Orbital Polarization and the Insulating Gap in the Transition-Metal Oxides

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It is shown that an orbital-polarization correction to a spin-polarized band-structure calculation leads to an insulating gap for CoO, in sharp contrast to a standard band calculation. Orbital-polarization instabilities, though, are not found for FeO and La_2CuO_4.

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One of the most intriguing problems in condensed-matter physics in the past several decades concerns the electronic nature of the 3d metal oxides. The standard (Mott) picture, reviewed in Refs. 1 and 2, asserts that the insulating state is a direct result of the large difference in energies between a ground state d^n configuration and its excited-state analog d^{n+1} due to the Coulomb repulsion parameter, U. This can be shown by starting from the atomic limit with U included, and then turning on the hybridization. As long as the bandwidth of the d states is not too large, a gap persists between the occupied and unoccupied states. If one starts from the band limit, though, and then turns on U, a problem occurs if no gap is present when U is not turned on, such as occurs for the 3d transition-metal oxides. One then has the difficulty that since there is no energy gap between occupied and unoccupied states, one cannot unambiguously apply U, since this quantity (equivalent to a self-interaction correction to band theory) distinguishes between occupied and unoccupied states, but the metallic (band) Fermi energy is an artificial separation between such states. This is equivalent to saying that since no unique Wannier transformation exists for the case of an unfilled band, one cannot apply U in an unambiguous manner. Thus, one would hope to understand the gap on symmetry grounds alone in order to construct a consistent theory. This problem was resolved for the cases of MnO and NiO by Slater's group.[3] They showed, as did Terakura *et al.*[4] in more detail, that an insulating gap can be induced for these two oxides if a spin-polarized band calculation is done in the observed type-II antiferromagnetic (AF) structure. Note that this gap will persist up to the Stoner temperature, which will be much higher than the moment-disordering Néel temperature, and so the system will remain insulating well above the magnetic transition temperature.[1] The gap, of course, is much smaller than that observed. This is to be expected, since the Coulomb U parameter primarily determines the size of the gap. (More formally, the gap is not a ground-state property, and the effective potential changes discontinuously across the gap.[5] This is the Mott picture, where occupied electrons see the potential of d^{n-1} electrons, whereas the unoccupied ones see that due to d^n electrons.[1]) In fact, the correct gap size of 4 eV for NiO has been calculated by taking the energy difference between a supercell where all the Ni sites have eight d electrons and a supercell where one Ni site has nine d electrons, and the rest have eight.[6]

The above picture, though, does not work for FeO and CoO. In the case of MnO, one has an empty t_{2g} band, and in the case of NiO a filled t_{2g} band. Therefore, FeO and CoO fill this band $\frac{1}{3}$ and $\frac{2}{3}$, respectively, and remain metallic, even in the magnetic state. Of course, one would expect an unquenched orbital moment in these cases, as first estimated by Kanamori.[7] This had led to the speculation that the orbital moment can induce a gap.[1] In particular, CoO has a body-centered tetragonal distortion with a complex magnetic unit cell composed of eight CoO units, the moments being canted off the $\langle 001\rangle$ axis,[8,9] and thus this distortion could lead to a gap. Simple model calculations by Wakoh[10] do lead to a gap if U is large enough. As emphasized by Terakura *et al.*,[4] though, one expects a gap not to occur at $\frac{2}{3}$ filling for a realistic calculation of CoO for a ratio of $c/a < 1$ as experimentally observed. These doubts were confirmed by the author, who showed that a spin-polarized calculation in the distorted crystal structure led to no change in the density of states (DOS) at the Fermi energy, E_F.[11] Moreover, inclusion of spin-orbit effects within the spin-polarized calculation also led to no change in the DOS at E_F.[11] Thus, the hope that one could understand the nature of the gap based on symmetry grounds seemed rather faint. The author therefore pessimistically concluded that one might need to go to a multideterminant formalism to understand the gap in CoO.

One problem with the calculation of Ref. 11 is that the calculated orbital moment was much smaller than one would expect based on the analysis of Kanamori.[7] A similar problem has been observed in actinide metals, where the calculated orbital moment appeared to be smaller than what one needed to explain experimental data.[12] Brooks thus proposed an orbital-polarization correction to account for the discrepancy. A crude estimate of this effect led to an improvement in the size of the moment.[12] Recently, Eriksson and co-workers[13] have developed a formal version of this correction and showed that it could obtain essentially a free-ion moment for cerium at large lattice constants, in direct contrast to when this correction is not included. It is the author's purpose here to show that such a correction also leads to an insulating gap in CoO, although it does not do so for the cases of FeO and La_2CuO_4. This is a first-principles verification of the proposal offered by Terakura *et al.*[4] that a population imbalance in the t_{2g} band leads to a gap, similar to an analogous proposal of Brandow.[2]

The basis for the orbital-polarization correction is as follows. First, a standard spin-polarized band calculation is supplemented by spin-orbit effects; this, in principle, takes into account Hund's first and third rules. The approximation used here[14] is similar to that used by Brooks.[12] The inclusion of spin orbit doubles the secular matrix. On the upper (lower) diagonal block, the spin-up (-down) potential is used to construct the spin-orbit matrix elements, whereas an averaged potential is used in the off-diagonal blocks. The resulting eigenvectors are combinations of spherical harmonics times spinors, from which one can construct spin potentials for the next cycle. One can also obtain the orbital moment as $\sum m n_{lms}$, where n_{lms} is the occupation number in the lms channel and the sum is over occupied states.[15] One deficiency of this treatment is that Hund's second rule is not taken into account. This is because the exchange-correlation functional is taken from the electron-gas problem, and an electron gas has no orbital moment; thus, the orbital moment contributes nothing to the energy. The suggestion by Brooks is to obtain the orbital-moment correction from Hartree-Fock theory.

The basic idea is that the difference in energy of the ground state of a particular ion relative to an average over configurations is proportional to a Racah parameter.[16] For d states, this is the B Racah parameter, which is a linear combination of F_2 and F_4 Slater integrals. The proportionality constant turns out to the $-\frac{1}{2}L^2$,[13] where L is the orbital moment, which the reader can verify from Ref. 16, noting that the average energy is the energy of the filled shell times the ratio of the number of electron pairs in the unfilled shell to the number of pairs in the filled shell. Functionally differentiating this, one obtains a correction equal to $-BLm$ for the d states in the secular matrix. This is especially easy to apply in the linearized muffin-tin-orbital (LMTO) formalism since the basis one uses is an lm basis. Self-consistency is achieved by determining B and L each iteration. One technical point is that one uses both a wave function, ϕ, and its energy derivative, $\dot{\phi}$, at the band center for a basis in each spin. Thus, it is necessary to write the Slater integrals that determine B as $F_l = \int \rho(r) V_l(r) \times 4\pi r\, dr$, where ρ is equal to $\phi\phi$, $\phi\dot{\phi}$, or $\dot{\phi}\dot{\phi}$ for each spin, depending on the matrix element considered, with V_l being determined solely from ϕ. Finally, note that the L considered is just L_z. Generalizations of this formalism involving the L_x and L_y terms have not been formulated yet. These terms would contribute to the off-diagonal blocks, and thus one would need to consider S_x and S_y terms also for consistency's sake.

TABLE I. Values of the spin and orbital moments (μ_B) and DOS at the Fermi energy [in (mJ/mol K^2)/(formula unit)] for FeO, CoO, and NiO in a type-II AF state. SO means spin orbit only and OP includes orbital polarization. ⟨111⟩ is an OP calculation with the z axis along the ⟨111⟩ direction.

	Spin	Orbital	DOS
FeO (SO)	3.47	0.12	4.5
FeO (OP)	3.47	0.28	4.7
FeO (⟨111⟩)	3.47	0.36	4.9
CoO (SO)	2.37	0.31	9.6
CoO (OP)	2.39	2.05	0.0
NiO (SO)	1.06	0.15	0.0
NiO (OP)	1.09	0.64	0.0

LMTO calculations were performed for FeO, CoO, and NiO in the type-II AF (trigonal) structure including combined correction terms to the standard atomic-sphere approximation.[17] Basis functions up to $l=2$ were kept on the metal and oxygen sites. Two empty spheres per formula unit were added at interstitial sites with basis functions up to $l=1$ on those sites. The oxygen sphere radius was taken to be 2.354 a.u., the empty sphere radius as 1.177, and the metal sphere radius as 2.354 (Ni), 2.457 (Co), and 2.5355 (Fe). The z axis was taken as the ⟨001⟩ axis (this defines L_z), although for FeO a calculation was done with the z axis along the ⟨111⟩ direction since experimentally the moment lies along the axis.[18] 30-k points in the irreducible wedge were used in the calculation, with the exchange-correlation potential being a spin-polarized variant of the Hedin-Lundqvist form.[19] Results are shown in Table I for calculations which included spin polarization and spin orbit (SO), and the two plus orbital polarization (OP). Additional calculations were also done for FeO and CoO with the metal sphere radius shrunk by about 20%, but the moments were only reduced by a few hundredths of a μ_B.

The interesting point to note from Table I is the large orbital-polarization instability found for CoO. This can be further seen in Fig. 1, where the DOS near E_F is plotted for the SO and OP cases. Note the drastic change in the DOS that opens a weak gap at E_F. This change is accompanied by a dramatic increase in the orbital moment from $0.31\mu_B$ to $2.05\mu_B$, leading to a total moment of 4.44. This moment, unfortunately, is larger than the experimentally observed values of 3.35 (Ref. 9) and 3.8 (Ref. 18) reported in the literature. Comparison to Kanamori's work[7] would indicate that the orbital moment is too large by a factor of 2. Note that a reduced orbital moment will act to close the gap, unless the Racah parameter increases to compensate. One might hope that a calculation in the distorted body-centered tetragonal structure would show a stabilization of the gap.

For the cases of FeO and NiO, orbital polarization

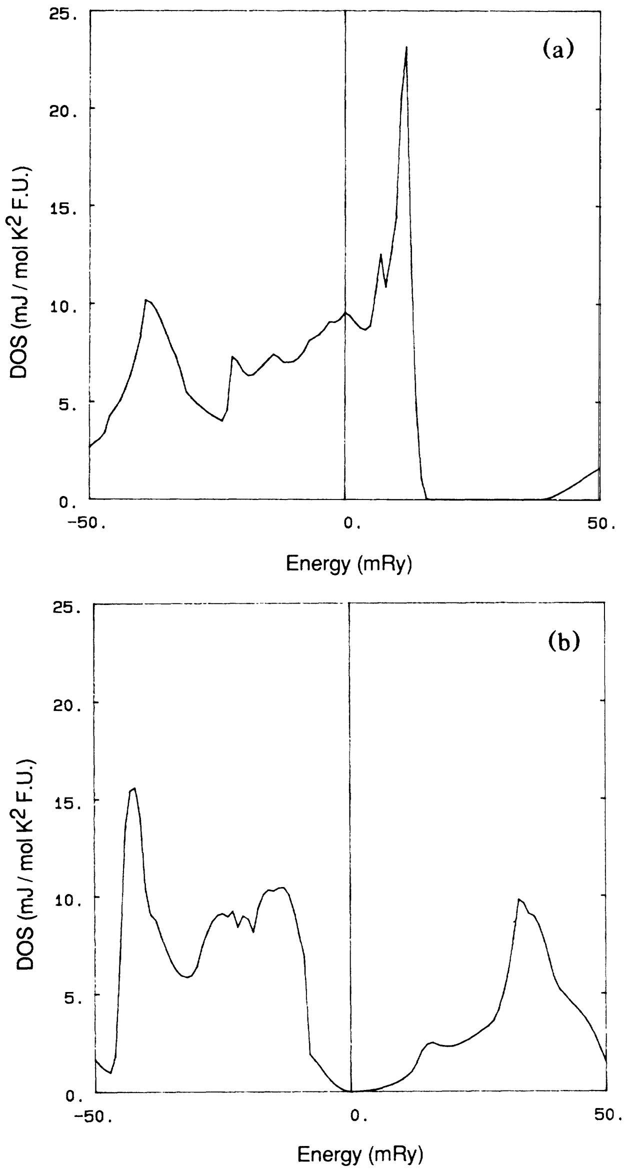

FIG. 1. Density of states [in (mJ/mol K^2)/(formula unit)] for CoO in a type-II AF state (a) with spin orbit only and (b) with orbital polarization. The Fermi energy is at zero.

had little effect on the electronic structure, although it does lead to a substantial enhancement of the orbital moment. In NiO, the band gap of about 0.33 eV is increased by only 0.03 eV when including orbital polarization. The inclusion of orbital polarization does boost the moment value close to its experimentally observed value of $1.77\mu_B$.[20] For FeO, the DOS was little affected by orbital polarization. An additional calculation was done with the z axis rotated onto the $\langle 111 \rangle$ direction. The orbital moment increased by 30%, indicating that the $\langle 111 \rangle$ direction is preferred over the $\langle 001 \rangle$ direction for the moment, as seen experimentally. As an additional test, the unit cell was elongated 0.8% along the $\langle 111 \rangle$ axis as seen experimentally, but this had little effect on the electronic structure. One might note that the calculated moment is already in excess of the experimental value of $3.32\mu_B$,[18] and so it would appear that the orbital moment is largely quenched, arguing against an orbital-polarization instability. Thus, the origin of the gap in FeO based on symmetry grounds has still to be resolved.

A related problem is the nature of the insulating gap in undoped La_2CuO_4. Spin-polarized band-structure calculations do not obtain a stable moment or an insulating state.[21] The author thus undertook calculations for tetragonal La_2CuO_4 using the orbital-polarization formalism, with the z axis along the experimentally observed moment direction (face-centered orthorhombic symmetry). The calculation included f states on the La sites and two empty spheres per formula unit as in Ref. 22, with a sphere radius of 2.2 a.u. for the Cu site. A standard spin-polarized calculation using an applied staggered field equivalent 3 mRy to start the calculation led to a spin moment of about $0.1\mu_B$, equivalent to what was obtained on the first iteration. This behavior indicates a metamagnetic state was formed, or the nonzero moment could be due to the sparse 30-k-point mesh used.[21] Turning on the orbital polarization with an assumed input orbital moment of $0.1\mu_B$ led to a rapid quenching of the orbital moment, and so no orbital instability was found.

Finally, a comment about the size of the Racah parameter B is in order. For the $\phi\phi$ term, B for up (down) spin in mRy are 14.4 (9.8) for FeO, 16.0 (12.8) for CoO, 17.5 (16.1) for NiO, and 19.5 (19.3) for La_2CuO_4. These values, of course, are sensitive to the sphere radius size chosen. Note that B increases with higher atomic number, consistent with increasing localization of the d electrons.

In conclusion, an orbital-polarization instability was found for CoO, leading to an insulating gap, in support of ideas earlier proposed by Terakura *et al.*[4] and Brandow.[2] Thus, it is now understood on symmetry grounds why there is an insulating gap in three of the metal oxides (MnO, CoO, and NiO). No such instability was found for FeO or La_2CuO_4. This indicates that a more sophisticated spin-orbital density-functional theory needs to be constructed in order to understand the nature of the insulating gaps in these two systems.

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