SURFACE STUDIES OF $Re_3Fe_5O_{12}$ GARNETS, $ReFeO_3$ ORTHOFERRITES AND $ReVO_4$ ORTHOVANADATES

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The X-ray photoelectron spectra for $Re_3Fe_5O_{12}$ garnets, $ReFeO_3$ ortho-ferrites and $ReVO_4$ orthovanadates have been measured by using Mg K_α radiation. The O $1s$, Re $4d$, Fe $2p$, and V $2p$ photoelectron spectra were studied. A very big difference was observed between $ReFeO_3$ orthoferrites and $ReVO_4$ orthovanadates, mainly the Fe $2p_{3/2}$ lines were double broader than V $2p_{3/2}$ ones, and the O $1s$ line is split by about 1.6 eV for orthoferrites, while this line is single for orthovanadates. The O $1s$ peak at 531.8 eV with intensity about 70% of the main peak is interpreted as originated from a charge fluctuation between oxygen and iron ions due to superexchange interaction.

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1. Introduction

The rare earth orthoferrites and garnets are widely studied series of compounds because of their possible applications as technological magnetic materials [1, 2].

The rare earth orthoferrites $ReFeO_3$ crystallize with the orthorhombic distortion of the perovskite structure [1]. There are two nonequivalent positions O(1) and O(2) of oxygen ions in the orthoferrite unit cell, where the number ratio O(2):O(1) = 2:1. The both O(1) and O(2) sites have four Re^{3+} neighbors at average distance equal to, e.g. in $DyFeO_3$ 2.79 Å and 2.76 Å, respectively, and two Fe^{3+} neighbors at distance 2.01±0.02 Å. The Fe–O–Fe geometry in both O(1) and O(2) cases is very similar (Fig. 1). In these compounds the iron lattice orders around 700 K and the rare earth lattice only at a few degrees Kelvin. Therefore at room
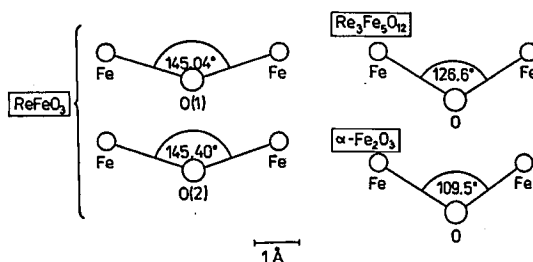
Fig. 1. The geometry of the Fe–O–Fe linkage in iron compounds: $ReFeO_3$ orthoferrite, $Re_3Fe_5O_{12}$ garnet and α-Fe_2O_3.

temperature the strongest interaction in the orthoferrites is the antiferromagnetic coupling of the iron moments [1].

The rare earth garnets $Re_3Fe_5O_{12}$ have rather complex structure even though the symmetry is cubic. They are ferrimagnetic with the Curie temperature above 550 K [2]. The total magnetic moment is parallel to a magnetic moment of an iron ion Fe_a^{3+} in the octahedral site and antiparallel to a magnetic moment of an iron ion Fe_d^{3+} in the tetrahedral site. The linkage geometry Fe_a–O–Fe_d (see Fig. 1) provides the superexchange interaction between iron ions in unlike sites.

For comparison another garnet $Ca_3Mn_2Ge_3O_{12}$ and orthovanadates $ReVO_4$ [3] were also studied.

2. Experimental

The X-ray photoelectron spectra have been measured by XSAM-800 photoelectron spectrometer using Mg K_α radiation. Single crystals of investigated materials were grown by Dr. H. Dąbkowska in the Institute of Physics of the Polish Academy of Sciences. The crystal growth and characterization of rare earth vanadates ($ReVO_4$) have been described in Ref. [4]. Crystals were powdered just before measurements. The samples were not treated by an ion bombardment. The binding energy scale was calibrated according to the binding energy C $1s$ equal to 285.0 eV.

3. Results and discussion

The O $1s$, Re $4d$, Fe $2p$, V $2p$, and Mn $2p$ photoelectron spectra were measured. The Re $4d$ spectra show a multiplet structure (Fig. 2), which is specific for a given Re ion. The Re $4d$ multiplet structure of investigated rare earth compounds is characteristic of 3+ valency. In Fig. 2 the measured spectra are compared with the theoretical Ho^{3+} $4d$ and Dy^{3+} $4d$ photoelectron spectra calculated in Ref. [5]. We would like to emphasize that obtained Dy $4d$ and Ho $4d$ spectra and these for other Re metals do not depend on the sample studied, consequently, Dy and Ho ions keep the 3+ valency in all measured compounds.

A very big difference in FWHM was observed between Fe $2p_{3/2}$ and V $2p_{3/2}$ spectra, mainly the Fe $2p_{3/2}$ lines (FWHM = 4.0 eV) in the samples studied were double broader than V $2p_{3/2}$ (FWHM = 2.0 eV). We have obtained the Fe $2p_{3/2}$ binding energy equal to 711.1 ± 0.2 eV.
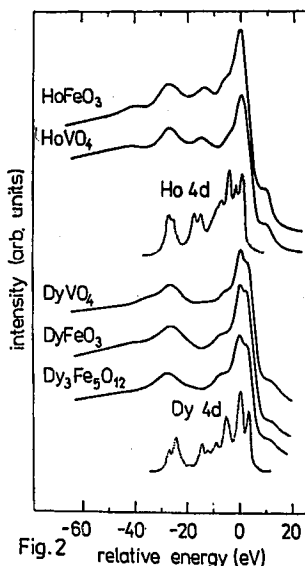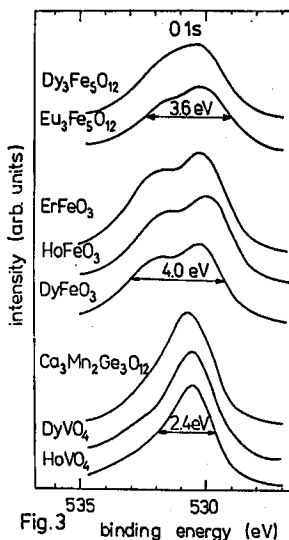
Fig. 2. The Re $4d$ photoelectron spectra obtained in this work and theoretical Ho^{3+} $4d$ and Dy^{3+} $4d$ spectra from Ref. [5].

Fig. 3. The O $1s$ photoelectron spectra of compounds studied.

In Fig. 3 the O $1s$ spectra of all samples are shown. The O $1s$ line is split by about 1.6 eV for iron garnets and orthoferrites, while this line is single for a manganese-germanium garnet and for vanadates. The binding energy of the O $1s$ peak maximum was 530.2 ± 0.2 eV for iron compounds and 530.6 ± 0.2 eV for vanadates.

The high energy O $1s$ peak shifted by about 1.8 eV relative to the main peak was already observed by other authors in some transition metal oxides. It was suggested that additional peak was a contribution from OH^- groups of a water contamination. Allen et al. [6] have studied a series of iron oxides. In the case of the hematite α-Fe_2O_3 they observed a narrow O $1s$ peak at binding energy 530.2 eV, whereas in the case of the magnetite Fe_3O_4 additional strong peak O $1s$ appeared at the binding energy 531.8 eV. The 531.8 eV peak was interpreted as contribution from chemisorbed water contamination, in spite of the fact that this peak remains strong even after heating treatment at temperature above 900 K [6]. Therefore their interpretation does not agree with the fact that a decomposition $FeO(OH) \rightarrow (1/2)\, Fe_2O_3 + (1/2)\, H_2O$ occurs already at the temperature 403 K in air.

It is, however, puzzling to underline that in some other magnetic oxides (nickel oxides) a similar splitting of the O $1s$ peak was observed [7, 8] and the origin of this splitting was not satisfactorily explained.

We tried to make a quantitative XPS analysis. We compared integral intensities of the O $1s$ and Re $4d$ lines measured for $HoFeO_3$ and $HoVO_4$, and the same for $DyFeO_3$, $Dy_3Fe_5O_{12}$ and $DyVO_4$. Applying this analysis we found that

the relative oxygen concentration is bigger for iron compounds than for vanadates by about 5% to 20% only. Therefore the high binding energy O 1s peak having about 70% of the intensity of the main peak cannot be explained as caused by an additional oxygen amount from a water contamination.

The superexchange interaction in transition metal oxides, in which metal ions are separated by more than 4 Å and the overlap of their atomic d shell wave functions is negligible, was first proposed by Kramers [9]. The theory of superexchange was developed by Anderson [10].

Let us consider linkage $Fe^{3+}-O^{2-}-Fe^{3+}$ responsible for the magnetic arrangement and properties of investigated compounds at room temperature. In the ground configuration both Fe^{3+} ions are in a $3d^5$ electronic configuration and the oxygen ion O^{2-} in a $2p^6$ configuration and has all electrons paired. As a result of excitation one p electron from the oxygen jumps into 3d or 4s state on one of ferric ions, which becomes a ferrous one. Thus the oxygen ion O^- is paramagnetic and can enter into interactions with iron ions.

Let us discuss the time scale of different experiments. The dynamical process of superexchange interaction causes fluctuations of magnetic moments. The Mössbauer effect can register only fluctuations which are slower than 10^{-8} s. The Mössbauer measurement and neutron scattering studies of $Y_3Fe_5O_{12}$ garnet [11] have shown that fluctuations of magnetic moments occur with relaxation rate 10^{-13} s $< \tau_m < 10^{-8}$ s, which is much longer than the lifetime of an X-ray level of the order of 10^{-14} s down to 10^{-15} s. Therefore photoelectron transitions in our X-ray photoelectron spectroscopy (XPS) experiments take place in time scale being much shorter than electron fluctuations predicted in Anderson's theory of superexchange [10]. Therefore, the O 1s photoelectron spectrum consists of the main peak of the ground state O^{2-} and additional peak of the excited state O^-. At the same time the Fe $2p_{3/2}$ photoelectron spectrum is broadened up to 4 eV due to the valency fluctuation $Fe^{3+}-Fe^{2+}$.

4. Conclusions

In our opinion the appearance of the splitting of the O 1s peak both in the iron perovskites and in the iron garnets is an evidence of the presence of both the O^{2-} and the O^- ions resulting from quick electron fluctuations between oxygen and iron ions following the superexchange interaction between iron ions via oxygen ions and could be explained on the basis of Anderson's theory of superexchange [10].

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