First-principles calculation of the structure and magnetic phases of hematite

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Rhombohedral $\alpha$-Fe$_2$O$_3$ has been studied by using density-functional theory (DFT) and the generalized gradient approximation (GGA). For the chosen supercell all possible magnetic configurations have been taken into account. We find an antiferromagnetic ground state at the experimental volume. This state is 388 meV/Fe atom below the ferromagnetic solution. For the magnetic moments of the iron atoms we obtain 3.4$\mu_B$, which is about 1.5$\mu_B$ below the experimentally observed value. The insulating nature of $\alpha$-Fe$_2$O$_3$ is reproduced, with a band gap of 0.32 eV, compared to an experimental value of about 2.0 eV. Analysis of the density of states confirms the strong hybridization between Fe 3d and O 2p states in $\alpha$-Fe$_2$O$_3$. When we consider lower volumes, we observe a transition to a metallic, ferromagnetic low-spin phase, together with a structural transition at a pressure of 14 GPa, which is not seen in experiment. In order to take into account the strong on-site Coulomb interaction $U$ present in Fe$_2$O$_3$ we also performed DFT+$U$ calculations. We find that with increasing $U$ the size of the band gap and the magnetic moments increase, while other quantities such as equilibrium volume and Fe-Fe distances do not show a monotonic behavior. The transition observed in the GGA calculations is shifted to higher pressures and eventually vanishes for high values of $U$. Best overall agreement, also with respect to experimental photoemission and inverse photoemission spectra of hematite, is achieved for $U=4$ eV. The strength of the on-site interactions is sufficient to change the character of the gap from $d$-$d$ to $O$-$p$-$Fe$-$d$.

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I. INTRODUCTION

Among the iron oxides, corundum-type $\alpha$-Fe$_2$O$_3$ (hematite) is the most common on earth. At ambient conditions, it crystallizes in the rhombohedral corundum structure (space group $R3c$), see Ref. 1. Below the Néel temperature, $T_N=955$ K, $\alpha$-Fe$_2$O$_3$ is an antiferromagnetic (AF) insulator showing weak ferromagnetism above the Morin temperature, $T_M=260$ K, due to a slight canting of the two sublattice magnetizations.\textsuperscript{2–5} Below $T_M$, the direction of the magnetic moments is parallel to the [111] axis of the hexagonal unit cell. The localization of the iron 3d electrons due to the strong on-site Coulomb repulsion results in a large splitting of the d bands and a band gap of 2 eV. As the upper edge of the valence band is dominated by oxygen p states, hematite is generally considered to be a charge-transfer rather than a Mott-Hubbard insulator.

There has been a considerable amount of experimental work on hematite, regarding its structural, magnetic, and electronic properties in bulk\textsuperscript{1–3,6–21} as well as in nanoparticles.\textsuperscript{22,23} Especially the nature of the high-pressure (HP) transition of $\alpha$-Fe$_2$O$_3$ has recently been discussed in detail.\textsuperscript{6–9,13,19–21} At pressures around 50 GPa a shrinkage of the crystal volume of about 10% together with a collapse of the magnetic moments and a concurrent insulator-metal transition due to the breakdown of the $d$-$d$ correlation has been observed. This transition was found to be isostructural, but subsequent to a change in crystalline structure.\textsuperscript{21} For quite a long time the HP phase of $\alpha$-Fe$_2$O$_3$ was considered to be of the orthorhombic perovskite type, containing Fe$^{3+}$ and Fe$^{4+}$ sites in the same amount.\textsuperscript{7,8,9,13} Recently, Pasternak et al.\textsuperscript{19} and Rozenberg et al.\textsuperscript{20} assigned the HP structure to a distorted corundum-type ($R2\overline{3}c$-II) phase with a single Fe$^{3+}$ cation.

From a theoretical point of view, the study of hematite is very attractive because of the challenges it poses to theory. The Fe $d$ electrons in Fe$_2$O$_3$ are strongly correlated, so methods beyond ordinary density-functional theory (DFT) in the local spin-density approximation (LSDA) are needed to correctly describe the system in terms of electronic and magnetic properties. As the rhombohedral primitive cell of hematite contains ten atoms (compared to only two atoms in simple transition-metal (TM) oxides with the rocksalt structure), considerable computational effort is required to obtain reasonable results concerning the crystalline, electronic, and magnetic structures of hematite.

This might be responsible for the fact that, in contrast to studies of NiO, FeO, and similar TM monoxides, which have been studied extensively using ab initio methods,\textsuperscript{24–30} there are only a few theoretical works\textsuperscript{32,33} concerning $\alpha$-Fe$_2$O$_3$. The Hartree-Fock (HF) study of Catti et al.\textsuperscript{31} already achieves the correct order of magnetic states at experimental volume, yielding an energy difference between antiferromagnetic and ferromagnetic (FM) alignments of the spins of 37 meV/(Fe atom), although the obtained mixing of oxygen $2p$ and iron 3d electrons is very weak. In addition, the energy gap is grossly overestimated while the predicted bandwidth is too small. Sandratskii et al.\textsuperscript{32} studied $\alpha$-Fe$_2$O$_3$ using conventional LSDA. They find an AF bilayer sequence for the Fe moments to be lowest in energy: 489 meV/(Fe atom) lower than the FM state. In a recent LDA+$U$ study, Punkkinen et al.\textsuperscript{33} concentrate on the density of states (DOS). They find that even a modest value of the on-site
Coulomb potential improves the prediction for the energy gap without, however, achieving satisfactory agreement for other physical properties. In the latter two studies no relaxation of the atoms inside the supercell and also no variation of the volume of the cell was taken into account.

In our study, we present results of a complete relaxation process of cell size and atomic positions, in the framework of DFT, based on the generalized gradient approximation (GGA) and the projector augmented wave (PAW) method. We also performed GGA + U calculations to account for the strong on-site Coulomb repulsion of the Fe d electrons. This paper is organized as follows. In Sec. II we describe the computational details, after that we briefly discuss in Sec. III how the on-site Coulomb interaction parameter U is introduced in the framework of DFT. We present results of the GGA calculations in Sec. IV, while results concerning GGA + U will be given in Sec. V. Concluding remarks and open key questions can be found in Sec. VI.

II. COMPUTATIONAL MODEL

The calculations have been performed on the basis of spin-polarized DFT with the Vienna ab initio simulation package VASP. For the exchange-correlation functional, we chose a semi-local form proposed by Perdew and Wang in 1991 using the GGA denoted hereby PW91. The spin interpolation of Vosko et al. was used. The Kohn-Sham equations were solved via iterative matrix diagonalized on the basis of the norm of the residual vector to each eigenstate and optimized charge- and spin-mixing routines.

A number of eight valence electrons for each Fe atom (3d^74s^1) and six valence electrons for each O atom (2s^22p^4) were taken into account. The remaining (core) electrons together with the nuclei were described by pseudopotentials in the framework of the PAW method proposed by Blöchl and adapted by Kresse and Joubert.

The one-electron Kohn-Sham wavefunctions as well as the charge density were expanded in a plane-wave basis set. The results reported in this paper correspond to an energy cutoff of 550 eV. It was checked that increasing the cutoff to 800 eV did not change total energies by more than 3 meV/atom. Energy differences were affected by less than 0.3 meV/atom. For the calculation of total energies, the integration over the total DOS have been calculated with a 16x16 x 16 k point mesh.

An increase to 20x20x20 k points did not lead to any visible change in the total DOS. The integration over the irreducible part of the Brillouin zone was carried out using the linear tetrahedron method with Blöchl corrections. The relaxation of the crystalline structure was performed using a Gaussian-smearing approach with a width of 0.2 eV to speed up convergence. Pressure and bulk modulus were derived from the calculated pressure-volume relation by fitting the data to a Murnaghan equation of state.

All calculations were carried out under rhombohedral symmetry constraints. The complete hexagonal unit cell of hematite is shown in Fig. 1, together with the rhombohedral primitive cell used in our calculation. All iron atoms have an equivalent octahedral environment. Therefore, electronic and magnetic properties will be the same at each iron site. The octahedra built by oxygen atoms and centered by iron atoms are slightly rotated against each other. We note that there are two types of pairs of Fe atoms, which are characterized by a short Fe-Fe distance (type A) and by a larger distance (type B) along the hexagonal axis. There are two internal degrees of freedom, commonly named z_{Fe} and x_{O}, by which the positions of the atoms inside the primitive cell can be described (see Table I). We have relaxed the positions of the

![Figure 1](image-url)
Some straightforward algebra one obtains

\[ D_{\text{FT}}E \]

This yields exactly the same energy as the DFT functional \( E_{\text{DFT}} \) in the limit of an idempotent on-site occupancy matrix \( \rho^\sigma = \rho^\sigma \) imposed by the second term in Eq. (3). For \( U/J \), the term is positive definite, since the eigenvalues \( \varepsilon_i \) of the on-site occupancy matrix are either 0 or 1,

\[ \rho^\sigma - \rho^\sigma \rho^\sigma = \sum_i \varepsilon_i^\sigma - (\varepsilon_i^\sigma)^2 > 0, \]

where the sum on the right-hand side is over all eigenvalues \( \varepsilon_i \) of the on-site occupancy matrix \( \rho^\sigma \). Hence the second term in Eq. (3) can be interpreted as a positive definite penalty function driving the on-site occupancy matrices towards idempotency, whose strength is parametrized by a single parameter \( (U-J) \). A larger \( (U-J) \) forces a stricter observance of the on-site idempotency, achieved by lowering the one-electron potential locally for a particular metal \( d \) orbital and in turn reducing the hybridization with, e.g., O atoms. The one-electron potential is given by the functional derivative of the total energy with respect to the electron density, i.e., in a matrix representation,

\[ V_{ij}^\sigma = \frac{\delta E_{\text{DFT}+U}}{\delta \rho_{ij}^\sigma} = \frac{\delta E_{\text{DFT}}}{\delta \rho_{ij}^\sigma} + (U-J) \left[ \frac{1}{2} \delta_{ij} - \rho_{ij}^\sigma \right]. \]

It is recognized that filled \( d \) orbitals, which are localized on one particular site, are moved to lower energies, by \( -(U-J)/2 \), whereas empty \( d \) orbitals are raised to higher energies by \( (U-J)/2 \). For the implementation of the DFT+U approach within VASP, see Ref. 52.

### III. DFT+U METHOD

The on-site Coulomb repulsion amongst the localized TM 3\( d \) electrons is not described very well in a spin-polarized DFT treatment. A conceptually better method (DFT+U) consists of combining the DFT with a Hubbard-Hamiltonian, thereby considering this Coulomb repulsion explicitly. In the present calculations we use a simple DFT+U version. It is based on a model Hamiltonian with the form \(^{49}\)

\[ \hat{H} = \frac{U}{2} \sum_{m,m',\sigma} \hat{n}_{m\sigma} \hat{n}_{m'\sigma} + U - J \sum_{m,m',\sigma} \hat{n}_{m\sigma} \hat{n}_{m'\sigma}, \]

where \( \hat{n}_{m\sigma} \) is the operator yielding the number of electrons occupying an orbital with magnetic quantum number \( m \) and spin \( \sigma \) at a particular site.

The Coulomb repulsion is characterized by a spherically averaged Hubbard parameter \( U \) describing the energy required for adding an extra \( d \) electron to an Fe atom, \( U = E(\hat{n}^{d+1}) + E(d^{n-1}) - 2E(d^n) \), and a parameter \( J \) representing the screened exchange energy. While \( U \) depends on the spatial extension of the wave functions and on screening, \( J \) is an approximation of the Stoner exchange parameter and almost constant \( J = 1 \) eV (see Ref. 50). The spin-polarized DFT+U energy functional is obtained by subtracting the Mott-Hubbard contributions already existing in the DFT functional (“double-counting” contributions) \(^{50}\) and after some straightforward algebra one obtains

\[ E_{\text{DFT}+U} = E_{\text{DFT}} + \frac{U - J}{2} \sum_{m\sigma} (n_{m\sigma}^2 - n_{m\sigma}). \]

This form is not invariant under a unitary transformation of the orbitals. However, when replacing the number operators by the on-site density matrix \( \rho_{ij}^\sigma \) of the \( d \) electrons, Lichtenstein et al. \(^{31}\) obtain a rotationally invariant energy functional, which in the present case is of the form

\[ E_{\text{DFT}+U} = E_{\text{DFT}} + \frac{U - J}{2} \sum_{\sigma} \text{Tr}[\rho^\sigma - \rho^\sigma \rho^\sigma]. \]

This yields exactly the same energy as the DFT functional \( E_{\text{DFT}+U} = E_{\text{DFT}} \) in the limit of an idempotent on-site occupancy matrix \( (\rho^\sigma)^2 = \rho^\sigma \) imposed by the second term in Eq. (3). For \( U/J \), the term is positive definite, since the eigenvalues \( \varepsilon_i \) of the on-site occupancy matrix are either 0 or 1,

\[ \rho^\sigma - \rho^\sigma \rho^\sigma = \sum_i \varepsilon_i^\sigma - (\varepsilon_i^\sigma)^2 > 0, \]

where the sum on the right-hand side is over all eigenvalues \( \varepsilon_i \) of the on-site occupancy matrix \( \rho^\sigma \). Hence the second term in Eq. (3) can be interpreted as a positive definite penalty function driving the on-site occupancy matrices towards idempotency, whose strength is parametrized by a single parameter \( (U-J) \). A larger \( (U-J) \) forces a stricter observance of the on-site idempotency, achieved by lowering the one-electron potential locally for a particular metal \( d \) orbital and in turn reducing the hybridization with, e.g., O atoms. The one-electron potential is given by the functional derivative of the total energy with respect to the electron density, i.e., in a matrix representation,

\[ V_{ij}^\sigma = \frac{\delta E_{\text{DFT}+U}}{\delta \rho_{ij}^\sigma} = \frac{\delta E_{\text{DFT}}}{\delta \rho_{ij}^\sigma} + (U-J) \left[ \frac{1}{2} \delta_{ij} - \rho_{ij}^\sigma \right]. \]

It is recognized that filled \( d \) orbitals, which are localized on one particular site, are moved to lower energies, by \( -(U-J)/2 \), whereas empty \( d \) orbitals are raised to higher energies by \( (U-J)/2 \). For the implementation of the DFT+U approach within VASP, see Ref. 52.

### IV. RESULTS AND DISCUSSION OF GGA CALCULATIONS

#### A. Crystal structure and magnetization

The total energies per atom and magnetic moments of the Fe atoms as a function of the volume per atom are displayed in Fig. 2. The curves belonging to different magnetic solutions are indexed according to the orientation of the local spin density around the Fe atoms. As zero energy the global energy minimum was taken, corresponding to an AF + + − − state, which means that Fe atoms belonging to type A pairs (short distance, see Sec. II) have opposite magnetic moment, while Fe atoms belonging to type B pairs (larger distance) have equal magnetic moments. Each point on every curve represents the result obtained after full relaxation of the cell shape (\( c/a \) ratio), atomic positions (under rhombohedral symmetry constraints), and magnetic moments for the corresponding volume.

For a discussion we first draw our attention to the order of states at experimental volume. Corresponding structural, energetic, and magnetic properties of the different magnetic solutions for a volume of 10.06 Å\(^3\) are presented in Table III. The energy differences between the AF + + − − and the other two AF states agree well with results of the LSDA calculation reported by Sandratskii and co-workers. \(^{32}\) The total energy of the FM solution is comparable to the corresponding value in the same publication, but considerably larger than the value found by Catti et al. \(^{31}\) within their HF study. The nonmagnetic (NM) solution is highest in energy.
In an ideal corundum-type structure the $c/a$ ratio is 2.8333. The unit cell of hematite is slightly shortened in $c$ direction with respect to this ideal cell, the experimentally measured $c/a$ ratio at zero pressure is 2.73 (Ref. 7). We find that the calculated values for the $c/a$ ratios for all three AF states agree well with this number, while the $c/a$ ratios for the FM and the NM state are somewhat larger and closer to the ideal value. The internal structural parameters (and hence the Fe-Fe distances) also show a pronounced dependence on the magnetic configuration. For the stable AF $++-+$ phase, we found good agreement with experiment, in the other magnetic configurations substantial differences are observed. These effects are largest in the FM configuration where smaller values of $z$ and larger $x$ parameters lead to a strongly increased difference of the bond lengths in Fe-Fe (A) and Fe-Fe (B) pairs. The contraction of the shortest Fe-Fe distances contributes to the quenching of the magnetic moments in the FM phase.

When comparing our results to other theoretical work we first note that we get the same order of states as Sandratskii et al. But while the energy differences between the AF phases are similar, we get the FM solution closer to the AF states by 110 meV per Fe atom. From a calculation of the total energy for the FM state at a volume of 10.06 Å$^3$ per Fe atom and a fixed $c/a$ ratio of 2.73, without relaxing the atomic positions, we obtained a value which is 135 meV above the corresponding energy obtained with full relaxation. Therefore we ascribe the discrepancy to the results of Sandratskii et al. To the fact that we have allowed for full relaxation of the cell shape ($c/a$ ratio) and the atomic positions inside the supercell. Sandratskii et al. present their results for a fixed geometry. This might also be the reason for their FM magnetic moments being about as large as the AF ones, while in our calculations the moments differ by more than 0.8μ$_B$. The small difference in energy between FM and AF states obtained by Catti et al. has already been explained$^{32}$ to be due to the complete neglect of correlation in HF theory.

When we consider lower volumes we observe a collapse of the magnetic moments, from a high-spin (HS) to a low-spin (LS) state, which occurs at 8.86 Å$^3$ for the AF $++-+$ solution, and around 9.1, 9.3 and 9.2 Å$^3$ for the

![Graph](image)

**FIG. 2.** Total energies (lower panel) and absolute values of magnetic moments of the Fe atoms (upper panel) as a function of the volume per atom. Dotted vertical lines mark the experimental value (Ref. 7) (10.06 Å$^3$/atom) for the volume per atom of hematite at ambient conditions and are drawn to guide the eye. As zero energy the global energy minimum is taken, corresponding to the AF $++-+$ state, at a volume of 10.00 Å$^3$/atom. The straight solid line is tangent to the AF $++-+$ and the FM $++++$ curves and marks a structural transition at a pressure of 14 GPa.

The AF solutions slightly vary in magnetic moments, with all moments being $\approx 3.4\mu_B$ in magnitude. This is about 1.5μ$_B$ lower than the experimental moments. In contrast to the results of Sandratskii et al.,$^{32}$ who obtain almost the same moments for AF and FM ordering, the moments of the FM solution are about 1.0μ$_B$ lower in our calculation. This reflects the frustration of the magnetic exchange interactions in the FM configuration.

<table>
<thead>
<tr>
<th>Magnetic state</th>
<th>Functional</th>
<th>Reference</th>
<th>Energy</th>
<th>Magnetic moment</th>
<th>$c/a$ ratio</th>
<th>Fe-Fe (A)</th>
<th>Fe-Fe (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF $++-+$</td>
<td>GGA</td>
<td>This paper</td>
<td>0</td>
<td>3.44</td>
<td>2.77</td>
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<td></td>
<td>LSDA</td>
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<td></td>
<td>HF</td>
<td>31</td>
<td>0</td>
<td>4.74</td>
<td>2.70</td>
<td>2.877</td>
<td>4.033</td>
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<td>GGA</td>
<td>This paper</td>
<td>211</td>
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<td>2.76</td>
<td>2.959</td>
<td>3.958</td>
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<td></td>
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<td></td>
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<tr>
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<td>GGA</td>
<td>This paper</td>
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<td>2.69</td>
<td>2.803</td>
<td>4.000</td>
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<td></td>
<td>LSDA</td>
<td>32</td>
<td>204</td>
<td>3.74</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>FM $++++$</td>
<td>GGA</td>
<td>This paper</td>
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<td>2.85</td>
<td>2.689</td>
<td>4.380</td>
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<tr>
<td></td>
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<td>3.73</td>
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<tr>
<td></td>
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<td>37</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NM</td>
<td>GGA</td>
<td>This paper</td>
<td>680</td>
<td>2.83</td>
<td>2.761</td>
<td>4.280</td>
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</tbody>
</table>

TABLE III. Order of the magnetic states at experimental volume, 10.06 Å$^3$/atom. Energies are in meV/(Fe atom), magnetic moments are in (μ$_B$/Fe atom), and distances are in Å (where NM stands for nonmagnetic).


+ + + + , + + + − , and + + + + solutions, respectively. Related to this are kinks in the energy vs volume curves. These HS-LS transitions are more pronounced for the AF states compared to the FM solution, resulting in two clearly visible minima at least in the AF + + + + and + + + − energy curves. In the LS phases, the magnetic moments decrease linearly with volume for the AF states, but stay almost constant around 1 \( \mu_B \) for the FM state. For very low volumes we did not succeed in stabilizing a LS AF + + + − phase. Below 7.6 Å\(^3\) we observe the collapse of the AF + + + − solution and obtain the NM state as the most stable solution.

We note that at low pressure the AF solutions are much more stable than the FM and the NM solutions. This is related to the strong superexchange interaction mediated by the O atoms. But we also note that at low volumes the FM solution is slightly lower in energy than the AF + + + − phase (although the energy difference is rather small, e.g., 2.5 meV/atom for a volume of 8.46 Å\(^3\)/atom, but this is not of importance for the further discussion), corresponding to a FM ground state at high pressures. By placing a common tangent to the FM and the AF + + + − curves, we obtain a value for the pressure, for which a HS-LS AF-FM transition will occur, of 14 GPa. The corresponding volume reduction is 10.5%. As the rhombohedral corundum-type structure has been reported to be the stable phase of \( \alpha\)-Fe\(_2\)O\(_3\) in the 0–50 GPa regime, we conclude that this transition is an artifact of the simulation method, namely, the DFT in combination with the GGA. It will be shown that when the GGA + \( U \) formalism is applied, the observed transition is shifted to higher pressures with increasing \( U \) and eventually disappears for large values of \( U \).

We have calculated structural parameters for each state by fitting the data in the volume regions corresponding to local minima of the energy curves to a third-order Birch-Murnaghan equation of state (Ref. 54). The results are given in Table IV. For two of the AF curves, structural parameters were calculated for both HS and LS phases. The equilibrium volume for the magnetic ground state agrees well with the experimental value, although the corresponding magnetic moment is too low. This is probably due to the overestimation of hybridization of Fe 3d and O 2p states in conventional GGA. We also obtain a value for the bulk modulus which is lower than the values found experimentally. However, it must be emphasized that the experimental value of the bulk modulus is subject to considerable uncertainty. Sato and Akimoto’s value of 231 GPa is derived by a fit over a very small pressure range of \( p < 3 \) GPa, whereas a fit to pressures up to 10 GPa leads to \( B_0 \sim 178 \) GPa closer to our calculated value. The most recent result of Rozenberg et al. is obtained by arbitrarily setting the pressure derivative \( B'_0 = \Delta B_0/\Delta p \) in the Murnaghan fit to \( B'_0 = 4 \).

The calculated bulk modulus for the FM state is considerably larger, which is due to the fact that it has been evaluated for a lower volume and coincides well with the experimental result that with increasing pressure hematite is becoming harder. This can be observed directly when comparing the bulk moduli for the HS and LS solutions of the AF + + + − and the AF + + + + phases.

Common to all magnetic states (and the experimental finding) is the dependence of the magnetic moment of the Fe atoms and the parameter \( z_{Fe} \) on the volume. For volumes of more than 10 Å\(^3\)/atom the moments are larger than 3 \( \mu_B \)/Fe atom and \( z_{Fe} \) is greater than 0.103. This results in a difference between Fe-Fe (A) and Fe-Fe (B) distances of about 1.0–1.1 Å. For volumes below 9 Å\(^3\)/atom the moments are smaller than 1.5 \( \mu_B \)/Fe atom and \( z_{Fe} \) is less than 0.098, leading to differences in Fe-Fe distances of more than 1.5 Å. We conclude that the volume reduction seems to result in an increase of Fe-Fe (B) distances and a strong decrease of Fe-Fe (A) distances. In contrast to that a clear trend is not visible for the parameter \( x_{Fe} \) and the \( c/a \) ratio.

As not only the volume, but also the magnetic order determine the structural parameters, we now stick to the experimentally observed AF + + + − state to examine further the dependence of crystalline structure of \( \alpha\)-Fe\(_2\)O\(_3\) on pressure. Figure 3 illustrates the dependence of the \( c/a \) ratio, the internal degrees of freedom \( z_{Fe} \) and \( x_{Fe} \), and the Fe-Fe and Fe-O distances on pressure for the AF + + + − phase. For comparison, experimental data from Ref. 19 is included. The straight solid lines mark the pressure of 14 GPa at which the AF-FM HS-LS transition takes place in our simulation. Up to that value, the structural parameters from our simulation change almost linearly with pressure. Around \( p_c \), a rapid change, especially in the \( c/a \) ratio, is observed, followed by nearly perfect linear behavior above \( p_c \). The HS-LS transi-

### Table IV. Ground-state parameters for the different magnetic states

<table>
<thead>
<tr>
<th>Magnetic state</th>
<th>( V_0 )</th>
<th>Moment</th>
<th>( z_{Fe} )</th>
<th>( x_{O} )</th>
<th>( c/a ) ratio</th>
<th>Fe-Fe (A)</th>
<th>Fe-Fe (B)</th>
<th>( B_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF + + + −</td>
<td>10.00</td>
<td>3.43</td>
<td>0.1057</td>
<td>0.3096</td>
<td>2.772</td>
<td>2.929</td>
<td>3.989</td>
<td>173</td>
</tr>
<tr>
<td>Expt. (Ref. 6)</td>
<td>10.06</td>
<td></td>
<td>0.1053</td>
<td>0.3056</td>
<td>2.731</td>
<td>2.896</td>
<td>3.977</td>
<td>178, 225 (231, 258)</td>
</tr>
<tr>
<td>AF + + + − (HS)</td>
<td>10.13</td>
<td>3.42</td>
<td>0.1073</td>
<td>0.3122</td>
<td>2.757</td>
<td>2.976</td>
<td>3.959</td>
<td>134</td>
</tr>
<tr>
<td>AF + + + − (LS)</td>
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<td>1.00</td>
<td>0.0979</td>
<td>0.3110</td>
<td>2.775</td>
<td>2.610</td>
<td>4.052</td>
<td>206</td>
</tr>
<tr>
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<td>10.13</td>
<td>3.48</td>
<td>0.1031</td>
<td>0.3047</td>
<td>2.690</td>
<td>2.812</td>
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<td>AF + + + + (LS)</td>
<td>8.88</td>
<td>1.17</td>
<td>0.0962</td>
<td>0.3120</td>
<td>2.714</td>
<td>2.526</td>
<td>4.038</td>
<td>212</td>
</tr>
<tr>
<td>FM + + + +</td>
<td>8.79</td>
<td></td>
<td>0.0960</td>
<td>0.3131</td>
<td>2.795</td>
<td>2.564</td>
<td>4.111</td>
<td>249</td>
</tr>
<tr>
<td>NM</td>
<td>8.73</td>
<td></td>
<td>0.0966</td>
<td>0.3150</td>
<td>2.811</td>
<td>2.582</td>
<td>4.102</td>
<td>271</td>
</tr>
</tbody>
</table>

\( ^a \)Reference 6.
\( ^b \)Reference 20.
tion is obviously accompanied by transitions in these structural parameters, whereas we do not see a transition in the experimental values.

The \( c/a \) values from our calculation are larger than the ones found in experiment.\(^6\),\(^7\),\(^20\) The agreement of all parameters and their pressure dependence with experiment is reasonable for pressures below \( p_c \). Due to the transition at \( p_c \), this agreement becomes poor for pressures above 14 GPa.

### B. Electronic structure

In order to analyze electronic properties of \( \alpha\)-Fe\(_2\)O\(_3\) we calculated the DOS for all energy minima of the curves. In Fig. 4 the partial DOS of Fe 3d \( (t_{2g} \text{ and } e_g) \) and O 2p states for the AF ++ --- solution at experimental volume are shown. A band gap of \( \approx 0.3 \) eV is clearly visible. As is usually the case for calculations based on DFT, this is much smaller (by about a factor of 6) than the experimental value of 2.0 eV (Ref. 55). For comparison, Punkkinen and co-workers,\(^33\) who applied GGA in combination with the linear muffin-tin orbital (LMTO) method in atomic-sphere approximation (ASA), obtained a value of 0.51 eV for the band gap. Sandratskii \textit{et al.}\(^32\) got a value of 0.75 eV by using

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**FIG. 3.** Variation of the \( c/a \) ratio (upper panel), the structural parameters \( x_0 \) and \( z_{Fe} \), plotted as \( z_{Fe} + 0.25 \) (middle), and Fe-Fe distances (lower panel) with pressure, together with experimental data taken from Ref. 20.

**FIG. 4.** Orbital projected DOS (PDOS) for the AF ++ --- solution of Fe\(_2\)O\(_3\), calculated within the GGA. The left (right) panel shows spin-up (spin-down) Fe \( e_g \), Fe \( t_{2g} \), and O 2p projections. The orbitals are projected onto Wigner-Seitz spheres.
LSDA and the augmented-spherical wave method (ASW), and Catti et al. calculated about 11 eV within HF. The small discrepancies between our and previous DFT calculations can be ascribed to the use of the ASA in the LMTO and ASW work (whereas we use a full-potential technique), the dramatic overestimation of the gap calculated within HF is due to the complete neglect of electronic correlations. The disagreement with experiment may be traced back to some extent to the amount of mixing of Fe 3d and O 2p states, which plays an important role in the characterization of the insulating nature of hematite. Whereas the mixing is nearly absent in the HF study and clearly underestimated in the LSDA calculations, a strong mixing across the entire range of the valence band is present in our calculations. At the upper edge of the valence band we observe Fe states and O states in comparable amounts. The Fe 3d DOS is even a bit larger than the O 2p DOS, whereas it is experimentally confirmed that the valence-band edge in α-Fe₂O₃ is dominated by oxygen 2p states, making hematite a charge-transfer insulator. This deficiency in our calculations originates from the underestimation of the on-site Coulomb interaction of the Fe d electrons and can be compensated by introducing an additional parameter in the density functional, as will be shown in Sec. VI.

Figure 5 shows the partial DOS’s for the FM solution at the equilibrium volume of the FM phase of 8.79 Å³/atom. We find half-metallic hematite under these conditions, the valence-band edge being clearly dominated by Fe 3d states. The HS-LS transition therefore turns out to be an insulator-metal transition.

V. CONCLUSIONS ON DFT CALCULATIONS

Using gradient corrections in the exchange-correlation functional we obtain a quite reasonable description of the structural properties at low pressures and the magnetic ground state of hematite. But still several evident shortcomings of the DFT remain. The magnetic moments of the Fe atoms and the band gap are too small, and the character of the gap contradicts the accepted charge-transfer character. Most importantly, however, we find α-Fe₂O₃ to be unstable under even modest compression against a HS-LS transition coupled to an isostructural transition. Furthermore, the energetic order of the possible magnetic phases changes upon the transition, with the FM phase being favored at pressures beyond ~ 14 GPa. This contradicts the observed stability of the corundum-type AF++−− phase up to about 50 GPa and demonstrates the need to account for electronic correlation effects.

VI. GGA+U CALCULATIONS

A. Crystal structure and magnetization

As discussed before, conventional DFT gives the correct stable antiferromagnetic ground state but underestimates the band gap and magnetic moments of α-Fe₂O₃. It also predicts the valence-band edge to be Fe 3d dominated, whereas the

FIG. 5. Orbital projected DOS (PDOS) for the FM solution of Fe₂O₃, calculated within the GGA. The left (right) panel shows spin-up (spin-down) Fe εgü, Fe t₂gü, and O 2p projections. The orbitals are projected onto Wigner-Seitz spheres.
experiment shows O 2p domination and therefore a charge-transfer type of band gap. Furthermore, the Fe 3d band energies from GGA are not in agreement with experimental valence-band spectra and conduction-band spectra. GGA also predicts α-Fe₂O₃ to undergo a magnetic phase transition at ~14 GPa, which is not found in experiment. On the other hand, the GGA prediction of the equilibrium volume agrees quite well with experimental data.

The inaccurate results for some of the ground-state properties of hematite obtained with GGA are attributable to the improper description of the on-site Coulomb repulsion between the localized Fe 3d electrons. The DFT+U method by explicitly taking into account the on-site Coulomb repulsion improves the predictions for the band gap, band energies, and magnetic moments. Figure 6 illustrates the dependence of equilibrium volume, Fe-Fe (A) distance, magnetic moments, and band gap on U. The parameter J was kept constant at 1 eV for all calculations.

GGA+U stabilizes the high-spin AF +++ − ground state as in the GGA limit, U = 1 eV. The experimental magnetic moment is reached only for U = 8–9 eV, whereas for the band gap full agreement is obtained for moderate values of U ~5 eV. The results for magnetic moment and band gap are in good agreement with former GGA+U calculations using the tight-binding LMTO-ASA method of Punkkinnen et al. using the experimental structure. The choice of an appropriate value for U is the same in both cases. The volume shows only a weak dependence on U. With increasing U, it increases first until at U = 5 eV a maximum value of ~10.3 Å³ is reached and then decreases slightly for larger U values. The agreement with experiment is reasonable throughout the entire U range. The Fe-Fe (A) distance reaches its maximum value of ~2.95 Å already for U = 2 eV and decreases slightly when further increasing U. The agreement with the experimental value of ~2.896 Å (Ref. 7) is best for U = 5 eV. The Fe-Fe distance reflects the behavior of the volume with varying U. The c/a ratio slightly decreases from c/a ~2.77 for GGA at an equilibrium volume of 10.00 Å³/atom to ~2.73 for GGA+U with U = 5 eV at an equilibrium volume of 10.30 Å³/atom and to ~2.72 for GGA+U with U = 7 eV at an equilibrium volume of 10.24 Å³/atom. Agreement with the experimental value of c/a = 2.73 is again best for U ~5 eV. Concerning the bulk modulus, we can observe an increase from the GGA value of 173 GPa at an equilibrium volume of 10.00 Å³/atom to the GGA+U value for U = 4 eV with 177.4 GPa at an equilibrium volume of 10.30 Å³/atom. For U = 7 eV, the bulk modulus increases to 178.8 GPa at an equilibrium volume of 10.24 Å³/atom. The bulk modulus remains too small compared to experiment even for large U parameters.

Figure 7 shows the volume dependence of the total energy and the magnetic moment for GGA+U with U = 1 (GGA), 4, and 7 eV. The tangent on the GGA curves mark the phase transition from the AF + + + − to the ferromagnetic phase for U = 1 eV.
Experimentally, Rozenberg et al. have shown that for the GGA case, the band gap closes abruptly. Whereas at a volume of \( \sim 7.4 \, \text{Å}^3/\text{atom} \), the band gap is \( \sim 1.2 \, \text{eV} \), it drops to zero at \( \sim 6.9 \, \text{Å}^3/\text{atom} \). However, as shown by Rozenberg et al., these transitions are preceded by a transition to a nonmagnetic orthorhombic Rh\(_2\)O\(_3\)(II)-type phase at about 50 GPa. This, however, is beyond the scope of the present study.

**B. Electronic structure**

The spin-polarized and orbital projected DOS, calculated in the GGA+\( U \) with \( U = 4 \, \text{eV} \) is shown in Fig. 9. The on-site Coulomb repulsion is found to have a profound influence on the electronic spectrum. The occupied Fe 3d states are shifted to higher binding energies, breaking the strong Fe 3d–O 2p hybridization characteristic for the electronic structure calculated in the GGA. The occupied states close to the Fermi energy are now entirely oxygen dominated, with only a small admixture of Fe 3d minority states. The empty Fe 3d minority states are up shifted, increasing the width of the gap. In contrast to the GGA predicting hematite to be an insulator with a very narrow gap created by the exchange splitting in the Fe 3d band, GGA+\( U \) with \( U = 4 \, \text{eV} \) leads to a charge-transfer type O 2p–Fe 3d gap of nearly 2 eV, in agreement with experiment.

Figure 10 shows the calculated intensities of the photoemission (PES) and inverse photoemission (IPES) spectra, compared with the experimental results of Fujimori et al.\(^{10}\) and Ciccacci et al.\(^{12}\) In spite of the fact that the one-particle DFT eigenvalues have no direct physical meaning, it is well established that calculated DOS and experimental PES can be compared on a qualitative basis, especially when the bands are very broad. In this sense the theoretical spectra are approximated by the sum over the partial DOS, weighted with the partial photoionization cross section of Yeh and Lindau,\(^{56}\) folded with a Gaussian to simulate the effect of a finite instrumental resolution. The analysis of the PES and IPES spectra confirms the conclusion that at least moderately strong on-site interactions must be included to achieve a correct description of the electronic structure of hematite. In the GGA limit and even with \( U = 2 \, \text{eV} \), the narrow gap at the Fermi level is completely covered by the finite resolution of the spectra, the lower edge of the valence band is found at too low binding energies, and the dominant peak in the conduction band is too close to the Fermi level. \( U = 4 \, \text{eV} \) leads to reasonable agreement with experiment. The structure in the valence band with separated peaks at \( E \sim -7 \, \text{eV} \) dominated by Fe 3d states and at \( E \sim -3 \, \text{eV} \) dominated by O 2p states is more pronounced than in experiment. This is a consequence of the fact that the on-site Coulomb potential acts only on the Fe 3d states, leading to a reduction of the Fe-O hybridization which is too strong. However, GGA+\( U \) with \( U = 4 \, \text{eV} \) leads undoubtedly to a marked improvement of the calculated electronic structure.

Punkkinen et al.\(^{33}\) found a value of \( U = 2 \, \text{eV} \) as an optimum from their DOS interpretation. They remarked that already for \( U = 3.5 \, \text{eV} \), the occupied Fe 3d states are shifted...
too much towards lower energies. The reason for the disagreement with our conclusions is twofold. 
(i) Punkkinnen et al. used a different version of the DFT+$U$ Hamiltonian which is not rotationally invariant.
(ii) There are significant differences already at the GGA level. As no information on the magnetic structure is given in the paper, the possibility that the calculation refer to a different antiferromagnetic configuration cannot be excluded.

VII. CONCLUSIONS

We have calculated structural, magnetic, and electronic properties of rhombohedral $\alpha$-Fe$_2$O$_3$ for different volumes of the primitive unit cell in the framework of DFT using the GGA. It could be shown that although ground-state properties such as $c/a$ ratio and atomic positions agree well with experimental data, electronic properties such as band gap, but also magnetic moments, are in substantial disagreement with experiment. Furthermore we observe a HS-LS AF-FM insulator-metal transition at a pressure of 14 GPa which is not seen in experiment. Above that pressure structural parameters differ strongly from the corresponding experimental values. This transition turns out to be due to the improper description of the on-site Coulomb interaction in conventional DFT in combination with the GGA. When introducing a Hubbard like term in the density functional (DFT+$U$), the transition is shifted to lower volumes with increasing $U$ and eventually disappears for $U \leq 4$ eV, resulting in strongly improved values for magnetic moments, internal degrees of freedom, and band gap as well as better agreement of the density of states with experimental PES and IPS spectra. A further increase of $U$ does not lead to better agreement, the band gap gets too large and occupied Fe $3d$ states are shifted to too low energies. We consider $U = 4$ to be the value for
which best overall agreement is achieved.

An important result of this study is the profound change in the semiconducting gap from a $d$-$d$ exchange gap to an O $2p$–Fe $3d$ charge-transfer gap, paralleled by the change of the frontier orbitals (the highest occupied valence states) from strongly hybridized O $2p$–Fe $3d$ to almost pure O $2p$ character. As the frontier orbitals determine the chemical reactivity of the surface of a material, we expect a non-negligible influence of the on-site Coulomb repulsions on the stable surface termination and on the adsorption of atoms and molecules on hematite surfaces. Recent work by two of us on the adsorption of small molecules such as CO on NiO(100) has demonstrated that the strong correlation effects present in these materials lead to a reduction of the adsorption energy by more than a factor of 2 and a qualitative change in the adsorption geometry (tilted vs perpendicular), markedly improving agreement with experiment. Although the on-site Coulomb repulsion is stronger in NiO than in Fe$_2$O$_3$ ($U=6.3$ eV vs $U=4$ eV), we expect similar effects in hematite as well. Due to the much more complex crystal structure, even the surface termination could be influenced.

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