

XPES and UVPES Studies of Iron Oxides*

S. VASUDEVAN, M. S. HEGDE, AND C. N. R. RAO†

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

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X-Ray and uv photoelectron spectra of FeO, Fe₂O₃, and Fe₃O₄ have been studied along with those of a few model compounds. It has been possible to assign distinct bands due to Fe²⁺ and Fe³⁺ in the 3*d*, 3*p*, 3*s*, and 2*p* bands of Fe₃O₄. The spectra of Fe₃O₄ do not show major changes through the Verwey transition.

1. Introduction

Core and valence levels in the photoelectron spectra (PES) of iron oxides have been investigated by a few workers, particularly by Brundle *et al.* (1) and McIntyre and Zetaruk (2). However, there is still some uncertainty with regard to the assignments of the valence bands and some of the core levels. Furthermore, earlier studies mainly employed X-ray PES (XPES) and there was need to investigate the valence bands carefully by UVPES. We have been investigating XPES and UVPES of iron oxides for some time and would like to report some of our important findings particularly on Fe₃O₄. In order to interpret the PES of Fe₃O₄ in terms of Fe²⁺ and Fe³⁺ levels, we have examined the spectra of a few model ferrites, as well as of Prussian blue, KFe [Fe(CN)₆]. In addition to the assignment of bands due to Fe²⁺ and Fe³⁺, we were interested in finding out whether PES of Fe₃O₄ shows differences as the temperature is varied through the Verwey ordering transition (3-5).

2. Experimental

All the samples studied were prepared by starting with high-purity starting materials following standard procedures. Since FeO is very susceptible to atmospheric oxidation, it was prepared *in situ* in the spectrometer preparation chamber by thermal decomposition of ferrous oxalate under a vacuum of 10⁻¹⁰ Torr.

Spectra were recorded with an ESCA3 Mark II spectrometer of V. G. Scientific Ltd., United Kingdom, fitted with a sample preparation chamber. The chamber in turn was fitted with an argon ion gun and a quadrupole mass spectrometer. The surfaces of the oxide samples were cleaned by heating (and etching where necessary) ensuring that no undesired reduction or oxidation occurred. The oxygen 1*s* signal was particularly employed to monitor the surfaces. AlK α (1486.6 eV) and HeII (40.8 eV) radiations were used for the spectra.

3. Results and Discussion

Valence bands of FeO and α -Fe₂O₃ in the XPES were found to be similar to those reported by McIntyre and Zetaruk (2). The

* Communication No. 13 from the Solid State and Structural Chemistry Unit.

† To whom all correspondence should be addressed.

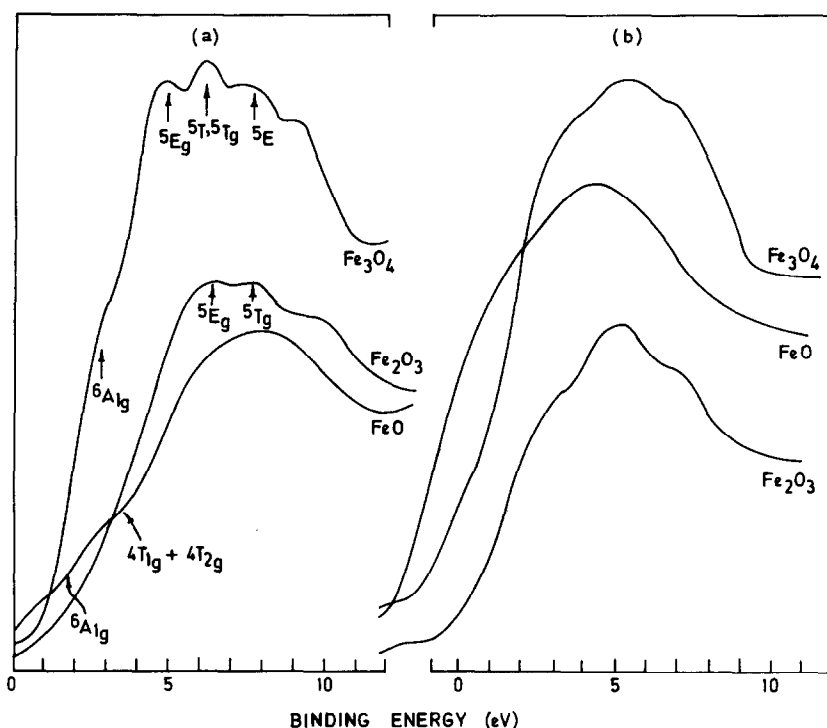


FIG. 1. Valence bands of iron oxides: (a) HeII spectra; (b) AlK α XPES spectra.

valence band of FeO was also similar to that of Bagus *et al.* (6). The valence band of Fe₃O₄ in XPES shows features of both FeO and Fe₂O₃ as expected (see Fig. 1). The valence bands showed considerably better structure when recorded with HeII excitation as can be seen in Fig. 1. We can interpret the valence bands of these oxides in terms of the atomic theory of the single-ion-in-a-crystal-field model accounting for final-state effects as suggested by Alvarado *et al.* (7). Thus, in FeO, the bands around 1.5 and 3.5 eV can be ascribed to ${}^6A_{1g}$ and (${}^4T_{1g} + {}^4T_{2g}$) states, respectively; a third band expected around 5 eV and other bands from valence-band final states probably occur as part of the broad band which also contains the O(2p) band (Fig. 1a). These assignments of the Fe(3d) bands of FeO are consistent with those of Bagus *et al.* (6). In the valence band of Fe₂O₃, we can readily assign two bands to the 5E_g and 5T_g states. In

Fe₃O₄, the band appearing around 2 eV may be assigned to the hole left behind after photoemission from Fe²⁺ at the B site (${}^6A_{1g}$). The Fe³⁺ ions in the B and A sites give rise to two peaks each due to 5E_g and 5T_g states, but which are inverted in order since the signs of the crystal field splitting at the A and B sites are opposite in sign. The band around 9 eV could arise from one of the final states of Fe²⁺ as in FeO (6). These assignments of Fe²⁺ in Fe₃O₄ are shown in Fig. 1a. The O(2p) band of Fe₃O₄ appears at considerably higher energies (>7 eV) than the Fe(3d) bands.

We have recorded the 3p, 3s, 2p_{3/2}, and 2p_{1/2} bands of Fe in FeO, Fe₂O₃, and Fe₃O₄; XPES of ZnFe₂O₄ and CuFe₂O₄ were also recorded in these regions to delineate features due to Fe²⁺ and Fe³⁺ in the spectrum of Fe₃O₄. In the case of the 3p and 2p bands of Fe₃O₄, we could assign the shoulders appearing on the low-energy side as due to

TABLE I
CORE-LEVEL BINDING ENERGIES IN
IRON OXIDES

	Fe(3p)	Fe(3s)	Fe(2p _{3/2})	Fe(2p _{1/2})	O(1s)
Fe	53.1	91.6	708.6	721.6	—
FeO	53.7	92.5	709.5	722.8	529.2
Fe ₂ O ₃	55.3	93.0	710.3	723.8	529.3
Fe ₃ O ₄ ^a	54.9	92.4	709.5	722.8	529.1
	55.8	93.2	710.5	724.0	
CuFe ₂ O ₄	55.7	93.5	710.8	724.0	529.2
ZnFe ₂ O ₄	56.4	93.1	710.3	723.9	529.1
LaFeO ₃	55.2	— ^b	710.5	724.1	529.0
EuFeO ₃	55.1	— ^c	710.2	724.7	529.5
HoFeO ₃	56.2	93.3	710.6	724.4	529.6

^a At 300°K.

^b La(4d) interferes with the Fe(3s) band.

^c Exact position could not be ascertained.

Fe²⁺ and we could readily decompose both these bands into the component bands of Fe²⁺ and Fe³⁺. The binding energies of 3p, 2p_{3/2}, and 2p_{1/2} of Fe³⁺ are 55.8, 710.5, and 724.0 eV, respectively, values which are close to those in CuFe₂O₄ and ZnFe₂O₄. Bands of Fe²⁺ in Fe₃O₄ appear at energies close to those in FeO (see Table I). These results are quite similar to those reported by McIntyre and Zetaruk (2) and will not be detailed here.

The 3s bands of iron oxides have not been discussed in much detail in the literature. Although detailed assignments of the 3s bands are generally complicated by final-state effects, we can draw some useful conclusions regarding Fe²⁺ and Fe³⁺ in Fe₃O₄ from a study of the 3s region. The 3s

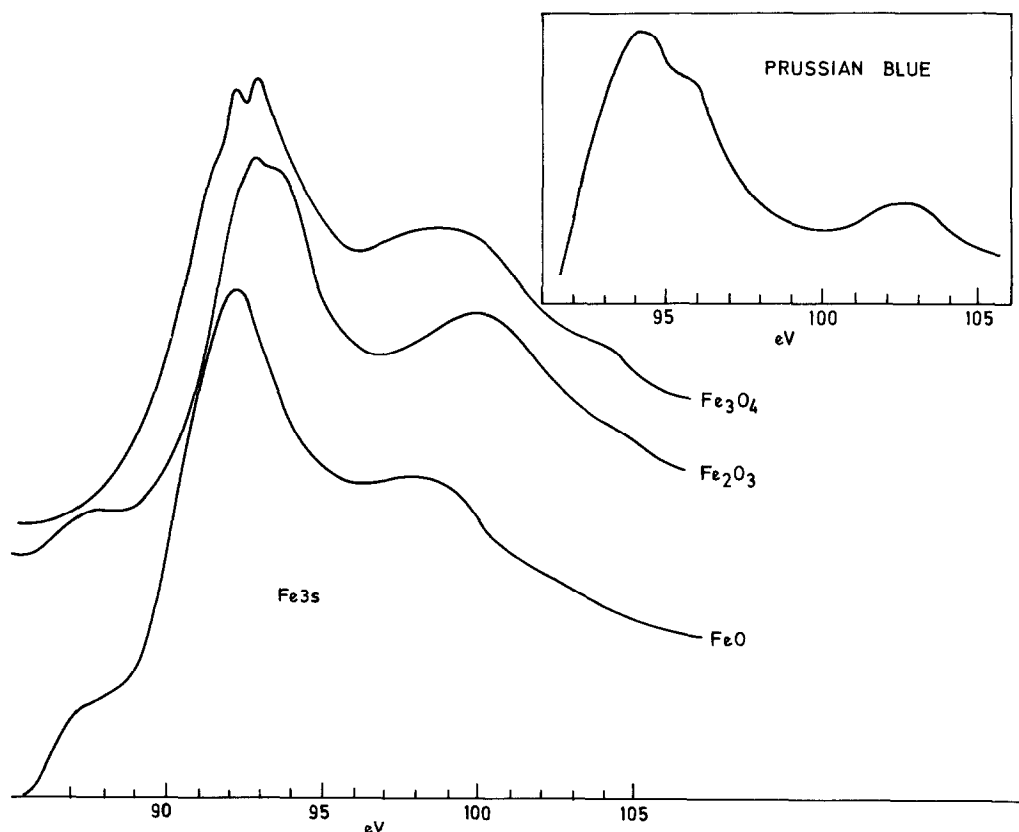


FIG. 2. Fe(3s) bands of iron oxides. The Fe(3s) band of Prussian blue is shown in the inset.

bands of the three iron oxides are shown in Fig. 2. In the case of Fe_3O_4 , we see features due to Fe^{2+} on the low-energy side of the main band; the main band (~ 93 eV) is itself due to Fe^{3+} and is similar to that in ZnFe_2O_4 and CuFe_2O_4 (93.1 and 93.5 eV, respectively). The broad band at ~ 98 eV in Fe_3O_4 also appears to have contributions from both Fe^{2+} and Fe^{3+} . The energy difference of ~ 5 eV between the two main bands in the $3s$ region is a sensible value for the exchange splitting. This assignment of the $3s$ band of

Fe_3O_4 finds support from the spectrum of Prussian blue (see inset of Fig. 2).

The binding energies of the important core levels of iron oxides are shown in Table I along with those of model compounds. In general, we see that the iron core-level binding energies vary in the order $\text{Fe} < \text{Fe}^{2+} < \text{Fe}^{3+}$ as expected; the $\text{O}(1s)$ binding energy is, however, constant. The Fe^{2+} and Fe^{3+} states in Fe_3O_4 can be distinguished in the $3p$, $3s$, $2p$, and the valence bands. The $3d$ bands in all the oxides are broad (~ 10 eV) as noted

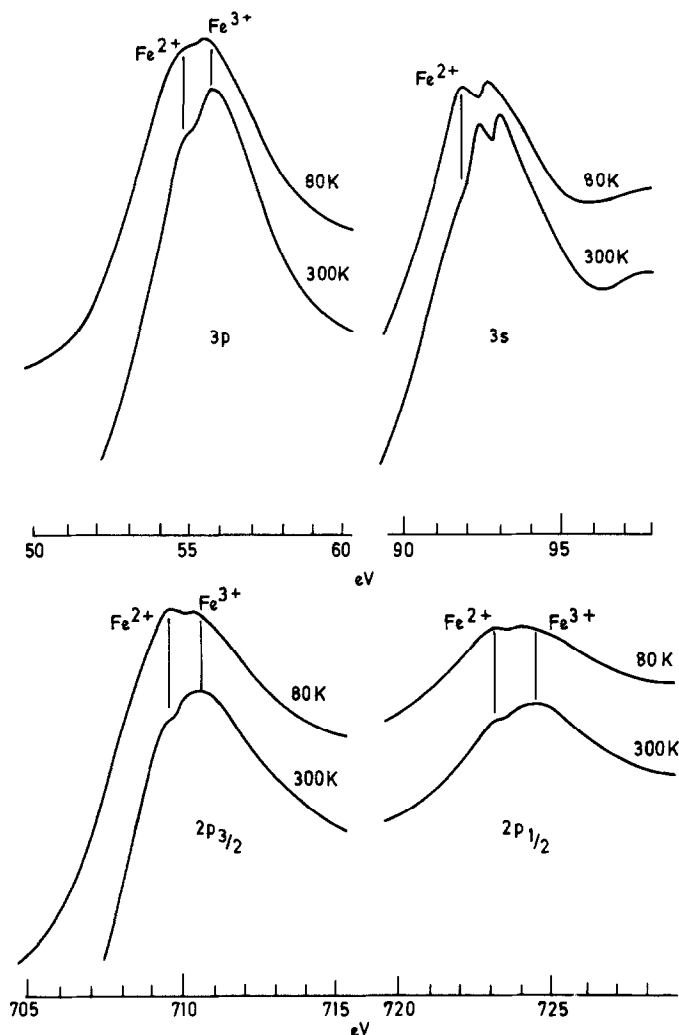


FIG. 3. $\text{Fe}(3p)$, $\text{Fe}(3s)$, and $\text{Fe}(2p)$ bands of Fe_3O_4 above and below the Verwey transition temperature.

by Brundle *et al.* (1) as well as Bagus *et al.* (6). The Fe core-level binding energies in the orthoferrites, LaFeO_3 , EuFeO_3 , and HoFeO_3 and in the spinels are not much different from those of the iron oxides (Table I). The $\text{O}(1s)$ binding energy in the orthoferrites, however, appears to vary with the central rare-earth ion of the perovskites, a point of interest in understanding binding in these structures.

Fe_3O_4 undergoes a phase transition around 120°K from cubic to orthorhombic structure; at this temperature, there is a 100-fold jump in resistivity (3–5). Above 120°K , there is rapid exchange between Fe^{2+} and Fe^{3+} while below this temperature they are ordered. The hopping frequency between Fe^{2+} and Fe^{3+} ions is estimated to be 10^{-11} sec (8). We have examined the valence-band and core-level spectra of Fe_3O_4 above and below the phase transition to see whether the ordering of Fe^{2+} and Fe^{3+} ions will have any effect on the spectra. Unlike in metal–insulator transitions in metal oxides (9), we found only negligible changes in the valence bands in both XPES and UVPS. However, in the core levels, we found that the features due to Fe^{2+} became prominent at low temperatures (in the ordered phase) as shown in Fig. 3. Considering that the time scale involved in the PES is of the order of 10^{-16} sec, these changes are indeed interesting. At this stage, we can only

surmise that the core-level bands of Fe_3O_4 seem to be somewhat sensitive to ordering of the cations (or electron hopping frequency), but are unable to comment any further on the mechanism of the observed changes in the photoelectron spectra.

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