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# Crystal-field polarization and the insulating gap in FeO, CoO, NiO, and $La_2CuO_4$

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An orbital-polarization correction to local-spin-density (LSD) theory is developed in a crystal-field basis, and applied to FeO, CoO, NiO, and $La_2CuO_4$. The result is a substantial enhancement of the LSD band gap for NiO, and the creation of an insulating ground state for FeO, CoO, and $La_2CuO_4$.

The long-debated issue concerning the nature of the insulating gap in transition-metal oxides has intensified with the recent interest in high temperature, copper oxide superconductors. Despite the recent success of interpreting positron annihilation and angle-resolved photoemission data using band-structure calculations, there still exists considerable mistrust of band theory due to the failure to obtain an insulating, magnetic ground state in the parent compound, undoped $La_2CuO_4$. Moreover, in the transition-metal oxide series MnO, FeO, CoO, and NiO, band theory predicts insulating behavior only in MnO and NiO.

The standard approach to understanding this problem is to invoke a Mott-Hubbard (self-interaction) correction to band theory. In such a theory, occupied $d$ electrons see the potential due to $N-1$ $d$ electrons on a metal site, whereas unoccupied $d$ electrons see that due to $N$ $d$ electrons on the site. This leads to an energy discontinuity $U$ between these states, causing an insulating gap in solids, if broken symmetry (non-Bloch) solutions are used. Recently, a realistic self-interaction correction has been employed by Svane and Gunnarsson[1] which leads to reasonable gaps and magnetic moments for the entire transition-metal oxide series.

A difficulty, though, is that formally such a Mott-Hubbard correction is classified as a derivative-discontinuity correction to density functional theory,[2] meaning that the effective potential changes discontinuously across the gap. By definition, then, such a correction is an excited-state effect. Although it has been suggested that the Mott discontinuity could be responsible for 100% of the gap, this cannot be true in general, since the Mott correction assumes a well-defined distinction between occupied and unoccupied states, which is not possible if the underlying ground-state calculation gives metallic behavior (i.e., the conduction and valence bands would be intermixed). To circumvent this difficulty, one would like to obtain a gap at the level of a density-functional ground-state calculation (no matter how small) so as to define the Mott-Hubbard correction in an unambiguous fashion.

This would imply, then, that the problem with band theory in transition-metal oxides is due to the use of the local-spin-density (LSD) approximation. One problem with local density theory is that all $d$ electrons of a certain spin see the same effective potential. This also occurs for orbitally averaged Hartree-Fock theory, which is the usual form applied in solids. In fact, spin-polarized Hartree-Fock calculations for NiO yield almost identical results as LSD, such as a small band gap.[3] This suggests that one should look at open shell Hartree-Fock corrections. In atoms, open shell corrections are evaluated at the total-energy level. In solids, though, one needs the correction at the eigenvalue level to see the effect on the bands. In general, this would involve substantially more effort than a standard band calculation. If, though, one assumes that the correction is diagonal in an on-site basis, then the effort involved is no greater than an orbitally averaged calculation. Obviously, the better choice of basis one makes, the better the diagonality approximation is.

In the past, the open shell correction was assumed to be diagonal in a spherical-harmonic basis. This is the basic assumption of the orbital-polarization correction developed by Eriksson, Brooks, and Johansson for $f$ electrons, an approximate ansatz which proved successful in describing the $\alpha$-$\gamma$ phase transition in cerium.[4] Using a similar correction for $d$ electrons leads to an increased orbital moment for FeO and CoO, but no insulating gap.[5] For $d$ electrons, it turns out that one can write down a formal open shell expression in a spherical harmonic basis.[6] Utilizing such a correction, the author was able to obtain an insulating gap for both FeO and CoO,[7] but the orbital moments were much too large. In NiO, the same correction leads to a reduction in the gap as well as a grossly large orbital moment. These huge orbital moments come about from the assumption of diagonality of the correction in a spherical-harmonic (free-atom) basis, and thus miss the effect of crystal-field quenching of the orbital moment. Obviously, a better approximation can be made if a basis appropriate to cubic symmetry is used.

In this paper, an orbital-polarization correction will be derived utilizing a crystal-field basis. The correction is valid for both high-spin and low-spin configurations. This formalism is then applied to NiO, $La_2CuO_4$, FeO, and CoO.

To derive an orbital-polarization correction which is assumed to be diagonal in a crystal-field basis, one looks at the various direct and exchange integrals between different crystal-field orbitals (Ballhausen,[8] p. 76). The total energy is then constructed, and the average interaction term (energy of the filled spin shell times the ratio of the number of electron pairs in the configuration to that in the filled shell), which is assumed to be included in local-spin-density theory, is subtracted out. The energy difference for like-spin electrons only involves the Racah $B$ parameter, which is a linear combination of $F_2$ and $F_4$

Slater integrals. For unlike-spin electrons, both the Racah $B$ and $C$ parameters are involved ($C$ is proportional to $F_4$).

An easy case is the interaction energy between like-spin electrons for cubic symmetry. One can easily see from Ballhausen's book that this is

$$\Delta E^{ss}=[-4n_e^s(n_e^s-1)-2.5n_t^s(n_t^s-1)\\ -2n_e^s n_t^s+1.75n^s(n^s-1)]B^{ss}\,, \tag{1}$$

where $n_e^s$ and $n_t^s$ is the number of $e_g$ and $t_{2g}$ electrons with spin $s$ and $n^s$ is their sum (the last term is the average interaction term). $B^{ss}$ is the Racah parameter $B$ involving radial functions of spin $s$. For unlike spins, we have

$$\Delta E^{ud}=(2n_e^u n_e^d+5/3n_t^u n_t^d+n_e^u n_t^d+n_t^u n_e^d-7/5n^u n^d)C^{ud}\,, \tag{2}$$

where $C^{ud}$ is the Racah parameter $C$ between up- and down-spin radial functions, with the total-energy correction being a sum of $\Delta E^{uu}$, $\Delta E^{dd}$, and $\Delta E^{ud}$.

The energy expression above (without subtracting out the average interaction term) gives the correct ground-state energy for every low-spin and high-spin $d$ configuration in a cubic environment (see Griffith,[6] p. 234).

For tetragonal symmetry, the cubic averaging of the interaction between $t_{2g}$ and $e_g$ electrons implicit in Eqs. (1) and (2) is not done, and thus in $\Delta E^{ss}$ we replace

$$-2n_e^s n_t^s \rightarrow n_1^s(-8n_3^s+n_4^s+n_5^s)+n_2^s(4n_3^s-5n_4^s-5n_5^s)\,, \tag{3}$$

where 1, 2, 3, 4, and 5 stand for $3z^2-r^2$, $x^2-y^2$, $xy$, $xz$, and $yz$, respectively. For the $ud$ term, we now have

$$\begin{aligned}\Delta E_B^{ud}&=(2n_1^u-2n_2^u-2n_3^u+n_4^u+n_5^u)\\ &\quad\times(2n_1^d-2n_2^d-2n_3^d+n_4^d+n_5^d)\,,\\ \Delta E_C^{ud}&=2n_1^u n_1^d+2n_2^u n_2^d+2n_3^u n_3^d\\ &\quad+(n_4^u+n_5^u)(n_4^d+n_5^d)-2/5n^u n^d\,,\end{aligned} \tag{4}$$

where $\Delta E^{ud}=\Delta E_B^{ud}B^{ud}+\Delta E_C^{ud}C^{ud}$.

The eigenvalue shifts for the orbital $n_i^s$ ($i$, the crystal-field orbital; $s$, the spin) is then found by differentiating $\Delta E$ by $n_i^s$. This correction, diagonal in the crystal-field basis, is then transformed back into a $Y_{lm}$ basis so as to use it in the secular matrix for an linear muffin-tin orbital band code. The correction is not diagonal in the $Y_{lm}$ basis (there are off-diagonal terms involving $Y_{2,2}$ and $Y_{2,-2}$ for the cubic and tetragonal cases discussed above).

The above formalism is applied as a correction to LSD calculations for NiO and $La_2CuO_4$ in their antiferromagnetic states (for specific details of the band calculations, see Ref. 5). For NiO, a double-sized secular matrix is solved so as to include the orbital moment. This moment is taken to point along one of the cubic axes (so the irreducible wedge is only $\frac{1}{4}$ of the zone). For $La_2CuO_4$, no spin-orbit effects were included. The symmetry for that case is face-centered orthorhombic (so the wedge is $\frac{1}{8}$ of the zone). Sixty $k$ points in the wedge were used in each calculation. $n_i^s$ is determined by integrating the charge densities of occupied LMTO eigenvectors inside the metal sphere, with the energy derivative terms not included since the radial functions connected with them are different. This is an approximation which needs to be checked for each specific case. For the above oxides, the $d$ orbitals which are completely filled have occupations ranging from 0.94 to 0.96, so the approximation is reasonable. For other cases, a tight-binding formalism may be necessary. Although the eigenvalue correction is found without using the energy derivative terms, when the matrix element of the eigenvalue correction is constructed for the secular matrix, different variants of $B$ and $C$ involving various combinations of the $l=2$ radial function and its energy derivative need to be calculated. Finally, the occupation numbers are taken to have tetragonal symmetry for the purposes of calculating the orbital-polarization correction (for NiO, the $n_i^s$ turn out to have cubic symmetry to within 0.1% despite the presence of the orbital moment).

In Table I, results are shown for NiO and $La_2CuO_4$, with density of states in the vicinity of the gap plotted in Fig. 1. For NiO, $B^{ud}$ is 0.15 eV and $C^{ud}$ is 0.56 eV; for $La_2CuO_4$, they are 0.16 eV and 0.60 eV, respectively. Note that for NiO, the spin moment on the Ni site has increased, bringing it into closer alignment with the experimental value of $1.77\mu_B$. Moreover, the band gap has increased from 0.3 to 1.4 eV. For the case of $La_2CuO_4$, a magnetically polarized ground state is found with a moment of $0.3\mu_B$ on the Cu site, and a gap of 0.2 eV. The gap value for both cases is consistent with the fact that most of the size of the gap is due to the Mott-Hubbard correction.

We now turn to a discussion of the orbital-polarization correction to the gaps and moments. For NiO, the important quantity for the gap is the splitting between occupied $t_{2g}$ down spin and unoccupied $e_g$ down spin. The orbital-polarization correction leads to an increased splitting of 1.0 eV, all of this due to the like-spin terms. For the moment, an increased exchange splitting of 1.4 eV is found for the $e_g$ states ($\frac{2}{3}$ due to like-spin terms, $\frac{1}{3}$ due to unlike-spin terms) and 0.6 eV for the $t_{2g}$ states ($\frac{1}{2}$ due to like-spin terms, $\frac{1}{2}$ due to unlike-spin terms). For the case of $La_2CuO_4$, the important quantity for both the gap and the moment is the splitting between $x^2-y^2$ up- and

TABLE I. Results of orbital-polarization calculations for FeO, CoO, NiO, and $La_2CuO_4$. LSD is the local-spin-density result, OP the orbital-polarization one. Tabulated are the spin and orbital moments ($\mu_B$) on the metal site, and the band gap (eV). No gap or moment is found within LSD for $La_2CuO_4$. For FeO, the moment is taken to be along ⟨111⟩, for the other cases along ⟨001⟩.

| | Spin | Orbital | Gap |
|---|---|---|---|
| FeO LSD | 3.47 | 0.16 | · · · |
| FeO OP | 3.57 | 0.79 | 0.4 |
| CoO LSD | 2.38 | 0.25 | · · · |
| CoO OP | 2.52 | 1.01 | 0.4 |
| NiO LSD | 1.08 | 0.15 | 0.3 |
| NiO OP | 1.43 | 0.12 | 1.4 |
| $La_2CuO_4$ OP | 0.30 | · · · | 0.2 |

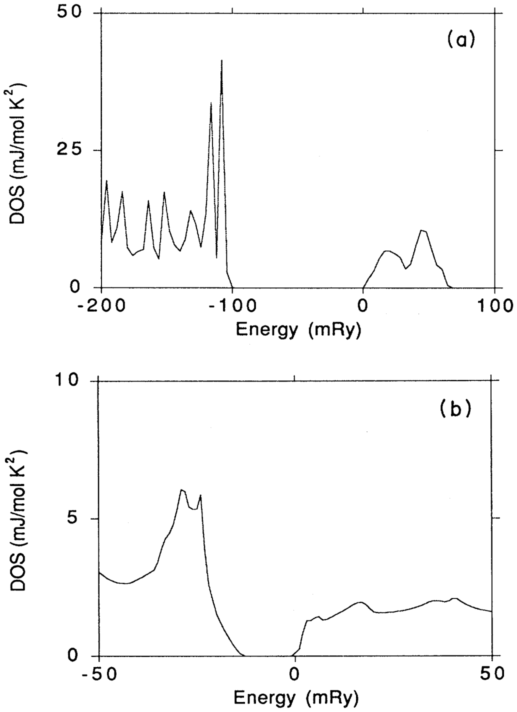

FIG. 1. Density of states (mJ/mol $K^2$/f.u.) for (a) NiO and (b) $La_2CuO_4$ in the vicinity of the gap from the orbital-polarization calculations.

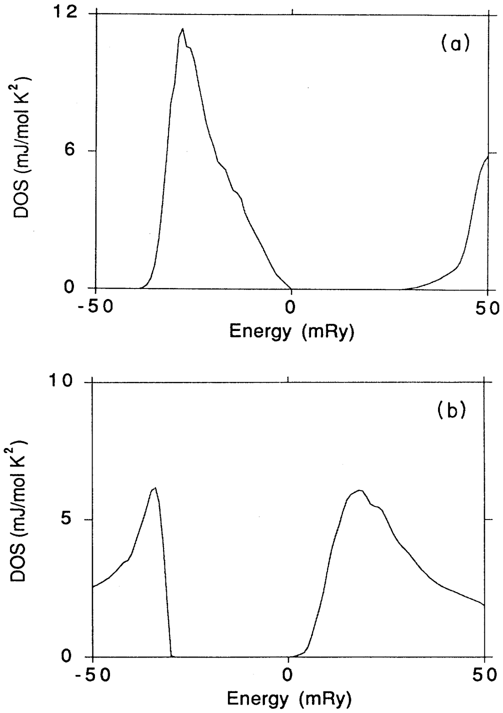

FIG. 2. Density of states (mJ/mol $K^2$/f.u.) for (a) FeO and (b) CoO in the vicinity of the gap from the orbital-polarization calculations.

$x^2-y^2$ down-spin orbitals. The orbital polarization increases this splitting by 0.75 eV ($\frac{1}{3}$ due to like-spin terms, $\frac{2}{3}$ due to unlike-spin terms). Virtually all of this is a negative shift of the up-spin eigenvalue, leading to an increased occupation of that orbital. Physically, the orbital-polarization correction is attempting to drive the system towards full spin polarization, but only partial polarization is achieved due to the strong hybridization with the oxygen $p$ electrons.

For the case of FeO and CoO, one must take into account the profound effect of the orbital moment on the crystal-field basis. In particular, an orbital moment instability is expected in the $t_{2g}$ band ($e_g$ states do not orbitally polarize). To accomplish this, we exploit a well-known isomorphism between $t_{2g}$ states and $p$ states which is discussed in Sect. 9.5 of Griffith's book,[6] and use as basis functions for $t_{2g}$ $Y_{2-1}$, $xy$, and $Y_{21}$ (corresponding to $m_l=-1,0,1$ for $p$ states). The energy for $p$ states, given on p. 80 of Griffith's book,[6] is then transformed by replacing $F_0$ by $A+\frac{5}{3}C$ and $F_2$ by $B+C/3$. This energy expression is (ignoring the $A$ Racah term, which drops out when the average interaction is subtracted out)

$$E_t=5/6n_t(n_t-1)C-[2.5n_t^2-10n_t+1.5L_t(L_t+1)+6S_t(S_t+1)](B+C/3) \qquad (5)$$

where $n_t$ is the total number of $t_{2g}$ electrons, and $L_t$ and $S_t$ are the $z$ component of the orbital and spin moment for the $t_{2g}$ states (note, $2S_t$ is equal to $n_t^u-n_t^d$). As this expression is valid for all values of the spin, a spin averaged $B$ and $C$ are assumed. This expression is then used as a replacement for the interaction between $t_{2g}$ electrons given in Eqs. (1) and (2). Finally, the basis set above assumes that the quantization axis is along a ⟨001⟩ direction. For FeO, the actual quantization axis is along ⟨111⟩. The basis set for $e_g$ and $t_{2g}$ in this case is given on p. 132 of Sugano, Tanabe, and Kamimura.[9] Details of the band calculations, similar to NiO, can be found in Ref. 5.

Results using this expression for FeO and CoO are shown in Table I and Fig. 2. Note that not only are insulating gaps obtained in both cases, but the orbital moments are much more reasonable than in Ref. 7, and, in fact, are close to the estimates of Kanamori.[10] The reduction in orbital moment as compared to a calculation using a spherical-harmonic basis is due to the fact that only $t_{2g}$ states are allowed to orbitally polarize as appropriate for cubic systems. The gaps are due to the splitting of the $t_{2g}$ band into $Y_{2-1}$, $xy$, and $Y_{21}$ subbands. The other intriguing result is that for FeO, a gap is obtained if the orbital moment lies along the correct ⟨111⟩ direction, whereas for a moment along the ⟨001⟩ direction, only a pseudogap is obtained (with a density of states at the Fermi energy of 8% relative to LSD). Therefore, an intimate connection is seen between the preferred moment direction and the electronic structure, a rather unusual finding.

In summary, an orbital polarization (open shell Hartree-Fock) correction to local-spin-density theory in a crystal-field basis leads to a stabilization of the LSD band gap in NiO, and to the creation of an insulating ground state in FeO, CoO, and $La_2CuO_4$. This indicates that although the size of the insulating gap in these oxides is determined by the Mott-Hubbard correction, the presence or absence of a gap is determined by Hund's rule effects.

*Note added in proof.* Calculations have now been done for $La_2CuO_4$ where the spin-polarization part of the LSD exchange energy has been replaced by the Hartree-Fock form $-DS(\mathbf{S}+1)$ where $D=7/6(5/2B+C)$. This results in a gap of 0.64 eV and a moment of 0.51 $\mu_B$ on the Cu site. Without the orbital polarization, a gap of 0.46 eV and a moment of 0.44 $\mu_B$ is found.

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