and the remaining part from intracluster binding and polarization. For Δ the situation is similar. Hence, it seems that a cluster must at least be embedded in an environment of point charges and polarizabilities.

It must be expected that intracluster excitations which bring about a large charge-redistribution effect, e.g., CT transitions, will also induce polarization in the rest of the crystal. For CT excitations this effect was estimated as follows. Two adjacent charges are placed in a NiO crystal: $-|e|$ at a Ni site and $|e|$ at an O site. The Mott-Littleton energy is then 1.8 eV. This situation would correspond to a fully localized O(2p) hole, so the FOCI-CI energy is corrected by this amount, after correction for the polarization of the five O^{2-} ions inside the cluster, which is 0.7 eV. So the CT energy is reduced by 1.1 eV. In these calculations, therefore, the optical CT gap is found to be 5.1 eV, close to the charge-fluctuation energies U and Δ. The optical dielectric constant of NiO is almost twice as large as ϵ_∞ in MgO:Ni. This partly explains the large decrease in CT excitation energy going from MgO:Ni to NiO. Other effects, such as the lattice polarization, may also contribute, but we feel that it is quite unlikely that a 1% change in the NiO distance alone may cause such a change.[31]

VI. CONCLUSIONS

The present analysis has shown that a good estimate for the charge-fluctuation energy in NiO can be obtained, based on calculations on a NiO_6^{10-} cluster. Bulk polarization effects, however, are large and must be accounted for.

It has, again, been established that it is important to go beyond one-electron models in the calculation of the wave function of the cluster. The specific open-shell correlation introduces effects which are underemphasized in Hartree-Fock theory. For $|d^n\rangle$ states an increased covalency results from interaction with $|d^{n+1}L^{-1}\rangle$ states. In O(2p) hole states, localization effects are introduced which have a large energy effect on Δ. Dynamic correlations are largely atomic.

Although there are still considerable uncertainties in the relative positions of the calculated Ni(3d) and O(2p) ionization energies, the results can be brought into good agreement with the experimental ionization spectrum.

A similar situation is found in case of U and Δ. They seem to be of the same order of magnitude, and both agree with the experimental value. The size and sign of their difference, however, is yet impossible to predict.

The importance of the bulk polarization is part of the explanation of why NiS is a conductor. The S^{2-} ions have a larger polarizability than the O^{2-} ions, so U and Δ will be reduced. Δ will get an additional reduction as the ionization energy of S^{2-} is expected to be smaller than that of O^{2-}. The combination of these two effects may well cause the gap to become zero.

It is apparent that, although the results from cluster calculations with semiempirical corrections agree well with the experimental data, it is desirable to develop a computational scheme which includes dynamic correlation and extracluster polarization.

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