six corners formed by the terminal O(1) atoms shows that one of the four unique Ca–O bonds can be characterized as preferrred, as was the case for $LiBO_2$. The ranking of the Ca–O bonds according to bond strength and the geometry of the polyhedron correspond to chemical intuition. Thus, the experimental electron density distribution allows the formation of the crystal to be rationalized in terms of moieties $[O(2)BO(1)]^-Ca^{2+}[O(1)BO(2)]^-$, which are joined *via* the free sp^2 hybrid orbitals of the B atoms in a three-dimensional framework. This picture is analogous to the binding model in $LiBO_2$.

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Electron-Microscopic Study of the Structure of Metastable Oxides Formed in the Initial Stage of Copper Oxidation. IV. Cu_4O-S_1 and Cu_4O-S_2

BY R. GUAN

Laboratory of Atomic Imaging of Solids, Institute of Metal Research, Academia Sinica, Shenyang, People's Republic of China

H. HASHIMOTO

Department of Applied Physics, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565, Japan

K. H. KUO

Laboratory of Atomic Imaging of Solids, Institute of Metal Research, Academia Sinica, Shenyang, People's Republic of China

AND T. YOSHIDA

Department of Applied Physics, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565, Japan

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Abstract

Besides Cu_4O, Cu_8O and $Cu_{64}O$ reported previously, two superstructures of the metastable copper oxides Cu_4O, called Cu_4O-S_1 and Cu_4O-S_2, have been observed by high-resolution electron microscopy in an early stage of oxidation of Cu together with Cu_4O. The atom positions of Cu and O have been determined by comparison of the observed structure images with simulated ones calculated using the theories of electron diffraction and image formation. Some O atoms in the superstructures occupy octahedral positions of the face-centered cubic lattice of Cu, while the others remain in tetrahedral positions

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as in Cu_4O. Possible interpretations for the occupation of the octahedral positions by O atoms are presented.

1. Introduction

A series of metastable oxides, *i.e.* Cu_4O (Guan, Hashimoto & Yoshida, 1984), Cu_8O (Guan, Hashimoto & Kuo, 1984) and $Cu_{64}O$ (Guan, Hashimoto & Kuo, 1985), which contain much less oxygen than the well known Cu_2O, were found by high-resolution electron microscopy (HREM) during the initial stage of oxidation of copper. In these suboxides, the O atoms occupy tetrahedral positions of the face-centered cubic (f.c.c.) lattice of copper rather than octahedral ones, although the latter has a much larger space for interstitial O atoms than the former. In the present paper, two superstructures with the same chemical composition as Cu_4O but with different structures are reported. The positions of O atoms in the superstructures located in the tetrahedral and octahedral sites of the Cu lattice have been determined using electron-microscope images. The reasons for the occupation by the O atoms of the octahedral positions are discussed.

2. Details of observation of superstructure

The observation of superstructures of metastable copper oxides Cu_4O has been reported (Guan, Hashimoto & Yoshida, 1984). Fig. 1 shows the HREM image reproduced from Fig. 2(*a*) of a previous paper (Guan, Hashimoto & Yoshida, 1984) and the corresponding electron diffraction pattern. The upper part of the micrograph (*A*) shows the suboxides with (001) orientation of Cu_4O, and the lower part (*B*) those with (100) orientation. The dotted line between them represents a boundary. It was confirmed in a previous paper (Guan, Hashimoto & Yoshida, 1984) that regions *E* and *D* located in part *A* and part *B*, respectively, represent the same suboxide Cu_4O but with different orientations. Moreover, some superstructure images can clearly be seen in the middle of Fig. 1, which are indicated by S_1 and S_2.

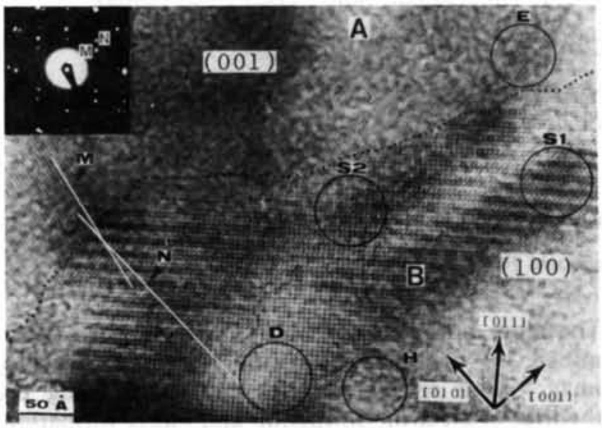
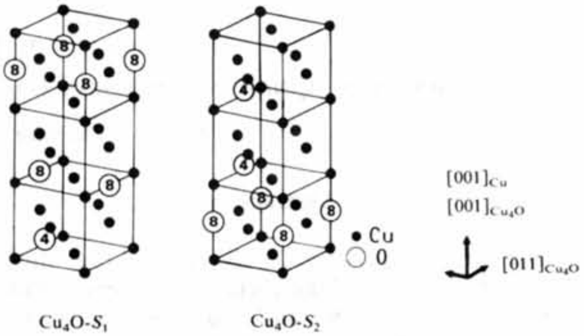


Fig. 1. High-resolution electron-microscope image of the metastable copper oxides of Cu_4O, containing superstructure of Cu_4O-S_1, Cu_4O-S_2.

Firstly, it was confirmed by optical selected-area diffraction patterns that the images of the superstructures shown in the regions S_1 and S_2 do not originate from the superposition of the grains *A* and *B*. It is clearly seen that there is no obvious boundary between the regions S_1, S_2 and *D*, so it is reasonable to expect that all the regions S_1, S_2 and *D* have the same (100) orientation. Moreover, since it was confirmed in the previous paper that the O atoms in the perfect region of Cu_4O appear as bright spots in the structure images, the O atoms in these superstructures will appear as bright spots. The reason for this point has been discussed in more detail in our recently published paper (Guan, Hashimoto & Kuo, 1986). It can be seen that the period of the regions S_1 and S_2 is three times that of the region *D* in the [011] direction, while the period still remains the same as that of *D* in the $[0\bar{1}1]$ direction. It is noted that such a threefold increase of the period in regions S_1 and S_2 corresponds to the extra diffraction spots of $\frac{1}{3}\mathbf{g}\,(001)_{\mathrm{Cu}}$.

3. Crystal structure

It is known that the O atoms in Cu_2O occupy two tetrahedral sites, while those in Cu_4O occupy only one tetrahedral site in each unit cell of copper. The shift of the bright spots and the change of their contrast in the images of the superstructures are probably due to the redistribution of O atoms among these tetrahedral and octahedral sites. Of the possible models, the two shown in Figs. 2(*a*) and (*b*) are in good agreement with the observations. In these models, the black dots represent the Cu atoms, while the open circles labeled 4 and 8 represent the O atoms located at the tetrahedral and octahedral sites respectively. It can be seen that the unit cells of both S_1 and S_2 contain 12 Cu and 3 O atoms within three unit



Cu_4O-S_1 Cu_4O-S_2

Fig. 2. Perspectives of the unit cell of Cu_4O-S_1 and Cu_4O-S_2.

cells of Cu. In model S_1, one of the three O atoms is located at the tetrahedral site, while the other two are at the octahedral site. In model S_2, however, two of the three O atoms are located at the tetrahedral site and only one at the octahedral one. These two models have the same chemical composition as Cu_4O, and are represented by Cu_4O-S_1 and Cu_4O-S_2, respectively.

4. Comparison of the observed images with the calculated contrast

Both structure models give the observed electron diffraction patterns schematically shown in Fig. 3. Figs. 4(*a*) and (*b*) respectively show the observed and calculated image of Cu_4O-S_1. Fig. 4(*c*) is a schematic illustration of the calculated image and Fig. 4(*d*) is the projection of atoms of Cu_4O-S_1 on $[010]_{Cu}$. From Fig. 4, it can be seen that the observed image agrees rather well with the calculated one and the bright spots in the images correspond to the positions of O atoms. However, by a careful comparison of Figs. 4(*a*), (*b*) and (*c*) with Fig. 4(*d*), it can be seen

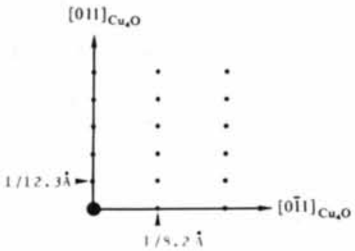


Fig. 3. Calculated electron diffraction patterns of Cu_4O-S.

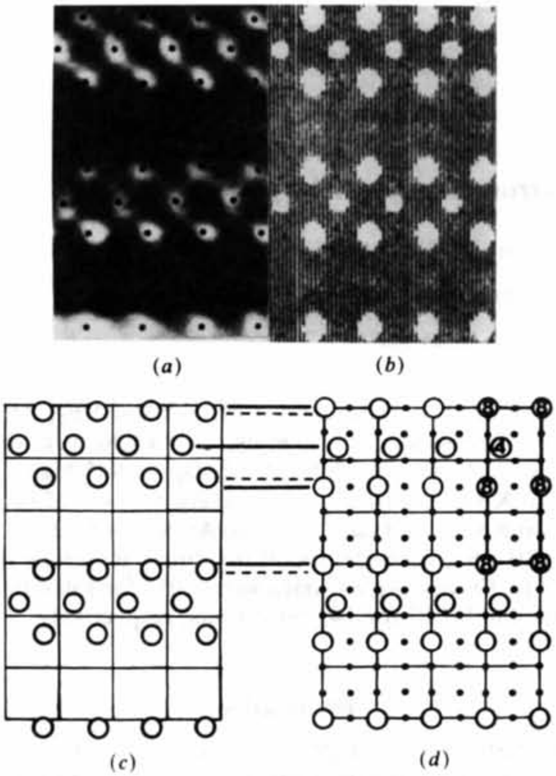


Fig. 4. Comparison of Cu_4O-S_1 atomic structure image and its calculated contrast. (*a*) Observed image. (*b*) Calculated image. (*c*) Schematic illustration of the calculated image. (*d*) Projection of atoms in Cu_4O-S_1 in Cu[010] orientation. Small spots and large open circles represent Cu and O atoms, respectively.

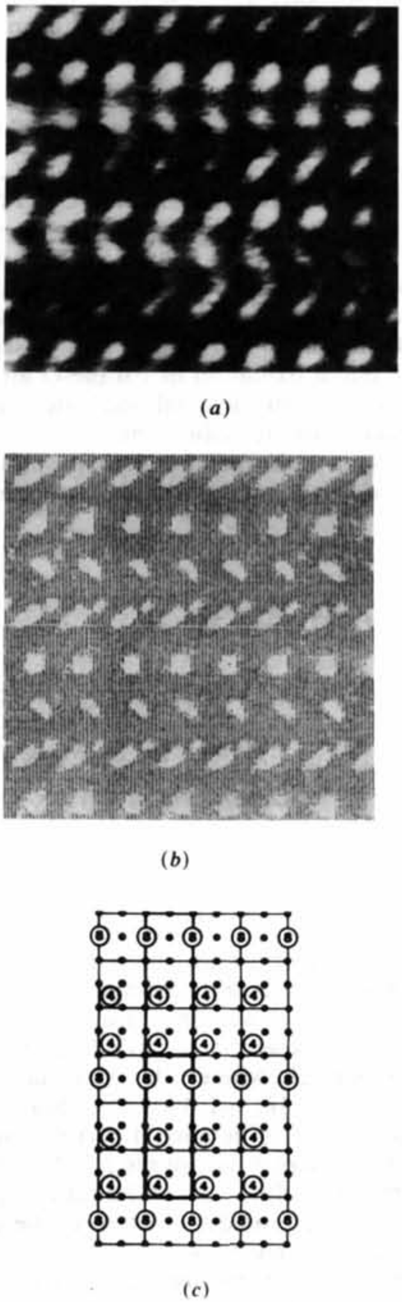


Fig. 5. Comparison between Cu_4O-S_2 atomic structure image and its calculated contrast. (*a*) Observed image. (*b*) Calculated image. (*c*) Projection of Cu_4O-S_2 model in Cu[010] orientation. Small spots and large open circles represent Cu and O atoms.

that the bright spots in the image do not correspond exactly to the positions of O atoms in the crystal. A similar shift of bright-spot images has already been observed in GaAs and AuAl (Hashimoto, Endoh, Takai, Tomita & Yokota, 1978-79) and in Si (Izui, Furuno & Otsu, 1977) and attributed to dynamic scattering of electrons in crystals and image formation with a limited number of waves (Krivanek & Rez, 1980). Similar comparisons and conclusions can also be made in the case of Cu_4O-S_2 as shown in Figs. 5(*a*)-(*c*). From these observations, it can be concluded that the suggested models are correct.

5. Discussion and concluding remarks

Two superstructures with the same chemical composition as Cu_4O, called Cu_4O-S_1 and Cu_4O-S_2, have been observed by HREM. In contrast to the structure of Cu_4O, a fraction of the O atoms in both Cu_4O-S_1 and Cu_4O-S_2 occupies the octahedral positions of the f.c.c. lattice of Cu. Since the space of the octahedra is larger than that of tetrahedra, it is possible that during the initial oxidation of Cu the O atoms may prefer to occupy first the octahedral sites then go to the tetrahedral sites to reduce the elastic interaction energy, until a uniform and perhaps more stable suboxide Cu_4O is formed. A similar phenomenon has been observed by Holley, Mulford, Ellinger, Kochler & Zachariasen (1955) and Korst & Warf (1956) in the hydrogen absorption of rare-earth metals, where the H atoms first go to the octahedral site of the f.c.c. lattice before the tetrahedra are filled by the H atoms, as confirmed by neutron diffraction and the measurements of the electric resistance. The present observation of superstructure may be explained as the occurrence of the same phenomenon.

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Asphericity Effects in the Electron Density of VF_2

BY M. M. R. COSTA AND M. J. M. DE ALMEIDA

Department of Physics, University of Coimbra, 3000 *Coimbra, Portugal*

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Abstract

The study of rutile-type structures has been undertaken in order to investigate the main features of the electron density in these compounds. The results of X-ray diffraction experiments carried out on VF_2 have been published elsewhere [de Almeida & Costa (1985). *Port. Phys.* **16**, 181-190]. Significant contour levels observed in difference Fourier maps were attributed to the asphericity of the 3*d*-electron distribution in the crystalline field of the rutile-type structure. Attempts were made to interpret these effects quantitatively by carrying out: (i) a fit of the parameters which represent the occupancy of each of the 3*d* orbitals, based on comparison of the observed structure factors with those calculated from 3*d* wave functions; (ii) a multipole refinement of the parameters which determine the occupation of the 3*d* orbitals in the crystal field. Crystal data: VF_2, $M_r = 88{\cdot}94$, tetragonal, $P4_2/mnm$, $a = 4{\cdot}806\,(10)$, $c = 3{\cdot}237\,(7)$ Å, $V = 74{\cdot}77$ Å^3, $Z = 2$, $D_x = 3{\cdot}945$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7017$ Å, $\lambda(\text{Ag } K\alpha) = 0{\cdot}5594$ Å, $\mu(\text{Mo } K\alpha) = 30{\cdot}3$ cm^{-1}, $\mu(\text{Ag } K\alpha) = 15{\cdot}2$ cm^{-1}, $F(000) = 82$, room temperature. Final R values for the Mo $K\alpha$ and Ag $K\alpha$ data were 0·014 for 190 reflections and 0·017 for 143 reflections, respectively.

Introduction

The study of rutile-type structures, MF_2, where M is a first-series transition metal, has been undertaken in our laboratory. The aim of this work is a careful determination of the electron-density distribution with a degree of accuracy which would enable a quantitative analysis of the charge-density asphericity

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