Electronic structure peculiarities of disordered Mn and Co diphosphates

V.L.Karbivskyy, S.S.Smolyak,
Yu.A.Zagorodniy, V.H.Kasiyanenko

G.Kurdumov Institute for Metal Physics, National Academy of Sciences of
Ukraine, 36 Acad. Vernadsky Blvd., 03680 Kyiv-142, Ukraine

Electronic structure peculiarities of disordered diphosphate — $Mn_{2-x}Co_xP_2O_7 \cdot 5H_2O$, with $x = 0$, 0.6, 1.0, 1.9, 2.0, were studied by XPS and X-ray emission spectroscopy. Substitution in the different degree of cobalt by manganese leads to a charge redistribution in the metal sublattice and results in increase of the chemical bond ionicity between oxygen anions and the metal cations. Such charge redistribution is responsible for formation of the states laying in the upper part of the valence band.

Методами рентгеновской фотоэлектронной и эмиссионной спектроскопии исследованы особенности электронного строения неупорядоченных дифосфатов — $Mn_{2-x}Co_xP_2O_7 \cdot 5H_2O$, где $x = 0$, 0.6, 1.0, 1.9, 2.0. Замещение в различной степени кобальта марганцем приводит к перераспределению электронной плотности в металлической подрешетке и к увеличению ионной составляющей химической связи между анионами кислорода и катионами металла, а также обусловливает формирование состояний, находящихся в верхней части валентной полосы исследуемых соединений.

1. Introduction

Disordered diphosphates are of scientific interest in terms of modifying their operational properties by varying the nature of the cations and their content in the structure. Among the phosphates studied for today the individual hydrated phosphates prevail. However the information about electronic characteristics of the hydrated diphosphates, in particular, cobalt and manganese diphosphates is absent in the literature.

The purpose of the present work was to study the peculiarities of the electronic structure of diphosphates on the basis of transition metals Co and Mn having the following composition: $Mn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ ($x = 0$, 0.6, 1.0, 1.9, 2.0).

2. Eperimental

X-ray photoelectron spectra (XPS) of the samples — $Mn_{2-x}Co_xP_2O_7 \cdot 5H_2O$, where $x = 0$, 0.6, 1.0, 1.9 and 2.0 were obtained on the photoelectron spectrometer of firm "JEOL" — "JSPM-4610" with using the non-monochromatic Al K_α (1486.6 eV) X-ray source. The necessity of using an aluminum anode with a larger width of K_α line is caused by the fact that the source with a magnesium anode leads to a significant excitation of KVV Auger line of oxygen in the $2p$ region of cobalt [1]. During the experiment, the vacuum in the analytical chamber was 10^{-7} Pa, the accuracy of the electrons binding energy definition — 0.1 eV. The samples were in the form of dispersed powder deposited on an aluminum substrate.

Since all the investigated samples are insulators, the emission of electrons during the spectrum acquisition led to the formation of a positive electrical charge on their surface and to an essential shift of corresponding lines. Calibration of X-ray photoelectron spectra taking into account the accumulated charge, was carried out by the

binding energy of 1s-level of carbon, which was accepted equal to 284.4 eV. It should be noted, however, that the vacuum required for obtaining the photoelectron spectra and heating of the samples by X-rays, led to some loss of water by the crystalline hydrate samples during the experiment. Such a change in the samples structure, apparently, led to the charge redistribution on the surface during the experiment and to a significant broadening of C1s line. Thus, on the basis of the data obtained it is impossible to reliably determine the binding energies for all of the samples with the accuracy required, but changes in the relative distances between the separate lines of the spectrum in a series of the investigated samples, has appeared to be informative enough in order to determine a changes in the electronic structure caused by the substitutions in their structure.

To determine the changes in the valence band, X-ray emission spectra of the studied compounds were obtained also. X-ray emission spectra were measured on the "SARF 1" spectrometer. During the experiment, the sample holder was cooled by water, thus avoiding essential heating of the samples under the influence of X- rays.

3. Results and discussion

From the structural data obtained for the studied samples, it is known [2] that the oxygen atoms of P_2O_7-groups together with the oxygen atoms belonging to the water molecules form an octahedral structure around the metal atoms.

The crystal field produced by such octahedral environment leads to the splitting of d-orbitals of the metal atoms. The magnitude of the crystal field produced by the oxygen, as well as the participation of d-orbitals in the formation of the chemical bond influence on the population of the splitted levels, that leads to the fact that the metal atoms can be in different possible spin states, characterized by the number of unpaired electrons.

It is known [1, 3] that for 2p lines of X-ray photoelectron spectra of cobalt being in different spin states, the existence of "shake-up" satellites is typical. The distance of these satellites to the main peak of the spectral line, as well as their intensity allow determining the number of unpaired electrons in the metal atoms and the nature of the chemical bond with their participation.

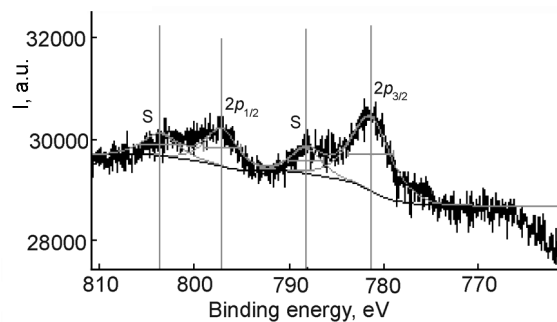For $Mn_{2-x}Co_xP_2O_7\cdot5H_2O$ compound with the value of $x = 0.6$, having the lowest co-

Fig. 1. X-ray photoelectron Co 2p spectrum for $Mn_{2-x}Co_xP_2O_7\cdot5H_2O$, $x = 1$. S — satellite.

balt content in its structure, it is impossible to resolve the "shake-up" satellites or different states of cobalt in the spectrum of 2p line of cobalt, while the half-width of approximately 2.8 eV indicates that cobalt in this compound is in more than one oxide state or geometric environment.

Further substitution of manganese by cobalt leads to appear of a pronounced satellite in the spectrum of the sample with the value of $x = 1$ at the distance approximately equal to 7 eV from the main peak of $2p_{3/2}$ line (Fig. 1).

Increase of cobalt content in the sample with the value of $x = 1.9$ (Fig. 2) accompanied by an even more pronounced "shake-up" satellite, and decrease in the distance between the main $2p_{3/2}$ peak and its satellite to the distance equal of about 5.8 eV.

Complete substitution of manganese by cobalt leads to the fact that spectrum of cobalt 2p line of compound $Co_2P_2O_7\cdot5H_2O$ has a half-width of ~4 eV, but such a line width and the presence of satellites do not allow to resolve unambiguously its individual components.

The structure of the "shake-up" satellites of cobalt lines, as it is known [1, 3, 5, 6], is associated with the mechanism of excitation of the atom, accompanied by the charge transfer from the ligand (oxygen) to the metal. Decrease of the distances between the main peak of cobalt 2p lines and its satellite, together with an increase of the satellite intensity, indicates that the charge transfer from the oxygen to the metal atom occurs at lower energies and with a higher probability. That points out on a change in the nature of the chemical bonding of cobalt atoms with the surrounding oxygen.

The position of cobalt satellite allows establishing the changes in the degree of covalence of the chemical bond depending on the content of cobalt in the sample. So the decrease of the distance between the satellite and the main peak indicates an increase of covalent component of the chemical bond [1].
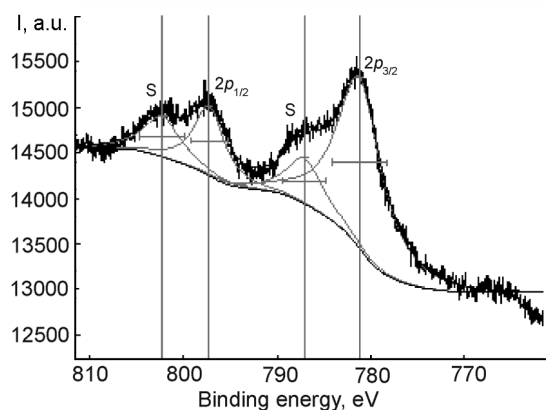
Fig. 2. X-ray photoelectron Co $2p$ spectrum for $Mn_{2-x}Co_xP_2O_7\cdot 5H_2O$, $x = 1.9$. S — satellite.

Variation in the distance between the satellite and the main peak indicates also the change in spin state of cobalt atom. Thus, for the diamagnetic cobalt Co^{3+} ($S = 0$) satellites are weak and located at a distance of about 10 eV. For cobalt Co^{2+}, being in the high-spin state ($S = 3/2$), occurred intensive "shake-up" satellites situated at a distance of about 6 eV or less. At the same time, the intensity of the satellites for cobalt in the state with $S = 3/2$ is higher than that for cobalt in the low-spin state with $S = 1/2$ [3].

Increase in the number of unpaired electrons of cobalt is also accompanied by an increase in the distance between $2p_{3/2}$ and $2p_{1/2}$ lines: for the diamagnetic cobalt Co^{3+} ($S = 0$) the distance $2p_{3/2}-2p_{1/2}$ is 15 eV, the low-spin cobalt is characterized by the distance between the lines of about 15.4 eV, whereas for Co being in the high-spin state, the distance between $2p_{3/2}$ and $2p_{1/2}$ lines increases to 16 eV [1, 3].

Presence of the pronounced satellite in $2p_{3/2}$ line of cobalt spectrum for compound $Mn_{2-x}Co_xP_2O_7\cdot 5H_2O$, $x = 1.9$ at a distance of 5.8 eV from the main peak, together with the fact that the distance between $2p_{3/2}$ and $2p_{1/2}$ lines is 16 eV (which for a given sample can be defined with good accuracy) indicates that cobalt ion in this compound has unpaired electrons in the outer shell [3] and is in the high-spin state with $S = 3/2$, that apparently is accompanied by changes in the geometry of its environment and must appear in ferro- or antiferromagnetic properties of the given compound.

Gradual decrease of the distance between the satellite and the main peak with increasing cobalt content indicates an increase of the covalent component of the chemical bond with participation of cobalt atoms as its content in the structure of the studied samples is increased.
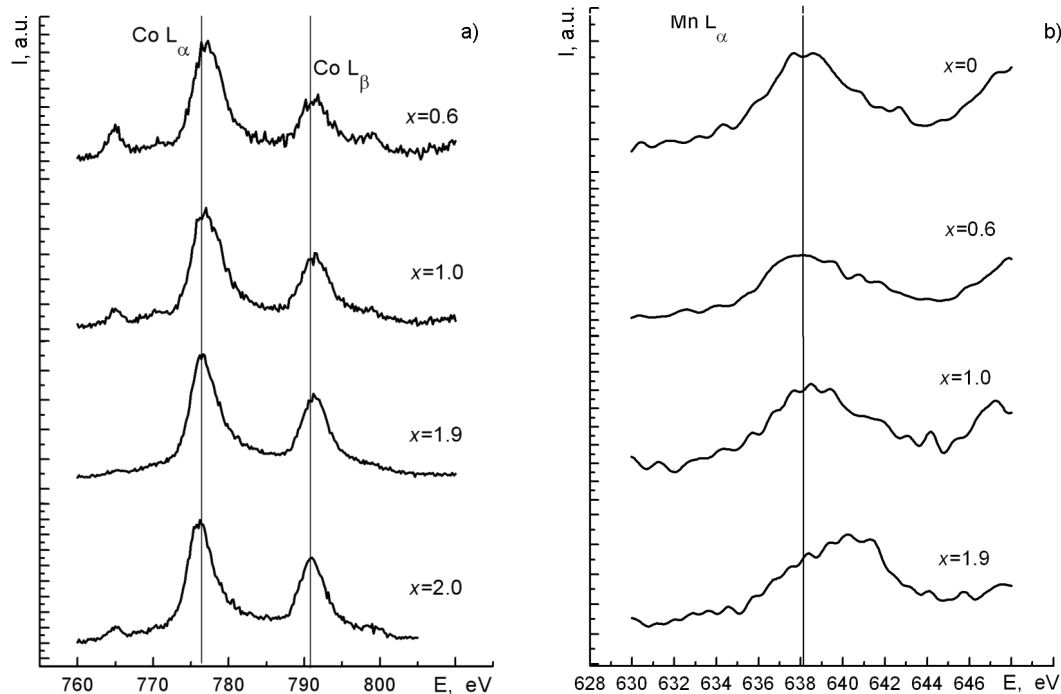

Fig. 3. L — spectra of cobalt (a) and manganese (b) for the samples $Mn_{2-x}Co_xP_2O_7\cdot 5H_2O$ with different values of x.

Such a change in the nature of the chemical bond with participation of cobalt with increase of its concentration manifest itself in some shift of $L_{\alpha1,2}$ line of cobalt X-ray emission spectrum to a lower energies (Fig. 3a) that may also indicate an increase of negative charge on cobalt.

Changes in $L_{\alpha1,2}$ — spectrum of manganese (Fig. 3b) are much more pronounced. In addition to the shift of $L_{\alpha1,2}$ line to lower energies with increasing amounts of manganese atoms, indicating the decrease of negative charge on the manganese, significant changes in the line shape are also take place. For the samples with low concentrations of manganese, the line is asymmetric, having bigger shoulder located in a low-energy region, while for the samples with higher content of manganese, a shift of the asymmetric shoulder towards higher ener-
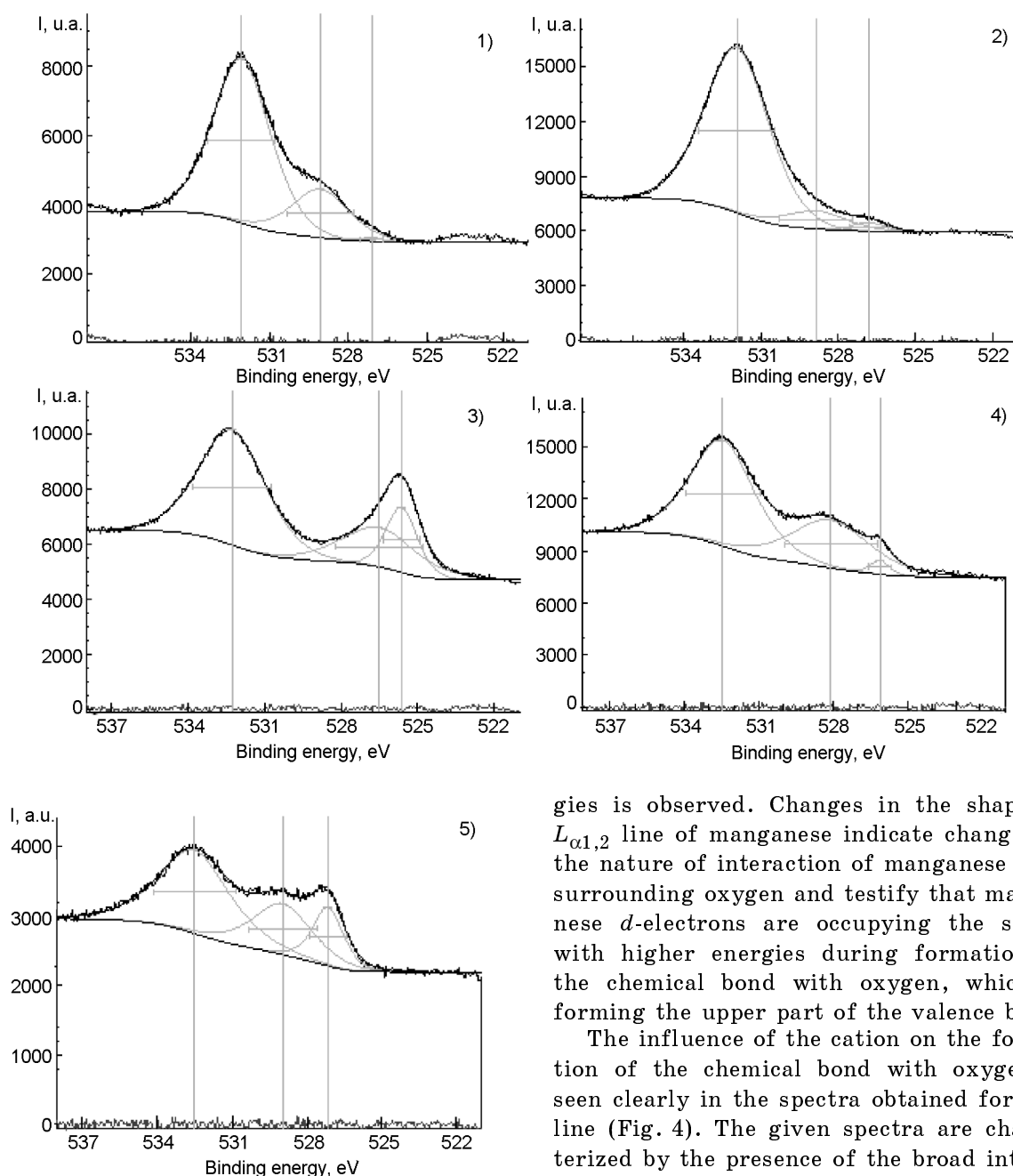
Fig. 4. X-ray photoelectron O1s spectra for $Mn_{2-x}Co_xP_2O_7 \cdot 5H_2O$: 1) $x = 2.0$, 2) $x = 1.9$, 3) $x = 1.0$, 4) $x = 0.6$, 5) $x = 0$.

gies is observed. Changes in the shape of $L_{\alpha1,2}$ line of manganese indicate changes in the nature of interaction of manganese with surrounding oxygen and testify that manganese d-electrons are occupying the states with higher energies during formation of the chemical bond with oxygen, which is forming the upper part of the valence band.

The influence of the cation on the formation of the chemical bond with oxygen is seen clearly in the spectra obtained for O1s line (Fig. 4). The given spectra are characterized by the presence of the broad intense line corresponded to the structural and adsorbed water on the sample surface, as well as by the line related to the oxygen of P_2O_7-groups.

The oxygen atoms belonging to P_2O_7-groups may form a various bonds with the surrounding elements, such as P–O–P, –P=O, P–O–M, where M — atom of the metal cation. Since the biggest change in the nature of the chemical bond occurs with the oxygen atoms being in the immediate vicinity of the metal atoms, the substitution of cobalt with manganese should be reflected in the O1s spectra in the energy area, which is characteristic for the oxygen forming P–O–M bond.

From the two possible bonds P–O–P and P=O, P–O–P bond is more covalent and is located towards higher energies in O1s oxygen spectrum with respect to the bond of P=O [4], whereas the energy position of 1s-level of oxygen participating in P–O–M bond depends on the cation type and ionicity degree of the chemical bond O–M. Hence, in the sample $Co_2P_2O_7 \cdot 5H_2O$, with the hundred-percent cobalt content, the rightmost peak (Fig. 4.1) obtained in the result of deconvolution refers to the forming the double bond of oxygen with phosphorus P=O, while a much more intensive lines reflect the energy state of oxygen forming the bonds P–O–P and P–O–M.

Substitution of cobalt by manganese leads to an increase of the feature located in the region corresponding to oxygen forming P=O bond in the sample $Co_2P_2O_7 \cdot 5H_2O$, therefore, 1s line of oxygen participating in the chemical bond with manganese falls to the region of lower binding energy in compare to oxygen forming the chemical bond with cobalt. An essential increase in the intensity of the given feature (Fig. 4), located in the region of low binding energies on O1s spectrum, with increasing manganese content indicates the decrease of 1s-electrons binding energy of oxygen and, consequently, an increase of an electron density on oxygen atoms belonging to P_2O_7-groups

and taking part in formation of the chemical bond with the atoms of the metal.

Thus, the substitution of cobalt by manganese is accompanied by an increase of the ionic component of the chemical bond O–M of manganese atoms with oxygen, meanwhile the increase of electron density on oxygen leads to a shift of valence electrons energy levels, being observed in L_α spectra of manganese (Fig. 3b).

4. Conclusions

The data obtained allow us to suggest that the substitution of manganese by cobalt is accompanied by both the redistribution of the electron density between the atoms of the metal sublattice, proceeding in accordance with their electronegativity values, and the change in the chemical bond nature between the metal atoms and the surrounding oxygen.

Increase of cobalt content leads to an increase of the covalent component of the chemical bond in the overall charge balance.

Substitution of cobalt by manganese is accompanied by an essential increase in the electron density on oxygen atoms involved in formation of the chemical bond with the metal atoms that leads to the formation of states laying in the upper part of the valence band of the investigated samples.

References

1. J.G.Dillard, C.V.Schenck, M.H.Koppelman, *Clays and Clay Minerals*, **31**, 69 (1983).
2. H.Assaaoudi, I.S.Butler, J.A.Kozinski, *J. Chem.Crystallography*, **36**, 723 (2006).
3. A.Mekki, D.Holland, K.Ziq, C.F.MCconville, *J.Non-Cryst. Solids*, **220**, 267 (1997).
4. G.D.Khattak, A.Mekki, L.E.Wenger, *J.Non-Cryst.Solids*, **355**, 2148 (2009).
5. S.C.Petitto, M.Langell, *J.Vac.Sci.Technol.A*, **22**, 1690 (2004).
6. F.Allegretti, G.Parteder, M.G.Ramsey et al., *Surf. Scie.*, **601**, L73 (2007).

Особливості електронної будови невпорядкованих дифосфатів Mn і Co

В.Л.Карбівський, С.С.Смоляк, Ю.О.Загородній, В.Х.Касіяненко

Методами рентгенівської фотоелектронної та емісійної спектроскопії досліджено особливості електронної будови невпорядкованих дифосфатів – $Mn_{2-x}Co_xP_2O_7 \cdot 5H_2O$, де $x = 0$, 0.6, 1.0, 1.9, 2.0. Заміщення різного ступеню кобальту марганцем призводить до перерозподілу електронної густини у металевих підгратах та до збільшення іонної складової хімічного зв'язку між аніонами кисню і катіонами металу, а також обумовлює формування станів, які знаходяться у верхній частині валентної смуги сполук, що досліджуються.