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Band theory for electronic and magnetic properties of α -Fe₂O₃

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Abstract. We report results of calculations that explain in the itinerant-electron picture magnetic and electronic properties of haematite, α -Fe₂O₃. For this we use the local approximation to spin-density functional theory and the ASW method incorporating spin-orbit coupling and noncollinear moment arrangements. The insulating character of the compound is obtained correctly and features in the density of states connected with Fe–O hybridization correlate well with experimental features seen in direct and inverse photoemission intensities. The total energy correctly predicts the experimentally observed magnetic order of the ground state, and, using total energies of different magnetic configurations, we can give a rough estimate of the Néel temperature. We also obtain a state showing weak ferromagnetism. The rate of change is calculated for the decrease of the insulating gap when an external magnetic field is applied.

1. Introduction

The itinerant-electron picture, as embodied in self-consistent energy-band theory, provides an accurate interpretation of a wide variety of magnetic phenomena. However, its application to the transition-metal oxides still remains in dispute; for a recent exposition, one may consult the review by Hüfner [1]. The work of Sarma *et al* [2] has thrown new light on the controversy by demonstrating the applicability of band theory to certain classes of transition-metal oxides (perovskites) for which the ratio of the electron–electron interaction strength and the hopping parameter was shown to be small enough to lead to delocalized d states.

We have recently determined the weak ferromagnetism of haematite, α -Fe₂O₃, i.e. we successfully obtained its basically antiferromagnetic structure in which, however, some small canting of the moments leads to an observable, ferromagnetic component [3]. Thus, in the itinerant-electron picture, we described correctly a rather complicated magnetic state together with the insulating nature of this compound. We therefore believe that haematite is in the same class as the perovskites studied by Sarma *et al* [2]. This motivates us here to give a full report of our calculations for α -Fe₂O₃ discussing computational details and new results concerning the electronic structure, in particular total energies of various magnetic states which allow us to estimate the Néel temperature. Furthermore, we show densities of states and determine the dependence of the band gap on an applied magnetic field. Where possible we compare our results with experimental data.

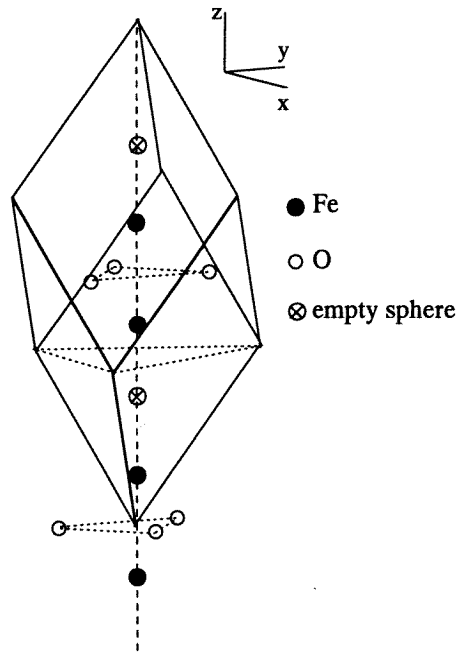


Figure 1. The crystal structure of α - Fe_2O_3 giving the rhombohedral unit cell.

2. Computational details

The crystal structure of α - Fe_2O_3 is shown schematically in figure 1 where we chose to display the primitive rhombohedral unit cell containing two formula units. Our self-consistent calculations are based on the local approximation to spin-density functional theory (LSDA). Since we use for the actual computations the ASW method [4] in the fully relativistic version [5], we are forced to make the atomic-sphere approximation which for the crystal structure at hand needs space-filling ‘empty’ spheres; they are placed at the positions shown in figure 1. Altogether the radii of the atomic spheres were chosen as follows: 2.237 au for Fe, 2.5 au for O and 2.237 au for the empty spheres, using for the lattice constants experimental values given by Wyckoff [6].

Table 1. The total energy E_{tot} (measured from the $(+ - - +)$ state), spin moment m_{sp} , orbital moment m_{or} and total moment m_{tot} for different magnetic configurations of Fe_2O_3 .

Configuration	E_{tot} (mRyd/(Fe atom))	m_{sp} (μ_B)	m_{or} (μ_B)	m_{tot} (μ_B)
(+ - - +)	0	3.69	0.03	3.72
(+ - + -)	14	3.77	0.03	3.80
(+ + - -)	15	3.71	0.03	3.74
(+ + + +)	36	3.70	0.03	3.73

3. Results and discussion

Since the unit cell of Fe₂O₃ contains four Fe atoms, we consider four magnetic sublattices and begin with by comparing the following magnetic configurations: (+++ +), (+-+-), (+--+) and (++--), where + and - designate up- and down-spin directions with respect to the *z*-axis (figure 1). In table 1 we collect together the total energies and the Fe magnetic moments of these configurations. In full agreement with experiment, the total energy is lowest for the (+-+-) configuration. The other two antiferromagnetic configurations are separated in energy by about 15 mRyd per Fe atom. The highest total energy is possessed by the ferromagnetic configuration which lies 36 mRyd above the ground state. In spite of the large differences in the total energies of the four magnetic configurations, the value of the atomic magnetic moment of Fe is quite stable, changing only little with magnetic structure. The calculated value of the atomic moment of iron is 3.72 μ_B in the ground state; this is somewhat smaller than the experimental estimates of 4.6–4.9 μ_B [7, 8]. Like Sarma *et al* [2] we believe that this difference may arise on one hand from an overestimate of the mixing of the O 2p with the Fe 3d states in the LSDA, but on the other hand it may originate in the analysis of the neutron diffraction data since the magnetic form factor is distorted by this mixing as well.

It is this stability of the magnetic moments with respect to changes of the magnetic configuration which was shown in [9] to establish a qualitative basis for the use of the Heisenberg Hamiltonian of classical spins to obtain a rough estimate of the magnetic transition temperature. Because of the equivalence of all Fe atoms we can write the magnetic energy of the crystal, calculated per Fe atom, as follows:

$$H = - \sum_{\nu} \sum_j J_{\nu j} S_0 S_{\nu j}. \quad (1)$$

Here the energy is calculated for an arbitrarily chosen ‘0th’ or ‘central’ atom. The sum extends over all atoms except for the central one, and ν numbers different magnetic sublattices and j the atoms within a sublattice. Without loss of generality we may assume that the 0th atom belongs to the first sublattice. Rewriting equation (1) in terms of the energies E_{ν} of the interaction of the 0th atom with the atoms of the ν th sublattice, we obtain

$$H = \sum_{\nu} E_{\nu}. \quad (2)$$

Since in the calculation of the four magnetic structures we only changed the *relative* direction of the atoms belonging to different sublattices, we have no numerical information on the exchange interaction, E_1 , between the 0th atom and the other atoms of the same sublattice. However, the leading contribution to E_1 comes from the sixth-nearest neighbours; thus this term does not influence the magnetic properties of Fe₂O₃ noticeably and can be neglected [10, 11]. Thus our estimates of E_2 , E_3 , and E_4 are 9.25, 8.75, and –1.75 mRyd, respectively. The mean-field approximation to the Hamiltonian given by equation (1) leads to the simple formula [12]

$$T_N = \frac{2}{3}(E_2 + E_3 + E_4) \quad (3)$$

for the Néel temperature and gives in our case a value of 1711 K. This is in fair agreement with the experimental value of 953 K, which, in view of the simplicity of the theory, must be considered satisfactory.

We next turn to the discussion of the calculated density of states (DOS) and show the total as well as some partial DOSs in figure 2. It is important to notice that the insulating

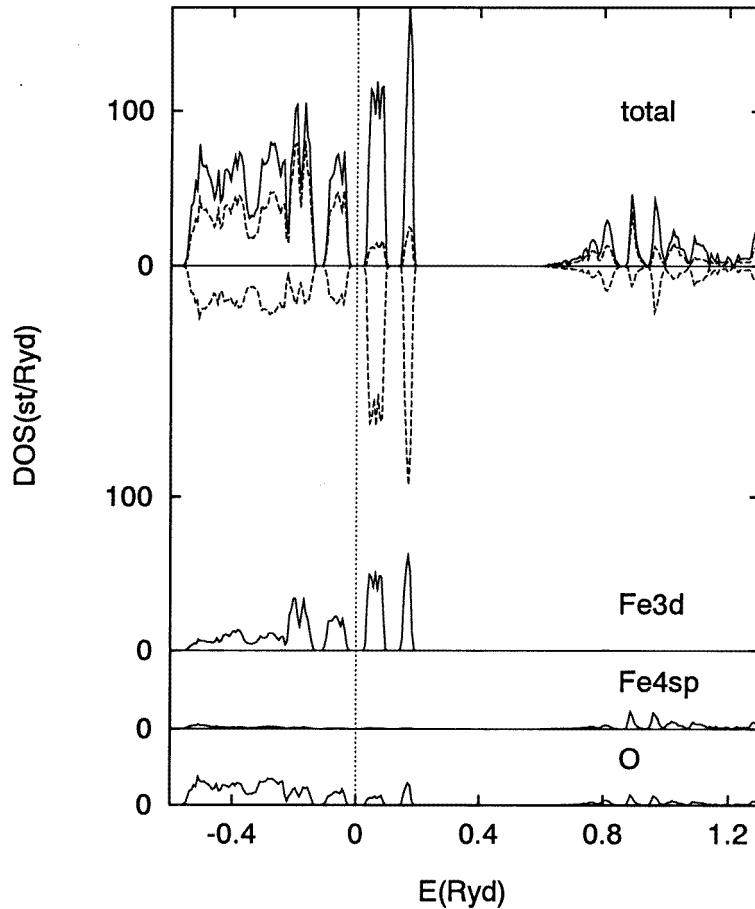


Figure 2. The density of states (DOS) of α -Fe₂O₃ for an antiferromagnetic ground state. Upper panel: solid line: total DOS; dashed line: spin-decomposed DOS; lower panels: partial Fe 3d, Fe 4sp and O DOS. The total DOS is given per chemical formula unit, while the partial DOS is per atom. The energy is measured from the Fermi energy.

nature of α -Fe₂O₃ is obtained correctly, although the calculated energy gap of about 0.75 eV is underestimated when it is compared with the optical gap of about 1.9 eV [13]. This deficiency of our LSDA approach is well known even for normal band semiconductors and insulators.

In figure 2 one sees that the upper part of the occupied states (the energy interval from -0.2 to 0 Ryd) as well as the lower part of the empty states (in the interval 0 – 0.2 Ryd) are formed by states with predominantly Fe 3d character, substantially mixed with O 2p states. Below -0.2 Ryd the states are still strongly hybridized but the O contribution now exceeds the Fe contribution. The states above 0.6 Ryd are Fe s–p states hybridized, again, with O states. Thus there is a substantial contribution of O states to all states in the energy interval from -0.6 to 1.3 Ryd. However, figure 2 also shows that different states originating from Fe alone, like the 3d and the 4sp states, are not mixed in this energy window.

The calculated DOS allows a comparison with available photoemission experiments. This is done in figure 3 for both the occupied and the empty states. To correct the gap

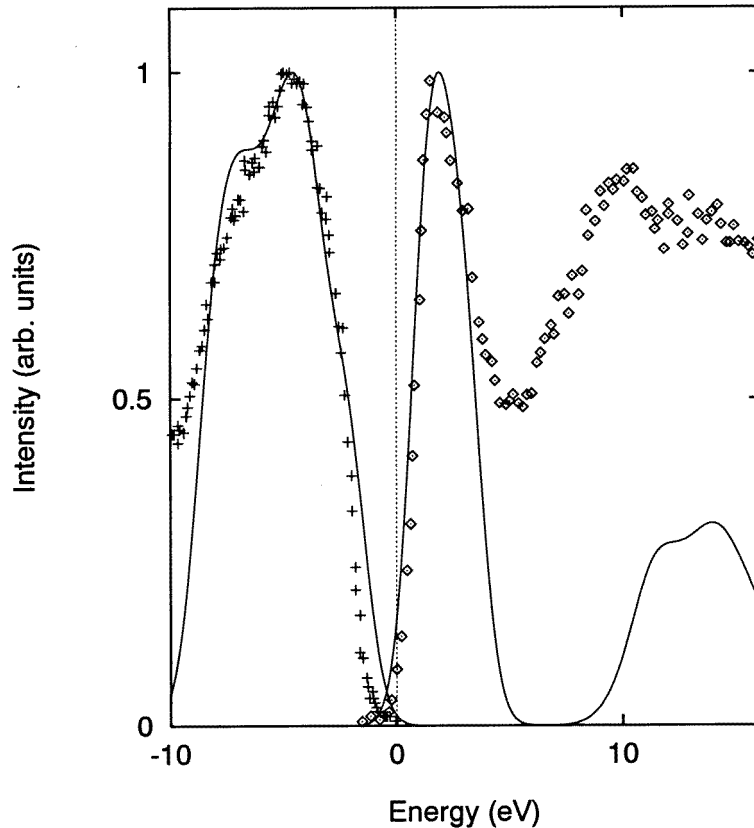


Figure 3. A comparison of calculated density of states (solid lines) with photoemission intensities (crosses) [14] and inverse photoemission (diamonds) [15]. The spectra are shifted to correct for the gap problem (see the text). To account for instrumental resolution and finite-lifetime effects the calculated DOS was broadened with a Lorentzian of 0.8 eV width.

problem the occupied and empty parts of the DOS were shifted relative to one another. In all other respects the agreement of the calculated DOS with the measured photoemission (direct and inverse) is good. In particular, the occupied part of the DOS possesses three obvious features which are also reflected in the measured intensities, confirming the conclusion of Fujimori *et al* [14] who attributed these features to the mixed Fe 3d–O 2p character of the electron states.

Concerning the empty states in figure 3 both theory and experiment [15] show the presence of two well-separated groups of states. In agreement with experiment the lower group of states is predominantly of 3d character, the contribution of the O states being rather small. The upper group of states originates mostly from the Fe 4sp states. The disagreement in the experimental and theoretical intensities at about 12 eV we believe results from background effects and our neglecting transition matrix elements.

Next we briefly describe the results of a numerical experiment to estimate the dependence of the energy gap on the value of an external magnetic field which we applied perpendicular to the magnetic moments. Under the influence of the field the magnetic moments deviate from the original antiparallel directions and tend to point toward the

magnetic field forming a canted magnetic structure. Evidently the canting angle increases with increasing field. Calculating the band structure for the canted states we find that the value of the energy gap decreases with increasing canting angle with a rate of change that can be estimated to be approximately 7 meV per degree. Unfortunately we know of no experiment on the field dependence of the insulating gap in α -Fe₂O₃.

For completeness we briefly touch on our calculations (published in detail elsewhere [3]) for weak ferromagnetism in α -Fe₂O₃ which is observed above 120 K and was explained by Dzialoshinski and Moriya (see [16] and [17]) some time ago in the localized-moment picture. In the itinerant-electron picture that is the basis of our work here the canted state that gives rise to a ferromagnetic moment of about $0.002 \mu_B$ is due to a combination of spin-orbit coupling and the particular crystal structure of α -Fe₂O₃ and is found as a self-consistent solution having a total energy that is, within our numerical accuracy, approximately the same as the ground-state energy. The magnetic moments in this case are arranged antiferromagnetically, being canted by a very small angle but essentially perpendicular to the z -axis (figure 1).

In closing we compare our results with those of previous calculations; these are the X_α -cluster calculation of [18] and the recent Hartree-Fock calculation of [19]. We agree with the results of [18] concerning the strong O 2p-Fe 3d mixing. But this is in contrast with the results of [19] which show a negligibly small O 2p-Fe 3d hybridization. Another point of difference between the present calculations and those of [19] is the value of the energy difference between the ground-state antiferromagnetic structure and the ferromagnetic structure. Our energy difference of 36 mRyd per Fe atom must be compared with 3.4 mRyd given in [19]. We believe that the small value in [19] is the result of the underestimation of the Fe 3d-O 2p mixing which leads to an underestimation of the effective exchange interaction between the Fe atoms. The value of 3.4 mRyd can hardly explain the rather high Néel temperature of 953 K in α -Fe₂O₃.

4. Conclusion

We have reported an LSDA calculation made in an effort to describe the electronic and magnetic properties of α -Fe₂O₃. In spite of the well-known problem that the LSDA has with a proper determination of the energy gap in semiconducting and insulating materials, we still succeeded in describing extremely well a number of important physical properties: the insulating character of the compound was obtained correctly and quite pronounced features in the density of states connected with Fe-O hybridization correlate well with experimental features seen in direct and inverse photoemission intensities. The total energy correctly predicted the experimentally observed magnetic order of the ground state, and total energies for a number of different magnetic configurations allow an estimation—although crude—of the Néel temperature. Also weak ferromagnetism, which is characteristic of α -Fe₂O₃ at higher temperatures, is borne out by our calculations. Finally, we determined the rate of change for the decrease of the insulating gap when the canting of the magnetic moments is increased by applying an external magnetic field.

Acknowledgments

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