Journal of Magnetism and Magnetic Materials 7 (1978) 12–15

THE OPTICAL ABSORPTION OF IRON OXIDES

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The first comprehensive study of the optical absorption spectra of the iron oxides FeO, Fe_3O_4 and Fe_2O_3 is reported. Combining the present results with previous data enables a reliable common one-electron energy level diagram for all three materials.

While progress was made in recent years in the understanding of the electronic structure of the transition metal oxides, only the gross features of this structure are conclusive. The fundamental question of whether the 3d electrons in these oxides are itinerant or localized is still unresolved [1]. Thus, the applicability of band structure calculations [2,3] is still in question and semi-empirical energy level schemes [4,5] are more representative of the present rudimentary understanding of the electronic structure in these materials. Furthermore, these are the only schemes that are amenable to comparison with experimental data.

The iron oxides represent a very typical example of the confusion that can arise from interpretation of various spectroscopic data when either a strictly "band" approach [3,4] or a strictly "atomistic" approach [5] was used. The only salient and generally acceptable [2–5] feature of the electronic structure in these materials is the separation between the oxygen 2P(O) band and the iron 4S(Fe) band which is estimated to be $\Delta_{ps} = 5$–6 eV. To construct a one-electron energy level diagram that includes the d-levels, one has to know three parameters: Δ_{cf}, the crystal field splitting, Δ_{ex}, the Hund's rule exchange splitting between the majority spin level (assumed spin down here) and the minority spin level, and Δ_{ds}, the relative position of one of the cation 3d bands and the 4S(Fe) band.

The values of these parameters were gathered previously from band structure calculations [4] or from experimental results on iron ions in various complexes [5]. A direct experimental determination of the parameters Δ_{cf} and Δ_{ex} in Fe_3O_4 and Fe_xO was reported only very recently be Alvarado et al. [6]. This enables the construction of a much more reliable energy-level scheme than was suggested before. From the "fully atomistic" approach that was used by Alvarado et al. to interpret their data, it is expected that Fe_xO, Fe_3O_4 and Fe_2O_3 should have the same spectroscopic behavior. In this paper we try to check this assumption, to determine Δ_{ds} from optical absorption data, and to find whether these optical data are in accord with the energy level scheme implied by Alvarado et al. [6].

For the measurements we have used crystals and films of the three compounds. Some details of the samples' preparation were already reported [7,8] and some will be reported elsewhere. The measurements from the near infrared to the ultraviolet spectral regions (0.5–6 eV) were carried out in a Carry 14 spectrophotometer while in the infrared region (0.1–0.5 eV) a Perkin Elmer 457 spectrophotometer was used. For all samples the reflectivity was measured separately and the optical absorption coefficient K was determined after the correction for the reflectivity [7] was considered.

The measurements on Fe_xO were taken on oxidized

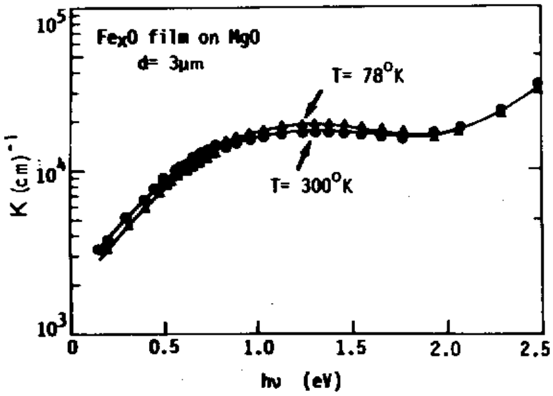

Fig. 1. The photon energy dependence of the absorption coefficient of an $Fe_{0.94}O$ film, at room temperature and at liquid nitrogen temperature. d is the film thickness.

iron films that were sputtered on an MgO (100) crystal. X-ray measurements have shown that the samples were highly oriented polycrystalline films with a lattice constant of $a = 4.300 \pm 0.004$ Å. Using the relation [9] $a = (0.4\,x + 3.932)$ Å we found that in the present samples $x = 0.94 \pm 0.01$. The photon-energy dependence of K for these films is shown in fig. 1. The most significant features of this dependence are the broad peak at 1.3 eV and a possible absorption edge at 2 eV. It is apparent that absorption processes [7] that prevent the measurement for small K values are present. These processes are typical to "black" transition metal oxides (e.g. V_2O_3), and prohibit a unique determination of the optical absorption edge as well as the fine features of the absorption spectra. The only other optical study [10] on Fe_xO films has exhibited the same features but the absorption edge was sharper. For the Fe_3O_4 study we have used natural crystals [7] and highly oriented polycrystalline films. The films were obtained by oxidizing iron which was sputtered on spinel (110) crystals [8]. The results for both types of Fe_3O_4 samples are shown in fig. 2. There are three features to be noticed in this figure. An "absorption edge" [7] at about 0.3 eV, a broad peak at 1 eV and a possible absorption edge at 2 eV. As for Fe_xO very few conclusions can be derived from such data when comparison with a many-level scheme is desired. We have thus referred to α-Fe_2O_3 for which an earlier study of Bailey [11] has indicated the feasibility of measurements in the small-K region.

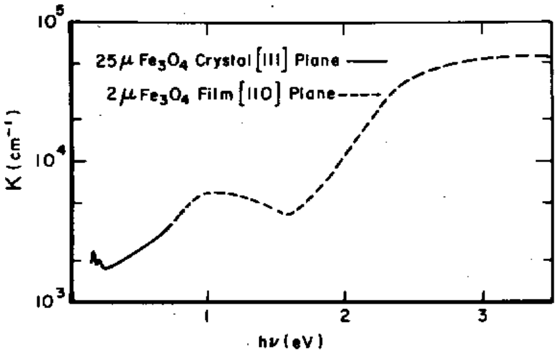

Fig. 2. The photon energy dependence of the absorption coefficient of Fe_3O_4. The samples' thicknesses are indicated in the figure.

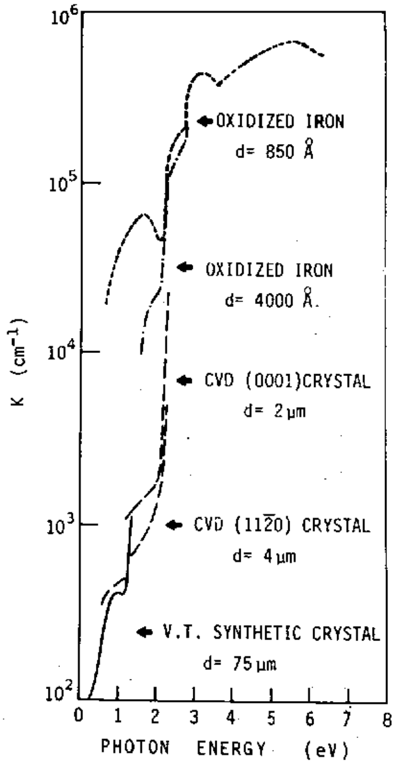

Fig. 3. The photon energy dependence of the absorption coefficient of α-Fe_2O_3 for samples of various thicknesses, d.

Prior to the present study, the results for α-Fe_2O_3 crystals [11] were limited to the $800 \leqslant K \leqslant 3500$ cm^{-1} range, while the very many results on oxidized iron films [12] yielded only the qualitative features of the large-K end. Hence, no absorption edge could have been identified with certainty. This identification is important since the determination of Δ_{ds} enables one to find the relative position of the d-levels within the 2P(O)–4S(Fe) gap. For the study of α-Fe_2O_3 we have prepared samples with various thicknesses, so that the entire K range could be measured. As far as we know this is the first study of optical absorption in the transition metal oxides where measurements are carried out over four orders of magnitude of K. For the small-K end, a synthetic crystal that was grown by vapour transport (VT) was used, while for the $10^3 \leqslant K \leqslant 10^4$ cm^{-1} range, single crystals that were grown epitaxially on sapphire by chemical vapour deposition (CVD) were used. At the large-K end we have used highly oriented polycrystalline films that were obtained by oxidizing iron films which were sputtered on sapphire substrates. The complete optical absorption data are shown in fig. 3. A well-defined absorption edge at about 2 eV and peaks at 1.5, 3.2 and 5.5 eV are clearly identified.

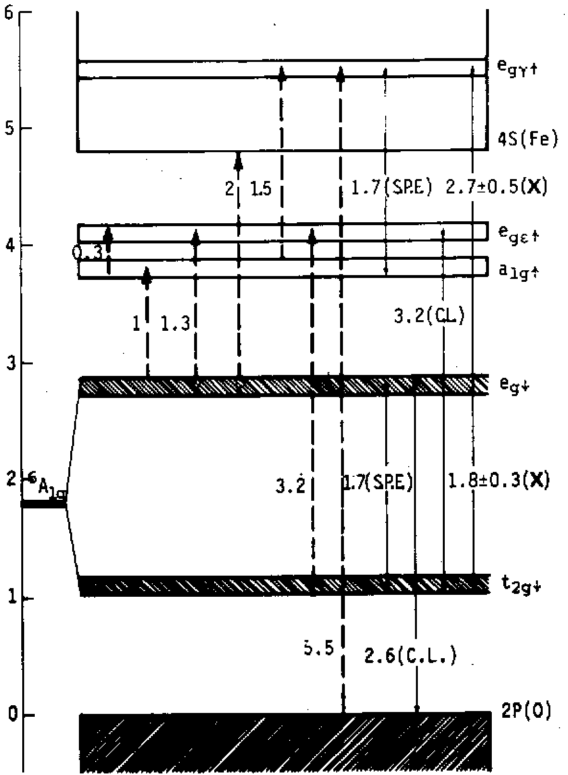

Fig. 4. A one-electron energy scheme of an octahedral site in Fe_3O_4. The interpretations of the various optical transitions are represented by the dashed arrows. Interpretations of other spectroscopic transitions are also indicated.

Having determined the position of the absorption edge we expect it to be associated with the optical transition from the last occupied d-band to the 4S(Fe) band [10]. Since this d-band is the majority spin $e_{g\downarrow}$ band (when the octahedral ligand environment of the iron ion is considered [4]), $\Delta_{ds} = 2$ eV. We can now, using the values of Alvarado et al. [6] of $\Delta_{ex} = 2.7$ eV and $\Delta_{cf} = 1.7$ eV, construct the one-electron energy level scheme. This scheme is shown in fig. 4. The optical transitions found in the present work (indicated by the dashed arrows) show that a common scheme can be suggested for all three materials. Of special interest is the $a_{1g\uparrow} - e_{g\epsilon\uparrow}$ splitting which we associate with the trigonal distortion of the lattice. Since in FeO the $a_{1g\uparrow}$ band is filled and in Fe_3O_4 it is half filled, one would expect a difference of about 0.3 eV between the corresponding transitions. This is indeed the energetic difference between the peaks that we found in the absorption of the two materials.

For completness we also show in fig. 4 our interpretation of other spectroscopic results on Fe_3O_4. The results are of spin polarized electron (SPE) study [6,13], cathodoluminescence (CL) study [4] and soft X-ray (X) study [14]. These results have been discussed in the past and their interpretation is not unique [4,5]. We believe, however, that the present interpretation is a reasonable combination of the knowledge of the corresponding spectroscopic transitions and the suggested one-electron energy scheme.

To conclude: the one-electron energy scheme which is based on the three parameters Δ_{cf}, Δ_{ex} and Δ_{ds} is compatible with the optical absorption data and is in accord with other spectroscopic data. The scheme indicates that the atomistic approach quite accurately yields the order and the separation of the energy levels. On the other hand, for considering the band widths of the d-levels additional interactions, such as admixture of orbitals, have to be considered.

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