Band theory and the insulating gap in CoO

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Results of three magnetic-polarized local-density calculations on the Mott insulator CoO are presented: (1) a spin-polarized calculation in the type-II antiferromagnetic (AF) state, (2) a spin-polarized calculation in the observed bct AF state, and (3) a moment-polarized calculation in the type-II AF state with spin-orbit coupling. In all three cases, a large density of states at the Fermi energy is found. It is concluded that the insulating behavior of CoO is intimately connected to the formation of a multideterminant ground state and is therefore outside the bounds of standard band theory.

The electronic structure of transition-metal oxides has been the focus of a continuing debate for the last several decades. It has been known for 20 years now that standard band theory can account for the insulating nature of MnO and NiO[1,2] below the Néel temperature. Insulating behavior above the Néel temperature can also be explained since local magnetic order should persist up to a "Stoner" temperature[3] (the Néel temperature being renormalized down from the Stoner temperature due to spin-fluctuation effects). One objection to this picture for NiO is that the calculated band gap is only about 0.3 eV (Ref. 2) as compared to 4.3 eV as determined from photoemission data.[4] The size of the band gap, though, is not a ground-state property, with the calculated gap always smaller than the actual gap. The latter difference is due to a discontinuity of the effective potential across the gap.[5] For atomiclike insulators, this discontinuity can be understood as follows: an electron in the valence band near a particular atom sees the potential of $N-1$ electrons from that atomic site (and that of N electrons from the other sites), whereas one in the conduction band sees the potential of N electrons on that atomic site.[3] This, in essence, is Mott's picture of the insulating nature of transition-metal oxides. The size of this discontinuity has been estimated for NiO by supercell calculations, where an additional d electron is forced on to a Ni site in the supercell, and the energy difference calculated with respect to the ground state. A value of 4 eV is found,[6] consistent with photoemission data.

A more serious objection, though, exists for the cases of FeO and CoO, where band theory predicts a metallic ground state. In the basic type-II antiferromagnetic (AF) ground state, one is filling a t_{2g} band which can accommodate three d electrons per metal site. This band is unfilled in the case of MnO and filled in the case of NiO. Therefore, one must obtain a metal for the cases of FeO and CoO where the band is $\frac{1}{3}$ and $\frac{2}{3}$ filled, respectively. Of course, one could conjecture that the above-mentioned discontinuity could be responsible for the entire gap, but one has the difficulty of how to distinguish between valence and conduction states. One way would be if there were some sort of symmetry breaking occurring. In fact, Mott has pointed out that the observed magnetic structure for CoO is body-centered tetragonal (due to an unquenched orbital magnetic moment), and thus that this symmetry lowering could potentially open up a gap.[3] In fact, Wakoh has performed a simplified unpolarized calculation for CoO assuming a fct lattice where the potential for a band calculation is supplemented by an intra-atomic self-exchange term (proportional to U), and has found that when U exceeds a certain value, a gap is opened up.[7] Terakura *et al.*[2] have emphasized, though, that the distortion seen in CoO would not only appear to be too weak to open a gap, but is the wrong type to open a gap at $\frac{2}{3}$ filling. They have proposed that the unquenched orbital magnetic moment itself is what is responsible for the opening of a gap. Brandow has gone further to emphasize that a multideterminant reference state may be necessary to understand the insulating gap,[8] although he also states that such a state could in principle be collapsed to a single-determinant form and that some sort of band theory should work.

In this paper, the effect of the observed tetragonal distortion and the effect of an unquenched orbital magnetic moment are investigated in the framework of ordinary band theory. It is shown that neither effect leads to the opening of a gap. It is then proposed that the existence of a gap in FeO and CoO is connected to the presence of a multideterminant ground state, as also observed in the magnetic insulator TmSe.

The band calculations were done within the linearized muffin-tin-orbital method (LMTO) utilizing combined correction terms to the standard atomic sphere approximation.[9] Basis functions up to $L=2$ were kept on both Co and O sites. Two empty spheres per CoO unit were added at interstitial sites due to the open nature of the rocksalt structure, with basis functions up to $L=1$ on these sites. The sphere radii (a.u.) were taken to be 2.457 for Co, 2.354 for O, and 1.177 for an empty site (with a lattice constant of 9.860). The type-II AF structure contains two formula units in a trigonal cell.[2] The bct AF structure has eight formula units in the primitive body-centered-tetragonal cell with $c/a=0.988$.[10] The spins in the type-II structure were assumed to lie along the trigonal z axis (they actually lie along the $\langle 111 \rangle$ axis, but the difference in angles is small). The spins in the bct struc-

ture were assumed to lie along the tetragonal z axis (they are actually canted 27° off this axis, but since a calculation without spin orbit was done for the bct structure, this canting would make no difference). The charge and spin densities were constructed on a 30-k-point mesh in the irreducible wedge using the tetrahedron scheme. The choice of exchange-correlation potential is that of Hedin and Lundqvist.[11] For the calculation which included orbital-moment effects, spin orbit was handled in a manner described in Ref. 12. Spin-orbit corrections induce coupling between up and down spins, so the size of the secular matrix is doubled. In the upper (lower) diagonal blocks, the spin-up (spin-down) potential is used to calculate the spin-orbit terms, whereas in the off-diagonal blocks, a spin-averaged potential is used. The resulting eigenvectors are combinations of "scalar" relativistic basis functions times spinors. From these, the spin density can be constructed for the next self-consistent cycle. Also, the orbital moment can be determined as $\mu_{\rm orb} = \sum_{l,m,s} m n_{lms}$, where m is the orbital quantum number and n_{lms} is the lm-projected occupation numbers in each spin channel, s. Finally, comparison calculations were done for the case of NiO, with sphere radii (a.u.) of 2.354 for both Ni and O, and 1.177 for an empty site (with a lattice constant of 9.667).

Results for all calculations (including a spin-only and a spin-orbit calculation for NiO in the type-II phase) are shown in Table I. Listed are (1) the spin part of the moment inside the metal sphere, (2) the orbital part of the moment, (3) the size of the gap (if any), and (4) the density of states (DOS) at the Fermi energy. Note that the size of the moment is sensitive to the choice of sphere radii,[2] so these numbers should not be regarded as absolutes. For the case of NiO, results equivalent to Ref. 2 are obtained (they obtain a spin moment of $1.09\mu_B$ and a gap of 0.3 eV). Note that in the present case, there is a weak orbital moment of $0.15\mu_B$ induced by hybridization effects. For the case of CoO, a spin moment of $2.37\mu_B$ is obtained (in Ref. 2, a spin moment of $2.35\mu_B$ is reported), as well as a large density of states at the Fermi energy. An orbital moment of $0.31\mu_B$ is found, which is rather small considering that a $0.15\mu_B$ orbital moment was found for NiO. The total magnetic moment ($2.7\mu_B$) is too small compared to the experimental value of $3.35\mu_B$.[13] This error is presumably due to the smallness of the calculated orbital moment (Kanamori estimates an orbital moment over three times larger[14]). The important thing to note is that spin orbit [at least within the local-density approximation (LDA) used here] has no effect on either the spin part of the moment or on the size of the DOS at the Fermi energy. This is the reason the author considered just the spin-only case for the bct structure (a spin-orbit calculation on this structure would be prohibitively expensive). From Table I, one sees that there is no difference between the results for the type-II and bct phases.

One could suppose, of course, that the failure to open up a gap could be rectified if a "more exact" exchange-correlation functional was used, presumably one that would depend on the orbital part of the moment[15] (the local spin-density functional depends only on the spin part of the moment). Still, the method presented above worked quite well for the heavy electron magnets $NpSn_3$ (Ref. 16) and UCu_5 (Ref. 12) (which are AF and have sizable orbital moments), not only for the total magnetic moment, but also for the degree to which the DOS at the Fermi energy was reduced when going from the paramagnetic phase to the magnetic phase (this reduction being induced by symmetry lowering in the magnetic phase). The exception to this was TmSe. In that case only about 86% of the DOS at the Fermi energy was removed when going magnetic, whereas experimentally the system is insulating in the magnetic phase.[17] Moreover, the size of the moment one obtained with local density ($\sim 4\mu_B$) is consistent with one's expectations, yet experimentally the moment is only $\sim 1.7\mu_B$. This reduction is due to multiplet effects, and is not representable by a single-determinant wave function.

The author therefore proposes that the case of FeO and CoO is similar to that of TmSe, being that the existence of a gap is connected with a multideterminant ground state as opposed to single-particle effects due to symmetry lowering in the magnetic state. The resulting multiplet corrections act to increase the size of the moment relative to the LDA for the metal oxides,[14] but decrease the size of the moment for TmSe,[17] giving moments in better agreement with experiment. Whether any exotic effects are associated with this correlation gap[18] remain to be seen.

TABLE I. Size of the spin and orbital magnetic moments in Bohr magnetons (columns 1 and 2), size of the gap in eV (column 3), and density of states at the Fermi energy expressed in specific-heat units of (mJ/mol K^2)/(formula unit) (column 4). The first four rows are for calculations in the type-II AF phase (SP refers to spin-polarized only and SO includes spin-orbit effects), and the final row is the spin-polarized calculation in the bct phase.

	Spin	Orbital	Gap	DOS
NiO (SP)	1.06		0.33	
NiO (SO)	1.06	0.15	0.33	
CoO (SP)	2.37			9.2
CoO (SO)	2.37	0.31		9.6
CoO (bct)	2.37			9.6

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