Fe_2O_3 within the LSDA + U approach

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Abstract. In the present work we concentrate on the electronic structure of haematite (Fe$_2$O$_3$) which shows two competing phenomena: correlation and hybridization. Using the tight-binding linearized muffin-tin orbital method with the on-site Coulomb interaction we show that, while haematite has considerable hybridization between different symmetries of electronic states, its on-site Coulomb interaction is also significant. The electronic structure is calculated by using LSDA and LSDA + U approximations to take into account the exchange–correlation effects. The LSDA + U potential describes many basic electronic properties of haematite better than the LSDA potential.

1. Introduction

In solid state physics the many-body problem is often treated by separating the many-electron Schrödinger equation into one-electron Schrödinger equations and replacing the original, nonlocal potential by a local, effective potential. Usually this is done within the (spin) density-functional formalism [1]. Unfortunately, the exact form of the total energy functional is not known. One has to approximate the unknown part, the exchange–correlation potential, in some way. The local (spin-) density approximation (L(S)DA) has been very successful for many systems in which the electrons are delocalized. For insulators and semiconductors the LSDA has been less successful. One reason for this is the fact that the LSDA does not take into account the on-site Coulomb interaction U of the strongly localized d electrons in a proper way. Moreover, the exchange–correlation potential is often treated as a spherical, orbital-independent potential. These facts appear specially as an inability to give a correct band gap for semiconductors and insulators. Many 3d-transition-metal oxides belong to this category, which makes them theoretically interesting. Moreover, they have special magnetic and electronic properties. There have been many investigations concerning transition-metal monoxides, because they have simple NaCl-type crystal structure [2]. Partly, the controversy has concerned the character of the gap of first-row transition-metal monoxides. Many suggestions have been proposed to improve the LSDA: generalized gradient approximation (GGA) [3, 4], self-interaction correction (SIC) [5, 6], orbital polarization correction [7, 8] and the L(S)DA + U method [9]. The L(S)DA+U method has been the most efficient method of these to produce the correct insulating state [9–12]. In this method the Coulomb on-site interaction is included in

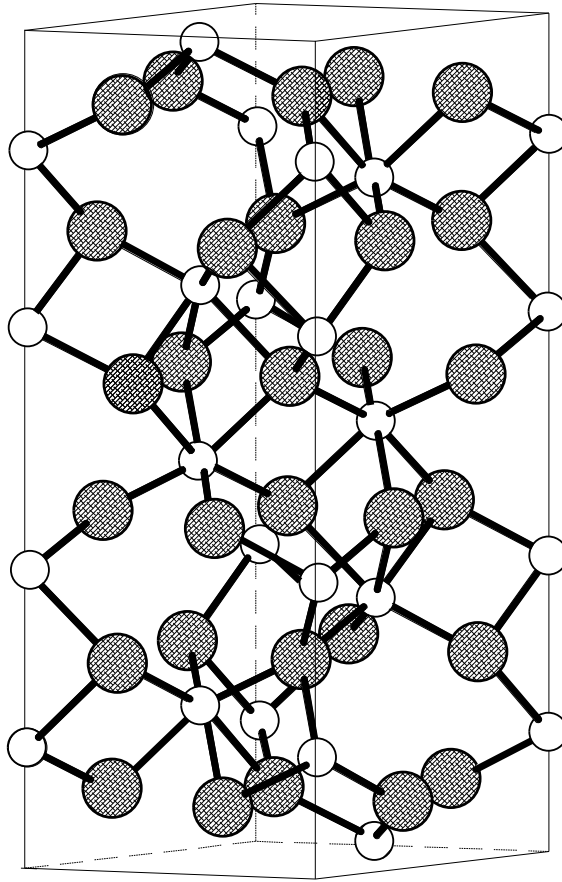¶ E-mail address: `marpunk@utu.fi`. Fax: +358-2-3336254.

Figure 1. The structure of Fe_2O_3. The iron atoms are shown by open circles and the oxygen atoms are shown by hatched circles.

the L(S)DA Hamiltonian. The non-local and energy-dependent self-energy is approximated by a non-local and energy-independent screened Coulomb potential [12]. One of the advantages of the method is the ability to treat delocalized and localized electrons simultaneously in the same computational scheme [12]. This is particularly advantageous if the localized d electrons hybridize significantly with other orbitals [12] as they do e.g. in the case of Fe_2O_3.

In this paper, we concentrate on haematite (Fe_2O_3), which has a rhombohedral primitive cell (space group $R\bar{3}c$). The structure of Fe_2O_3 is shown in figure 1. Haematite is an antiferromagnetic insulator below the Morin temperature ($T_M = 250$ K). The iron atoms are located in the holes of the trigonally distorted oxygen octahedra and the spins are aligned with the hexagonal [001] axis. There have been only a few electronic structure calculations taking into account the full crystal symmetry of the haematite: Hartree–Fock calculations [13] and ASW (augmented spherical wave method) LSDA calculations [14]. However, the results of the calculations concerning basic properties such as the magnitude of the band gap, magnetic moment, the strength of the hybridization and local partial DOS differ from each other. The basic problem concerning haematite is that both the localization of the valence states and the mixing of the oxygen p states and iron d states are considerable. In this paper, we consider

haematite in the LSDA + U framework. The Hubbard U-parameter is treated as an adjustable parameter. In this way, our goal is twofold: the LSDA results are brought into better agreement with experimental results by adjusting U and at the same time we obtain information about the on-site Coulomb interaction and the nature of the bonding in the system.

2. Methods of calculations

The calculations were performed by using the scalar-relativistic linear muffin-tin orbital (LMTO) method in the orthonormal tight-binding representation and the atomic-sphere approximation (TB–LMTO–ASA) [15–17]. We used a 36-atom hexagonal unit cell, which consists of three primitive, rhombohedral cells. Six empty spheres were introduced because of the open crystal structure of haematite. The Wigner–Seitz radius was 2.2279 au for iron atoms and empty spheres and 2.5175 au for oxygen atoms. The lattice parameters and the positional parameters x and z, which give the locations of the atoms in the unit cell, were taken from [18] and are for the hexagonal cell: $a = 5.0347$ Å, $c = 13.7473$ Å, $x(O) = 0.3056$ and $z(Fe) = 0.3553$. The basis-function set for the valence electrons consists of s, p and d functions. The calculations were done using 80 k-points in the irreducible wedge of the Brillouin zone. We used about 1300 vectors in the Bloch sum to calculate the (k-dependent) crystal structure constants. Iron 3d and 4s states and oxygen 2p states were treated as valence states. Oxygen 2s states were treated as semi-core states by another energy panel. Other states (core states) were held fixed throughout the self-consistent cycles of the valence electrons (frozen-core approximation). The exchange–correlation effects were taken into account by using the Perdew–Burke–Ernzerhof (LDA) exchange–correlation potential [19] and the orbital correction potential (for d electrons), which is [10]

$$V_{m\sigma} = V^{LSDA} + U \sum_{m'} (n_{m'-\sigma} - n^0) + U \sum_{m' \neq m} (n_{m'\sigma} - n^0) - J \sum_{m' \neq m} (n_{m'\sigma} - n_{\sigma}^0)$$

where V^{LSDA} is the LSDA potential, n^0 is the average d-orbital occupation number, n_{σ}^0 is the average spin–orbital occupation number and J is the exchange parameter for which a value is obtained from the LSDA calculation (1.05 eV). The occupation numbers were calculated self-consistently. At first the converged LSDA potential was obtained, and then the orbital correction was switched on and the potential was iterated to convergence again. Self-consistency was assumed when the magnetic moment was stabilized and the position of the Fermi level differed by about 0.0001 Ryd or less in successive iterations using a value of 0.10 for the parameter, which determines the mixing of the charge density. In this form, the exchange–correlation interaction works in a proper way by lowering the energy of a single-particle level (orbital) when it is filled, and increasing the energy of a single-particle level when it is emptied.

3. Results and discussion

Our LSDA calculation yielded quite similar results to those of Sandratskii *et al* [14]. The total DOS and spin-polarized d DOS of iron are shown in figures 2 and 3 (all curves are slightly smoothed). The oxygen p states and iron d states are more strongly mixed in haematite than in FeO (see also figure 6 and, for example, [10] and [11]). This might be partly due to the trivalent nature of Fe in haematite [20]. The iron 3d levels are lowered due to the smaller d-state occupation [20]. Moreover, in haematite the Fe–O distance is shorter than in FeO and the symmetry of the crystal structure is lower thus spreading the iron and oxygen states in the energy scale. The quite strong hybridization takes place over the whole valence band. This is in
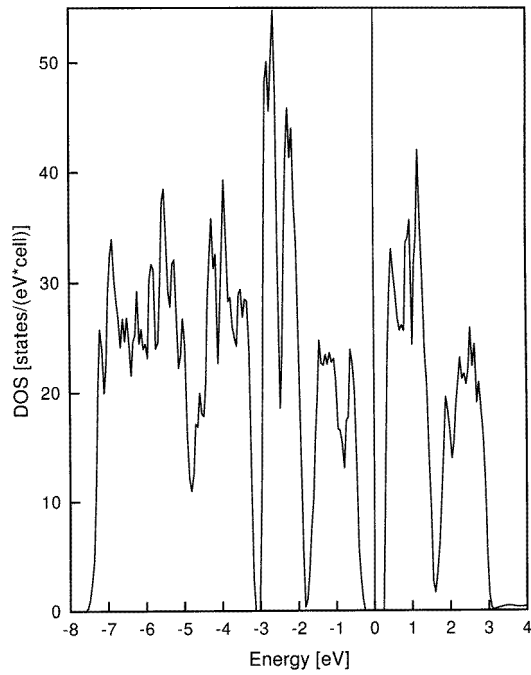
Figure 2. Total DOS within the LSDA approximation. The position of the Fermi energy is indicated by a vertical line.
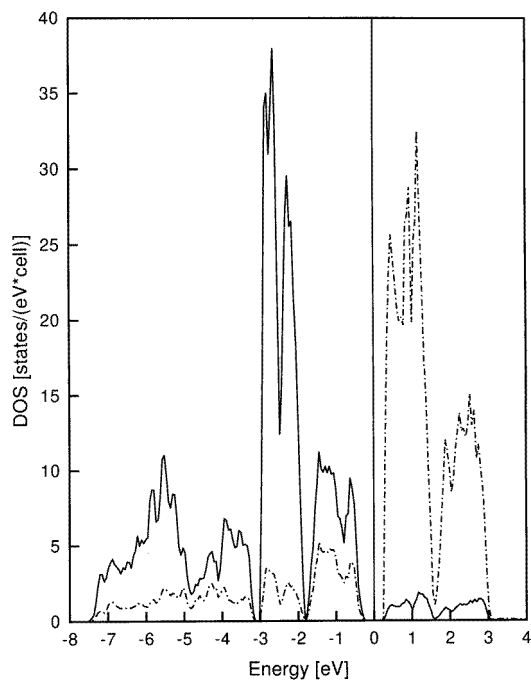

Figure 3. Spin-polarized d DOS of iron within the LSDA approximation. The spin-up and spin-down DOS are indicated by full and chain curves, respectively.
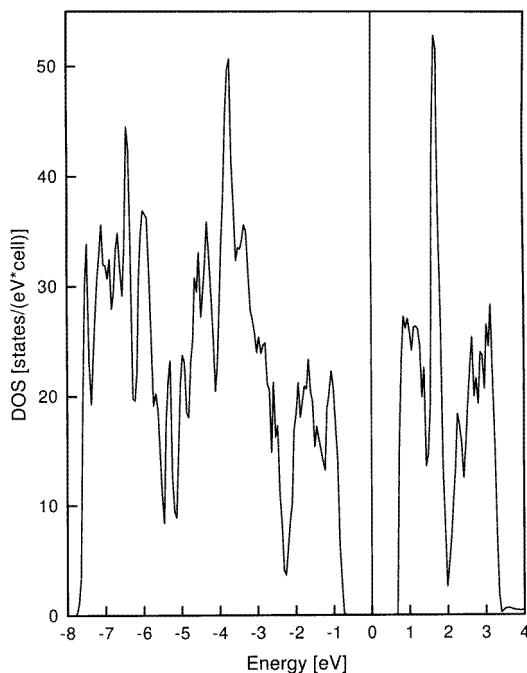
Figure 4. Total DOS within the LSDA + U approximation ($U = 2.0$ eV).

good agreement with the spectroscopy results [20, 21], but is contrasted with the results of the HF calculation, which shows very small oxygen 2p–iron 3d hybridization [13]. Although the DOS data cannot be directly compared with the spectroscopy results, there are several features in the DOS and various spectra which can be related to each other. Additional matrix elements describing the transition probabilities should be included in the theoretical investigations to critically assess e.g. the meaning of the photoemission results. Because of the hybridization, it is instructive to compare our local partial DOS with the x-ray emission and absorption spectra due to their selective nature because of the dipole selection rules. Although the total DOS of the LSDA calculation agrees quite well with the photoemission results of Fujimori *et al* [20], the partial iron d DOS of the LSDA calculation does not agree with the x-ray emission results [21] (even if one disregards the problems of the LSDA calculation with the band gap) or with the Fe 3d-derived emission spectrum [22]. The Fe Lα x-ray emission spectrum shows a broad peak, much broader than the Fe L$_3$ XAS peak, which probes the unoccupied part of the Fe 3d DOS. The peak is centred at the binding energy of 5 eV with respect to the centre of the gap [21]. The maxima near the Fermi level are at 3.1 eV and 6.2 eV according to the Fe 3d-derived emission spectrum [22]. However, the LSDA calculation shows a narrow maximum for the Fe 3d DOS at about 2.5 eV.

Other basic properties in which we are interested are the magnitude of the energy gap and the magnetic moment. The energy gap turns out to be of the charge-transfer type also according to our calculations in agreement with the experiments [20–22]. Our LSDA calculation yielded 0.51 eV and 3.43 μ_B for the energy gap and spin moment, respectively. The experimental values are about 2.0 eV [23] and 4.9 μ_B [24].

We used different values (2.0–5.0 eV) for the on-site Coulomb interaction U. The value of 2.0 eV gives best agreement with all considered experimental results. The total DOS and spin-polarized d DOS of the LSDA + U calculation ($U = 2.0$ eV) are shown in figures 4 and 5.
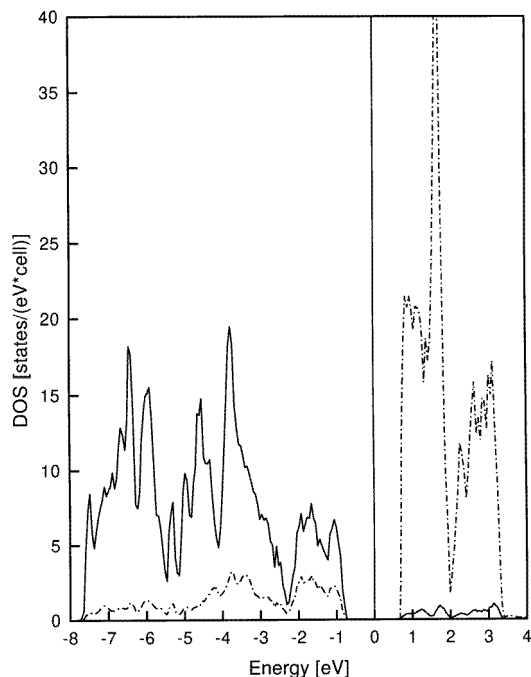
Figure 5. Spin-polarized d DOS of iron within the LSDA + U approximation ($U = 2.0$ eV). The spin-up and spin-down DOS are indicated by full and chain curves, respectively.

The obtained total DOS is very similar to the total DOS of the LSDA calculation irrespective of the larger band gap and slight modifications in the occupied DOS. There is one peak at the centre of the valence band instead of two peaks. However, the occupied part of the iron 3d DOS of the LSDA+U calculation is not predominantly concentrated near the top of the valence band as in the case of the LSDA. If one takes into account the energy-dependent lifetime broadening, the obtained results are in quite good agreement with the x-ray emission spectrum [21] and the Fe 3d-derived emission spectrum [22]. The local DOS of oxygen of the LSDA (broken curve) and LSDA + U (full curve) are shown in figure 6. The LSDA + U calculation increases the amount of the oxygen states and decreases the amount of the iron states at the top of the valence band. Therefore, an increase in the value of U brings a better agreement with the results of the HF calculation according to which the states at the top of the valence band are predominantly oxygen states [13]. Moreover, according to the photoemission measurements the states near the valence-band maximum are assigned to d^{5}L final states (L is a ligand hole) [20–22]. The LSDA + U calculation also increases the hybridization over the whole valence band in agreement with experiments, which show strongly hybridized structures in different spectra [20, 21]. However, one should note that the photoemission spectrum is composed of different final state configurations [20–22]. Therefore, one cannot expect exact correspondence between the calculational and experimental results, especially at higher binding energies, because the wave function is a single Slater determinant both in the LSDA and LSDA + U methods. This appears clearly as an inability to explain the high-binding-energy satellite. The satellite is related to the localized nature of Fe 3d electrons [20].

   The LSDA + U calculation (using a value of 2 eV for U) yielded 1.42 eV for the energy gap and 3.84 μ_B for the spin-moment, respectively. The orbital moment is almost quenched
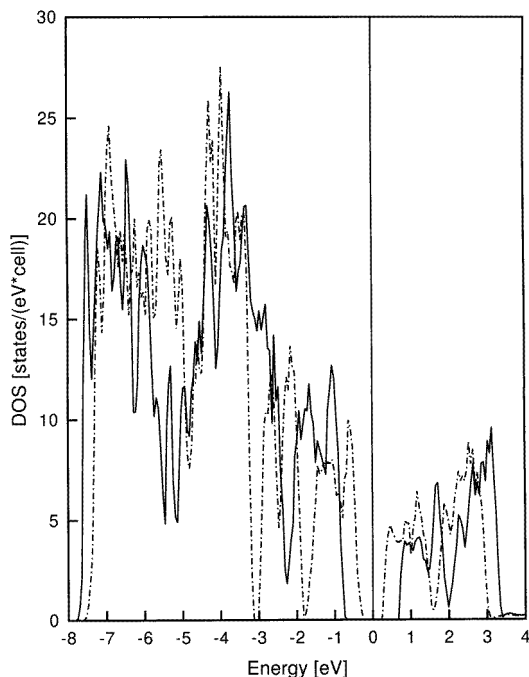
Figure 6. Local DOS of oxygen within the LSDA approximation (chain curve) and the LSDA + U approximation (U = 2.0 eV) (full curve).

(0.01 μ_B) and the crystal field splitting has about the same magnitude as in FeO. The value of 3.5 eV for U yields an energy gap of the experimental size: the energy gap is 2.04 eV and the spin moment is 4.01 μ_B (orbital moment is 0.01 μ_B). However, the Fe 3d states are shifted strongly to the bottom of the valence band and one cannot find a good agreement with spectroscopy data. It is possible that the experimental value for the magnetic moment from the neutron diffraction measurements is overestimated, because the magnetic form factor is distorted by the strong mixing of the oxygen 2p and iron 3d states [14]. The negligibly small hybridization and the overestimation of the band gap (about 1 Ryd) of the HF calculation appear as a large value for the magnetic moment (4.74 μ_B) [13].

Our results show that the correlation effects due to the localized nature and small bandwidth of the iron 3d electrons are significant also in haematite. The LSDA + U potential describes many basic electronic properties better than the LSDA potential. However, the value of U is quite small. This is partly because of the screening of the on-site Coulomb interaction in Fe$_2$O$_3$ due to the charge transfer between the oxygen 2p states and iron 3d states. The larger value of U in FeO (3.5 eV according to experiments) [25] compared to that in haematite is partly due to the larger Fe–O distances in FeO. Another reason for the quite small value of U in iron oxides is that the strong exchange interaction (which tends to stabilize the screened high-spin d^5 state) is screened less than the repulsive part of the Coulomb interaction [25]. The exchange interaction is possibly even stronger in haematite than in FeO because of the more significant oxygen 2p–iron 3d hybridization which strengthens the superexchange mechanism and increases iron 3d–iron 3d hybridization mediated via the oxygen orbitals. The exchange interaction appears as a non-vanishing energy gap also in the LSDA calculation and a smaller value for U than in FeO. The experimental determination of U is difficult partly because

of the several many-body interactions involved in experiments [26]. Although the explicit inclusion of U improves the agreement with the experimental results in many respects, the size of the experimental energy gap is not achieved with a value of U which gives the best overall agreement with experiments. This is probably due to the strong Fe 3d–O 2p hybridization. The hybridization can take place also between different excited-state configurations thus making the character of the energy gap more exotic [25].

Full potential treatment (instead of the ASA approximation) might have led to better agreement with experiments. The ratio of the Wigner–Seitz radii of the atomic spheres affects slightly the investigated quantities. Using a ratio of 0.8333 (2.1474 au for iron atoms and empty spheres and 2.5769 au for oxygen atoms) yields 0.57 eV for the energy gap and 3.46 μ_B for the spin moment (orbital moment is 0.01 μ_B). The corresponding results of the LSDA + U calculation ($U = 2.0$ eV) are 1.48 eV and 3.85 μ_B. The net amount of the charge transfer from a particular sphere depends naturally on the value of the radius of that sphere. A decrease in the radius of the iron atoms (from 2.2279 au to 2.1474 au) increases iron net charge transfer from -1.80 e (electrons) to -1.97 e in the LSDA calculations and from -1.86 e to -2.03 e in the LSDA + U calculations. The frozen-core approximation is expected to work well for the investigated system and quantities, because the core states are very well separated from the valence and semi-core states in energy scale. Moreover, the experimental lattice parameters are used. If one treats the oxygen 2s states as core states, the energy gap and magnetic moment are decreased. For example, the energy gap of the LSDA calculation is decreased by about 0.2 eV.

However, one should note that haematite is a very difficult system to investigate theoretically. The localized nature of d electrons leads to correlation effects. On the other hand, the hybridization of oxygen 2p states and iron 3d states and the screening of the on-site Coulomb interaction tend to lead to a band-like behaviour.

4. Summary and conclusions

In summary, the electronic band structure of haematite is calculated within the LSDA + U approximation using different values for the on-site Coulomb interaction U. Best agreement with all considered experimental results is obtained by using a value of 2.0 eV for U. The introduction of U increases the energy gap and magnetic moment in agreement with the experimental results. Moreover, the local partial d-DOS of iron is described better in the LSDA + U than in the LSDA. The LSDA + U calculation increases the amount of the oxygen states at the top of the valence band. The value of U for haematite is quite low. This is because of the strong exchange interaction and the screening of the on-site Coulomb interaction due to the charge transfer and hybridization. In spite of this, our calculations show that the correlation effects beyond the LSDA are important in haematite due to the localized nature of iron 3d states.

Acknowledgments

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