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Generalized-gradient-approximation description of band splittings in transition-metal oxides and fluorides

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The local-spin-density approximation yields a metallic ground state for the antiferromagnetic insulators CoO, FeO, FeF_2, and CoF_2. By using the generalized gradient approximation (GGA) we find the difluorides to be insulators, while in CoO the GGA splits the bands near E_F and opens a direct gap, but a small indirect band overlap remains. For FeO a significant improvement is found but not quite enough to make it an insulator. The magnetic moments and gaps increase. The GGA improves angular (and also in-out) correlations and thus affects the energy bands, a feature in addition to the total-energy improvement.

I. INTRODUCTION

The local-spin-density approximation[1] (LSDA) for treating exchange and correlation effects within the density-functional theory (DFT) is well established in first-principles calculations for describing the ground-state properties of solids. Although the LSDA has been very successful, there are shortcomings and failures that call for an improvement of it. For example the cohesive energies of most solids and the binding energy of molecules are overestimated and the respective equilibrium distances are often too short;[2] the ground state of iron is predicted[3] to be the nonmagnetic fcc rather than the ferromagnetic bcc phase observed experimentally; the insulating antiferromagnetic transition-metal oxides (like MnO, CoO, or NiO) are computed to be metallic or show only a tiny gap,[4] while the undoped parent compounds of the high-T_c superconductors (such as $YBa_2Cu_3O_6$, La_2CuO_4, and $CaCuO_2$) are nonmagnetic metals instead of antiferromagnetic (AF) insulators.[5,6] Since the LSDA is based on results of the homogeneous electron gas, it is natural to try gradient expansions to improve it, but a straightforward second-order expansion violates important sum rules.[7] Recently, however, various forms of generalized gradient approximations (GGA) for the exchange and/or the correlation energy were introduced[2,7,8,9] which yield better cohesive energies and equilibrium distances, at least for molecules and solids containing light atoms up to the 3*d* elements. These results have dramatically changed the view of quantum chemists who now often use DFT (with the Becke-Perdew[2,9] GGA) in their calculations of large molecules. The applications of GGA to solids has led to the correct ground state of Fe (Refs. 10–12) and to improved equilibrium lattice parameters for many solids.[2,13] However, it was found that in systems containing heavier elements (such as Pd), where already LSDA predicts good equilibrium volumes, GGA yields too large values[13,14] and in certain cases overestimates magnetism.[14]

Leung, Chan, and Harmon[12] reported for the transition-metal oxides almost no difference in the band structures using LSDA or GGA potentials and thus they argued that for these highly correlated systems GGA [in the Perdew-Wang (PW-I) version[8]] is insufficient and other techniques must be used. For example, self-interaction corrected (SIC) LSDA calculations[15,16] found localization of the metal (*M*) *d* states and a large band gap between occupied O 2*p* and unoccupied *M* 3*d* states. The occupied *M* 3*d* states were found below the O 2*p* band in contrast to LSDA results, so that these systems were described as charge-transfer insulators instead of Mott-Hubbard insulators. A different approach was taken by Norman,[17] who applied an *ad hoc* orbital polarization correction (OPC) in a proper basis and obtained an insulating ground state for FeO and CoO. He argued that Hund's second rule, which is not properly taken into account in LSDA, must be satisfied to yield an insulator.

In this paper, we show that a careful and complete implementation of GGA can split bands to yield insulators. We investigate the electronic structure of AF solids, the monoxides (MnO, FeO, CoO, and NiO) and difluorides (MnF_2, FeF_2, CoF_2, and NiF_2) of transition metals (TM), by means of the full-potential linearized-augmented-plane-wave (LAPW) method[18] using GGA as parametrized by Perdew *et al.*[2] All Fe and Co compounds are metallic (Mn and Ni compounds have a tiny gap) when calculated within LSDA, but we show that GGA makes the relevant bands more localized and splits them such that these compounds become insulators or develop at least a band structure with a direct gap and a small indirect band overlap. Thus we demonstrate that GGA not only affects and improves the total energy, but can alter the energy band structure significantly.

II. METHOD

We use the full-potential LAPW method as embodied in the WIEN93 code[18] in a scalar relativistic version without spin-orbit coupling. In LSDA the exchange-correlation energy (E_{xc}) is just a functional of the local electron spin densities $n_\uparrow$ and $n_\downarrow$

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$$E_{\mathrm{xc}}^{\mathrm{LSDA}}[n_\uparrow,n_\downarrow]=\int n\epsilon_{\mathrm{xc}}(n_\uparrow,n_\downarrow)d^3r\ ,$$

while in GGA it is a functional of these densities and their gradients

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n_\uparrow,n_\downarrow]=\int f(n_\uparrow,n_\downarrow,\nabla n_\uparrow,\nabla n_\downarrow)d^3r\ .$$

We have implemented this formalism for E_{xc} and the corresponding exchange-correlation potential V_{xc} (which involves higher derivatives) into our LAPW code using the PW-II form.[2] Since in the WIEN93 code the potential and charge density is described without any shape approximations,[18] we can compute all required gradients; inside the *atomic spheres* we obtain radial gradients (based on a spline interpolation on a dense r mesh) as well as angular gradients (analytically) of the charge density, and include both in the calculation of V_{xc} and E_{xc}; in the *interstitial region* the density is fitted with a second-order polynomial from which the gradients are obtained analytically.

We use a well-converged basis of about 500 (800) plane waves for the TM oxides (fluorides) corresponding to $R_{mt}K_{\max}=8.0$ (with atomic sphere radii R_{mt} of 2.0 and 1.75 a.u. for the TM and nonmetal atoms, respectively) and include local orbitals[19] for TM $3s,3p$ and O $2s$ orbitals. The charge density and potentials are expanded into lattice harmonics up to $L=6$ inside the spheres and into a Fourier series of about 600 (900) K stars for the TM-oxides (fluorides) in the interstitial region. The Brillouin-zone integration was done with a modified tetrahedron method using 60 special k points.

III. TM OXIDES

The TM oxides mentioned above crystallize in the sodium chloride structure, and some show small distortions which we neglect. They are insulators with an antiferromagnetic type II structure (Fig. 1), where the spin alignment is parallel in the (111) plane. This AF-II structure can be described with a doubled, rhombohedral unit cell leading to space group $R\bar{3}m$. In Fig. 2 we show for CoO (at the experimental volume) the band structure around the Fermi energy (E_F) and some partial densities of states (DOS) computed with GGA or LSDA. For details of LSDA results the reader is referred to the paper by Terakura *et al.*,[4] whose results agree well with our present LSDA calculation. In the LSDA band structure (dotted lines) there is no indication of a gap, whereas using GGA the bands at E_F change drastically and split into subbands (full lines) producing a direct gap of almost 1 eV at, for example, Γ or Z, while a small indirect overlap of bands between different **k** regions remains. In the cubic case the d levels split into e_g and t_{2g} states, whereas in the trigonal AF-II structure[4] of CoO the "t_{2g}" bands are further split into bands corresponding to a twofold e_g (denoted below as e_g') and an a_{1g} symmetry (Fig. 2). The LSDA-DOS shows a strong mixing between e_g' and a_{1g} symmetry indicating that the crystal-field interactions, where t_{2g} is still a good description, dominates. In the GGA-DOS, however, the bands with a_{1g} symmetry have been raised (lowered) in energy for the spin-down (spin-up) states, and are separated from e_g' due to angular correlations as will be shown below.

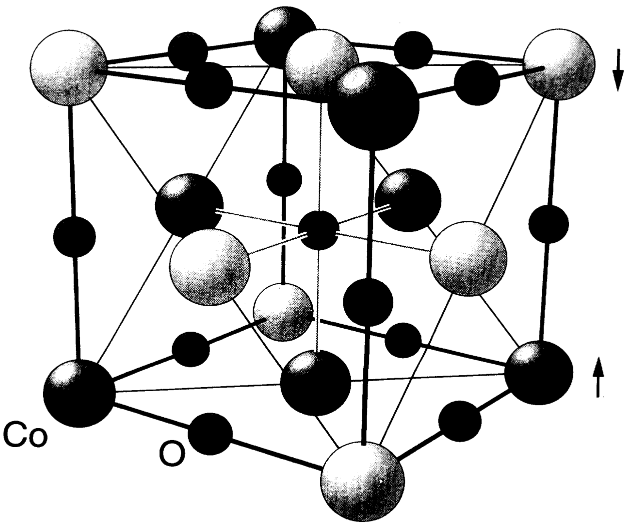

FIG. 1. Antiferromagnetic AF-II structure of CoO.

After having described the effect we now analyze the calculations in order to find the physical origin of these shifts. For that purpose we compare the spin-up densities $n_\uparrow$ of CoO between LSDA [Fig. 3(a)] and GGA [Fig. 3(b)]. We show a section of the (010) plane, where the two types of Co atoms, Co(1) and Co(2), are displayed with an O atom in between (corresponds to edge in Fig. 1). The spin-up density $n_\uparrow$ is the majority spin for Co(1), but the minority for Co(2). Both Co(1) and O [in Fig. 3(a) and 3(b)] have an almost spherically symmetric $n_\uparrow$ while at Co(2) an anisotropy with t_{2g} symmetry appears. Since the t_{2g} states split into e_g' and a_{1g} subbands according to the trigonal symmetry of the AF-II structure, the density around a Co site does not need to have fourfold symmetry, but in LSDA this fourfold character remains, to a large extent (with maxima at 5.2 and 4.8 e Å^{-3}), consistent with the fact that the partially filled t_{2g} bands are hardly split into subbands (Fig. 2). In GGA, however, this anisotropy around Co(2) is enhanced (with maxima at 5.8 and 4.1 e Å^{-3}), since only the e_g' subbands are occupied, while the a_{1g} band remains almost empty [Fig. 3(b)]. The lobe with the smaller (larger) peak points towards a Co with the same (opposite) spin orientation (Fig. 1).

We try to find the origin of these changes in the densities by investigating the exchange correlation potential V_{xc} and thus plot the difference $\Delta V_{\mathrm{xc}}=V_{\mathrm{xc}}^{\mathrm{GGA}}-V_{\mathrm{xc}}^{\mathrm{LSDA}}$ for the spin-up electrons [Fig. 3(c)]. At the Co(1) and the O site the corresponding densities are almost spherically symmetric and thus in ΔV_{xc} only radial density gradients show up with in-out correlation, which causes the wave functions to become more localized, as has been discussed by Langreth and Mehl.[7] At the Co(2) position, however, the density is no longer spherically symmetric so that angular correlations (gradients) become effective. ΔV_{xc} shows a strong attractive potential of -180 mRy pointing along 45° towards Co(1) with the opposite spin (see

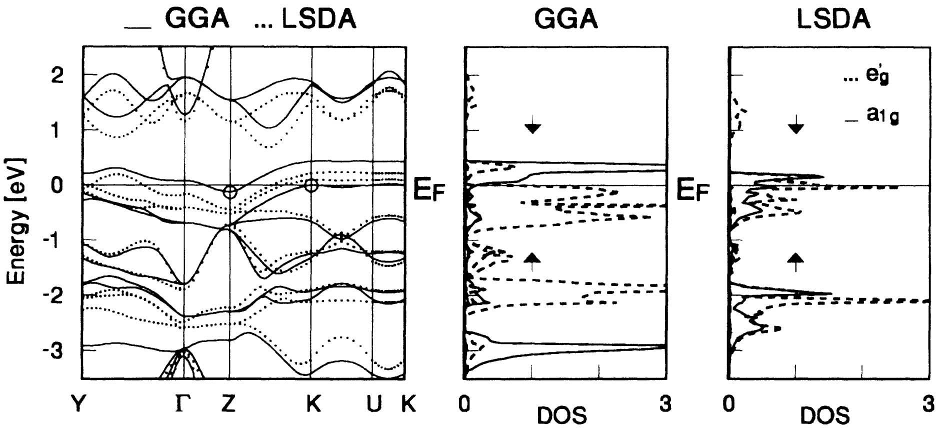

FIG. 2. Band structure (left panel) and symmetry decomposition of the t_{2g} DOS of CoO (in states per eV) for GGA and LSDA.

Fig. 1) in contrast to the perpendicular component towards Co(2) with the same spin. Therefore, angular gradients in GGA enhance the asphericities and lower V_{xc} for the e_g' symmetry, while V_{xc} remains about the same as in LSDA for the a_{1g} symmetry. This attractive potential (which is only partly compensated by the Coulomb potential) lowers the corresponding bands with respect to the others, so that the latter split off and become unoccupied. Thus GGA yields an effect similar to Norman's *ad hoc* orbital polarization corrections,[17] but from first principles. It should be mentioned that the asphericity in V_{xc} has been seen before, but for example in the work on iron by Singh, Pickett, and Krakauer[11] it did not play a crucial role in describing the stabilization of the magnetic state (bcc versus fcc).

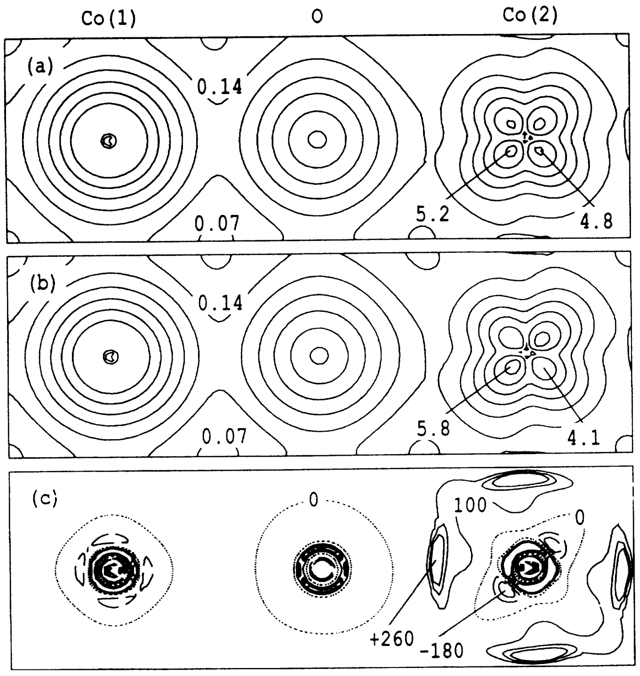

FIG. 3. Spin-up electron density $n_\uparrow$ of (a) LSDA and (b) GGA calculation with contour values from 0.07 to 4.48 e Å^{-3} (in multiples of 2); (c) spin-up $\Delta V_{xc} = V_{xc}^{GGA} - V_{xc}^{LSDA}$; negative contours (dashed), zero (dotted) and positive contours (full line) with contour lines at 0, ±100, ±150, and ±200 mRy.

As mentioned in the Introduction, Leung, Chan, and Harmon[12] did not find any effect on the energy bands of TM oxides in contrast to the present work. This calls for an explanation. We have repeated our calculations using the same PW-I version[8] of GGA as in their work, but still obtain substantial changes of the energy bands and almost the same results as with the more recent GGA form. On the other hand, when we perform a GGA calculation omitting all angular gradients inside the atomic sphere but keeping just the radial gradients, we obtain very similar energy bands as with LSDA. This might explain why Leung, Chan, and Harmon[12] did not find an improvement of GGA over LSDA and these test calculations illustrate the importance of angular gradients.

It has been demonstrated in several papers in the literature that GGA affects the total energy and thus cohesive properties. Figure 4 shows the total energy as a function of the lattice parameter for LSDA and GGA. The LSDA equilibrium lattice constant is about 3% too small (as in many other systems), while GGA leads to almost perfect agreement between theory and experiment. The bulk modulus obtained within LSDA is 260 GPa and

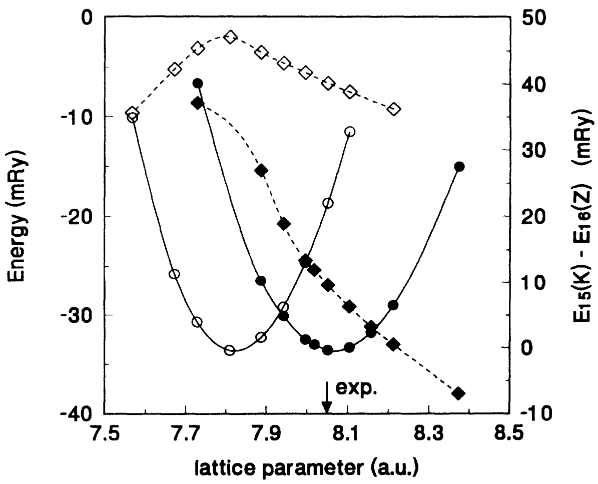

FIG. 4. Relative total energies (circles) adjusted at the minimum and band overlap (gap) $\Delta E = E_{15}(K) - E_{16}(Z)$ (diamonds) of CoO as a function of lattice constant for LSDA (open symbols) and GGA (closed symbols).

drastically decreases to 180 GPa within GGA, very close to the experimental value[20] of 190 GPa. We have repeated the calculation with GGA omitting all angular gradients. Although in this case the energy bands differ from the full GGA bands and are very similar to the LSDA bands as emphasized above, the equilibrium lattice constant is almost the same (0.5% smaller) as that of the full GGA. This demonstrates that radial gradients affect mainly the total energy, while angular gradients can modify the energy bands.

The main emphasis of the present paper is on the energy bands in connection with the metal-insulator behavior. We can take the energy difference ΔE between band 15 at K and band 16 at Z (marked by circles in the GGA band structure in Fig. 2) to define a good measure for the indirect band overlap (or gap). In the LSDA calculations ΔE is about 40 mRy, positive (overlap), and shows only a small volume dependence. For GGA, however, ΔE decreases strongly with volume reaching a negative value (gap) at a lattice parameter about 2% larger than equilibrium, where one even obtains an insulating ground state. We did not perform any calculations with the small tetragonal distortion observed experimentally ($c/a=0.988$),[21] which could lead to an insulator within GGA, but probably not in LSDA.

If the band splitting of the t_{2g} manifold in FeO were qualitatively similar to CoO a metallic state would occur, since FeO has one valence electron less than CoO and this would lower the Fermi energy into the e_g' subband which can accommodate two electrons. In order to make FeO an insulator within a band picture the ordering of the onefold and twofold subbands must be reversed with respect to CoO, so that the spin-up a_{1g} subband is the lower (fully occupied) of the t_{2g} complex, while the higher lying e_g' subband remains unoccupied. In both LSDA and GGA this is not the case, but with GGA convergence is poor, indicating that the metallic and the insulating configurations are almost degenerate. In fact, we can stabilize the a_{1g} band below the e_g' by artificially adding and subtracting 5 mRy to the V_{40} term of the potential for the two spin directions, respectively.[6] A shift of 20 mRy already opens a gap, while within LSDA shifts of 50 and 100 mRy would be needed to obtain similar effects. Better GGA versions with more emphasis on angular correlations (or Hund's second rule) might solve this in future. The present version goes in the right direction, but is not sufficient to yield the correct ground state.

LSDA calculations for MnO and NiO yield an insulating ground state, but the gap (Table I) and the spin-magnetic moments (Table II) are smaller than the experimental data. Using GGA the magnetic moments are slightly enlarged, approaching experimental, SIC,[15,16] and OPC[7] results. Note that the choice of atomic sphere radii (although it is not crucial in our full-potential calculation) determines the attribution of the spin density to a particular atom and thus the respective magnetic moment depends on R_{mt}, e.g., for MnO a calculation with $R_{\mathrm{Mn}}=2.0$ (2.3) a.u. yields a moment of $3.72\mu_B$ ($4.28\mu_B$).

TABLE I. Energy gap [eV] according to our LSDA and GGA calculations and comparison to literature.

	LSDA	GGA	SIC(OPC)	Exp.
MnO	1.0 (0.8[a])	1.4	3.98[a]	3.6–3.8[b]
NiO	0.4 (0.2[a])	1.2	2.54[a] (1.4[c])	3.0[d],4.3[e]
MnF_2	2	2.4		
FeF_2	0	0.4		
CoF_2	0	0.6		
NiF_2	0.8	1.4		

[a]Reference 15.
[b]Reference 26.
[c]Reference 17.
[d]Reference 23.
[e]Reference 22.

Within density functional theory it is well known that the energy bands (Kohn-Sham eigenvalues) do not represent excitation energies (gaps) but nevertheless they are often used for that purpose as a first approximation. Using GGA the band gaps increase, e.g., in NiO from 0.4 to 1.2 eV, which is close to the results of Norman[17] and thus is no longer a small fraction of the experimental gap of 3.0–4.3 eV.[22,23] The nature of the gap is widely discussed: SIC calculations find the occupied M $3d$ states below the O $2p$ states,[15,16] while we find them above the O-$2p$ bands and near E_F in both LSDA and GGA. The experimental results are ambiguous but we want to stress that d-d transitions are dipole forbidden and can only be seen at small excitation energies.[23]

IV. TM DIFLUORIDES

Other compounds where the metal-insulator problem occurs are the AF TM difluorides, which crystallize in the rutile structure. Some of them, namely MnF_2 and NiF_2, have recently been investigated using LSDA calculations and an insulating ground state in agreement with experiment was obtained.[24] For FeF_2 (Fig. 5) and CoF_2, however, LSDA leads to metals, where E_F lies in the middle of the t_{2g} manifold (in the rutile structure the TM atoms are coordinated by F atoms forming a slightly distorted octahedron[25]). These t_{2g} states form three subbands with d_{xy}, d_{xz+yz}, and d_{xy-yz} symmetry.[25] The GGA band structure of FeF_2 (Fig. 5) and the correspond-

TABLE II. Spin-magnetic moments [μ_B] according to our LSDA and GGA calculations and comparison to literature.

	LSDA	GGA	OPC	SIC	Expt.
MnO	3.72 (4.45[a])	4.15		4.49[b]	4.58[c],4.79[d]
FeO	3.33 (3.43[a])	3.38	3.57[e]	3.54[b]	3.32[d]
CoO	2.36 (2.35[a])	2.42	2.52[e]	2.53[b]	3.35[f],3.8[d]
NiO	1.21 (1.09[a])	1.38	1.43[e]	1.53[b]	1.64[g],1.9[c]
MnF_2	4.43	4.47			
FeF_2	3.47	3.51			3.75[h]
CoF_2	2.54	2.62			
NiF_2	1.56	1.64			1.61[i]

[a]Reference 4.
[b]Reference 15.
[c]Reference 27.
[d]Reference 28.
[e]Reference 17.
[f]Reference 29.
[g]Reference 30.
[h]Reference 31.
[i]Reference 32.

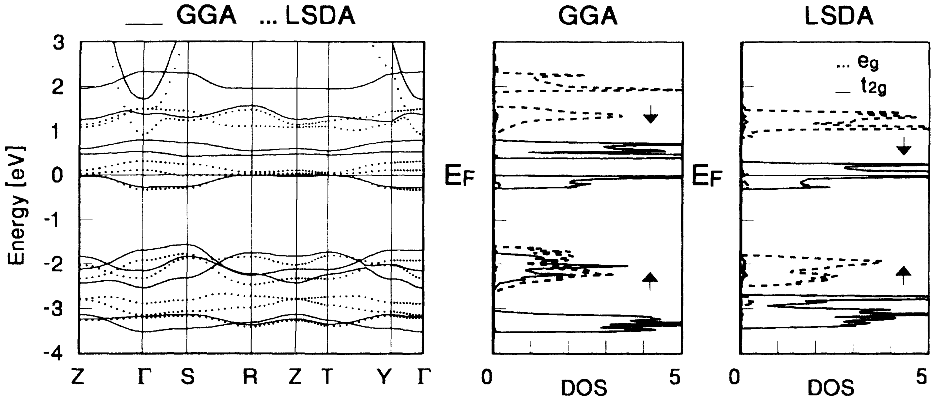

FIG. 5. Band structure (left panel) and symmetry decomposed DOS of FeF_2 (in states per eV) for GGA and LSDA.

ing DOS show that for spin-down electrons one band from the t_{2g} complex, namely, that with d_{xy} symmetry, is lowered and splits off opening up a gap of about 0.5 eV. (Note that for spin-up electrons the corresponding band moves up about 1 eV mixing into the two e_g bands.) For CoF_2 (not shown here) the GGA lowers two of the t_{2g} subbands (with d_{xy} and d_{xy+yz} symmetry) below E_F leading to a gap of about 0.5 eV. An analysis of V_{xc} (similar to that of CoO) shows that again angular gradients are responsible for this effect.

Similar to the TM-oxide (MnO and NiO) results, LSDA calculations for MnF_2 and NiF_2 yield an insulating ground state, but the gap is very small (Table I). Using GGA the gap is increased and the spin-magnetic moments are in agreement with the few experimental data available (Table II).

V. DISCUSSION AND CONCLUSIONS

We found that GGA yields a significant improvement over LSDA calculations for the metal-insulator problem when angular gradients are taken into account, while the radial gradients alone are insufficient. We applied these gradient corrections self-consistently, so that V_{xc} can shift some relevant energy subbands leading to more localized bands and opening a (direct) gap. For example, we find FeF_2 and CoF_2 to be insulating, whereas a standard LSDA calculation fails (making them metallic); for MnO and NiO the gap is enlarged, while for CoO a direct gap opens but a small indirect overlap remains. Note that in connection with magnetic instabilities Singh and Pickett[6] applied GGA to $CaCuO_2$ and found that it moves the system towards an AF solution but the corrections are too small to produce the AF ground state.

We conclude that radial gradients (in-out correlations) affect mainly the total energy and thus are important, for example, for cohesion or thermochemical properties, while the angular gradients (angular correlations) can shift and localize energy subbands selectively according to the magnetic quantum number *m* obeying Hund's second rule. Thus the important orbital polarizations, which Norman[17] has introduced on an *ad hoc* basis, come out naturally (but still too weak) in GGA. In LSDA there is a tendency to reduce charge asphericities, since the electron-electron Coulomb repulsion often dominates over exchange-correlation contributions, while GGA includes nonlocal effects that can enhance such asphericities. Therefore, GGA must be used within the self-consistency cycle rather than as a perturbation correction at the end of a calculation. Already the present version of GGA yields for certain systems substantially better results, but further work is needed to improve the specific form of GGA. The present results suggest trying further improvements by satisfying additional constraints mainly on V_{xc} rather than on the related E_{xc} as often done in the literature. GGA does not solve all difficulties occurring in LSDA, but can already lead to better results in solid-state and molecular calculations.

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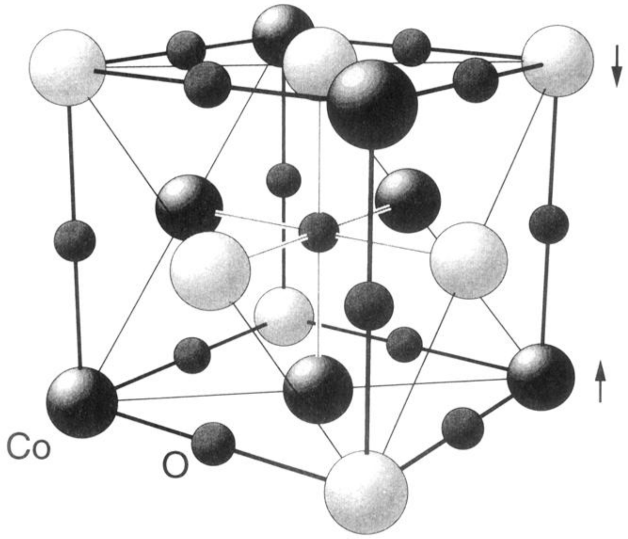

FIG. 1. Antiferromagnetic AF-II structure of CoO.