

## ARTICLES

## Soft-x-ray-emission study of the influence of Li<sup>+</sup>-doping, irradiation, and plastic deformation on CuO

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The influence of Li<sup>+</sup> doping, shear under pressure, and irradiation with He<sup>+</sup> or electrons on the oxygen 2*p*-band and valence states of copper ions in CuO was studied using soft-x-ray emission spectroscopy. In the case of irradiation and shear under pressure the transformation of the spectrum shape is explained by the appearance of Cu<sub>2</sub>O. The doping with lithium leads to the appearance of copper ions with formal valency of 3+. It was also established that the presence of lithium ions prevents Cu<sub>2</sub>O phase forming without a dependence on the plastic deformation value. The reasons and possible mechanisms of the CuO→Cu<sub>2</sub>O transitions in the oxides studied are discussed. [S0163-1829(99)01402-2]

### I. INTRODUCTION

Various properties of some materials are determined by the presence of differently charged ions. In the case of copper compounds, cations of dissimilar charge can order to form a single-crystalline phase according to electroneutrality of the involved cations and anions. LiCu<sub>3</sub>O<sub>3</sub>,<sup>1,2</sup> LiCu<sub>2</sub>O<sub>2</sub>,<sup>1,3,4</sup> and Cu<sub>4</sub>O<sub>3</sub> (Ref. 5) are among such compounds. Ions with different valence states may also appear in a system as a result of some kind of external effects, thermal treatment, deviations from strictly stoichiometric proportions, etc. Cupric oxide, CuO, can be considered as a suitable example of such a system.<sup>6</sup> Doping, irradiation with charged particles (high-energy electrons, He<sup>+</sup> ions, etc.), and strong plastic deformation also result in the appearance of ions with other charges than the basic ones.

Doping of CuO with light alkali metals should lead to appearance of copper ions with formal valency of 3+ if oxygen takes 2-. According to a simple ionic model, the 50% substitution, Li<sub>0.5</sub>Cu<sub>0.5</sub>O, should yield only trivalent copper. There exists a cation-ordered compound at this composition, LiCuO<sub>2</sub>.<sup>7,8</sup> For the isostructural NaCuO<sub>2</sub>, it was established<sup>9</sup> that, in the ground state, the *d*<sup>9</sup>*L* configuration is dominant (formal Cu<sup>3+</sup>, being Cu<sup>2+</sup> plus an oxygen *p* hole) rather than *d*<sup>8</sup> (real Cu<sup>3+</sup>). The corresponding situation takes place in the Li<sub>*x*</sub>Ni<sub>1-*x*</sub>O system<sup>10</sup> and in copper-based high-temperature superconductors.

The nearest neighbor 3*d* transition-metal oxide NiO tolerates doping by lithium to a large extent without changing its structure, but CuO does not,<sup>2</sup> and annealing cannot improve the situation. The difference in behavior is due to the square ligand coordination in CuO while the environment in NiO is octahedral, also suitable for Li<sup>+</sup>.

Among other suitable methods for affecting the structure and properties of materials, irradiation with charged particles and plastic deformation under pressure are considered. Un-

fortunately, there is a limited number of papers concerning the influence of charged particles irradiation on the properties of CuO.<sup>11,12,14</sup> As for papers concerning the influence of plastic deformation on valence states of copper ions in CuO, they are absent till now. Thus, the processes of formation of ions with different valence states in CuO that can be caused by irradiation and shear under pressure are also of direct interest.

Soft x-ray emission spectroscopy (XES) is an efficient method of studying chemical bonding and to determine the valence states of ions in various systems. In this paper, we present the results of an XES study of the influence of Li<sup>+</sup> doping, irradiation with He<sup>+</sup> and electrons, and shear under pressure on the appearance of ions with dissimilar valence states and on phase transitions in copper monoxide CuO.

### II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

Pressed pellets of CuO were prepared from commercial powder of 99.9% purity by annealing at 1220 K in air during 50 h. Li<sub>0.01</sub>Cu<sub>0.99</sub>O and Zn<sub>0.02</sub>Cu<sub>0.98</sub>O samples were obtained using the solid-state phase reaction method (annealing at 970 K during 24 h) from appropriate mixtures of CuO, Li<sub>2</sub>CO<sub>3</sub>, and ZnO powders. Grinding, compacting, and final heat treatment at 1220 K were performed. This gave single-phase specimens of Li<sub>0.01</sub>Cu<sub>0.99</sub>O and Zn<sub>0.02</sub>Cu<sub>0.98</sub>O. X-ray powder-diffraction phase analysis was used for characterizing the products. On doping by lithium or zinc, CuO changed its lattice parameters. The resulting cell parameters of the samples obtained are given in Table I. The concentrations of the involved lithium and zinc were estimated according to Vegard's rule using these cell parameters. LiCuO<sub>2</sub>, used as a reference material, was made by delithiating Li<sub>2</sub>CuO<sub>2</sub>.<sup>7</sup>

TABLE I. Crystallographic parameters for CuO,  $\text{Li}_{0.01}\text{Cu}_{0.99}\text{O}$ , and  $\text{Zn}_{0.02}\text{Cu}_{0.98}\text{O}$  samples with monoclinic lattice.

Sample	$a \pm 0.002$ (Å)	$b \pm 0.002$ (Å)	$c \pm 0.002$ (Å)	$\beta \pm 0.04$ (°)
CuO	4.685	3.423	5.128	99.58
$\text{Li}_{0.01}\text{Cu}_{0.99}\text{O}$	4.686	3.416	5.124	99.60
$\text{Zn}_{0.02}\text{Cu}_{0.98}\text{O}$	4.684	3.408	5.126	99.54

For the preparation of a  $\text{Li}_{0.05}\text{Cu}_{0.95}\text{O}$  solid solution a method of mechanochemistry (shear under pressure) was used. The composition of this specimen was assumed to be the nominal according to the amounts of CuO and LiOH taken. Powder mixtures of these components were pressed up to 6–8 GPa between two flat anvils, one rotating relative to each other. The rotation velocity was 1 revolution per minute and the number of revolutions  $n$  varied from 1 to 5. The strain is related to the number of revolutions  $n$ . The relation is determined by the expression  $\varepsilon = \ln(\varphi r/h)$  (here  $\varphi$  denotes the revolution angle,  $h$  is the sample thickness, and  $r$  is the distance between the center of a specimen and a selected point),<sup>13</sup>  $n=1$  corresponding to  $\varepsilon \sim 5.5$  and  $n=5$  to  $\varepsilon \sim 7$ . Unfortunately we cannot estimate the concentration of the involved lithium from the x-ray-diffraction data, because the strong mechanical stresses arising in this specimen under such conditions result in x-ray diffraction line broadening that impede the precision measurements of the cell parameters and the phase analysis. For quantitative analysis of the composition measurements of the resistivity  $\rho$  have been performed. It is well known that  $\text{Li}^+$ -doping should decrease resistivity, on the other hand, deformation should lead to increasing resistivity. Our measurements showed that the room-temperature value of  $\rho$  is about  $0.5 \Omega \text{ cm}$  for  $\text{Li}_{0.01}\text{Cu}_{0.99}\text{O}$ , and  $0.1 \Omega \text{ cm}$  for the specimen prepared by mechanochemistry. These facts confirm the increase of Li content up to  $\sim 5$  at. % for the mechanochemically synthesized specimen.

Irradiation of single-crystal CuO samples with electrons was performed with the help of a linear particles accelerator at the Institute of Metal Physics, Ekaterinburg, Russia (electron energy 5 MeV, flux  $\sim 3 \times 10^{18} \text{ cm}^{-2}$ ). During the process of irradiation the sample temperature did not exceed 250 K. Irradiation with  $\text{He}^+$  ions was performed with the help of an U-120 cyclotron in the Ural State Technical University, Ekaterinburg, Russia (particles energy 4.65 MeV, beam density  $1.2 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ , flux  $\sim 3 \times 10^{17} \text{ cm}^{-2}$ ). In this case the sample temperature was not more than 370 K. All the irradiated specimens were 1–2 mm thick. From here on we shall separate the surfaces of irradiated samples into two categories. The surface which was directly affected with the beam of charged particles will be called an “irradiated surface” while the opposite surface, not facing any charged particles, will be called a “nonirradiated surface.”

The O  $K\alpha$  x-ray emission spectra (XES) were obtained with a JCSA-733 electron-probe microanalyzer, specially adjusted for precise measurements of XES fine structure,<sup>15</sup> where the x-ray tube operated at 5 kV and 100 nA. We used the O  $K\alpha$  spectrum of MgO (525.4 eV) for calibrating. The instrumental broadening of the O  $K\alpha$  spectra was about 0.5 eV.

### III. RESULTS AND DISCUSSION

Figure 1 shows O  $K\alpha$  ( $2p \rightarrow 1s$  electron transition) x-ray emission spectra (XES) for the deformed CuO,  $\text{Li}^+$ -doped CuO and untreated CuO. These spectra reflect the contribution of O  $2p$  density of states to the valence band and clearly exhibit two spectral features, named A and B, which are situated at about 524.4 and 526.2 eV, respectively. Here, the B feature reflects the admixture of antibonding oxygen  $2p$ -copper  $3d$  states, while the A feature belongs to the bonding states.<sup>16</sup> As for the Zn-doped specimen, we found no influence on the spectral shape. Neither were there any differences between the front and backward surfaces. Therefore, we present no further data. We have arranged the XES O  $K\alpha$  spectra measured for different specimens but obtained under the same deformation conditions in pairs (doped samples are the upper spectrum, undoped are the lower spectrum). Recall that the magnitude of plastic deformation is indicated by the number of revolutions,  $n$ .

As one can clearly see from Fig. 1, the shear under pressure strongly affects the XES O  $K\alpha$  spectrum shape for CuO. This results in a decrease of the B feature intensity with respect to that of the A feature (as inferred from comparing the  $n=0$  and  $n=5$  spectra). It should be mentioned that the spectrum shape of CuO for  $n=5$  specimen is closer to some

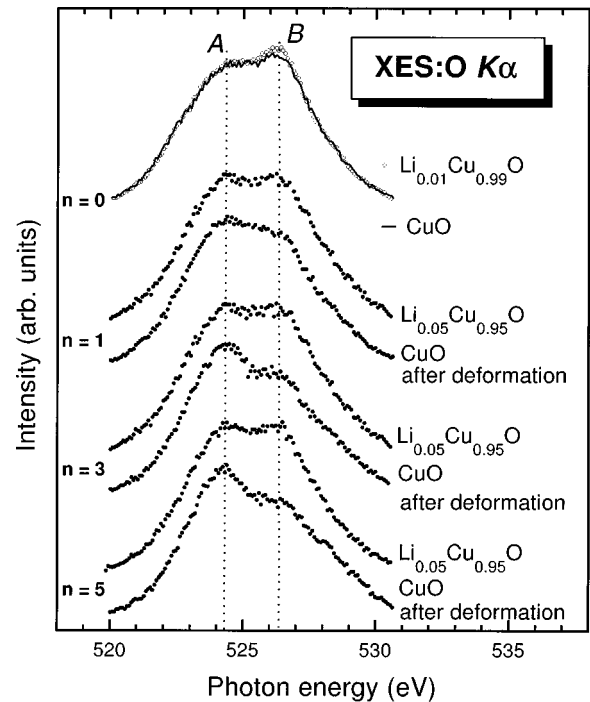


FIG. 1. O  $K\alpha$  x-ray emission spectra for CuO subjected to different values of shift deformation ( $n=0,1,3,5$ ) and  $\text{Li}^+$ -doped CuO.

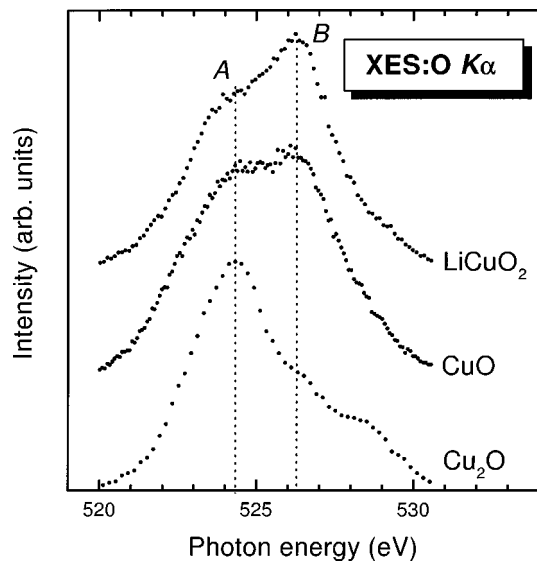


FIG. 2. O  $K\alpha$  x-ray emission spectra for  $\text{LiCuO}_2$ ,  $\text{CuO}$ , and  $\text{Cu}_2\text{O}$ .

extent to that of  $\text{Cu}_2\text{O}$  (see Fig. 2). Figure 2 shows the spectra for reference samples of  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$ , and  $\text{LiCuO}_2$  that contain  $\text{Cu}^{1+}$ ,  $\text{Cu}^{2+}$ , and formally  $\text{Cu}^{3+}$  ions, respectively.

An interesting result was obtained for the  $\text{Li}^+$ -doped  $\text{CuO}$  specimens. According to our data, the presence of lithium in a small concentration (1%) only slightly changes the spectrum shape whereas the higher level of doping (5%) transforms it essentially. The latter leads to a redistribution of intensity of A and B features. One can point out that the spectrum shape is practically independent of the plastic deformation value for  $\text{Li}_{0.05}\text{Cu}_{0.95}\text{O}$  samples (Fig. 1).

One can see from Fig. 1 that the process of  $\text{Li}^+$ -doping results in an increase of the B-feature intensity for the sample with  $n=0$  (no plastic deformation) in comparison with that for “pure”  $\text{CuO}$ . A strong B feature is present in the spectrum of  $\text{LiCuO}_2$ , where copper ions adopt a formal valency of 3+ (Fig. 2). Thus, we advocate that the process of doping  $\text{CuO}$  with  $\text{Li}^+$  leads to formal  $\text{Cu}^{3+}$  valence states, in analogy with the XES O  $K\alpha$  spectrum of  $\text{LiCuO}_2$  (and  $\text{NaCuO}_2$ .) Accordingly, the independence of spectrum shape on the plastic deformation value is explained by the competition between two processes: on the one hand, the appearance if  $\text{Cu}_2\text{O}$  takes place and, on the other, the formal  $\text{Cu}^{3+}$  valence states emerge ( $d^9L$ ). The  $\text{Li}^+$ -doping prevents the growth of the  $\text{Cu}_2\text{O}$  phase and rather leads to the presence of both  $\text{Cu}^{1+}$ ,  $\text{Cu}^{2+}$ , and, formally,  $\text{Cu}^{3+}$  valence states in the doped and simultaneously deformed samples.

Figure 3 shows the XES O  $K\alpha$  spectra for  $\text{CuO}$  after irradiation with  $\text{He}^+$  and electrons. One can see from this figure that the process of electron irradiation changes the spectrum shape in the same manner as the shear under pressure: the intensity of the B feature is decreasing in O  $K\alpha$  spectrum. We measured the spectra for both the irradiated and the nonirradiated surface, no difference being detected between them.

As for the  $\text{He}^+$ -irradiated sample, an unexpected result was obtained. While the spectrum of the  $\text{He}^+$ -irradiated surface was only slightly changed, the spectrum of the nonirra-

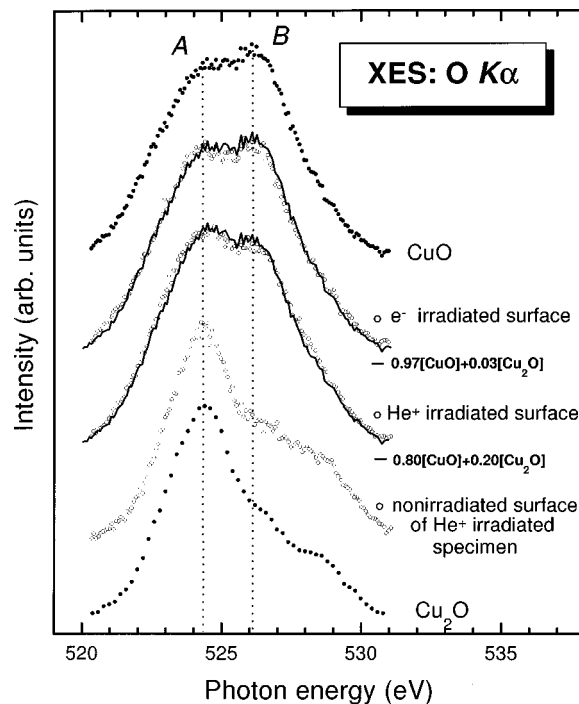


FIG. 3. O  $K\alpha$  x-ray emission spectra for  $\text{He}^+$  and electron-irradiated  $\text{CuO}$ .

diated surface was similar to that of “pure”  $\text{Cu}_2\text{O}$  (see Fig. 3).

We assume that the cases of electron and  $\text{He}^+$  irradiation should be interpreted differently. During the process of electron irradiation, the specimen undergoes copper-oxygen bond breaking, and the  $\text{Cu}_2\text{O}$  phase forms. This point of view is supported by the absence of any dramatic differences in the shape of O  $K\alpha$  spectra for both surfaces of an irradiated specimen compared with the case of plastic deformation. Such a result can be clearly understood by taking into account that electrons are able to penetrate through the whole specimen. The maximum penetration depth of 5 MeV electrons in  $\text{CuO}$  is estimated to be about 4 mm. Moreover, the experimental XES O  $K\alpha$  spectrum for the electron-irradiated sample can be simulated to a good approximation by a sum of O  $K\alpha$  spectra of  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  taken in a ratio 0.97:0.03 (see Fig. 3, solid line curve).

The situation for the  $\text{He}^+$ -irradiated specimen is not compatible. Here, significant differences between the spectra for nonirradiated and irradiated surfaces were established. This effect was established in independent studies.<sup>14,17</sup> In our opinion, the phenomena mentioned can be interpreted as follows. During irradiation of the specimen with  $\text{He}^+$  particles, that have much lower penetration ability ( $\sim 10 \mu\text{m}$ ) than electrons, shock waves form at the ends of particle tracks. Such shock waves cause atomic excitations and bond breaking while extending over the whole specimen volume. Under these conditions, irradiation-stimulated diffusion enhances the formation of the new phase near the surface that is opposite to the irradiated one. During the process of irradiation the surface is subjected to dynamic annealing due to the release of the energy that is connected with ionization losses. In this case, dynamic annealing of the defects near the irradiated surface takes place and leads to a partial restoration.

Thus, only a small  $\text{Cu}_2\text{O}$  phase content appears on the irradiated surface while the nonirradiated one consists practically of “pure”  $\text{Cu}_2\text{O}$ . However, further study is necessary to describe this phenomenon in more detail. It should be noted that, during  $\text{He}^+$  irradiation, the temperature of the specimen was too low ( $<370$  K) to explain the reduction of defects in the irradiated specimen on a thermal basis. In a similar manner as before, the O  $K\alpha$  spectrum simulations have been performed (Fig. 3). The process of irradiation also leads to the formation of  $\text{Cu}_2\text{O}$  similar to the effect of shear under pressure but with some deviations in each case, as mentioned above.

#### IV. CONCLUSIONS

Taking our data into consideration, the following conclusions were made.

Shear under pressure and irradiation with  $\text{He}^+$  or electrons essentially change the phase composition of copper oxide as well as the valence states of copper ions. In all these cases, the  $\text{Cu}_2\text{O}$  phase is formed. The process of  $\text{Li}^+$ -doping leads to the appearance of copper ions with formal valency

of 3+. During electron irradiation the  $\text{Cu}_2\text{O}$  phase is distributed over the whole specimen volume, whereas the irradiation with  $\text{He}^+$  particles results in accumulation of  $\text{Cu}_2\text{O}$  phase at the nonirradiated surface of a specimen due to a shock-wave mechanism. The process of  $\text{Li}^+$  doping, together with shear under pressure, impede the formation of  $\text{Cu}_2\text{O}$  phase so that  $\text{Cu}^{1+}$ ,  $\text{Cu}^{2+}$ , as well as formal  $\text{Cu}^{3+}$  valence states are present in the doped and simultaneously deformed samples. However, no effects were detected on  $\text{Zn}^{2+}$  doping. The high efficiency of soft x-ray emission spectroscopy for studying phase transitions in oxide systems has been demonstrated.

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