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Electronic structure of the antiferromagnetic *B*1-structured FeO

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Density functional theory (DFT) famously fails to correctly describe the electronic band structure of Mott insulators, such as FeO. Here, we present calculations on the structural, elastic, and electronic properties of antiferromagnetic, NaCl-structured (B1) FeO, employing hybrid functionals that combine fractions of the Becke and Fock exchange in combination with the Lee-Yang-Parr correlation functional. We find that in detail different properties of FeO require the inclusion of different amounts of Fock exchange in order for the simulation to reproduce the experimental values, correctly, e.g., geometry, band gap, and elastic constant; but in general between 30%–60% Fock-exchange gives a good description of lattice parameters, bulk modulus as well as the electronic structure, and this approach is therefore an alternative to the LDA+U method that has traditionally been used in the past.

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I. INTRODUCTION

The simplest Fe-containing oxide, FeO, adopts a rhombohedrally distorted NaCl-structure (B1) at low pressures and temperatures approaching 0 K.[1] The local magnetic moments on the Fe ions are responsible for the insulating behavior of FeO, as demonstrated by optical spectroscopy and by *ab initio* calculations,[2,3] which have shown that the band gap of FeO lies between the Fe 3*d*/O 2*sp* and Fe 4*s* states and has a weak absorption of ~0.5 eV. However, a much stronger transition of 2.4 eV has been reported between the Fe 3*d*/O 2*sp* and Fe 3*d* states.

Despite its simple crystal structure, FeO represents a computational challenge, and the most widely used DFT approach, based on the local density approximation (LDA) method, fails to describe the magnetic properties of highly correlated systems such as FeO, incorrectly predicting as it does that the B1-structure of FeO is metallic. Moreover, not even the generalized gradient approximation (GGA) manages to recover the failure of the LDA Hamiltonian, which is due to the inexact cancellation of the electron self-interaction (SI) in the local exchange functional used in DFT. Several approaches to overcome this short coming in DFT have been proposed. Thus, employing a self-interaction correction (SIC) to the LDA Hamiltonian has been used successfully in modeling rare-earth materials,[4] as well as Mott insulators.[5,6] The SIC methods have also been applied to model properties of atoms and molecules (e.g., electron affinities, excitation energies, and NMR shifts), for which comparisons are made to high-level wave-function calculations (see, for example, Refs. 7–13).

Another approach is to add an effective on-site repulsion term (U) of a Coulombic-type to the LDA Hamiltonian (the LDA+U method[14–16]). However, the U term is difficult to calculate accurately, and depends on the covalency of the system (e.g., Ref. 17). As a consequence, the U term may vary for the same element in different polymorphs, and needs to be fitted for each structure under investigation. Despite this limitation associated with the U term, the LDA+U method has been shown to successfully reproduce the electronic structure, including the band gap, and structural properties of FeO, at both zero[18,19] and high pressures[20,21] as well as to a range of other correlated systems (e.g., Ref. 22).

An alternative approach to SIC or LDA+U, is one which improves the description of electron self-interaction by making use of the exact cancellation between the Coulomb and exchange terms in the Hartree-Fock theory. This involves the use of hybrid DFT exchange functionals, of which Becke's three-parameter exchange [often used in combination with the Lee-Yang-Parr (LYP) correlation functional; B3LYP[23]] is the most well known. Because the U term in LDA+U has a similar effect to the Fock-exchange contribution, this approach seems a reasonable one to pursue.

Calculations on small molecules containing main group elements (e.g., Ref. 24) have shown that the use of hybrids of the B3LYP Hamiltonian which contain 20% Fock exchange, improve the description of both geometric and electronic properties when compared with standard LDA and GGA functionals. For the solid state, however, it has been suggested that slightly more Fock exchange would be needed to reproduce structural, magnetic, and electronic properties.[25] The hybrid functionals have been shown to significantly improve the electronic description of Mott insulators (such as MnO and NiO).[26,27] The magnetic coupling constants have also been shown by Martin and Illias[27,28] to be correctly reproduced by such hybrid functionals. In another study, Moreira *et al.*[29] suggested that for NiO a hybrid functional described by 35% Fock exchange in combination with a 65% LSDA exchange and correlation energy reproduces the experimental value of the magnetic coupling constants.

The aim of this investigation is to establish whether a mixing between the Becke and Fock exchange can reproduce the band structure, band gap, geometrical structure, and elastic properties of the antiferromagnetic, cubic B1 structure of stoichiometric FeO. Factors associated with the structural distortion and nonstoichiometry of FeO are to be investi-

TABLE I. Geometric and electronic properties for antiferromagnetic FeO, as a function of Fock and Becke exchange in combination with the LYP correlation functional. Mulliken charges on the O ions are the same as Fe, but with opposite sign. For the UHFLYP and UHF methods the presented transitions refer to Fe $4sp \rightarrow$ Fe $4s$: Fe $3d$.

Hamiltonian					Mulliken charges (a.u)
HF	Becke	a(Å)	K_0 (GPa)	Fe $3d$/O $2sp\rightarrow$ Fe $4s$:Fe $3d$ (eV)	Fe
0	100	4.344	195	0:0	1.596
10	90	4.371	177	2.11:1.89	1.656
20	80	4.374	175	3.91:3.70	1.700
30	70	4.371	181	5.41:5.65	1.737
35	65	4.367	181	5.65:6.53	1.753
40	60	4.364	185	6.40:7.63	1.765
50	50	4.358	186	7.63:9.40	1.788
60	40	4.346	193	9.04:11.15	1.808
80	20	4.329	209	11.51:14.63	1.839
100	0	4.311	247	14.05:18.06	1.862
UHF		4.417	186	7.77:10.68	1.881
B3LYP		4.365	191	3.70:3.73	1.703
PW91		4.291	199	0:0	1.622
LSDA		4.179	237	0:0	1.598
Exp.		4.302[37]	153[37]	0.5:2.4[2,3]	-
Exp.		4.34[35]	179[36]	-	-
LDA+U[7]			1.3:2.2		
LDA+U[9]		4.297	189	0.5:1.9	-
SIC[6]		-	-	3.25	-

gated in later studies. In this current set of simulations, we modeled the magnetic structure of FeO as a double unit cell containing planes of Fe with α and β spins along the [111] direction, which is the experimentally reported magnetic structure.[1]

II. METHOD

All calculations were performed with the CRYSTAL 2003 code (CR03).[30] In this program the crystal-like orbitals are expressed as linear combinations of Bloch functions, which in turn are built up from Gaussian-type functions. In CR03, periodic self-consistent-field (SCF) calculations can be performed both within the Hartree-Fock (HF) scheme, as well as with various implementations of DFT. It is possible to combine different exchange and correlation functionals, but it is also possible to mix the HF and DFT exchange functional to any degree desired. In the work described in this paper we mixed the unrestricted Hartree-Fock (UHF; also referred to as the Fock exchange) and the Becke (B) exchange functionals with the Lee-Yang-Parr (LYP) correlation functional according to:

$$\mathbf{F}_{xc} = y\mathbf{F}_x(\mathrm{UHF}) + (1-y)\mathbf{F}_x(\mathrm{B}) + \mathbf{F}_c(\mathrm{LYP}),$$

where the subscripts x and c are denoting exchange and correlation, respectively. By tuning the y value between 0 and 1, we can follow the series from the pure BLYP to the UHFLYP Hamiltonians. These hybrids are, hereafter, expressed as percentages, and referred to as $\mathrm{H}_x\mathrm{B}_{100-x}$LYP. In addition to this hybrid functional, we discuss the more traditional Hamiltonians namely UHF, local spin density approximation (LSDA),[31] Perdew-Wang91 (PW91),[32] and B3LYP.[23] All calculations were spin polarized.

The exchange-correlation potential was expanded numerically, and the cutoff threshold parameters (ITOLs) for the evaluation of the Coulomb and exchange contributions were set to $\{8\ 8\ 8\ 8\ 16\}$. We used a k-point mesh of $10\times10\times10$, expanded according to the Monkhorst-Pack scheme. The Broyden mixing, as implemented in CR03,[30] was employed for the metallic solutions, while for the insulating solutions we employed the level shifting technique[30] for faster convergence. In all calculations we used an all-electron basis set: 86-411d41[33] and 8-411Gd1[34] for Fe and O, respectively. The same atomic basis sets were used both in the Hartree-Fock and the different DFT-based techniques.

III. RESULTS

We find that FeO is described as an ionic compound; the UHFLYP Hamiltonian shows net Mulliken charges close to the formal values of Fe(+2) and O(−2) (see Table I). In agreement with the calculations on NiO by Moirera *et al.*,[29]

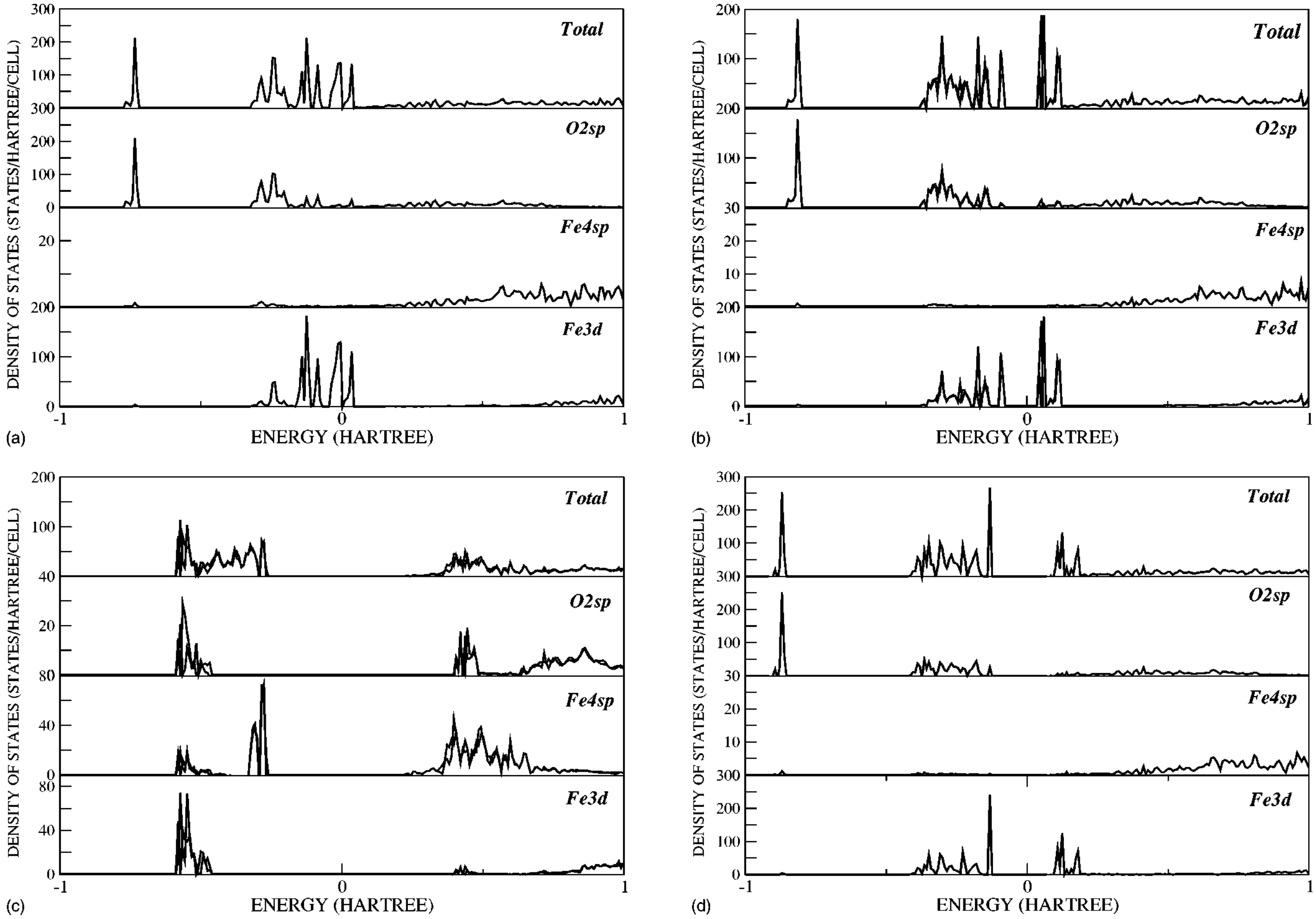

FIG. 1. Total denisity of states (DOS) and partial density of states (PDOS) for the (a) BLYP, (b) B3LYP, (c) UHF, and (d) $H_{35}B_{65}LYP$ Hamiltonians. Energies are given in Hartree.

we also find that on increasing the Becke exchange, the ionic contribution is decreased. Besides the more delocalized charge distribution, BLYP shows metallic behavior with a zero band gap [see Fig. 1(a)]. The UHFLYP method, on the other hand, results in an unphysical band gap of ~14 eV (see Table I).

We stress that the calculated band gaps are derived from the one-electron description, and it is well known that the UHF method fails to reproduce the virtual orbitals by overestimating the excitation energies, while DFT should be used only to describe ground states and thus only provides a correct description of the electron density under such conditions. Nevertheless, there have been a number of successful attempts to simulate an insulating state in FeO, employing LDA+U (Refs. 18–20) and SIC (Refs. 5 and 6) calculations. However, the SIC method fails to reproduce the nature of the band gap in the series of transition metal oxides from MnO to NiO: all oxides are predicted as charge-transfer insulator, which contradicts the experimental indications that the series changes character from being a Mott-Hubbard to a charge-transfer type of transition. This effect is considered to be a consequence of the latter method's tendency to favor *d* bands in their pure orbital state, i.e., to poorly describe the hybridization between the Fe 3*d* and O 2*sp* orbitals. In contrast, the LDA+U method[18] predicts an insulating state because the *d* electrons in the occupied t_{2g} state are stabilized by a mixing between the Fe 3*d* and the O 2*sp* orbitals, with the result that the unoccupied e_g band is energetically stabilized above the Fe 4*s* band, thus creating a band gap described by a Fe 3*d*/O 2*sp*–Fe 4*s* transfer in agreement with the experimental data. However, the energy of the electronic transitions are dependent on the U value chosen by the user: the band gaps predicted by Mazin and Anisimov[18] (employing a U of 5.1) are 1.3 and 2.2 eV for the Fe 3*d*/O 2*sp*–Fe 4*s* and Fe 3*d*/O 2*sp*–Fe 3*d* transitions, respectively, while Garmasch *et al.*[20], who employed a U of 4.6, instead reported band gaps of 0.48 and 1.9 eV.

To analyze the effect of Fock exchange on the electronic structure we compare the character of the highest energy level in the valence band and the lowest level in the conduction band with the results from the LDA+U calculations,[18] and we find the effect of the Fock exchange is similar to that produced by the use of the U factor. From our hybrid functionals we learn that the contributions from the occupied Fe 3*d* orbitals are energetically stabilized on increasing the Fock exchange, and the *d* electrons in the occupied t_{2g} states hybridizing with the O 2*sp* orbitals. Hence, the highest occupied energy level in the valence band shown in Fig. 2 for the UHFLYP is characterized by the Fe 4*sp* orbitals, while for the pure DFT (BLYP) and the Hamiltonians described by

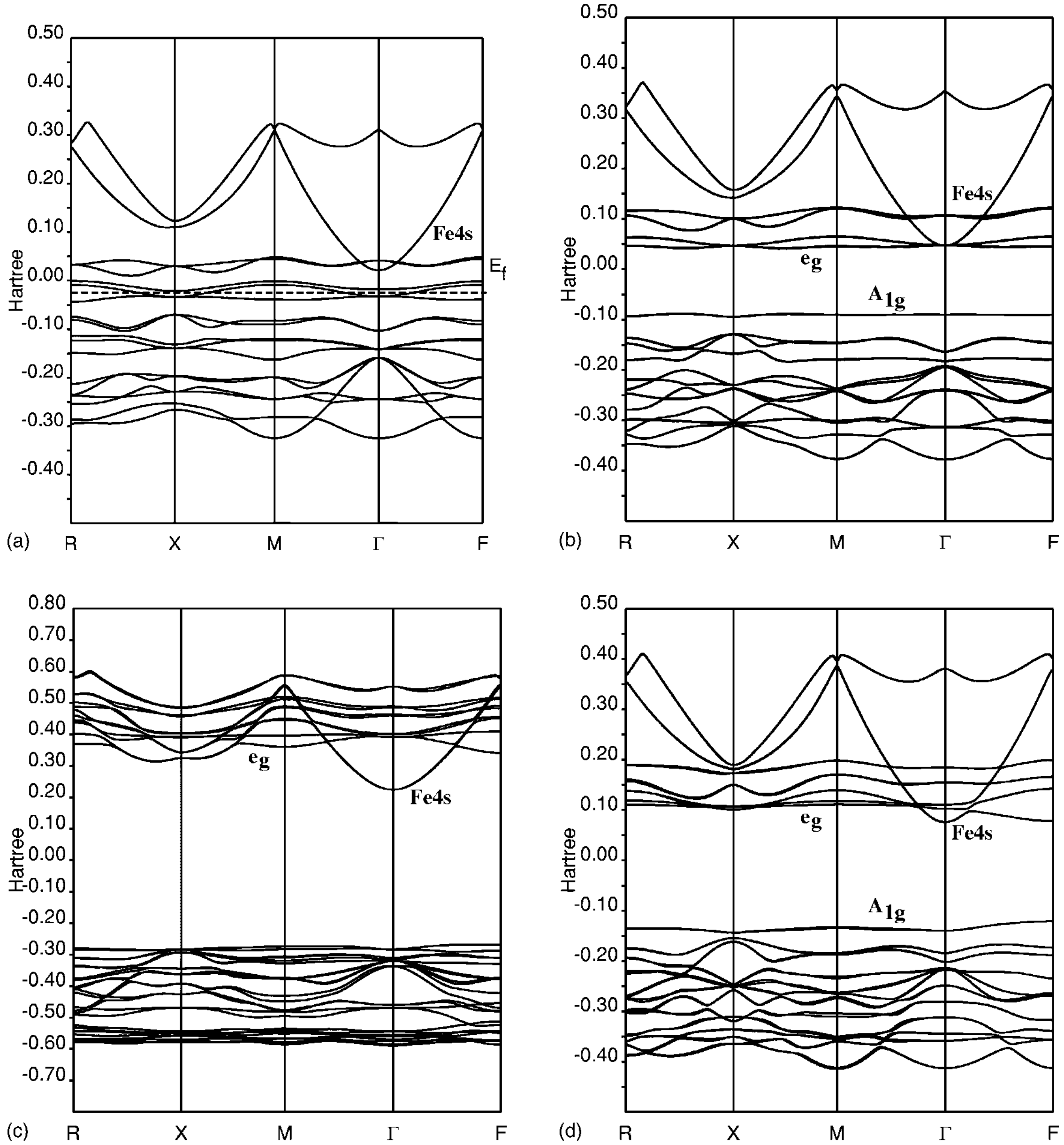

FIG. 2. Band structure for the (a) BLYP, (b) B3LYP, (c) UHF, and (d) $H_{35}B_{65}LYP$ Hamiltonians. Energies are given in Hartree.

minor amounts of Fock exchange (B3LYP and $H_{35}B_{65}LYP$), the energy level is characterized by the A_{1g} symmetry d orbital, in agreement with the LDA+U calculations.[18] In Ref. 18 the occupied t_{2g} states are described as a linear combination showing the A_{1g} symmetry: $A_{1g}=(xy+yz+zx)/\sqrt{3}$. This is possible because the rhombohedral field on the Fe^{2+} ions, which is caused by the antiferromagnetic structure. The A_{1g} states are marked in Fig. 2.

The unoccupied d electrons in the e_g state, gradually become more energetically destabilized compared to the Fe 4s orbitals as the amount of Fock-exchange increases (see Figs. 1 and 2). The lowest energy levels in the conduction band is, thus, characterized by an important d contribution in the BLYP and B3LYP Hamiltonians, while for $H_{35}B_{65}LYP$ the character is instead best described as Fe 4s. However, because the larger flexibility of our basis set (also 5sp and 4d are included in the basis set) compared to the LDA+U calculations the description of our band structures are slightly more complex than those reported in Ref. 18, but the character of the highest occupied bands, employing the hybrid functionals and the LDA+U method, are in agreement.

This finding is a consequence of the fact that the self-interaction correction is more important for the localized Fe 3d than for the delocalized Fe 4sp orbitals. The result is that for pure UHF the character of the band gap is described as a transition between the Fe 4sp and Fe 4s states, while the B3LYP functional describes the band gap as a transition between the Fe 3d/O 2sp to Fe 3d. Only for a Fock exchange between 30% and 60% is the character of the band gap described in accordance with the experiment, i.e., between the Fe 3d/O 2sp and Fe 4s states. These Hamiltonians [e.g., $H_{35}B_{65}LYP$; Fig. 2(d)] also give band structures that are in good agreement with the cubic structure reported from LDA+U calculations by Mazin and Anisimov.[18] However, as can be seen in Table I, the absorption energies for the band gap (calculated according to Koopman's theorem) for the $H_{35}B_{65}LYP$ Hamiltonian are in poor agreement with the experimental values.

Table I also shows the large effect the LYP correlation makes on the band gap (compare UHF and UHFLYP values). We, therefore, consider that in the future it should be possible to improve on the values of the calculated band gaps by changing the correlation functionals, which have previously been discussed by Bredow.[26]

The results given in Table I show that the lattice parameter increases from 4.34 to 4.37 Å for BLYP to $H_{20}B_{80}LYP$ after which the lattice parameter decreases as a function of the amount of Fock exchange. The change in the trend of the lattice parameter follows the change in the electronic structure as discussed above. We find that about 60% Fock exchange predicts a lattice parameter in good agreement with an experimental value obtained by fitting the lattice parameter for stoichiometric FeO [4.34 Å; (Ref. 35)]. For comparison we also report lattice parameters for the more traditional Hamiltonians (LSDA, PW91, UHF, and B3LYP). The LSDA Hamiltonian underestimates the lattice parameters by almost 4%, while the PW91 method underestimates the lattice parameter by $\sim 1\%$. In fact, our PW91 value agrees with the LDA+U value reported by Garmasch *et al.*[20]

Finally, we find that the bulk modulus follows a similar trend to the lattice parameter: decreasing for a Fock-exchange of 20% or less, and increasing for larger amounts of Fock exchange. The experimental value (obtained by extrapolating to a value corresponding to stoichiometric FeO; (Ref. 36) of 179 GPa suggests that about 30%–35% of Fock exchange give a reasonable result.

IV. CONCLUSIONS

By employing a mixing scheme between the Becke and UHF exchanges we have found that different properties of FeO require a slightly different amount of Fock exchange to reproduce the experimentally reported values and behavior correctly. However, given the uncertainties of extrapolating the experimental data to obtain estimated values for stoichiometric FeO, it would seem that in general between 30% and 60% of Fock exchange is needed to correctly model the structural properties of FeO. The band gap in best agreement with the experimental values require not more than 10% Fock exchange, but to correctly reproduce the electronic structure about 30%–60% Fock exchange is needed. In contrast, the B3LYP method, parameterized for molecular systems, does not give a band structure in agreement with either experimental observations or LDA+U calculations. We also notice the large effect the LYP correlation makes on the predicted band gap, and therefore we consider that in the future it should be possible to improve on the values of the calculated band gaps by changing the correlation functionals. Future work is now planned to investigate this and to establish the success of the hybrid functionals in describing other aspects of the FeO system.

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