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## X-ray emission spectroscopy study of the Verwey transition in $\text{Fe}_3\text{O}_4$

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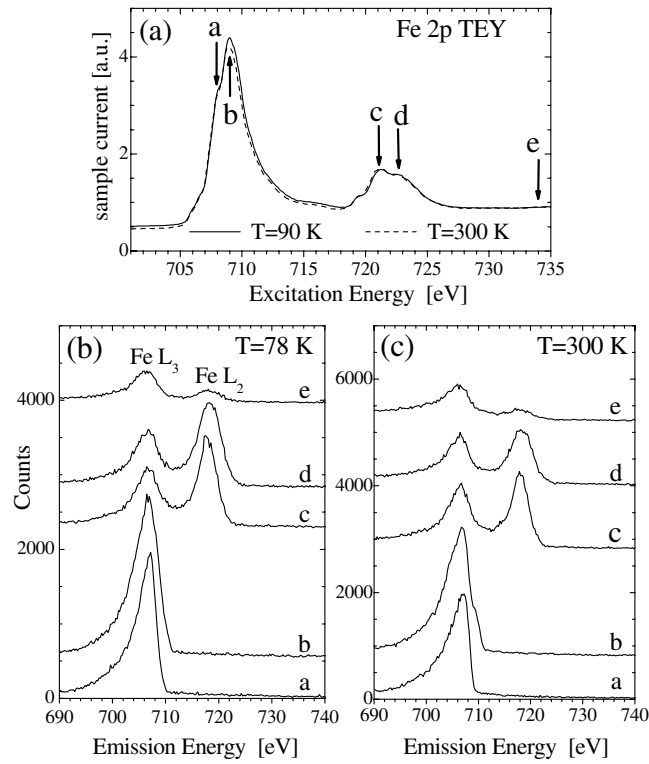
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### Abstract

The temperature-dependent Verwey transition in a 500 Å (111) thin film of  $\text{Fe}_3\text{O}_4$  (magnetite) has been studied using soft-x-ray emission spectroscopy at room temperature and below the transition temperature  $T_V$ . The Fe  $L_{2,3}$  x-ray emission spectra show an increase in the intensity of the  $L_2$  emission relative to the  $L_3$  emission below  $T_V$ . This is independent of the excitation energy and is attributed to a metal–insulator transition across  $T_V$ . Comparison of the Fe  $L_3$  emission and O  $K\alpha$  spectra with LDA band structure calculations supports the suggestion of charge ordering in  $\text{Fe}_3\text{O}_4$  at low temperature.

$\text{Fe}_3\text{O}_4$  (magnetite) is a ferrimagnet displaying an inverted cubic spinel structure at room temperature [1].  $\text{Fe}_3\text{O}_4$  undergoes a first-order phase transition referred to as the Verwey transition, at a temperature  $T_V = 122$  K, in which the electrical conductivity decreases by two orders of magnitude upon cooling to  $T < T_V$  (see [2]). At room temperature, one third of the Fe atoms are located at the centres of oxygen tetrahedra (referred to as A-sites) as  $\text{Fe}^{3+}$  ions, while the remaining two thirds of the Fe ions (with formal valence  $\text{Fe}^{2.5+}$ ) reside at the centres of oxygen octahedra (B-sites). This is expressed by the nomenclature  $[\text{Fe}^{3+}]_{\text{tet}}[\text{Fe}^{2+}\text{Fe}^{3+}]_{\text{oct}}\text{O}_4$ . Although metal-to-insulator transitions are generally considered to result from an order-to-disorder transformation, Verwey suggested an ordering of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions in octahedral B-sites in the low-temperature insulating phase [2]. Mott, on the other hand, pointed out that transfer of 3d electrons should not be ignored and that the low-temperature transition should be considered as due to band splitting caused by correlation effects [3].

Local spin density approximation (LSDA) calculations (see [4] and [5]) and LSDA +  $U$  band structure calculations [6] as well as various spectroscopic measurements [7, 8] have

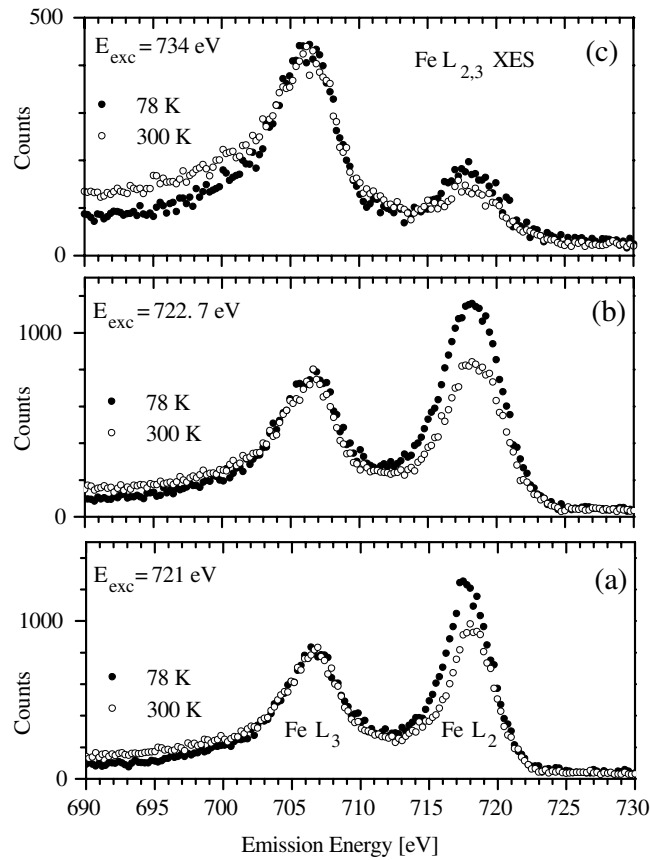


**Figure 1.** Fe 2p absorption (a) and Fe  $L_{2,3}$  emission measurements for  $Fe_3O_4$  measured below (b) and above (c) the Verwey transition temperature.

been performed to elucidate the electronic structure of  $Fe_3O_4$ . LSDA calculations point to a metallic solution without charge ordering and with partially filled bands (containing one electron per two B-sites) originating from  $t_{2g}$  spin-down 3d orbitals of Fe ions in octahedral B-sites. The LSDA +  $U$  model (the modified local density approximation which includes the on-site Coulomb interaction correction) predicts a change in electrostatic potential associated with a transition to a completely disordered state [6].

Ultraviolet photoemission spectroscopy (UPS) measurements were taken and show that  $Fe_3O_4$  is an insulator even above  $T_V$  but with smaller band gap [7]. Other photoemission measurements report that above  $T_V$ , magnetite is metallic but with a very low density of states (DOS) at the Fermi level that increases with increasing temperature [8].

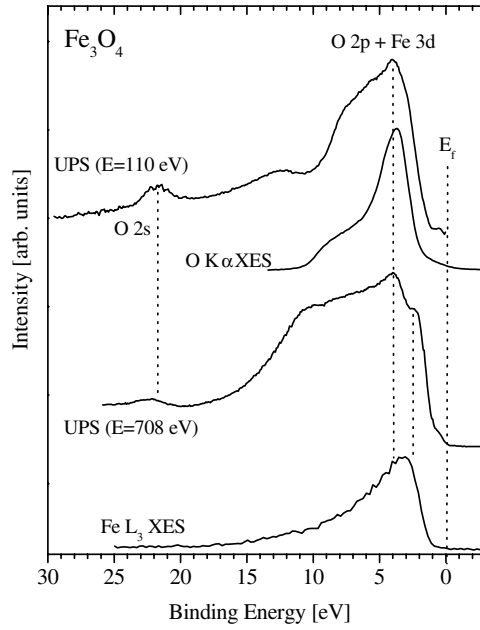
In the present paper we report soft-x-ray emission spectroscopy (XES) measurements taken either side of  $T_V$ . Using tunable synchrotron radiation from beamline 8.0.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory and the associated soft-x-ray fluorescence end-station [9], we have measured the resonant and non-resonant Fe  $L_{2,3}$  ( $3d4s \rightarrow 2p$  transition) and non-resonant O  $K\alpha$  ( $2p \rightarrow 1s$  transition) emission spectra. The excitation energy for Fe  $L_{2,3}$  emission was varied between 707 and 734 eV. The O  $K\alpha$  spectrum was excited at 560 eV. The corresponding x-ray absorption spectroscopy data (XAS) were also recorded with a resolving power of 5000. The Fe  $L_{2,3}$  XES measurements were recorded with an energy resolution of about 0.7 eV using an excitation bandwidth of 0.4 eV. The sample was a highly ordered epitaxially grown 500 Å thick film of  $Fe_3O_4$  [111] on an  $Al_2O_3$  [0001] substrate [10].



**Figure 2.** Comparison of Fe  $L_{2,3}$  emissions of  $\text{Fe}_3\text{O}_4$  measured at 78 K and room temperature for non-resonant (a) and resonant ((b), (c)) excitation.

Due to dipole selection rules and the element specific excitation of the constituents, the Fe  $L_{2,3}$  emission spectra probe the local Fe 3d DOS. The 4s contribution to the spectral intensity can be neglected. Figure 1 shows XAS and XES data near the Fe 2p threshold. The absorption spectra (figure 1(a)) are recorded in the sample current mode at room temperature and at 90 K, which is well below the Verwey transition temperature. No significant change in the unoccupied 3d DOS may be deduced from these measurements, which are practically identical above and below  $T_V$ . They are in good agreement with previous measurements [11, 12]. The Fe  $L_{2,3}$  emission spectra were recorded at 78 K (figure 1(b)) and at room temperature (figure 1(c)). The emission spectra are excited resonantly (as indicated by arrows a–d) and non-resonantly (arrow e).

Non-resonant excitation well above the  $L_{2,3}$  ionization thresholds leads to normal x-ray emission and reflects the 3d occupied DOS modified by matrix transitions and radiationless Coster–Kronig (CK) transitions. Selective excitation to just above the  $L_3$  edge brings into play the excited state multiplet structure. The effect on the resonant emission depends on the relative decay rates of the core hole and excited electron states. In other words, resonant emission corresponds to the decay from the  $\text{Fe } 2p^5 3d^{n+1}$  state, though the intermediate state may first decay to  $2p^5 3d^n$  and yet be too close in energy to be distinguishable. Note that the overall picture will be more complex, since excitations may also occur toward Fe 3d–



**Figure 3.** Comparison of Fe  $L_3$  and O  $K\alpha$  [17] soft-x-ray emissions with the UPS [7] of  $\text{Fe}_3\text{O}_4$ .

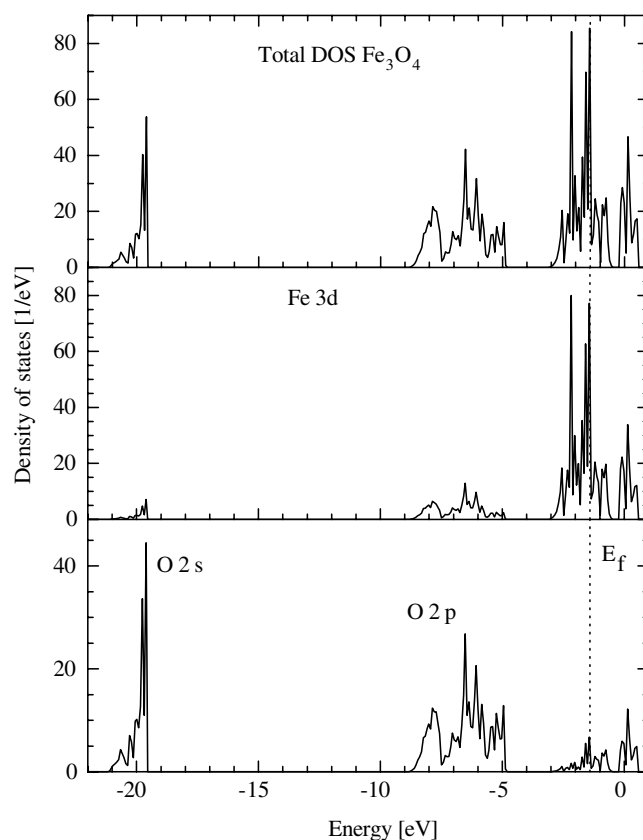
O 2p hybridized states which decay to different final states. In the spectrum taken above  $T_V$  and at energy (b), the shoulder to the high-energy side corresponds to an elastic peak ( $2p^6 3d^n \rightarrow 2p^5 3d^{n+1} \rightarrow 2p^6 3d^n$ ). The main peak contains, indistinguishably, contributions from energy loss structure and normal x-ray emission reflecting the extent of the 3d DOS. Below  $T_V$  the elastic peak is weaker, but otherwise the shape of the main peak is unchanged. An excitation close to the  $L_3$  edge (a) does not reveal an elastic peak and the shape of the spectrum remains unchanged below  $T_V$ .

We assume that excitation to (b) is associated with well localized unoccupied d states. It marks a distinct difference in the electronic structure of magnetite either side of  $T_V$  though it is not possible to use this information to precisely interpret the presence of charge ordering below  $T_V$  without the help of model calculations. This point will be discussed later in the context with our band structure calculations.

The spectra taken at (c) are clearly little affected by the change in temperature. The  $L_2$  emission observed for excitation energy (d) is very similar in shape to that of the normal x-ray emission band. Its intensity is enhanced, however, relative to that of the  $L_3$  x-ray emission as a result of resonant excitation.

The strongest change across the phase transition is in the intensity in the  $L_2$  peak relative to the  $L_3$  line. This is emphasized in figure 2 where the spectra taken above and below  $T_V$ , corresponding to excitations at energies (c)–(e), are shown. The spectra are normalized to the corresponding  $L_3$  amplitudes. In all three cases the  $L_2$  intensity is weaker in the high-temperature phase.

As already mentioned, the spectra are affected by CK transitions. Excitation energies (c)–(e) are sufficient to create an  $L_3$  core hole but, in addition, the non-radiative  $L_2 L_3 M_{4,5}$  CK channel enhances the relative intensity of the  $L_3$  radiative decay channel. We see that this CK probability *decreases* below  $T_V$ . In order to evaluate the intensity ratio  $I(L_2)/[I(L_2) + I(L_3)]$  we may assume as a first approximation that the total spectral intensity is unchanged above



**Figure 4.** The DOS calculated for  $\text{Fe}_3\text{O}_4$ .

and below  $T_V$ . The relative intensities are therefore  $I(\text{L}_2)_{>T_V}/I(\text{L}_2)_{<T_V}$ . We obtain values of 0.73, 0.71 and 0.76 at 721.0, 722.7 and 734.0 eV, respectively. The differences in these relative intensity values are most probably within the experimental limits and therefore not significant.

It is known that the CK process depends among other factors on the chemical state of the element [13]. For 3d metal spectra and their alloys, the ratio  $I(\text{L}_2)/[I(\text{L}_2) + I(\text{L}_3)]$  is smaller (0.22–0.25) than the ratio that would be expected in the absence of the CK decay (0.33). At the same time, the probability for non-radiative  $\text{L}_2\text{L}_3\text{M}_{4,5}$  CK transitions is lower for 3d transition metal oxides as a consequence of the band gap and the reduced possibility of collective 3d electron excitations. We conclude that the behaviour shown in figure 2 is compatible with a transition from the metallic to the insulating phase.

UPS data [7, 14] for  $\text{Fe}_3\text{O}_4$  are compared to the Fe  $\text{L}_3$  and O K emissions in figure 3. Binding energies of 710.3 eV for Fe  $2p_{3/2}$  (see [7]) and 529.1 eV for O 1s [15] are subtracted from the emission energies to bring the XES data to the common binding energy scale. The energy position of the O  $\text{K}\alpha$  emission coincides with the maximum intensity of the UPS data (excited at  $E = 110$  eV). This is expected since both spectra probe O 2p states. The photoelectron spectrum excited at the Fe 2p threshold ( $E = 708$  eV) exhibits an additional feature at 2.5 eV caused by Fe 3d states. This picture emphasizes the strong overlap between Fe 3d and O 2p states in the valence band of  $\text{Fe}_3\text{O}_4$ .

In order to calculate the band structure of  $\text{Fe}_3\text{O}_4$ , we have used the self-consistent tight-binding (TB) linear muffin-tin orbitals method (LMTO) in the atomic sphere approximation

(ASA) [16]. Atomic coordinates were taken from [4]: space group  $Fd3m$ , Fe (A):  $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ , Fe (B):  $0\ 0\ \frac{1}{2}$ , O:  $\frac{1}{4} + u\ \frac{1}{4} + u\ \frac{1}{4} + u$ ;  $a = 8.394\ \text{\AA}$ ,  $u = 0.0048$ .

Figure 4 displays the TB-LMTO-ASA band structure calculations of  $\text{Fe}_3\text{O}_4$ . According to these calculations, O 2p bands together with hybridized Fe 3d states are located well below the Fermi energy ( $E_F$ ). The latter is situated in the middle of an Fe 3d band extending over some 6 eV.  $E_F$  is located near a very narrow peak in the density of states, indicating a ferromagnetic instability within the Stoner model that is consistent with the magnetic nature of the compound. One of the features of these calculations is that they indicate a splitting in states above  $E_F$  into two narrow bands. The upper band (roughly 2 eV above  $E_F$ ) could explain the relatively strong elastic peak observed in the high-temperature spectrum taken at energy (c) (figure 1(c)). On the other hand, when on-site Coulomb interaction is introduced to describe the low-temperature charge-ordered phase, the empty states form an almost continuous band above  $E_F$  [6]. Instead there is formation of a gap at  $E_F$ . Thus at low temperatures a more itinerant intermediate excited state would be compatible with a weaker elastic peak and charge ordering.

To summarize, the decrease in the  $L_2$  intensity in the normal x-ray emission spectrum above  $T_V$  is direct spectroscopic evidence for the transition to the metallic state of  $\text{Fe}_3\text{O}_4$ . The resonant emission data confirm this finding. This also tends to confirm the band structure calculations, which show significant changes in the band structure above  $E_F$  when Coulomb interaction energy is included to account for charge ordering. Such modifications are not detected by high-resolution XAS because of core-hole broadening effects.

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