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## BRIEF COMMUNICATIONS

# Investigation of Mineralogical and Synthetic $Cu_2O$ by HREM and CBED

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Natural and synthetic cuprite, $Cu_2O$, have been examined to investigate the radiation stability of the two samples and to find methods of specimen preparation suitable for convergent beam electron diffraction analysis. In this investigation the mineralogical form, stable in the electron beam at room temperature, is found to contain copper-deficient 110 fault planes which would contribute to its three-dimensional rigidity. The defect-free form, obtained by high-temperature annealing, or, as a synthetic crystal, is by comparison radiation sensitive and can only be examined by electrons at liquid nitrogen temperature. © 1988 Academic Press, Inc.

## Introduction

$Cu_2O$ is an interesting compound in that its structure consists of two interpenetrating rafts of identical composition covalently bonded internally, but related, one to the other, by second neighbor Cu–Cu bonds along ⟨110⟩ directions, together with, presumably, weak ionic coupling between Cu–O inter-raft neighbor ion pairs. Intermetallic bonding is commonly found in organo-metallic compounds, but is unique to the $Cu_2O$ structure among simple, small unit cell inorganic compounds. It has recently received attention in several other laboratories (*1–3*). Our interest relates to determining the bonding structure by convergent beam electron diffraction (CBED) intensity measurement (*4*). For this we need to determine stable conditions of study for the cuprite phase, metastable at room temperature and pressure (*3*), and have examined mineralogical and synthetic samples with this in mind. The following results have accrued.

## Results

The mineralogical sample, from Ongania, Namibia, proved to have fault planes perpendicular to the ⟨110⟩ vector, and separated by roughly 30 to 100 unit cell inter-

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vals, as determined by high-resolution electron microscopy (HREM) at room temperature. These planes appear to arise from a slight nonstoichiometry, given by the stacking sequence:

$$\begin{gathered}\ldots.\mathrm{Cu} + \mathrm{O}, \mathrm{Cu}, \mathrm{Cu} + \mathrm{O}, \mathrm{Cu},\\ \underline{\mathrm{Cu} + \mathrm{O}, \mathrm{Cu} + \mathrm{O}}, \mathrm{Cu}, \mathrm{Cu} + \mathrm{O}, \ldots,\end{gathered}$$

where the underlining indicates a copper-deficient CuO-phase plane. The average composition is therefore $Cu_{2-x}O$, with $0.01 < x < 0.02$, or a composite oxide with a ratio $CuO/Cu_2O$ of 1 to 2%.

The above analysis is made from 1-D and zonal micrographs, as shown in those of Fig. 1. Figure 1a shows a single stacking variant of deduced CuO composition using an off-zone orientation to image the (110) planes. Figure 1b shows a [100] zone axis image, with moire fringes typical of a sample containing an inclined planar defect, indicating rotation across the defect. These micrographs are consistent with a 110 planar compositional defect given by the removal of one plane of Cu atoms followed by a translation of $\frac{1}{2}$, $\frac{1}{2}$, 0 between the remaining lattices. This fault structure is shown in Figs. 2a and 2b, giving the relative disposition of planes before and after the formation of the fault. The coordination of atoms within this structure is such that the O atoms retain their tetrahedral coordination, with the Cu atoms being bonded to three oxygens, and a nominal valence state of $1 + \frac{1}{2}$. A photograph of a model of the defect, Fig. 2c, shows double planes of distorted squares of CuO, similar to sections from the (010) face of the tenorite structure CuO. A consequence of extended planes of this coordination is that additional three-dimensional rigidity would arise from the distorted-square Cu–O bonding which would link a series of the otherwise unbonded cuprite rafts.

The fault planes in the mineralogical sample can be removed by careful annealing, but then the radiation sensitivity is such that decomposition to Cu and $Cu_2O$ overtakes any observation at room temperature (*5*).

The synthetic sample, supplied by the Smithsonian Institute (Catalog No. 163531), has similar properties in the beam to the annealed natural sample, but is fault-free over larger regions. It requires cooling to liquid nitrogen temperatures before electron microscope examination. This is particularly so for CBED where beam density is higher than in HREM. Mechanical grinding readily induces fault planes, predominantly along 110 planes (*6, 7*). Preparations for CBED were therefore obtained by a minimal grinding under ethanol. The resulting grains, examined in a Phillips 430 electron microscope with a Gatan low-temperature side-entry stage, showed occasional thin ledges, permitting all three major zones ([100], [110], [111]) to be examined at 86°K (Gatan read-out temperature). Figure 3 shows the [100] zone for the thin and thicker ledges. These patterns show the typical CBED thickness-dependent structure within the disks, expected for patterns taken with a 20-nm probe cross section beam from a perfect but wedged crystal, indicating a relative freedom from point defects.

An additional observation was a notable absence of TDS streaking in over-exposed point patterns taken at 86°K.

## Discussion

The following observations have been made from the above study of cuprite from two sources:

1. The geologically stable form of cuprite contains extensive planar copper-deficient defects.

2. The synthetic $Cu_2O$ sample may be examined in the electron microscope provided it is held at 86°K. At room tempera-

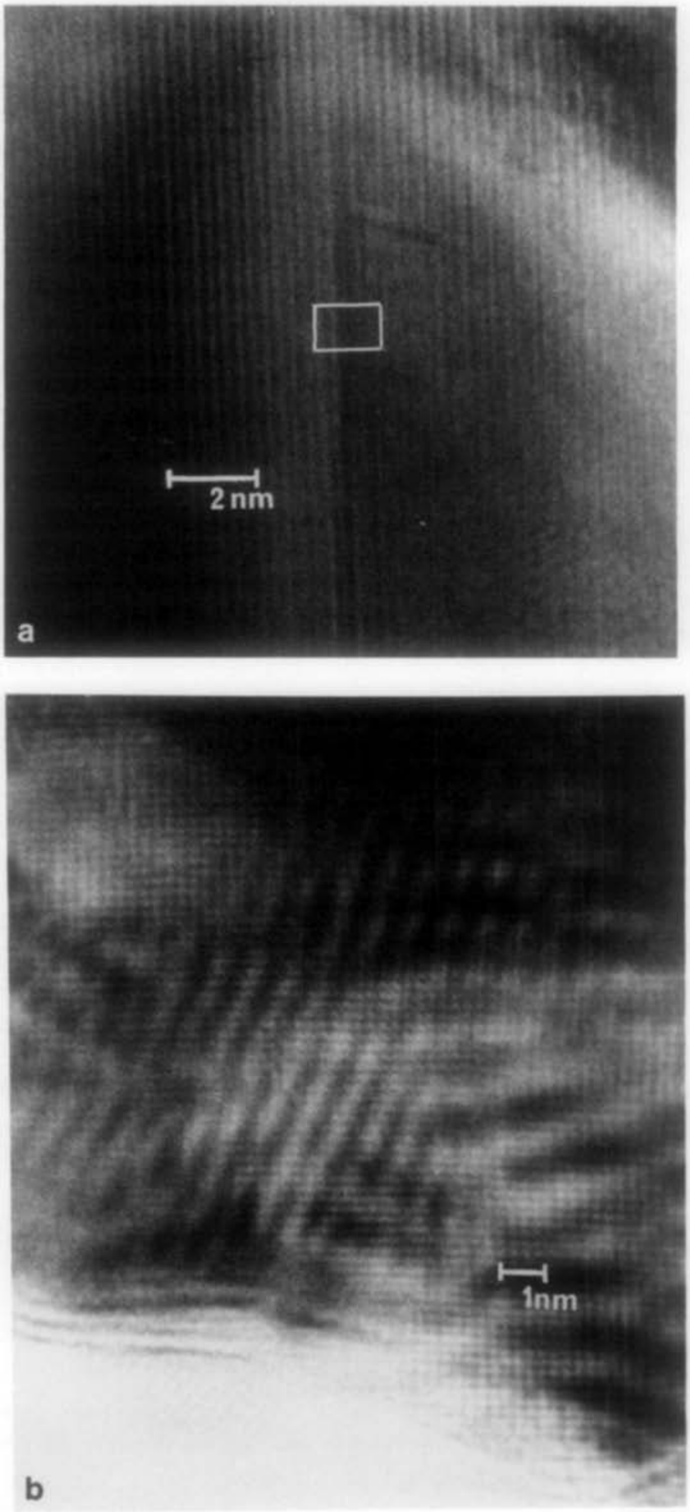

FIG. 1. HREM images taken using the top-entry JEOL 200CX electron microscope. (a) 1-D lattice image of the ⟨110⟩ planes in natural cuprite, with a single stacking sequence fault plane indicated center image by a drawn box. (b) [100] Zone axis image, with domained moire fringes.

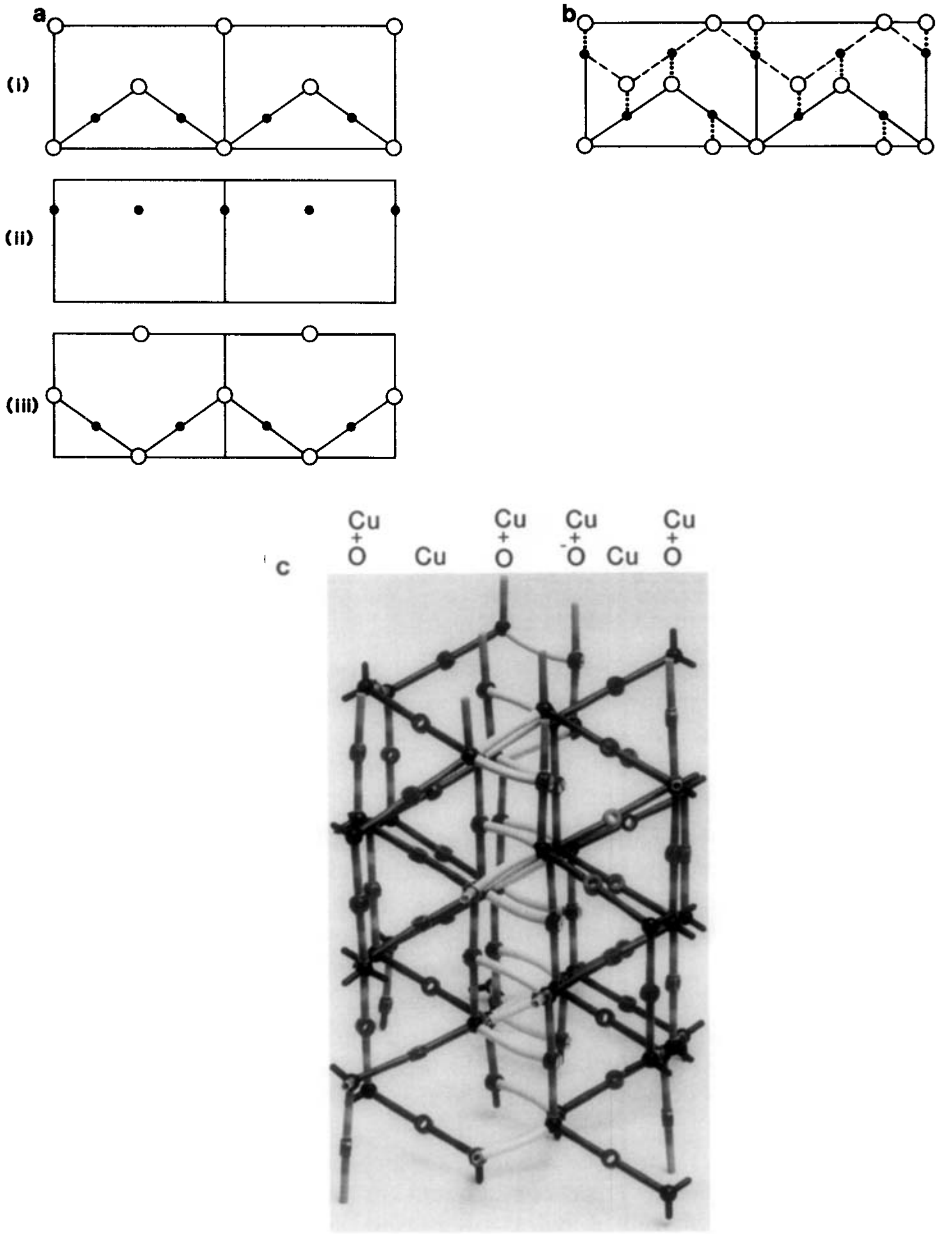

FIG. 2. Structural model of compositional fault phases in mineralogical cuprite. (a) Atomic arrangement in three successive (110)-indexed planes of perfect cuprite. (b) Atomic arrangement within the double Cu–O (110) fault plane after the elimination of the Cu plane (ii) of (a); the two Cu–O planes (i) and (iii) are distinguished by broken and full-line bonds, while the relation between these planes through Cu atoms with 3 coordination is shown by dotted lines. (c) Photograph of modelled structure for the cuprite compositional planar defect, which is central in the model, showing Cu–O bonds, linking the two interpenetrating lattices of cuprite, in white.

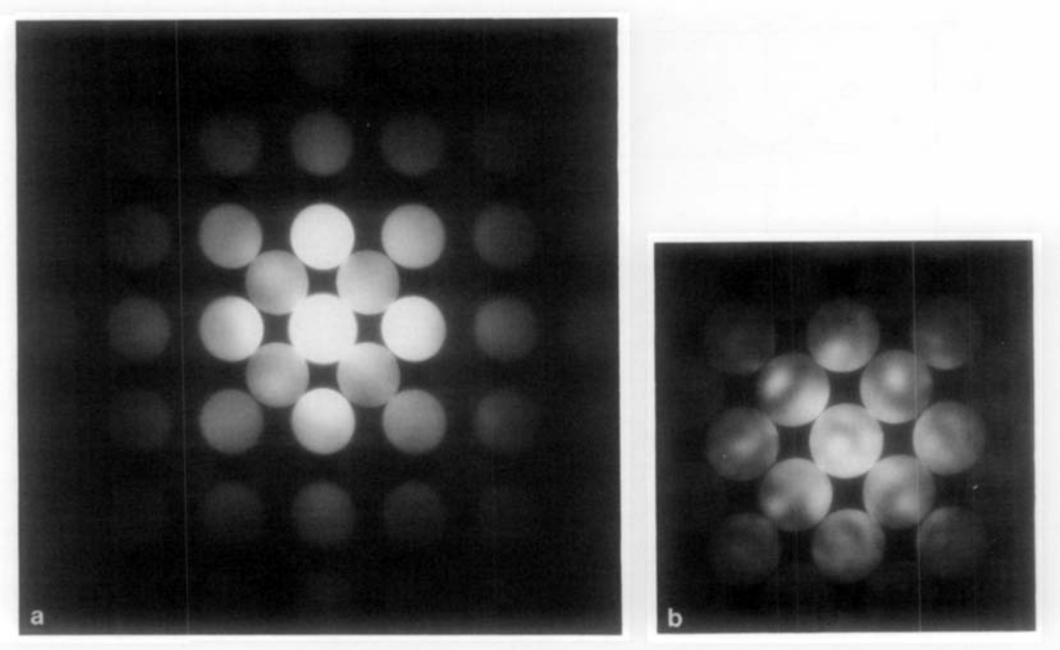

FIG. 3. CBED patterns from the [100] zone axis of synthetic $Cu_2O$ taken on the Phillips 403 electron microscope and with the Gatan stage, at 86 K. (a) Thin region CBED pattern. (b) Thicker region CBED pattern.

ture it rapidly decomposes to Cu metal plus CuO under irradiation, as previously reported (*5*), while excessive grinding induces planar defects, predominantly $\{110\}$ $\langle 1\bar{1}0\rangle$ (*6, 7*).

3. Electron diffraction patterns from the low-temperature $Cu_2O$ sample show no detectable thermal streaking indicating a reasonably isotropic thermal behavior for the Cu atoms.

From observations 1 and 2 we can conclude that the stability of the mineralogical sample is somehow related to the existence of extensive composition planes of 110 index. This could readily be understood since the deduced mechanism of these fault planes would result in a three-dimensional Cu–O bonding at irregular intervals throughout the bulk structure, connecting the two interpenetrating rafts characteristic of the perfect cuprite lattice. It is interesting to note further that the compositional faults which occur naturally (Fig. 2), and those most readily induced by room temperature deformation (*6*), involve the same displacement direction, $\langle 1\bar{1}0\rangle$, within the 110 plane. A further interest, which we intend to pursue, is the extent and manner in which these types of fault affect the carrier density of the *p*-type semiconductivity.

Observation 3 on the other hand was made on fault-free cuprite. It is therefore necessary to understand a degree of thermal isotropy coexisting with the low, $\bar{3}m$, Cu site symmetry. This behavior can in fact be fitted to theoretical predictions for $Cu_2O$ indicating strongly directed Cu–O bonds (*8*) by assuming deformable Cu–O–Cu bonds and easy relative displacement of the rafts. Much more quantitative data is therefore required in order to further refine the bonding structure of cuprite.

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