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LETTER TO THE EDITOR

A theoretical and experimental investigation of the electronic structure of α -Fe₂O₃ thin films

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Abstract. Ground and excited states of α -Fe₂O₃ have been investigated by determining the spin-polarized wavefunctions and eigenvalues of an embedded Fe₂O₉²⁻ cluster using the discrete variational X_α method. The computed transition energies compare reasonably well with the recorded experimental spectrum of high-purity α -Fe₂O₃ thin films obtained by the sol-gel technique. The theoretical data herein reported predict a very high valence-conduction band gap incompatible with the experimental outcomes, which were routinely interpreted as originated by an interband transition. In contrast to this, the lowest-energy optical transitions have a charge transfer nature, involving excitation of electrons from the occupied O 2p-based spin down levels to the empty Fe atom-like spin down orbitals.

Iron (III) oxide thin films are particularly appealing for experimental and theoretical investigations in view of their technological applications. Actually, they can be used as catalysts in dehydrogenation reactions [1], magnetic devices [2], temperature and water sensors and optical filters [3, 4]. Furthermore, the applicability of Fe₂O₃ thin films in the relatively new field of non-linear optics has been suggested [5].

The UV-VIS absorption spectra of ferric oxides have received great attention in the past in order to understand the role of the ground and excited electronic states in determining their electronic properties. Unfortunately, in the case of measurements carried out on bulk samples, a very strong absorption starting at about 2.45 eV obscures a large section of the UV-VIS spectrum, preventing any analysis of the energy region above such an edge. As a consequence, in these kinds of sample, the only bands for which an assignment can be attempted are the very weak ones lying at about 1.85 eV, which, on the basis of crystal field calculations [6, 7], are assigned as a whole to the formally doubly forbidden d-d electronic transitions within the d⁵ configuration of the iron (III) ion.

In a recent contribution, some of us [8] investigated by means of x-ray photoelectron (XPS), UV-VIS and Mössbauer spectroscopies high-purity Fe₂O₃ thin films prepared by the sol-gel technique. In detail, XPS measurements revealed that iron is only present (within the sensitivity of the technique, <1%) in the ferric form and that films without any carbon contamination are obtained at temperatures above 400 °C. The absence of any absorption in the near-IR range confirmed the absence of the ferrous species for all the heat treatment temperatures. Furthermore, Mössbauer spectroscopy detected exclusively the presence of iron (III) ions with an octahedral environment in the amorphous phase as well as in

nanocrystals. As far as the UV-VIS data are concerned, a fairly resolved structure in the 2.5–6.0 eV spectral region was obtained for films heated above 500 °C.

In the present letter we extend the analysis to UV-VIS spectra for Fe₂O₃ coatings heated from 200 °C to 1000 °C. Moreover, a detailed assignment of absorption bands for samples heated above 500 °C [9] is reported. The theoretical analysis of the experimental data is based on calculations carried out within the discrete variational (DV) X_α approach [10] through the use of the cluster embedding procedure of Ellis *et al* [10], which, incidentally, has been widely applied in the last decade to study the electronic structure of metal oxides and of defect centres in these materials [11].

The DV X_α procedure [10] has been used to determine the spin-polarized wave functions and the eigenvalues of a cluster. The rest of the solid has been mimicked by providing an electrostatic crystal field and charge field in which the cluster is embedded (see the article by Ellis *et al* [10]). This is done by generating a microcrystal surrounding the cluster and placing the atoms at specified lattice positions. This approach has proved to be very appropriate to investigate systems where the conventional band structure formalism turns out to be intractable or computationally expensive. More details about the computational procedure are reported by Bertonecello *et al* [11].

Numerical atomic orbitals (AOs) generated by Hartree-Fock-Slater calculations on free Fe³⁺ and O²⁻ ions were used as basis functions. An extended basis set was used for both atoms (1s–4d for Fe and 1s–3p for O). Spherical wells (2 Ryd deep) having internal and external radii of 4.0 and 6.0 au, respectively, were added to the atomic potentials.

The crystal structure of haematite, α-Fe₂O₃, is typified by that of corundum, rather common in sesquioxides (α-Al₂O₃, Cr₂O₃, Ti₂O₃, α-Fe₂O₃). The hexagonal unit cell, containing 12 Fe cations and 18 O anions is shown in figure 1, while in figure 2 the rather small cluster (Fe₂O₉) we have adopted to carry out our calculations is displayed (see below). Geometrical parameters relative to the cluster employed have been taken from [12], where the crystal structure of hexagonal Fe₂O₃ is reported.

The Fe₂O₃ precursor solution was prepared by dissolving Fe(OCH₂CH₃)₃ in dehydrated ethanol. Iron (III) ethoxide was synthesized in our laboratory according to the published procedure [13]. The oxide concentration in the solution was 20 g l⁻¹. Films were obtained by dipping spectrograde silica slides in the precursor solution with a withdrawal speed of 12 cm min⁻¹. Depositions were carried out at room temperature and at a relative humidity of 60%. Heat treatments were performed in air by using a programmable furnace (Heraeus Thermicon P) from 200 °C to 1000 °C, holding the samples for 1 h at each temperature. Films 1000 (± 100) Å thick, as measured by a Tencor Alpha Step profilometer, were obtained. The UV-VIS spectra were finally recorded using a double-beam CARY5E spectrophotometer with a spectral bandwidth of 1 nm. The contribution due to the silica substrate was subtracted.

In a series of papers dealing with the electronic structure of sapphire (with both bulk and surface states taken into account) Ellis and coworkers [11] have pointed out that only for quite large and compact clusters, containing more than 30 embedded atoms, does the density of states (DOS) not show significant variations when increasing the cluster size. With this in mind, our first numerical experiments were carried out by running spin-polarized DV X_α calculations on an embedded 33-atom cluster of symmetry C_{3v} containing 15 Fe atoms. As usual, when carrying out molecular cluster calculations, the first problem to be solved is the choice of the correct number of electrons to be used to fill the DV X_α self-consistent cluster energy levels. In principle, any number of electrons between the neutral cluster and the ionic extreme would be correct [14]. In this regard, it is worthwhile to mention that in a rather ionic material such as ZnO the use of the ionic extreme provided very good results (see the

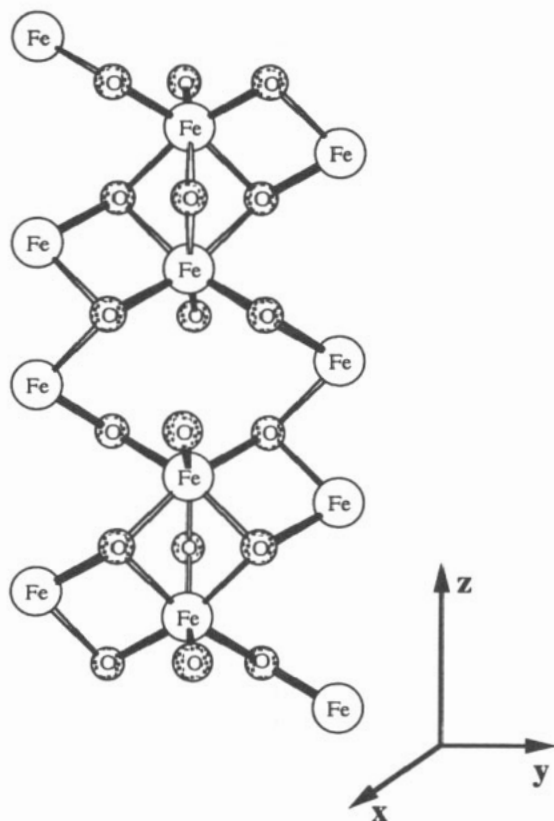


Figure 1. A schematic representation of the hexagonal unit cell of haematite. The dark thick lines correspond to the short Fe–O bonds (1.97 Å) while the thin ones refer to the long Fe–O (2.12 Å) bonds.

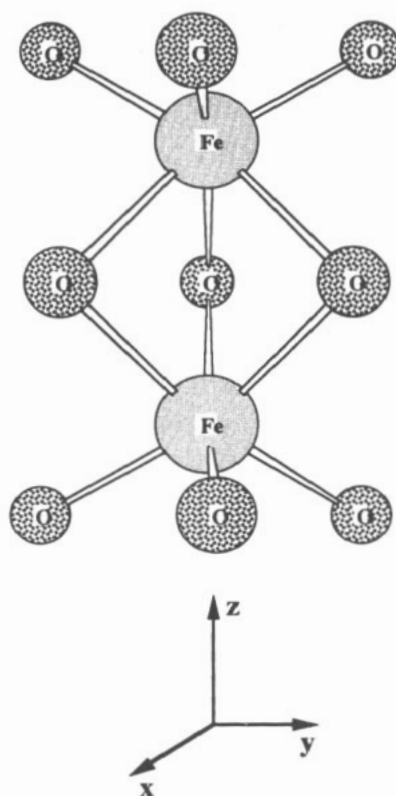


Figure 2. A schematic representation of the Fe_2O_9 cluster. In the adopted framework the z axis is coincident with the Fe–Fe internuclear axis.

articles by Bertocello *et al* [11]), so in all the clusters investigated we assumed that each Fe and O atom contributes five (Fe^{3+}) and eight (O^{2-}) electrons, respectively. As a matter of fact, in a cluster of 33 atoms including 15 Fe centres, the number of 3d Fe AOs is quite large ($5 \times 15 \times 2 = 150$; the two is due to the spin-polarized treatment) and the relative cluster MOs are very closely spaced. In these conditions, we verified that the spin polarization was completely lost, because for each Fe-based spin up level the corresponding spin down partner was also occupied. On this basis, within the adopted theoretical framework, the size of the cluster has been determined by the requirement of finding the correct number of unpaired electrons on each Fe centre (approximately five). The largest cluster having the required features is the one reported in figure 2, which consists of two equivalent Fe atoms short bonded to six axial O ions and long bonded to the three equatorial ones. The symmetry properties of the $\text{Fe}_2\text{O}_9^{12-}$ cluster refer to the C_{3v} point group.

In figure 3 the DOS of the $\text{Fe}_2\text{O}_9^{12-}$ cluster is reported together with the Fe and O partial DOSSs (PDOSSs). These plots were obtained by applying a Lorentzian broadening to the cluster eigenvalues and scaling the energies with respect to the highest occupied molecular orbital (HOMO).

The distinction between *octahedral* t_{2g} -like and e_g -like Fe contributions to the Fe PDOS is prevented by the mixing of $d_{x^2-y^2}$ with d_{xz} and d_{xy} with d_{yz} as a consequence of the use of the threefold axis as the axis of quantization [15]. Nevertheless, it is still possible to recognize contributions from the Fe $3d_{z^2}$ AO, which transforms, in C_{3v} , in a unique way and consequently is a *pure* t_{2g} -like level.

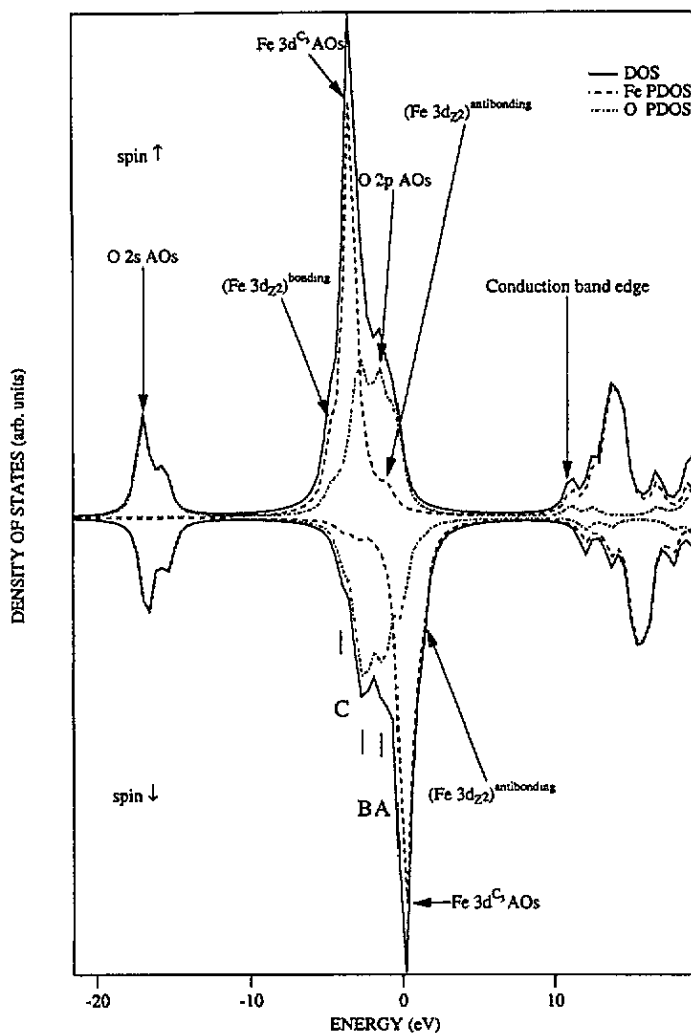


Figure 3. The DOS of the Fe_2O_3 cluster. Spin up levels have positive values while the spin down ones have negative values. The O and Fe PDOSs are also outlined.

The bonding contribution between the Fe $3d_{z^2}$ AO and a suitable linear combination of O 2p levels gives rise to the low-energy shoulder in the spin up Fe PDOS outlined in figure 3. The ΔE (1.22 eV) [16] between this Fe $3d_{z^2}$ component and the accidentally degenerate $d_{x^2-y^2}$; d_{xz} ; d_{xy} and d_{yz} (hereafter $3d^{C_3}$) roughly corresponds to the crystal field splitting of the Fe 3d AOs induced by oxide ions. The obtained value is in reasonable agreement

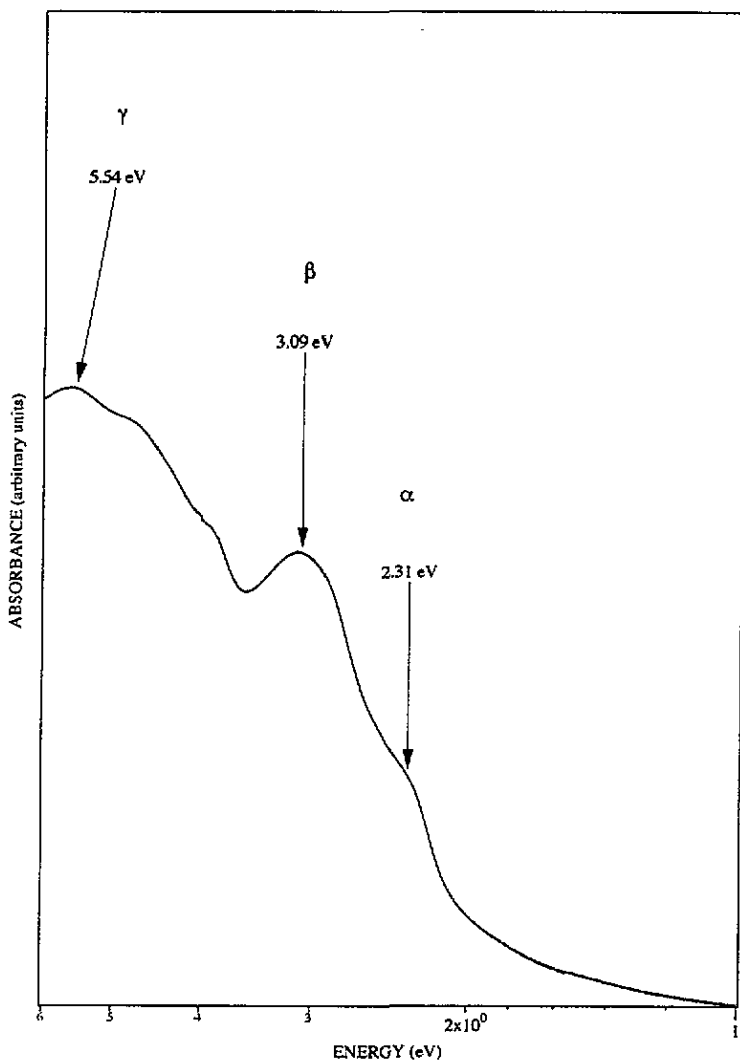


Figure 4. The spectrum of the α - Fe_2O_3 thin film heated at 1000 °C. The energy scale is logarithmic.

with experimental data reported by Baiocchi *et al* [18] for glasses containing Fe^{3+} ions in a pseudo-octahedral coordination. The Fe and O gross atomic charges obtained from the Mulliken [19] population analysis are 2.02 and -1.78 , respectively, while the Fe magnetic moment, evaluated by taking the difference between the Mulliken populations for Fe spin up and spin down electrons (3d, 4s, 4p, 4d) [20] is $3.81 \mu_B$. It is also interesting that the composition of the lowest spin up unoccupied MO (LUMO), which, in agreement with theoretical results pertaining to other rather ionic oxides such as ZnO (see the article by Bertoncello *et al* (1992) [11]) and α - Al_2O_3 (see the article by Shangda *et al* [11]), is significantly localized over Fe 4s AOs with non-negligible contribution from O 3s levels. The HOMO(\uparrow)-LUMO(\uparrow) energy difference, which can be associated with the fundamental band energy gap (see figure 3), is ~ 11 eV [21]. This result is fairly close to those obtained

by Shangda *et al* and Guo *et al* (1992) [11] by means of the same theoretical approach as employed here for the isostructural α -Al₂O₃.

In figure 4 we present the first complete UV-VIS spectrum up to ~ 6 eV of a perfectly transparent and crystalline α -Fe₂O₃ thin film [22] ever reported. This spectrum is readily assigned making reference to our theoretical calculations. It is evident from figure 3 that the allowed transitions will involve a charge transfer from the occupied O-based spin down levels (indicated as A, B and C) into empty Fe atom-like spin down 3d orbitals (the accidentally degenerate 3d^{C₃} and the pure 3d₂, antibonding in character). It is noteworthy that such an assignment is substantially different than that proposed by Hashimoto *et al* [23] who associated the shoulder (~ 2.5 eV) and the single peak (~ 3.1 eV) present in their spectra to the excitations from the Fe³⁺ 3d AOs into the conduction band and from the O²⁻ 2p bonding levels into the conduction band, respectively. In relation to this, it is of relevance to point out that the assignment proposed by Hashimoto *et al* [23] is definitely in contrast with trivial energetic considerations. Actually, it is hard to believe that transitions involving $\Delta E < 5$ eV imply a charge transfer from Fe³⁺ ions, characterized by a very high ionization energy, to O²⁻ ions having a very low electron affinity.

Our computed orbital energy differences [16] are 1.64 eV, 2.86 eV, 4.08 eV and 5.31 eV. Transition state calculations [17] have been also carried out in order to take care of relaxation effects upon excitation; negligible differences have been obtained with respect to ground state orbital energy differences.

With reference to figure 4, at least three clearly evident features (labelled as α , β , γ) are present in the 2–6 eV energy region. The absorption coefficient is about 2×10^5 cm⁻¹ at the band maximum (~ 5.6 eV), clearly indicating that the transitions involved are fully allowed. Their assignment results a straightforward matter by making reference to figure 3. The lowest-energy feature (α in figure 4) can be confidently associated with the excitation from the shoulder A (see figure 3) to the 3d^{C₃}. The stronger intermediate feature β in figure 4 is, according to our theoretical data, the convolution of two distinct transitions, one involving the excitation from B to Fe 3d^{C₃} AOs, the other from A to the Fe 3d₂ AO. The last poorly resolved band envelope γ , peaking at 5.54 eV, is then assigned to the remaining transitions involving the shoulder C of figure 3 and the Fe 3d₂ AO. It is worthwhile to note that under this band envelope the two transitions from C to 3d^{C₃} and from B to the Fe 3d₂ AO are also hidden.

For the first time the spectrum up to 6 eV of a perfectly transparent and crystallized thin film of α -Fe₂O₃ has been presented. The complementary use of UV-VIS spectroscopy and DV X_α calculations within the embedded molecular cluster model has allowed a detailed description of all the spectral features. The most relevant result of the present contribution is that, in contrast to previous assignments of the UV-VIS spectrum of α -Fe₂O₃ thin films, the lowest-energy optical transitions have to be associated with a charge transfer from the occupied O 2p-based spin down levels to empty Fe-based spin down orbitals within the valence band. In other words, the observed spectral features are due to intraband excitation rather than to interband transitions.

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