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PHOTOEMISSION ELECTRONIC STATES AND CORRELATION ENERGIES OF MAGNETITE BASED COMPOUNDS*

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The photoemission spectra (XPS/UPS) for iron oxides, stoichiometric magnetite and for selected Ti and Zn doped magnetite single crystals are presented. From the Fe-3s split lines the exchange energies for FeO, Fe_2O_3 and magnetite based samples were estimated. It was shown that Ti and Zn ions are of 4+ and 2+ valency, respectively. The correlation energies were estimated from the Fe $2p_{3/2}$ core-level spectra and from the L_3-$M_{4,5}$,$M_{4,5}$ Auger lines. The type of insulating gap in these compounds was discussed.

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1. Introduction

Magnetite Fe_3O_4 has received wide attention within the last 60 years mainly due to the Verwey transition at $T_V \approx 120$ K at which anomalies in many physical properties were found. It is commonly believed that the electronic motion on octahedral iron positions is strongly influenced by the interionic Coulomb interaction, as well as the electron–phonon coupling [1]. These interactions participate in the freezing out of octahedral electrons below T_V. Since the existing experimental data does not provide the clear picture for the electronic and band structure of magnetite [2–4] photoemission studies of magnetite based materials were undertaken.

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2. Experimental results and their analysis

Single crystalline stoichiometric magnetite, zinc ferrite $Fe_{3-x}Zn_xO_4$, and titanomagnetite $Fe_{3-x}Ti_xO_4$ samples with small doping levels x, were grown as described *e.g.* in [1]. In addition, for comparative purposes, single crystalline iron oxides Fe_2O_3 and Fe_xO ($x = 0.95$) were prepared by the Floating Solvent Traveling Zone Melting method.

Photoemission measurements were carried out by the XPS/UPS Leybold LHS10 spectrometer. All the experiments were performed under vacuum better than 10^{-9} Torr. The samples were cleaved to open a fresh surface just before recording the spectra. No significant differences among the recorded spectra above and below T_V were found.

The XP and UP room temperature valence band spectra shown in Fig. 1a may apparently be divided into two lines: the one at –3.5 eV is attributed to Fe-$3d$ emission and that at -6.5 eV to O-$2p$ emission [3,4]. The $3d$ emission is composed of two final state spin configurations $3d^5$ out of Fe^{2+} ($3d^6$) initial state and one quintet final state spin configuration $3d^4$ out of Fe^{3+} ($3d^5$) initial state. The lower energy sextet final state, barely seen below –1 eV (marked with arrows in Fig. 1a), and the higher energy quartet final state of the Fe^{2+}-$3d^5$ configuration are separated by the quartet–sextet exchange interaction energy which is usually of about 3 eV.

From the double-peaked Fe-$3s$ core level spectra (non-shown here), the exchange-splitting energies $\Delta E_{\mathrm{ex}} = 5.7 \pm 0.2$ eV and 6.5 ± 0.2 eV for $Fe_{3-x}Zn_xO_4$ with $x = 0.008$ and 0.03, respectively, were estimated. The $3s$ exchange splitting energies of Fe_3O_4, Fe_2O_3 and Fe_xO were 4.7 eV, 5.2 eV and 4.5 eV, respectively, and were scaled linearly with the magnetic moment μ per iron ion. The significantly larger value of the exchange splitting for Zn-substituted samples is not clear at present.

Fig. 1b shows the Fe $2p_{3/2}$ and $2p_{1/2}$ XP (Al-K_α) core-level spectra for all investigated specimens. In the Fe-$2p$ spectra the main lines at about 709.0 eV ($J = 3/2$) and at 722.0 ($J = 1/2$) are very similar for all magnetite compounds, giving the spin-orbit splitting of about 23.0 eV. Each main line for magnetite samples was assigned to the two-component $2p^{-1}3d^4$ and $2p^{-1}3d^3$ final state configurations out of the $2p^6 3d^4$ and $2p^6 3d^3$ initial state configurations of Fe^{2+} and Fe^{3+} ionic states, respectively. As a result, the best fit for those samples is obtained with two Gauss lines. For Fe_2O_3 (and Fe_xO) where nearly pure trivalent (divalent) ionic state of Fe is expected, single line fit produces best results (see Fig. 1b). Energy positions of the $2p$ lines of Zn- and Ti- $2p$ spectra match very well with those for ZnO and TiO_2, resulting in $+2$ and $+4$ valence states for Zn and Ti, respectively.

The Fe-$2p$ core-level spectra of Fe_2O_3 and Fe_xO exhibit the broad satellites S at the 718 eV and 716.5 eV binding energies, respectively (see Fig. 1b).

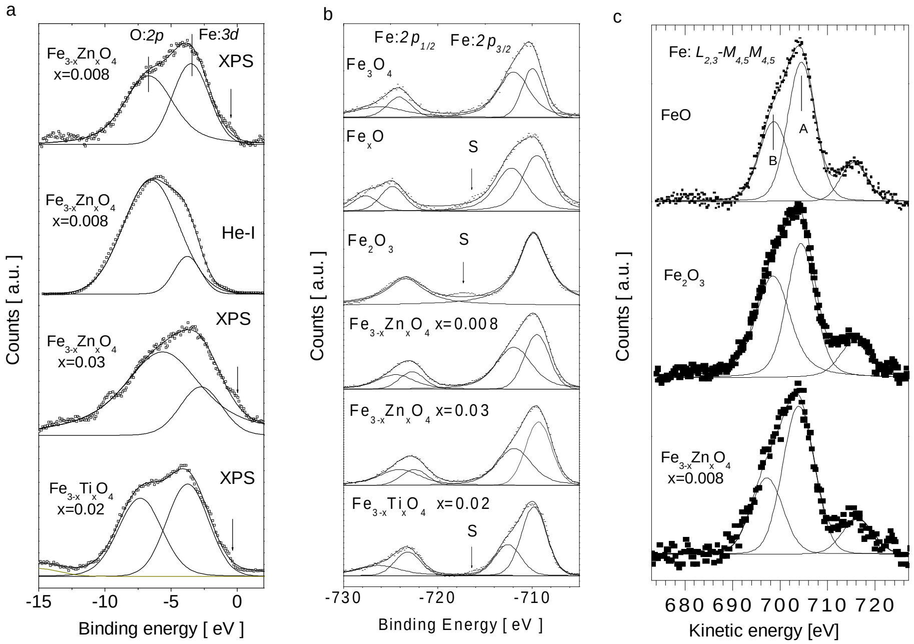

Fig. 1. a — The XP spectra (Al-K$_\alpha$) and UP spectra (He-I) of valence bands for magnetite-based samples. b — The XP spectra (Al-K$_\alpha$) of Fe-2p core-levels for investigated samples; fits are marked with solid lines. *S* indicates the energy positions of the satellites. c — Auger lines of Fe-$L_{2,3}$-$M_{4,5}$,$M_{4,5}$ with the best fitted lines.

The S satellites are hardly seen for magnetite and zinc ferrites due to the superposition of Fe^{2+} and Fe^{3+} valent states; only some trace of the satellite is observed for Ti-substituted samples. The satellites result from multiplet splitting effects due to the correlation energy U_{cd} between the $2p$ core hole and the $3d^6$ or $3d^5$ electronic configurations in the final state of the photoemission process [4–6]. It was established [3] that the satellites have roughly the same location for different iron oxides even though the main lines occur at significantly different energies. This helps to estimate the energy positions of the satellites and their energy separation $\Delta E_{\mathrm{M-S}}$, from the main lines also in magnetite. Hence, as an estimate for $\mathrm{Fe_3O_4}$ we have assumed for the Fe^{2+} and Fe^{3+} satellites the same energy positions as those for $\mathrm{Fe}_x\mathrm{O}$ (Fe^{2+}) and $\mathrm{Fe_2O_3}$ (Fe^{3+}), respectively. The satellite to main peak energy distance was described by the Zaanen, Sawatzky and Allen (ZSA) theory and is expressed as [4–6]:

$$\Delta E_{\mathrm{M-S}} \cong \sqrt{(U_{cd}-\Delta)^2+4t^2}\,, \tag{1}$$

where Δ is the charge transfer energy for the excitation of an electron from a ligand ion onto the d-hole state of metal ion, and t is the hybridization term between p and d states or the so-called transfer integral. To apply the above formulae to the analysis of the experimental data the independent estimates of two quantities out of Δ, U_{cd} and t are needed. In addition, we can also use the relation $U_{cd} \cong 1.4U_{dd}$ which is consistent with a number of experimental results [3, 4].

One can obtain the independent estimates of U_{cd} and U_{dd} from the analysis of Fe L_3-$M_{4,5}$,$M_{4,5}$ and the O K-$L_{2,3}$,$L_{2,3}$ Auger lines. These lines and the best fits for iron oxides and the Zn-substituted magnetite sample are shown in Fig. 1c. Each Auger line consists of the main high-kinetic energy component (A) at E_{A} and the lower-kinetic energy component (B) at E_{B}. The main peak A is due to a correlated two-hole final state and the peak B is due to transitions into the uncorrelated two-hole final states [7]. The line A was attributed to the $3d^5$ final state configuration for the Auger process starting from a $2p_{3/2}3d^7$ intermediate state, while the line B was assigned to the $3d^4$ final configuration from a $2p_{3/2}3d^6$ intermediate state. The separation between A and B lines is linked to the Coulomb correlation energies U_{dd} and U_{cd} [7]:

$$E_{\mathrm{A}} - E_{\mathrm{B}} \cong 2U_{dd} - U_{cd} \cong 0.6U_{dd} \tag{2}$$

Taking the experimental value of $E_{\mathrm{A}} - E_{\mathrm{B}}$, Table I and Fig. 1c, one can calculate both U_{dd} and U_{cd}. We have then used the relation (1) to calculate the charge transfer energy Δ taking into account the relevant Fe-2p main line to satellite separation energies $\Delta E_{\mathrm{M-S}}$ and the average value $t = 2$ eV calculated in [3]. These estimates are listed in Table I.

TABLE I

The energy separations, $\Delta E_{\mathrm{M-S}}$, $E_{\mathrm{A}} - E_{\mathrm{B}}$ and the correlation energies: U_{dd}, U_{cd} and Δ from Eqs. (1) and (2). The error of U_{dd}, U_{cd} and Δ is about ±0.5 eV. The $\mathrm{Zn}_{0.008}$ stands for $\mathrm{Fe}_{2.992}\mathrm{Zn}_{0.008}\mathrm{O}_4$.

		$\Delta E_{\mathrm{M-S}}$	$E_{\mathrm{A}} - E_{\mathrm{B}}$	U_{dd}	U_{cd}	Δ
	Fe^{2+}	5.7	4.6			6.6
$\mathrm{Fe}_3\mathrm{O}_4$				7.7	10.7	
	Fe^{3+}	6.9	4.6			5.6
$\mathrm{Fe}_x\mathrm{O}$	Fe^{2+}	5.0	5.9	9.8	13.7	10.7
$\mathrm{Fe}_2\mathrm{O}_3$	Fe^{3+}	6.6	5.9	9.8	13.7	8.5
	Fe^{2+}	5.4	6.6			11.8
$\mathrm{Zn}_{0.008}$				11.0	15.4	
	Fe^{3+}	6.9	6.6			9.8

According to ZSA phase diagram [5,6] the investigated compounds might be classified, either as the Mott–Hubbard compounds if $U_{dd} < \Delta$, like FeO, as the charge transfer compounds if $U_{dd} > \Delta$, like Fe_2O_3, and as a mixed type of insulator if $U_{dd} \cong \Delta$. The investigated magnetite oxides might be classified as the mixed type compounds, most likely due to the mixture of Fe^{2+} and Fe^{3+} ions, although some tendency to the charge transfer behavior is seen from the values presented in Table I.

3. Summary and conclusions

1. Two peaks at −3.5 eV and −6.5 eV in the valence band spectra (Fig. 1a) arise mainly from the Fe $3d$ states and the O $2p$ states, respectively.

2. The $3s$ exchange splitting energies of Fe_3O_4, Fe_2O_3 and Fe_xO scale with the magnetic moment per iron ion. The exchange splitting for two Zn-substituted samples are larger than for magnetite.

3. The Fe-$2p$ main lines (Fig. 1b) were assigned to the two-component of Fe^{2+} and Fe^{3+} ionic states. The Zn and Ti-$2p$ core level spectra prove that valence states of Zn and Ti are 2+ and 4+, respectively.

4. The correlation energies U_{dd}, U_{cd} and the charge transfer energy Δ were estimated from the Fe-$2p$ spectra and the Fe L_3-$M_{4,5}$,$M_{4,5}$ Auger lines (see Table I). According to the Zaanen–Sawatzky–Allen phase diagram iron oxide $Fe_{0.95}O$ behaves more like the Mott—Hubbard insulator and Fe_2O_3 as well as Fe_3O_4 behave more like the charge transfer insulators. The investigated zinc ferrites- and titanomagnetite are situated on the border between Mott–Hubbard and charge transfer type insulators with some tendency towards the charge transfer behavior.

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