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ESCA Studies of Copper Oxides and Copper Molybdates

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Valence band, Cu $2p_{3/2}$, O $1s$, Mo $3d$, and Cu $L_3M_{45}M_{45}$ photoelectron and X-ray-induced Auger spectra were recorded for metallic copper, Cu_2O, CuO, $Cu_2Mo_3O_{10}$, $Cu_6Mo_4O_{15}$, $CuMoO_4$, $Cu_3Mo_2O_9$, and $Cu_{3.85}Mo_3O_{12}$. Cu $2p_{3/2}$ binding energy is 0.9 eV lower for Cu^+-containing molybdates than for Cu_2O and 0.7 eV higher for Cu^{2+}-containing molybdates with respect to that of CuO. Calculation of net chemical shift demonstrates the influence of Madelung potential on the binding energy of core electrons. On the basis of differences in binding energy it was possible to distinguish between various Cu-containing phases and to follow the surface redox processes of copper molybdates which, as it was seen, follow the same reactions as in the bulk processes. Auger spectra suggest the presence of a very thin layer of "surface phase" common for all five studied molybdates and independent of bulk structure and composition.

1. Introduction

Binding energy (B.E.) of core electrons measured by photoelectron spectroscopy depends on the formal valency of the element. For simple and composed oxides the observed chemical shift frequently amounts to 0.5–1 eV per valency unit and thus most surface redox processes may be easily followed by ESCA technique. It may be expected also that the configuration of the first coordination sphere (coordination number, symmetry, and interatomic distances) of studied atoms or ions should influence the value of chemical shift. However, direct experimental evidence of this effect is lacking.

It was found, e.g., that the B.E. of the Mo $3d$ doublet is the same for a series of Mo(VI) compounds as MoO_3, $CoMoO_4$, Bi_2MoO_6, $Bi_2Mo_2O_9$, $Bi_2Mo_3O_{12}$ (*1–3*) as well as for MoO_3 supported on Al_2O_3, SiO_2 (*1*), and MgO (*3*) in spite of different octahedral or tetrahedral coordination. Also the B.E. of inner electrons of Bi shows the same values for Bi_2O_3 and all three above quoted bismuth molybdates (*2*). There are some data in the literature (*4–6*) suggesting that the B.E. of Co $2p$ electrons changes on passing from the octahedral (CoO) to the tetrahedral (Co_3O_4) coordination of the Co^{2+} ion.

Earlier results concerning Co ions based on comparison of the experimental data obtained in different laboratories (*7*) do not find any confirmation in the most recent studies (*8*, *9*).

The lack of a more pronounced influence of matrix upon chemical shift in photoelectron spectroscopy makes it difficult to study the surface properties of multicomponent samples, e.g., mixed oxide catalysts, and it was impossible to detect the difference between oxysalts or solid solutions, on the one hand and an ordinary mixture of simple oxides, on the other.

It seemed that the question concerning the matrix effects in chemical shift should have been most easily answered by studies of the compounds of an element which readily

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accepts very different coordination numbers. Copper was thus chosen for the present investigation.

The studies of the following samples are described in this paper:

—Metallic copper with cubic close-packed structure and interatomic distances of 2.556 Å (*10*).

—Cu_2O of cuprite *Pn*3 structure (*10*) in which each metal has only two close oxygen neighbors at the distance of 1.85 Å. The closest Cu–Cu separation is 3.01 Å.

—CuO of tenorite *C*2/*c* structure (*10*) in which copper is surrounded by an approximate square of oxygens with Cu–O distances of ca 1.88 and 1.96 Å.

—$CuMoO_4$ belonging to the $P\bar{1}$ space group (*11*). Two of the copper atoms occupy axially distorted octahedra of oxygen atoms; Cu–O bond distances are equal to 4 × 1.933 and 2 × 1.980 Å. The third copper atom occupies a distorted tetragonal pyramid with basal CuO distances ranging from 1.894 to 1.895 Å and an apical Cu–O bond of 2.341 Å.

—$Cu_3Mo_2O_9$, belonging to the *Pnam* space group (*12*). Two Cu atoms occupy CuO_6 octahedra distorted in two ways with Cu–O bonds ranging from 1.79 to 2.27 Å and from 1.92 to 2.53 Å. The third Cu atom has a distorted tetragonal pyramidal arrangement with Cu–O bonds ranging from 1.90 to 2.18 Å.

—$Cu_{4-x}Mo_3O_{12}$ ($x \leqslant 0.15$), space group $P2_12_12_1$ (*13*). Two Cu atoms are located in two types of distorted, elongated octahedra of Cu–O bonds ranging from 1.946 to 2.429 and from 1.982 to 2.408 Å. One Cu atom is placed in a deformed square pyramid (Cu–O between 2.035 and 2.814 Å) with a more distant oxygen atom (3.269 Å) completing a deformed triangular prism. Some copper atoms (~0.85) are in chains of face sharing octahedra with Cu–O distances between 2.08 and 2.42 and short Cu–Cu distances across the face equal to 2.51 Å, which is even less than in metallic copper. The problem of valency of copper in this compound has not been answered before, but the combination of 3Cu(II) and 0.85 Cu^0 seems most plausible.

—$Cu_6Mo_4O_{15}$ (*14*, *15*) and $Cu_2Mo_3O_{10}$ (*16*). The structures of these compounds are not known but the magnetic susceptibility measurements (*16*) showed that they contain Cu(I) and Mo(VI).

As the experiments involved redox treatments of samples it may be appropriate to mention that according to our previous studies (*16*) the following bulk reactions at temperatures not exceeding 450°C were identified by X-ray analysis:

$$
\begin{aligned}
&Cu_2Mo_3O_{10} \xrightarrow{\text{ox}} 2CuMoO_4 + MoO_3; && (1)\\
&Cu_6Mo_4O_{15} \xrightarrow{\text{ox}} 4CuMoO_4 + 2CuO; && (2)\\
&Cu_{3.85}Mo_3O_{12} \xrightarrow{\text{ox}} 3CuMoO_4 + 0.85CuO; && (3)\\
&10CuMoO_4 \xrightarrow{\text{red}} 2Cu_2Mo_3O_{10} + Cu_6Mo_4O_{15}; && (4)\\
&2Cu_3Mo_2O_9 \xrightarrow{\text{red}} Cu_6Mo_4O_{15}; && (5)\\
&2Cu_{3.85}Mo_3O_{12} \xrightarrow{\text{red}} 1.28Cu_6Mo_4O_{15} + 0.87MoO_3. && (6)
\end{aligned}
$$

At more drastic conditions of reduction with hydrogen all copper molybdates reduce to Cu and MoO_2. On reoxidation CuO and MoO_3 are formed which may react to $CuMoO_4$.

2. Experimental Details

2.1. Preparation of samples. A sample of metallic copper was obtained by evaporation of spectral pure Cu in the preparation chamber of the spectrometer. After exposure to oxygen at atmospheric pressure and 400°C for 3 min CuO was formed and its spectra were registered. On subsequent heating at 300°C in vacuum for 5 hr the sample was reduced to Cu_2O. The above procedure of sample preparation was adopted after Kim (*17*). Certain small amounts of Cu^{2+} and Cu^{+} ions on the surface of Cu_2O and CuO, respectively, cannot be excluded, but the presence or absence of Cu $2p$ satellites as discussed further seems to be a good test of proper preparation of both oxides.

All other samples, i.e., $CuMoO_4$, $Cu_3Mo_2O_9$, $Cu_6Mo_4O_{15}$, $Cu_2Mo_3O_{10}$, and $Cu_{3.85}Mo_3O_{12}$ were obtained by solid state reactions between MoO_3, CuO, and/or Cu_2O at 450–600°C in air or in the evacuated sealed quartz tubes and were controlled by X-ray analysis as described in (*16*, *18*). All these samples were then deposited from acetone suspension of finely ground powder onto the sample holder.

2.2. Measurements. Electron spectra were recorded using an ESCA-3 Vacuum Generators spectrometer. The Au $4f_{7/2}$ peak was taken as a reference line with the B.E. assumed as 84.0 eV. The B.E. value of the C $1s$ line, due to carbon contamination visible in the photoelectron spectra of fresh powdered samples close to 285 eV, was used in certain cases as an internal calibration standard. The estimated accuracy of determination of peak positions was better than ±0.2 eV.

The experimental procedure consisted in registration of the spectra of fresh samples, which then were subjected to following treatments:

—reduction (decomposition) by outgassing (10^{-7}–10^{-9} Torr) the sample for several hours at moderately elevated temperatures (100–400°C);

—reduction in about 10^{-5} Torr of hydrogen at 200–400°C for several minutes;

—oxidation by exposure to oxygen at atmospheric pressure at 300–400°C for several minutes.

3. Results and Discussion

3.1. General remarks. In the present study valence bands, Cu $2p$, X-ray-induced Auger Cu $L_3M_{45}M_{45}$, O $1s$ and Mo $3d$ lines were recorded for all samples quoted in the Introduction. All determined energy parameters are summarized in Tables I and II. The Cu $2p$, O $1s$, and Cu $L_3M_{45}M_{45}$ spectra of metallic copper and copper oxides are shown in Fig. 1 whereas the valence band region is shown in Fig. 2. Examples of Cu $2p$ and Cu $L_3M_{45}M_{45}$ spectra of investigated oxysalts after various redoxy treatments are illustrated in Figs. 3–5. Figures 6 and 7 show valence band and Mo $3d$ photoelectron spectra, respectively, for all investigated "fresh" molybdates. The O $1s$ line in copper molybdates was a single narrow line

TABLE I

ELECTRON ENERGY PARAMETERS OF COPPER OXIDES AND COPPER MOLYBDATES (ELECTRON VOLTS)[a]

Sample	Cu $3d$	$\Delta 3d$	Cu $2p_{3/2}$	$\Delta 2p_{3/2}$	Cu $L_3M_{45}M_{45}$	$\Delta L_3M_{45}M_{45}$	ΔE_{chem}
Cu metal	3.3	—	933.1	—	918.2	—	—
Cu^{I}_2O	3.6	0.3	933.1	0	916.0	−2.2	−0.6
$Cu^{II}O$	3.9	0.6	934.0	0.9	917.6	−0.6	−0.3
$Cu^{I}_2Mo_3O_{10}$	2.4	−0.9	932.2	−0.9	916.3		0.9
$Cu^{I}_6Mo_4O_{15}$	2.4	−0.9	932.2	−0.9	916.4		0.9
$Cu^{II}MoO_4$			934.7	1.6	916.4		
$Cu^{II}Mo_2O_9$			934.7	1.6	916.4		
$Cu_{3.85}Mo_3O_{12}$			933.1	0	916.4		
			934.7	1.6			

[a] XPS lines in binding energy scale. Auger lines in kinetic energy scale. Chemical shift Δ given as ion–metal difference. Net chemical shift ΔE_{chem} calculated as explained in the text.

TABLE II

BINDING ENERGIES (ELECTRON VOLTS) OF O 1*s* AND Mo 3*d* ELECTRONS IN COPPER OXIDES, COPPER MOLYBDATES, AND MoO$_3$[a]

Sample	O 1*s*	Mo 3$d_{5/2}$	Mo 3$d_{3/2}$
Cu$_2^{I}$O	530.8		
Cu^{II}O	529.8		
MoO$_3$	530.8	232.8	236.0
Cu$_2^{I}$Mo$_3$O$_{10}$	530.5	232.6	235.9
Cu$_6^{I}$Mo$_4$O$_{15}$	530.6	232.3	235.6
Cu^{II}MoO$_4$	530.8	232.9	236.2
Cu$_3^{II}$Mo$_2$O$_9$	530.8	233.0	236.3
Cu$_{3.85}$Mo$_3$O$_{12}$	530.7	232.7	236.1

[a] MoO$_3$ values are taken from our previous work (*2*) (recalibrated).

for all samples with nearly the same (see Table II) B.E. values and thus are not shown in the figures.

The discussion given in this paper is confined mainly to the Cu 2$p_{3/2}$ and Cu $L_3M_{45}M_{45}$ spectra.

As regards the Mo 3*d* spectra, differences between copper molybdates and MoO$_3$ are not large, yet not negligible (cf. Fig. 7 and Table

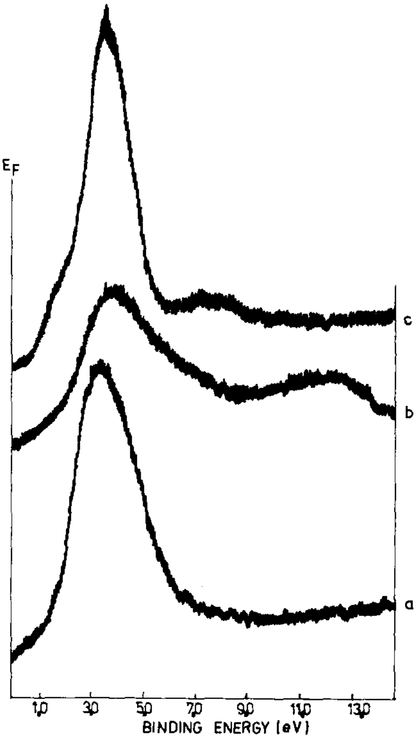

FIG. 2. Photoelectron spectra of valence band region of samples in Fig. 1.

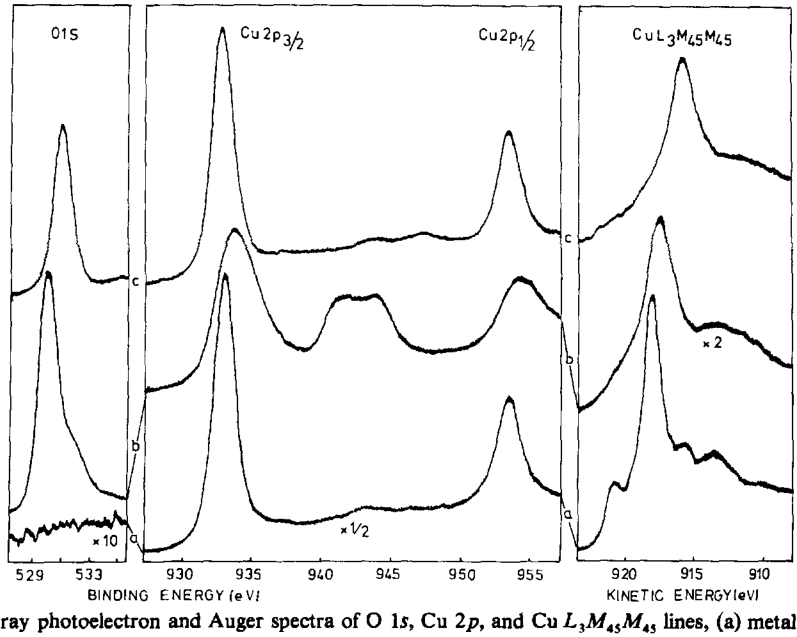

FIG. 1. X-ray photoelectron and Auger spectra of O 1*s*, Cu 2*p*, and Cu $L_3M_{45}M_{45}$ lines, (a) metallic copper film, (b) CuO obtained by exposure of the Cu film to oxygen at atmospheric pressure at 400°C, (c) after subsequent heating under vacuum at 300°C for 5 hr.

II). They are particularly evident for Cu^+-containing molybdates and may be assumed to be due to the variation of the Madelung potential in these compounds. Unfortunately, no final conclusions can be drawn because of the lack of structural data for the compounds in question. More detailed interpretation of the Mo 3*d* spectra together with some quantitative aspects of the present ESCA study is in progress (*19*).

Also the spectra of the valence band, although showing the fine structure, are at present not very informative. They have been registered mainly to be used for the calculation of net chemical shifts.

3.2. Spectra of copper and copper oxides. Metallic copper, copper oxides, and some other copper compounds have already been the subject of a number of XPS studies (*8*, *9*, *17*, *20–36*). Most of the authors agree that the B.E. shift of the Cu $2p_{3/2}$ line between Cu_2O and metallic Cu is very small, whereas that between CuO and metallic Cu equals about 1 eV (*8*, *29*, *30*, *35*). It has also been established (*9*, *17*, *27*, *34*) that in the Cu 2*p* photoelectron region of Cu^{2+} compounds satellite lines (or so-called shake-up lines) appear which are never present in the spectra of Cu^+ ions. The last feature facilitates the identification of copper in different valency states.

At variance with other authors our results for CuO and Cu_2O were obtained for oxides prepared *in situ* in the spectrometer. They agree well with most of the above-mentioned commonly accepted literature data. Note the difference of about 1 eV in the position of the O 1*s* line in Cu_2O as compared with that in CuO, in agreement with the recent work (*8*) and our suggestions (*37*). It can be seen from Figs. 1 and 2 (curves b) that the widths of CuO lines are larger as compared with the same lines of Cu and Cu_2O. This is frequently interpreted as resulting from multiplet splitting (*17*, *27*) but we believe that in part this broadening is due to the presence of some amount of Cu^+ ions at the surface of CuO. The similar phenomenon (in case of Co 2*p* lines) has been discussed recently for cobalt oxides (*6*). In this case, however, the K.E. (kinetic energy) shift between Co^{2+} and Co^{3+} ions (and also the proportion of Co^{3+} (Co^{2+} ions)) was sufficiently large to produce in the Auger Cu $L_3M_{45}M_{45}$ region two unresolved peaks (*38*) and this fact enables the detection of both Co ions present simultaneously at the surface. Apparently this is not the case for Cu oxides where the Auger shift between Cu^+ and Cu^{2+} ions is too small.

3.3. Cu 2p spectra of oxysalts. The results we have obtained indicate that both $2p_{3/2}$ B.E. values for Cu^+ and Cu^{2+} ions in copper molybdates differ considerably from those in copper oxides. Curve a in Fig. 3 shows the

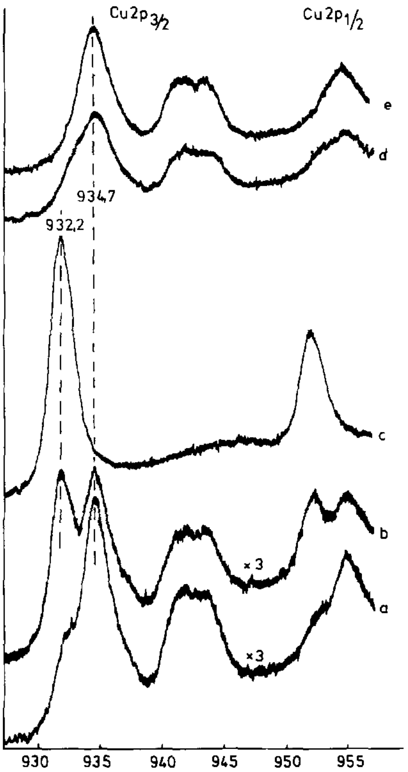

FIG. 3. Cu 2*p* photoelectron spectra: (a) fresh $CuMoO_4$ sample, (b) $CuMoO_4$ after heating under vacuum at 300°C for 1 hr, (c) $Cu_6Mo_4O_{15}$ after heating under vacuum at 250°C for 6 hr, (d) fresh $Cu_3Mo_2O_9$, (e) $Cu_3Mo_2O_9$ after exposure to oxygen at 350°C and atmospheric pressure for 5 min.

main Cu $2p_{3/2}$ line from fresh $CuMoO_4$ placed at 934.7 eV and followed by satellite. This line may be assigned to Cu^{2+} ions. It may be noted that its width is distinctly smaller than that obtained for CuO. After reduction of the sample (curve b) by heating under vacuum a new peak appears in the spectrum with B.E. equal to 932.2 eV, the same as observed for Cu^{+}-containing salts (curve c). In fact, according to X-ray data (*16*) $CuMoO_4$ reduces—as shown by Eq. (*4*)—to $Cu_2Mo_3O_{10}$ and $Cu_6Mo_4O_{15}$ but not to Cu_2O. It may thus be concluded that for Cu^{+}-containing salts such as $Cu_2Mo_3O_{10}$ and $Cu_6Mo_4O_{15}$, the Cu $2p_{3/2}$ B.E. value is 932.2 eV, being 0.9 eV lower than that for Cu_2O; for Cu^{2+}-containing salts such as $CuMoO_4$ and $Cu_3Mo_2O_9$ it amounts to 934.7 eV, i.e., 0.7 eV more than for Cu^{2+} ions in CuO.

On the basis of the results described above the Cu $2p$ spectra of $Cu_{3.85}Mo_3O_{12}$ presented in Figs. 4a,b may be easily interpreted. The main Cu $2p_{3/2}$ line from the fresh sample (curve a) is composed of two poorly resolved peaks. Comparison with the Cu $2p_{3/2}$ spectra of metallic copper and $CuMoO_4$ summarized in Fig. 8 indicates that the two components of the Cu $2p_{3/2}$ line of $Cu_{3.85}Mo_3O_{12}$ correspond to the peak of metallic copper at 933.1 eV and the peak of Cu^{2+} ions at 934.7 eV. The satellite peak characteristic for Cu^{2+} ions is also visible. It may be thus concluded that the $Cu_{3.85}Mo_3O_{12}$ compound contains copper in two valence states, namely, Cu^{2+} and Cu^{0}. After partial decomposition of the sample by vacuum heating (Fig. 4b) the intensity of the Cu^{2+} (934.7 eV) peak and its satellite decreases. Simultaneously the left peak increases its intensity, its maximum being shifted to

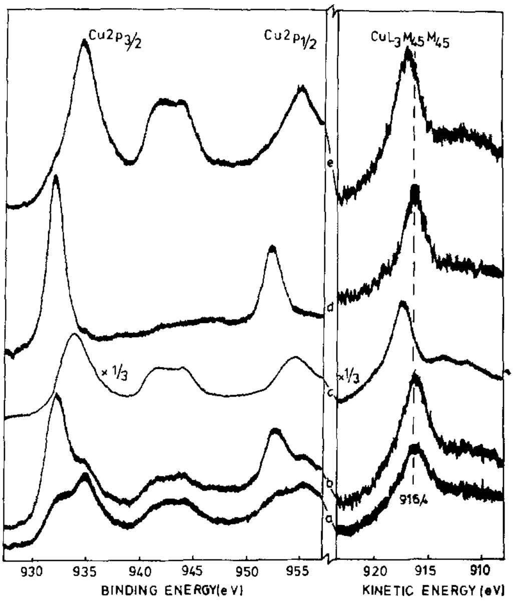

FIG. 4. Cu $2p$ and Auger Cu $L_3M_{45}M_{45}$ spectra: (a) fresh $Cu_{3.85}Mo_3O_{12}$ sample, (b) $Cu_{3.85}Mo_3O_{12}$ after heating under vacuum at 130°C for 15 hr, (c) $Cu_{3.85}Mo_3O_{12}$ after subsequent exposure to oxygen at 400°C and atmospheric pressure for 5 min, (d) $Cu_2Mo_3O_{10}$ after heating under vacuum at 250°C for 2 hr, (e) $Cu_2Mo_3O_{10}$ after subsequent exposure to oxygen at 350°C and atmospheric pressure for 5 min.

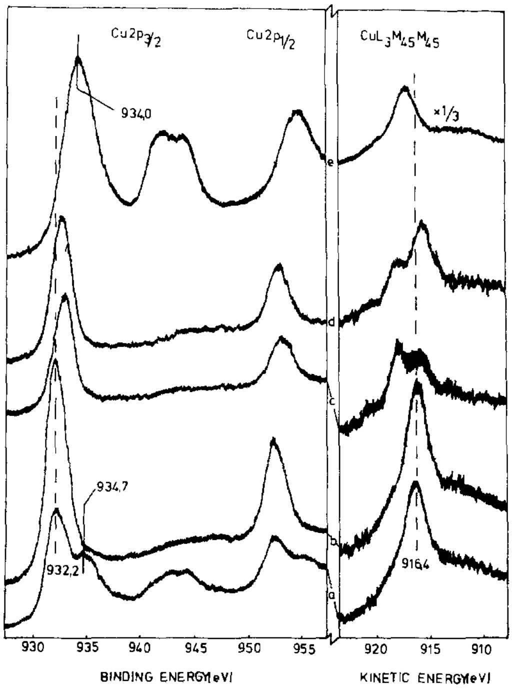

FIG. 5. Cu $2p$ and Auger Cu $L_3M_{45}M_{45}$ spectra: (a) fresh $Cu_6Mo_4O_{15}$ sample, (b) $Cu_6Mo_4O_{15}$ after heating under vacuum at 250°C for 6 hr, (c) $Cu_6Mo_4O_{15}$ after subsequent reduction in 1×10^{-5} Torr of hydrogen at 200–400°C for 5 min, (d) $Cu_3Mo_2O_9$ after reduction in hydrogen in conditions as above, (e) sample $Cu_3Mo_2O_9$ after subsequent exposure to oxygen at 400°C and atmospheric pressure for 5 min.

932.2 eV, the value characteristic for Cu^+ containing molybdates. This indicates that reaction (*6*) took place, resulting in the formation of $Cu_6Mo_4O_{15}$. At the right slope of the 932.2-eV peak (Fig. 4b) a shoulder is seen which may be assigned to Cu^0 in the unreacted part of $Cu_{3.85}Mo_3O_{12}$.

Our results enable us also to draw some conclusions concerning the shape of the Cu $2p_{3/2}$ satellite line. Kim (*17*) and Brisk and Baker (*39* suggested that the complex structure (doublet) of shake-up satellite peaks in some Cu^{2+} compounds is due to the Jahn–Teller effect. They argued that CoO and NiO, in contrast to CuO, show a single satellite structure due to high symmetry of NaCl-type structure. We have observed, however, only negligible changes of the shape and position of satellites in all Cu^{2+} compounds studied here (see Figs. 1b, 3, 4a–d, and 5e) in spite of very different coordinations. Thus it seems that some other interpretation than that proposed in (*17*, *39*) must be looked for.

3.4. Auger $CuL_3M_{45}M_{45}$ spectra. It is striking that despite a 2.5-eV difference between Cu $2p_{3/2}$ B.E. on passing from Cu^{2+} to Cu^+ ions in copper molybdates, no difference can be detected in the respective Auger spectra. The Cu $L_3M_{45}M_{45}$ peak looks unchanged in Fig. 4, curves a, b, and d though very dramatic

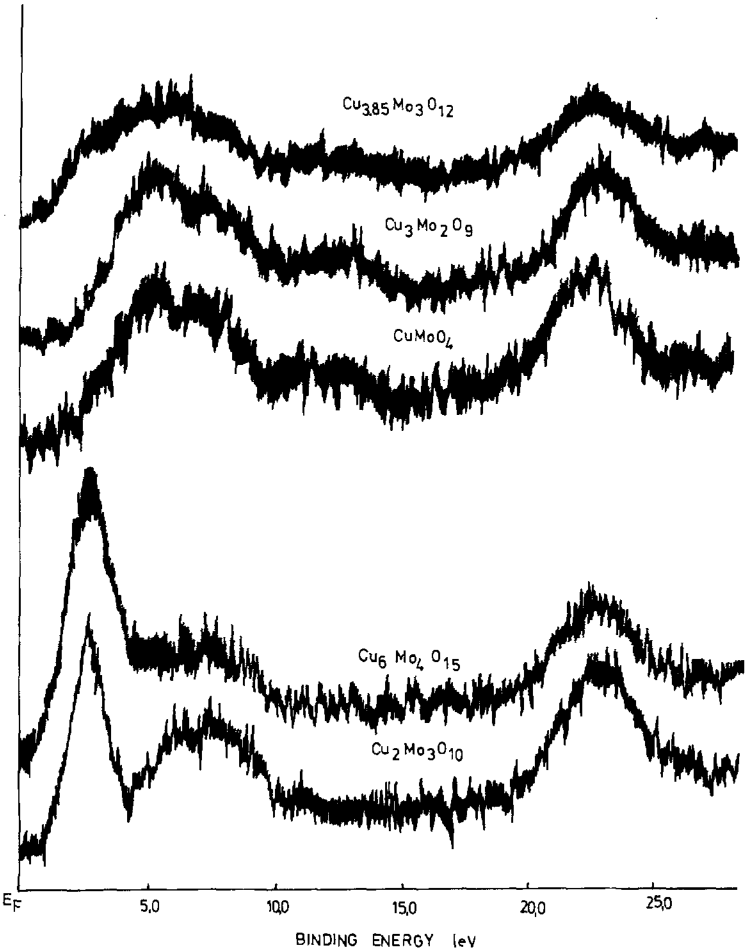

FIG. 6. Photoelectron spectra of the valence band region of copper molybdates.

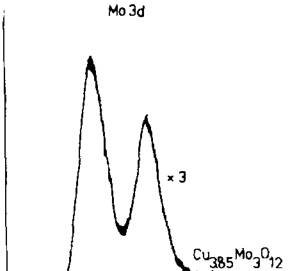

FIG. 7. Mo 3*d* photoelectron spectra of MoO_3 and copper molybdates. MoO_3 spectrum is taken from our previous work (2).

changes are visible in corresponding Cu 2*p* spectra. This is also the case in Figs. 5a,b. In fact we found that the Cu $L_3M_{45}M_{45}$ peak has practically the same position (see Table I) for all five copper molybdates. This position is intermediate between that characteristic for Cu^+ ions in Cu_2O and that characteristic for Cu^{2+} ions in CuO.

This is rather surprising in view of the frequent observations (*46*) that for a given compound the observed shift of the Auger line is much larger than the corresponding shift of the photoelectron line.

The following interpretation of the unusual stability of Auger peaks in copper molybdates may be suggested. As first pointed out by Brundle (*40*, *41*) and confirmed in our previous paper (*38*) Auger spectra may in some cases be more sensitive than XPS spectra for the properties of the outermost layers of the surface. Our results could then indicate that all studied oxysalts are covered with a very thin layer of "surface phase" common for all preparations and independent of the composition and structure of the bulk.

It should be emphasized that this phase is reappearing also after the redox experiments have been performed *in situ* in the spectrometer (cf., e.g., Figs. 4a–c). Thus it seems that this phase is thermodynamically stable in the conditions, whereat the spectra are registered and not accidentally formed during the preparation or deposition of the powder on the sample holder.

Only after rapid reoxidation or reduction of compounds were we able to note some changes in the Auger spectra. This mav be illustrated by the spectra of $Cu_6Mo_4O_{15}$ and $Cu_3Mo_2O_9$ registered after reduction in hydrogen (Fig. 5, curves c and d). In both cases two poorly resolved Auger peaks appear. The kinetic energy of the left one equals 918.2 eV and thus indicates the presence of metallic copper, its formation being in agreement with the course of bulk reduction. The position of the second Auger component at 915.8 eV may be interpreted as due to Cu^+-containing molybdates. It therefore seems reasonable to assume that the surface of Cu^+-containing salt freshly formed or exposed during the short period of reduction may not yet be covered by the above discussed surface phase. Therefore the peak under discussion could be assigned to the surface layer with the same composition as the bulk or to a certain intermediate state between that of bulk and equilibrated surface phase.

In view of the proposed explanation the apparently single Cu $2p_{3/2}$ line of reduced $Cu_6Mo_4O_{15}$ and $Cu_3Mo_2O_9$ should be composed of two lines, namely, one characteristic for metal (933.1 eV) and another characteristic for Cu^+ ions in oxysalts (932.2 eV). In fact, the position of the Cu $2p_{3/2}$ peak in

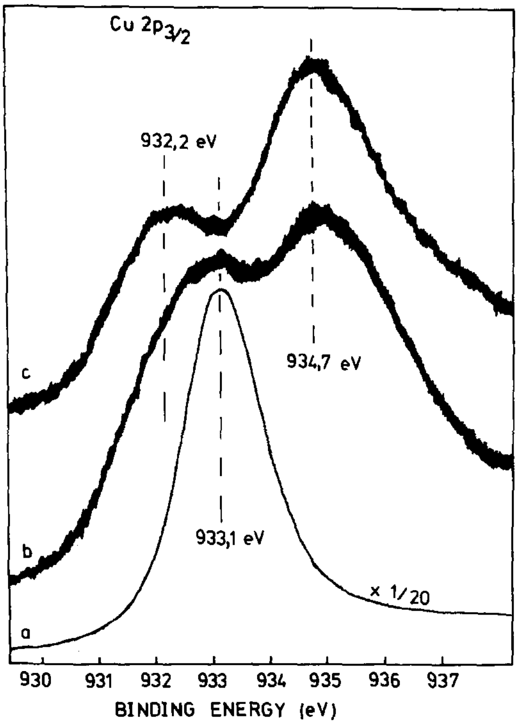

FIG. 8. Cu $2p_{3/2}$ photoelectron spectra: (a) metallic copper film, (b) fresh $Cu_{3.85}Mo_3O_{12}$ sample, (c) $CuMoO_4$ sample after heating under vacuum at 400°C for 1 hr.

spectra c and d of Fig. 5 is intermediate between metallic copper and Cu^+ salt. The reduction in case d is less extensive since the left Auger peak is smaller than that in spectrum c and accordingly the position of the Cu $2p_{3/2}$ line (932.6 eV) is shifted further from the metallic copper (933.1 eV) than the peak in spectrum c (932.9 eV).

3.5. Chemical shifts. According to Chuang *et al.* (*6*) the measured B.E. or K.E. shifts are due to the combination of three effects, namely: initial state charge, Madelung potential, and final state relaxation energy. The first two components can be treated together as an effective nucleus charge producing "net chemical shift" (*42*). Kowalczyk *et al.* (*43*) have proposed an equation enabling approximate calculations of net chemical Auger line shift. It may also be assumed (*44–46*) that the absolute value of net chemical shift should be approximately the same for both the Auger and XPS lines, as it depends only on the effective nucleus charge. For copper the equation derived in (*43*) may be formulated as follows:

$$\text{net } \Delta E_{\text{chem}} = \Delta \text{B.E.}(2p_{3/2}) - 2\,\Delta \text{B.E.}(3d).$$

The net ΔE_{chem} has been calculated (see Table I, last column) for Cu_2O, $Cu_2Mo_3O_{10}$, $Cu_6Mo_4O_{15}$, and with somewhat less accuracy (due to line broadening) for CuO. For other salts net chemical shift cannot be obtained since their valence band spectra do not show a sufficiently sharp Cu $3d$ peak to permit the calculations.

It should be mentioned, however, that after heating under vacuum a peak of growing intensity appeared in the valence band spectra of Cu^{2+}-containing molybdates, similar to that visible in the spectra of $Cu_2Mo_3O_{10}$ and $Cu_6Mo_4O_{15}$. As shown above, such vacuum treatment results in the formation of Cu^+ molybdates; the discussed peak may thus be assigned to Cu $3d$ electrons from Cu^+ ions.

The calculated net chemical shift for Cu_2O is higher than for CuO, suggesting that the effective nucleus charge is higher for Cu^+ than Cu^{2+} ions in these oxides.

Net chemical shift of Cu $2p_{3/2}$ B.E. in Cu^+ containing salts is equal to the value measured experimentally. This means that the relaxation energy term for Cu $2p_{3/2}$ electrons is approximately the same for metallic Cu- and Cu^+-containing molybdates.

The negative B.E. shift observed for Cu^+ ions in molybdates with respect to metallic copper must thus be due to the difference in the Madelung potential. Apparently this factor is also responsible for the large difference of 0.9 eV in B.E. values of $2p$ electrons of Cu^+ ions in Cu_2O and Cu^+ molybdates.

The situation is less clear in the case of Cu^{2+} molybdates. Cu $2p_{3/2}$ B.E. of Cu^{2+} ions increases on passing from CuO to Cu^{2+}-containing molybdates. This may be due to a lower relaxation energy or/and to a respective change in Madelung potential. The question as to which of those two effects is more important remains open and further studies are needed.

It should be emphasized that the influence of the lattice structure on the chemical shift has been observed so far only for the case of large differences in coordination of the studied ion, as, e.g., exist between Cu oxides and copper oxysalts. On the other hand, as described in the Introduction the Cu^{2+} molybdates contain copper in two different octahedral and pyramidal coordinations. This fact is not reflected in the spectra by splitting of lines, but may be one of the reasons for their broadening.

In some cases the discussed contributions of relaxation energy and Madelung potential to the observed shift may compensate each other. This could explain the fact that Oku and Hirokawa (*9*) have not observed the influence of matrix effects on B.E. studying XPS spectra of $Cu_xMg_{1-x}O$ solid solutions.

3.6. Redox treatments. Previous results(*16*) quoted in the Introduction and concerning bulk redox transformations of copper molybdates indicate that these processes proceed frequently with the change of the Cu/Mo atomic ratio and in certain cases with the formation of CuO and MoO_3, copper or molybdenum being in stoichiometric excess in relation to the composition of the respective final copper or cuprous salt. It was already mentioned that under vacuum or oxygen treatment at relatively low temperatures (300–400°C) and short oxidation time (several minutes) the surface reduction or oxidation of the studied compounds takes place. The differences in B.E. of the Cu $2p_{3/2}$ peak of Cu^{2+} and Cu^+ ions in oxides and salts make it possible to answer the question as to whether the surface processes follow the same equations (1)–(6) as the bulk ones.

We have already shown that the vacuum treatment of $CuMoO_4$ (Figs. 3a, b) and $Cu_{3.85}Mo_3O_{12}$ (Figs. 4a, b) leads to the formation of Cu^+ molybdates ($Cu_2Mo_3O_{10}$ or $Cu_6Mo_4O_{15}$), whereas Cu_2O or Cu^0 are never seen in the spectra. The result agrees with the course of reactions expressed by Eqs. (4) and (6), respectively.

Similar conclusions can be drawn from XPS spectra of the $Cu_3Mo_2O_9$ sample. The fresh sample spectrum (Fig. 3d) and that after vacuum treatment (not shown) are analogous to that of fresh and vacuum treated $CuMoO_4$ (Fig. 3a, b) confirming that reaction (5) has taken place. Reoxidation of $Cu_3Mo_2O_9$ previously reduced in hydrogen results in shifting the Cu $2p_{3/2}$ line to 934.0 eV and in the appearance of a satellite (Fig. 5e) revealing the presence of CuO at the surface. The same conclusion can be drawn from the Auger Cu $L_3M_{45}M_{45}$ peak which is now placed at 917.6 eV (CuO). The result is thus consistent with Eq. (2) and the bulk reoxidation mechanism of Cu and MoO_2 mixture.

The same conclusion has been obtained from the spectrum of reoxidized $Cu_{3.85}Mo_3O_{12}$, previously reduced by vacuum treatment (Fig. 4c). Here also the Cu $2p$ and Cu $L_3M_{45}M_{45}$ peak positions reveal the presence of CuO as a predominant phase at the surface after reoxidation. The result agrees with the course of reactions (6), (2), and (3).

From the viewpoint of the mechanism of bulk oxidation the reaction (1) describing oxidation of $Cu_2Mo_3O_{10}$ represents the only exception. Namely, in this case CuO cannot be formed. The ESCA study shows that the surface oxidation of $Cu_2Mo_3O_{10}$ follows the same mechanism as the bulk one. Before oxidation (Fig. 4, curve d) the Cu $2p_{3/2}$ peak is placed at the position characteristic for Cu^+ salts. After oxidation (curve e) it is shifted to 934.7 eV, i.e., the value characteristic for $CuMoO_4$ which is the product of oxidation of $Cu_2Mo_3O_{10}$ according to reaction (1). Note that the Cu $L_3M_{45}M_{45}$ peak is also shifted after oxidation from 916.3 to 917.0 eV. It seems that this new position of the Auger peak cannot be interpreted as due to the mixture of Cu-containing salts and CuO, since: (1) the distance of 1.2 eV would be sufficient to produce two resolved peaks or at least distinct shoulders, and (2) the presence of CuO should also produce a shift of the Cu $2p_{3/2}$ peak to the position lower than 934.7 eV, which is not the case. Apparently also in this case the equilibrated surface phase has not been formed and the value 917.0 eV is close to the K.E. of the Cu $L_3M_{45}M_{45}$ electrons from Cu^{2+} ions in Cu^{2+} molybdates.

Finally we would like to remark that the valence state of copper at the surface usually differs somewhat from the bulk composition. This is demonstrated by several examples. In the spectrum of fresh $CuMoO_4$ (Fig. 3a) the main Cu $2p_{3/2}$ line at 934.7 eV shows a left side shoulder which may be ascribed to a small amount of Cu^+ ions at the surface and which under vacuum treatment grows up into a well-resolved peak characteristic of Cu^+-containing molybdates. A similar shoulder is seen in the spectrum of fresh $Cu_3Mo_2O_9$ (Fig. 3d), disappearing after oxidation (curve e). On the other hand, a fresh $Cu_6Mo_4O_{15}$ sample (Fig. 5a) shows an addition to the Cu $2p_{3/2}$ peak at 932.2 eV a maximum at 934.7 eV and shake-up satellite, both of much lower intensity. They indicate the presence of a small amount of Cu^{2+} salts at the surface and disappear after vacuum treatment (Fig. 5b). It is noteworthy that the positions of these additional maxima or shoulders suggest the presence of Cu^+ of Cu^{2+} ions rather in the form of Cu-containing salts than the respective oxides.

Summarizing the results described in Section 3.4 it may be concluded that in all cases redox surface processes of copper molybdates follow the same equations as the bulk ones.

4. Conclusions

The studies described in the present paper lead to four main conclusions:

(1) It was demonstrated experimentally that the B.E. of core electrons depends on the Madelung potential. Two factors may be responsible for the lack of experimental evidence of this dependence in earlier works, namely: too small differences in the coordination of the studied atom and/or compensation effect due to opposite influence of the changes of Madelung potential and that of relaxation energy on B.E., cancelling each other.

(2) For copper atoms, accepting very different coordinations in oxygen surrounding the influence of Madelung potential is clearly manifested and thus it is possible: (a) to distinguish between different copper compounds even of the same valency, (b) to follow surface redox processes of copper molybdates, and (c) to show that they follow the same equations as in the bulk.

(3) It is argued that the surface of all copper molybdates is covered with a very thin "surface phase" common for all salts and independent on bulk structure and composition.

(4) It was shown that XPS and X-ray-induced Auger spectra provide the complementary information and simultaneous registration of both extends the characterization of complex oxide surfaces.

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