

## ELECTRICAL CONDUCTIVITY OF PURE AND IMPURE POLYCRYSTALLINE CUPROUS OXIDE

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The electrical conduction mechanism of polycrystalline cuprous oxide prepared from spectroscopically pure and electrolytic copper has been studied in the temperature range from 1080°C down to 80°C. The effect of the surrounding atmosphere and different impurities on the conduction mechanism has also been discussed.

### *Introduction*

Many metallic oxides show an appreciable measure of electronic or positive hole conduction even at relatively low temperatures and can therefore be classified among semi-conducting materials.

Verwey and coworkers found that the introduction of foreign ions in a compound semiconductor may have a pronounced effect on its conductivity.

Cuprous oxide is one of the prototype of oxides whose properties were investigated as being governed by their departure from the exact stoichiometry in the direction of excess oxygen. Its electrical properties depend markedly on the thermodynamic conditions of preparation and the purity of the initial material used. When cuprous oxide is heated *in vacuo* a reduction in its conductivity would be produced; it loses oxygen and approaches its stoichiometric composition  $\text{Cu}_2\text{O}$ . But if heated in oxygen its conductivity becomes greater. Small amounts of impurities when present affect the electrical conductivity of such semiconducting compound.

It was the aim of this work to investigate the electrical properties *i.e.* the conduction mechanism of polycrystalline cuprous oxide samples prepared from both spectroscopically pure and electrolytic (less purity) copper in the temperature range from 1080°C down to 80°C. The effect of the surrounding atmosphere and the role of the impurities on conduction mechanism has been studied and discussed.

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### Experimental procedures

The crystals used in the experiments with pure cuprous oxide were plates of spectroscopically pure copper 99.9999%, while those with impure cuprous oxide were of electrolytic copper 99.7%. Samples of dimensions  $9.6 \times 6.91 \times 1.33 \text{ mm}^3$  were first freed from oxide layers by emery paper; mechanically polished using carborundum polishing powder of different grades, then etched in 2 N nitric acid. They were degreased using acetone, washed with distilled water and finally dried. Conductivity leads were made by wrapping platinum wires around the ends of the copper plates prior to oxidation. The oxidation of the samples took place in a furnace at  $1030^\circ\text{C}$  either in an air atmosphere or in nitrogen atmosphere of about 2% oxygen content. The nitrogen was introduced to the furnace by flowing with a suitable rate. After complete oxidation the temperature was raised to  $1050^\circ\text{C}$  and the crystals were left for about one hour to attain equilibrium with the atmosphere. The conductivity was measured using the circuit shown in Fig. 1. A double reverse switch was employed

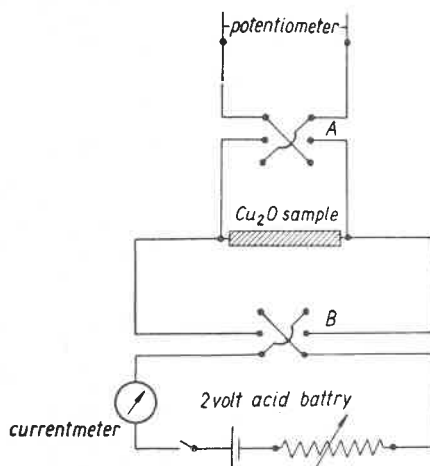


Fig. 1

to prevent the time lag between the successive readings of the potentiometer in the opposite directions of current passing in the sample. Conductivity was measured in heating and cooling cycles from  $80^\circ\text{C}$  up to  $1010^\circ\text{C}$  in a period of about 6–8 hours *i.e.* with  $2\text{--}3^\circ\text{C}/\text{min}$  rate.

### Results and discussion

Conductivity  $\sigma$  as a function of temperature was measured at two different oxygen pressures for spec. pure cuprous oxide (sample 1). The results are plotted in Fig. 2. Curve 1 is that for the sample treated in nitrogen atmosphere, while curve 2 represents the results for the sample treated in air atmosphere. The results were taken throughout two successive runs on heating and cooling. From curve 1 the conductivity was found to vary from  $10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$  at  $80^\circ\text{C}$  to about  $3 \text{ ohm}^{-1}\text{cm}^{-1}$  at  $1000^\circ\text{C}$ . The increase in conductivity is governed by the increase of holes which are thermally agitated, since the hole mobility was

found to vary from  $50 \text{ cm}^2 \cdot \text{v}^{-1} \cdot \text{s}^{-1}$  at room temperature, to about  $20 \text{ cm}^2 \cdot \text{v}^{-1} \cdot \text{s}^{-1}$ , at  $1000^\circ\text{C}$ . Such variation of hole mobility is to be expected since the hole motion can be looked upon as wave propagation in the lattice structure. So the hole waves suffer dispersion by thermal vibrations of the lattice ions during propagation and then the mean free path should decrease with rise of temperature.

The activation energies of charge carriers in the two conductivity regions above and below  $484^\circ\text{C}$  are calculated to be  $2.25 \text{ eV}$  and  $0.51 \text{ eV}$  at room temperature respectively.

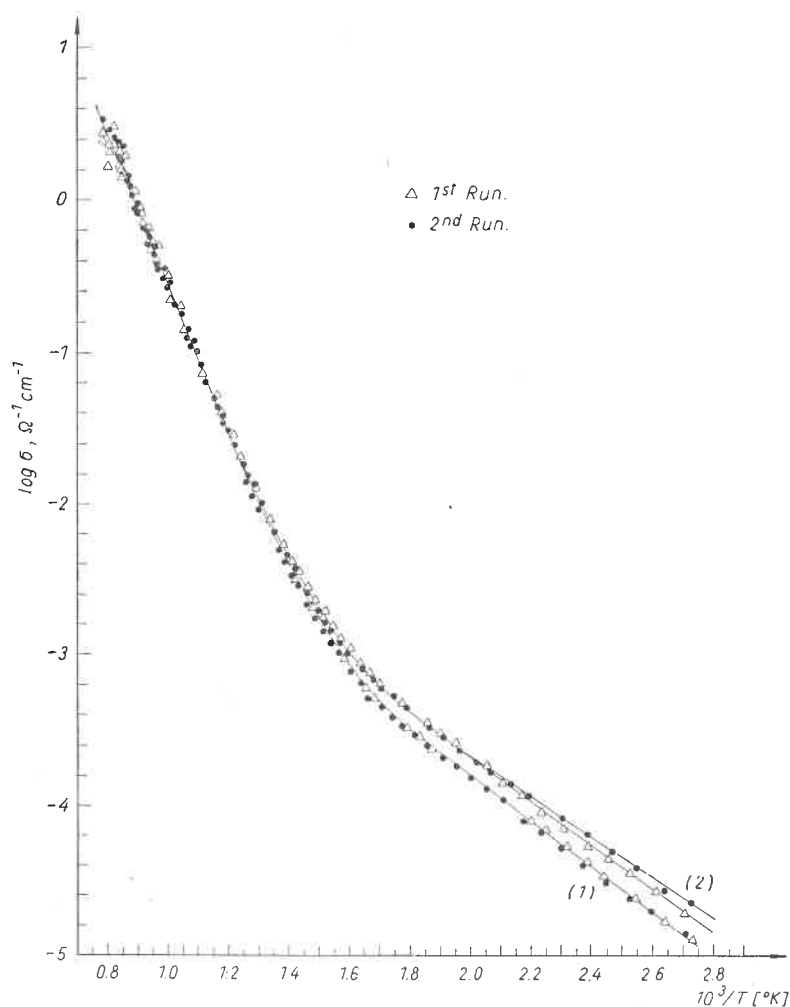
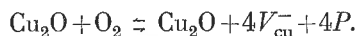


Fig. 2

The low activation energy was found to be constant indicating that there is one type of defect centers (copper vacancy centers formed during preparation) while the high temperature activation energy gives rise to the conduction due to nonstoichiometric composition of  $\text{Cu}_2\text{O}$  as the temperature increases.

Curve 2 represents the results of sample 1 treated in an air atmosphere with two cooling rates. From this curve the low temperature activation energy was found to be 0.52 eV and 0.56 eV for cooling rates of 3°C/min and 2°C/min respectively. The observed increase in conductivity which is accompanied by a decrease in activation energy as the surrounding atmosphere changed from nitrogen (with 2% oxygen content) to air is expected since the concentration of defect centers  $V_{\text{cu}}$  depends on the oxygen pressure during preparation at high temperature.

According to Wagner and using Brouwer approximate method, the excess oxygen adsorbed on the  $\text{Cu}_2\text{O}-\text{O}_2$  interface leads to the migration of  $\text{Cu}^+$  ions promoting the creation of vacant lattice sites according to the following electronic equilibrium



Taking into consideration that the concentration of  $V_{\text{cu}}^-$  equals that of the holes, we have  $P = [V_{\text{cu}}^-] = (K_{\text{ox}}p_{\text{O}_2})^{1/8}$  where  $K_{\text{ox}}$  is the equilibrium constant of the process,  $p_{\text{O}_2}$  is the applied oxygen pressure and  $P$  being the concentration of the holes.

Now the electric conductivity should be proportional to the 8<sup>th</sup> root of the oxygen pressure, since conductivity depends on the hole concentration.

The formation of such defect centers affect the exact stoichiometric composition of cuprous oxide ( $\Delta$ ), any deviation from this composition can be determined by the relation

$$\Delta = \Sigma[V_{\text{cu}}^-] - 2\Sigma[V_{\text{O}}]$$

since the exact stoichiometric composition requires the existence of two copper vacancies for every oxygen vacancy. At high oxygen pressures which is our case, at which the concentration of  $V_{\text{cu}}$  centres is large, the last relation reduces to  $\Delta = [V_{\text{cu}}^-]$ .

For instance the cooling rate would affect the nonstoichiometric factor  $\Delta$  and also the observed conductivity. As the cooling rate increases,  $\Delta$  also increases giving more conductivity and lower activation energy. This can be shown in the lower part of the log  $\sigma$  versus  $10^3/T$  relation Fig. 2.

On the other hand the high temperature activation energy is 2.29 eV, which is higher than that obtained in nitrogen atmosphere (2.25 eV) giving an evidence for the formation of the new solid phase CuO during the cooling, with that originally formed under preparation conditions at 1030°C.

The results obtained for log  $\sigma$  against  $10^3/T$  relation for pure cuprous oxide (sample 1) together with that for cuprous oxide prepared from electrolytic — impure — copper (sample 2), both treated in nitrogen (with 2% oxygen content) atmosphere and in air are shown in Fig. 3. Sample 2 has lower conductivity values in both the higher and lower temperature regions. The low temperature activation energy amounts 0.69 eV, whereas the high temperature activation energy is almost the same as that for sample 1. The initial electrolytic copper was analysed spectroscopically and found to have quantitatively the following metallic impurities.

Element	Si	Fe	Mg	Pb	Mn	Al	Ba	Zn	Ag	Ni
Quantity	F.T.	V.F.T.	T.	F.T.	V.F.T.	F.T.	V.F.T.	T.	T.	F.T.

T = trace (0.1–1%), F.T. = faint trace (0.01–0.1%) V. F. T. = very faint trace (0.001–0.01%).

Since small amounts of metallic impurities are put into oxygen excess cuprous oxide and may be considered as replacing  $\text{Cu}^+$  and  $\text{Cu}^{++}$  ions, leaving the total number of vacancies almost unchanged, our electrolytic copper may be looked upon as containing Mg, Ag and Zn impurities. Such impurities may certainly be incorporated into cuprous oxide as  $\text{Ag}^+$ ,  $\text{Mg}^{++}$

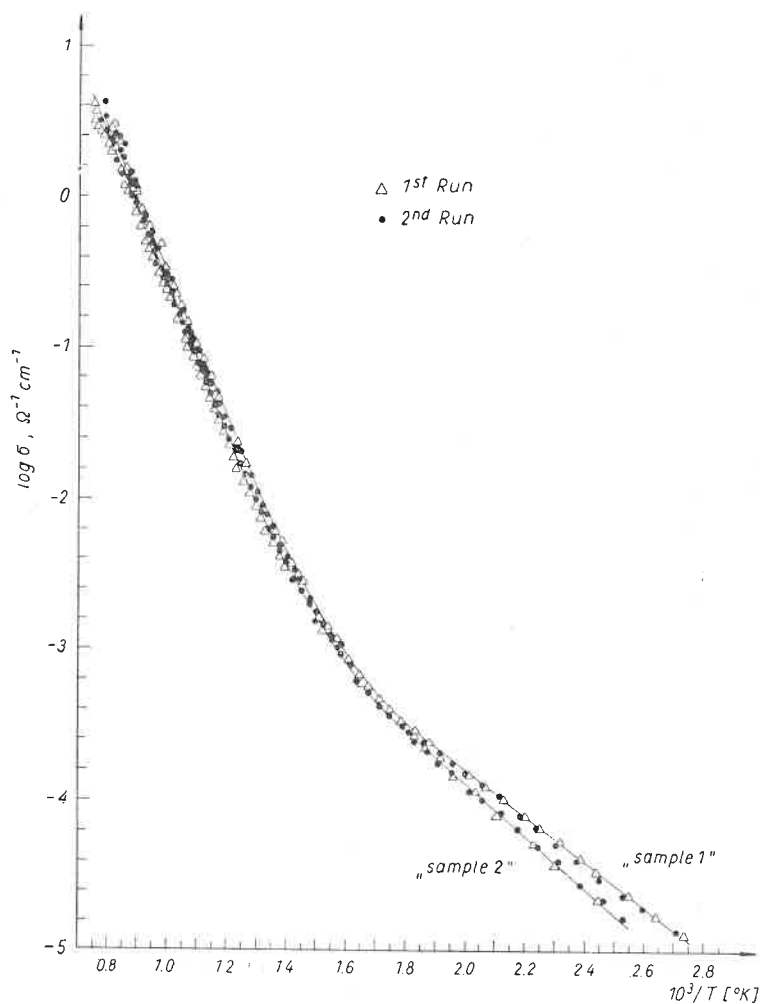


Fig. 3

and  $\text{Zn}^{++}$ . These ions will increase the number of cation vacancies and reduce the number of free positive holes since they go in substitutionally or interstitially. The expected effect is therefore that the conductivity should decrease and the activation energy increase. Our results confirm these obtained by O'Keefe *et al.* on polycrystalline cuprous oxide doped with beryllium. They pointed out that the identification of low temperature activation energy is rather more difficult, but gives support to the idea that as the number of holes decreases the activation energy for impurity conduction increases.

Fig. 4 represents the conductivity as a function of temperature for the impure cuprous oxide prepared from electrolytic copper treated in air and in nitrogen atmosphere. It could be noticed that as the oxygen pressure increases the conductivity increases also. This is naturally expected but with more probability since the impurity ions have higher vacancies.

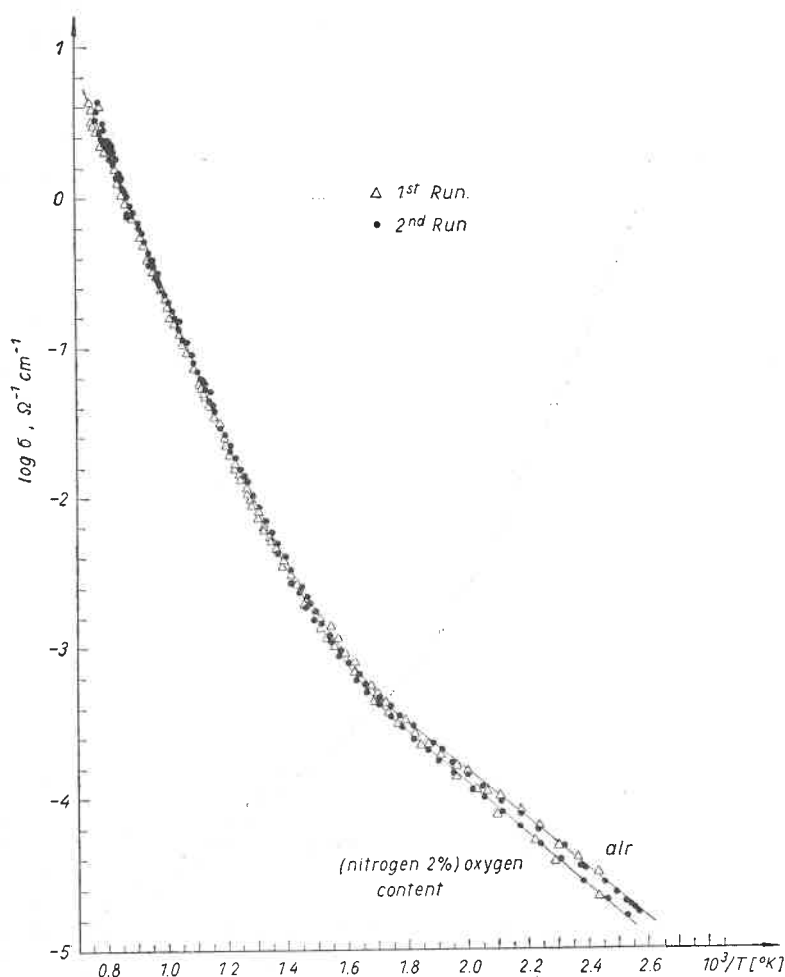


Fig. 4

### Conclusion

It can be concluded that the thermodynamic conditions — oxygen pressure and temperature — of preparation affect the defect nature of the nonstoichiometric *P*-type cuprous oxide. The presence of a certain concentration of foreign atoms reduces the conduction by the formation of new impurity centers. The impurity atoms are expected to replace the copper vacancies by occupying them, and may occupy also interstitial positions.

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