

The Defect Structure of Cuprous Oxide*

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Measurements have been made of the Hall effect in single crystals of cuprous oxide below 200°C. In this range the hole mobility is given by $\mu=3.1 \times 10^5 T^{-3/2}$. The number of frozen-in acceptors is much less than the number of cation vacancies. It is suggested that vacancies with their associated positive holes pair on cooling to form a complex electronically analogous to H₂. This model is in accord with magnetic measurements. At high temperatures the paired holes are dissociated; the high density of acceptors results in a merging of the acceptor levels with the valence band. In accord with this model it is shown that the number of free holes varies as the 1/4 power of oxygen pressure at high temperatures. Infrared absorption bands previously ascribed to defects are shown to arise from lattice vibrations. Diffusion measurements indicate that a very small fraction of the excess oxygen occurs as interstitial atoms.

It has long been established that the majority defect in cuprous oxide is a cation vacancy and associated positive hole, the electrical conductivity always being *p*-type¹⁾. The thermodynamic aspects of the formation and migration of this defect have recently been discussed in some detail²⁾. In this paper we present new results leading to a comprehensive theory of the defect structure, which resolves some apparent inconsistencies in the experimental data (cf. (1)).

A. Electrical Properties

The electrical properties of single crystals of cuprous oxide at high temperatures (room temperature to the melting point) have already been reported^{1),3)}. We have now made measurements of conductivity and Hall effect down to 77°K. All measurements to be described were made with single crystals.

Unless considerable care is taken to ensure a homogeneous sample, low temperature measurements will be dominated by surface effects. This is because at temperatures below about 200°C cuprous oxide will adsorb and incorporate considerable excess oxygen into the surface layers⁴⁾, which become highly conducting and effectively short out the bulk material. It was found that a sample prepared by cooling from 1050°C to 500°C in oxygen at

1 mm and subsequently cooling to room temperature in an oxygen pressure of less than 10⁻⁵ mm was essentially homogeneous. The conductivity is then approximately 10⁻⁶ ohm⁻¹ cm⁻¹ and the Hall mobility 60 cm² v⁻¹ sec⁻¹ at 20°C. Exposure to the atmosphere results in a slightly enhanced conductivity and a decrease in the Hall mobility to about 40 cm² v⁻¹ sec⁻¹.

Subsequent illumination with visible light in air greatly enhances these surface effects. Fig. 1 shows the results of illumination of one sample; the slow processes involved are believed to be adsorption and incorporation of oxygen into the surface layers. After this treatment, the apparent Hall mobility at room temperature is 22 cm² v⁻¹ sec⁻¹. These results emphasize the need for extreme caution in interpreting experiments on photoconductivity, luminescence, etc., on materials for which surface effects have not been eliminated.

The concentrations of positive holes for a number of samples have been calculated from the measured Hall coefficients. Some results are shown in Fig. 2. In this figure, curves A and B show surface effects at low temperatures. From the conductivity above 150°K the energy for dissociation of a hole from a vacancy is calculated to be 0.66 ev. The number of frozen-in vacancies is calculated to be 8 × 10¹³ cm⁻³ for a sample given the heat treatment described above.

The Hall mobility calculated for homogene-

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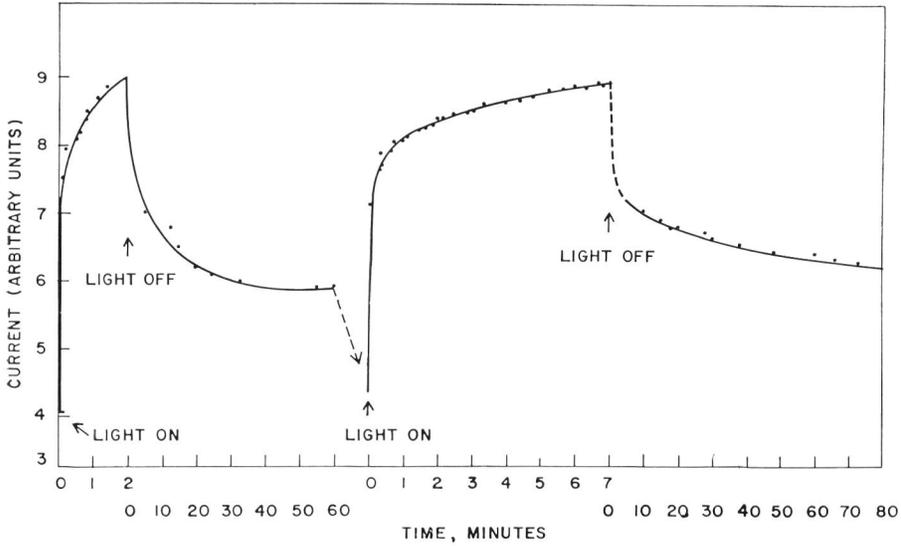


Fig. 1. Photoconductivity of cuprous oxide in air at room temperature.

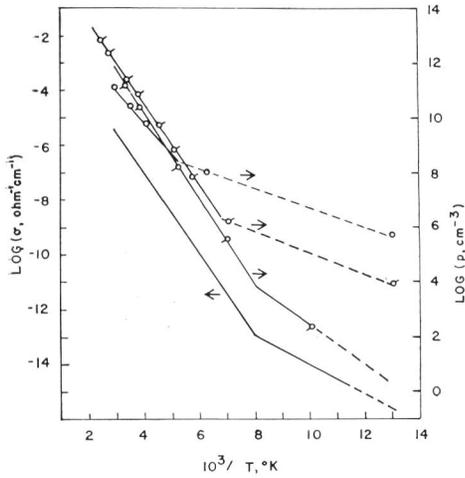


Fig. 2. Hole concentration and conductivity as a function of temperature for cuprous oxide single crystals.

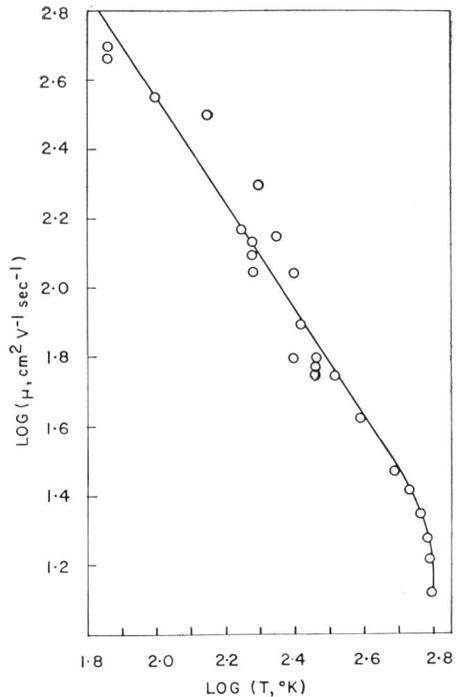


Fig. 3. The Hall mobility as a function of temperature for cuprous oxide single crystals.

ous samples is shown in Fig. 3. Below $250^\circ K$ the results are well represented by $\mu=3.1 \times 10^5 T^{-3/2} \text{cm}^2 \text{v}^{-1} \text{sec}^{-1}$, the temperature dependence being that expected for acoustical mode scattering.

It is of considerable interest that for a sample quenched from $1050^\circ C$ in air the number of acceptors (vacancies) frozen in is only 10^{15}cm^{-3} instead of about 10^{20} expected²⁾. We interpret this decrease as due to aggregation of vacancies to form electrically neutral complexes even in rapid quenching. O'Keeffe

and Stone⁴⁾ came to the same conclusion on the basis of magnetic measurements. The rapid decline in mobility above $250^\circ C$ is believed to be related to this effect, "impurity" scattering becoming the factor that limits mobility.

These results and our failure to measure a Hall voltage at high temperatures have led us to the conclusion that the mobility in the high temperature range is rather small, suggesting that the number of free holes is approximately the same as the number of vacancies. Thus at 1000°C we have $\sigma = 6 \text{ ohm}^{-1} \text{ cm}^{-1}$ and the number of vacancies, $N_v = 5.5 \times 10^{19} \text{ cm}^{-3}$. If the number of holes, $p = N_v$, we have $\mu = 0.7 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ (cf. $\mu = 7 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ obtained by extrapolation of the low temperature results.) If the number of free holes is equal to the number of vacancies, the same dependence on oxygen pressure might be expected for conductivity and for vacancy concentration. On the contrary, however, $\sigma \propto P_{O_2}^{1/7}$ and $N_v \propto P_{O_2}^{1/3}$. We can resolve this difficulty as follows.

The conductivity is given by $\sigma = p|e|\mu$. If "impurity" controlled, the mobility will depend on the number of vacancies and hence on oxygen pressure. We have, therefore, $\sigma = \text{const } P_{O_2}^x \mu(P_{O_2})$ where $P_{O_2}^x$ represents the true pressure dependence of hole concentration. To calculate x from the experimental data we

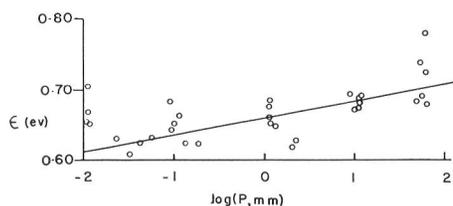


Fig. 4. The activation energy for conductivity of cuprous oxide for oxygen pressures from 10^{-2} to 100 mm. Data from Toth, Kilkson and Trivich³⁾.

use the observations: (a) $\log \sigma$ vs. $1/T$ plots are accurately linear, (b) the apparent activation energies, ϵ , derived therefrom depend on pressure. Fig. 4 shows the results obtained by Trivich *et al.*³⁾ In this figure the straight line is a least-squares fit of the data and is given by $\epsilon = (0.66 + 0.0105 \ln P)$ ev. Thus $\sigma = \text{const} \cdot P_{O_2}^x \cdot \exp \{(-0.66 - 0.0105 \ln P)/kT\}$.

The pressure dependence of conductivity is given by

$$m = \frac{\partial \ln \sigma}{\partial \ln P_{O_2}} = x - \frac{0.0105}{kT}$$

In Table I, x has been calculated for various temperatures by means of the values of m

reported in reference (1). The mean value of x is 0.25 ± 0.005 . This is close to the result obtained by O'Keeffe and Moore²⁾; $N_v \propto P_{O_2}^n$, $n = 0.27 \pm 0.015$. Thus, within experimental error, we have the same pressure dependence for the concentrations of holes and vacancies.

Table I. Pressure dependence of conductivity and hole concentration

$T^\circ\text{C}$	m	x
794	0.129	0.243
844	0.139	0.248
880	0.148	0.253
940	0.141	0.241
957	0.158	0.257
1050	0.152	0.244
1100	0.154	0.253
1135	0.164	0.251

The explanation of this result is that at high vacancy concentrations and high temperatures, the "impurity" levels merge into the valence band⁵⁾, and the vacancies are fully ionized. It should be noted that this interpretation of the high temperature conductivity is different from, and supersedes that given in reference (1).

B. Diffusion Measurements

The diffusion of copper by means of cation vacancies has already been discussed²⁾. In this paper we present new results on the diffusion of oxygen in cuprous oxide. Experimental details and the temperature dependence of the diffusion coefficient have already been given⁶⁾. Fig. 5 shows the pressure dependence of the diffusion coefficient at 1050°C. From the slope of the $\log D$ vs. $\log P$ plot, we find $D \propto P^n$ with $n = 0.5 \pm 0.09$. The combined pressure and temperature dependence is given by $D = (6.50 \pm 3.6) P_{O_2}^{1/2} \exp \{(-39.3 \pm 6.5 \text{ kcal})/RT\}$ where P_{O_2} is in atmospheres.

Assuming that $D = D_i X_i$, where D_i is the intrinsic diffusion coefficient of a defect of mole fraction X_i , we have

$$D = \frac{kT a^2}{h} \exp \{(\Delta S_f + \Delta S^\ddagger)/R\} \\ \times \exp \{(-\Delta H_f - \Delta H^\ddagger)/RT\}$$

where a is a jump distance and the subscript

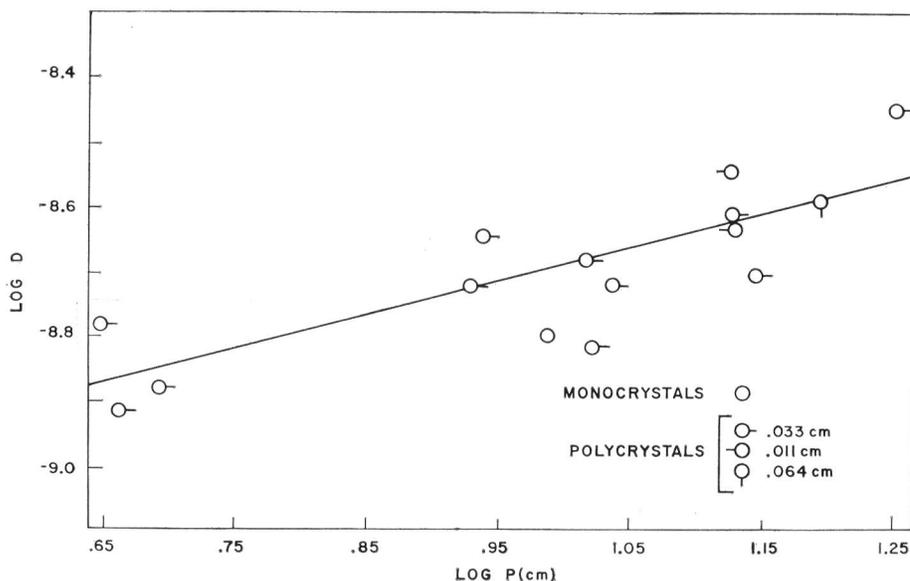


Fig. 5. The variation with oxygen pressure of the diffusion coefficient for ^{18}O in cuprous oxide.

f refers to the formation of the defect.

The pressure dependence of D leads us to the conclusion that the most probable defect is an oxygen interstitial atom produced by $\text{O}_2 \rightarrow 2\text{O}_i$. Thus we take for a the distance between two tetrahedral interstitial sites in the f. c. c. Cu^+ lattice and obtain for 1000°C ,

$$\Delta S_f + \Delta S^\ddagger = 0.3 \pm 1 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f + \Delta H^\ddagger = 36.6 \pm 6.5 \text{ kcal mole}^{-1}.$$

If it is assumed that the interstitial atom has the same vibration frequency as the lattice we can calculate the value of ΔS_f as $-15.1 \text{ cal deg}^{-1} \text{ mole}^{-1}$ so that $\Delta S^\ddagger = 14.8 \text{ cal deg}^{-1} \text{ mole}^{-1}$. It does not appear possible to make a realistic calculation of ΔH_f or ΔH^\ddagger at present, however, if we assume (as is likely) that $\Delta H^\ddagger > 10 \text{ kcal mole}^{-1}$, we find $N_i > 6.5 \times 10^{14} \text{ cm}^{-3}$. This result implies that there is a significant concentration of oxygen interstitials in cuprous oxide at elevated temperatures. It is tempting to identify this defect with the acceptor center having an ionization energy of 0.2 eV, which is apparent in the low temperature electrical conductivity (see Fig. 2).

C. Optical Properties

Apart from the strong absorption in the region of the Reststrahlen frequency, cuprous oxide has a number of absorption bands in the infrared, the most prominent being at

1122 and 794 cm^{-1} . Several authors have ascribed one or the other of these bands to free holes or lattice defects. We have prepared Cu_2^{18}O by oxidation of thin copper foils in $97\%^{18}\text{O}_2$. We find that these bands are isotopically shifted to 1079 and 766 cm^{-1} ; the shift is very close to that expected for optical lattice vibrations. The tentative assignment is $1122 \text{ cm}^{-1} = 2\nu_t$, $749 \text{ cm}^{-1} = \nu_l$, where ν_t and ν_l are the frequencies of the transverse and longitudinal optical modes.

In pure crystals we have observed no absorption directly due to vacancies, although there is a small shift of the absorption edge to lower frequencies with increasing oxygen content. In a crystal previously irradiated with $3 \times 10^{18} \text{ neutrons cm}^{-2}$, there is a continuous absorption from 5000 cm^{-1} up to the absorption edge.

D. Magnetic Properties

We have observed no EPR in pure crystals, even those quenched from 1050°C in air. This result supports the thesis that vacancies aggregate on cooling with consequent spin-pairing. In a neutron bombarded ($3 \times 10^{18} \text{ n cm}^{-2}$) sample, a broad (200 gauss) EPR line at $g=2.15$ was observed. This signal is believed to be due to a hole trapped on the Cu^+ nearest neighbors of a cation vacancy (*i. e.* Cu^{2+}). If the hole is shared equally among the 12 nearest neigh-

bor Cu^+ ions, there should be 37 hyperfine lines. These would probably require very low temperatures for resolution. It is of interest in this connection that the 'Bohr radius' of the vacancy-hole complex is 9.2 \AA (see below), which would imply interactions out to considerably further than nearest neighbor distances.

E. Conclusions

The major conclusions reached in this paper are as follows: At high temperatures ($>750^\circ\text{C}$) in equilibrium with oxygen, cuprous oxide contains a high concentration of cation vacancies which are completely ionized; *i.e.*, for each vacancy there is a free positive hole in a band which has merged with the conduction band. Conversely, at low temperatures ($<200^\circ\text{C}$), the majority of the frozen-in defects are associated, and there is only a small concentration of single vacancies which behave as acceptor centers about 0.65 eV above the valence band. We have shown that this theory adequately accounts for the magnetic properties of cuprous oxide and for the dependence of conductivity on oxygen pressure. It is clear that the apparent activation energy of conductivity is not amenable to a simple interpretation, because the mobility is not constant. However, the heat of formation of a cation vacancy will be the main factor contributing to this activation energy in the range where cuprous oxide is thermodynamically stable (cf. (1)).

To account for the behavior of holes at low temperatures, it is helpful to treat the vacancy center as a shallow acceptor state and to use the effective mass approximation⁷. The ionization energy of the center is then

given by $\epsilon = 13.6 \kappa m^*/m \text{ eV}$ where κ is the static dielectric constant. Taking $\kappa = 13$ (O'Keeffe: unpublished) and $m^* = 0.75 m^{\text{B}}$ we have $\epsilon = 0.63 \text{ eV}$ in good agreement with the $\epsilon = 0.66 \text{ eV}$ from the conductivity data. The 'Bohr radius' is given by $r = r_0 \kappa m/m^*$ where r_0 is the Bohr radius for the H atom, whence $r = 9.2 \text{ \AA}$. A logical extension of this model is to the case of two adjacent vacancy+hole "atoms" with a separation of the same order or magnitude as the Bohr radius. By analogy with the H_2 molecule, the ground electronic state for this system will be a singlet state in which the "hole spins" are paired. The result is a deeper lying acceptor level that is nonmagnetic.

Clearly, if this proposal of a vacancy-pair "molecule" should prove correct it will have many interesting applications. For example, we may speculate that the as yet unidentified levels observed in the luminescence of cuprous oxide arise from such a complex.

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DISCUSSION

Igaki, K.: 1) Have you any idea about the equal-composition curve or your P - T - x diagram? Have you already got the temperature dependence of equilibrium constant? 2) Have you some experimental evidence for your assumption that the specimen equilibrated at low temperature to very low oxygen pressure is stoichiometric? 3) Will you give me the order of magnitude of the lowest specific conductivity of your specimen at room temperature?

O'Keeffe, M.: 1) We do not know the exact conditions necessary to obtain stoichiometric Cu_2O . We only know the temperature dependence of vacancy concentration. 2) We do not assume that a specimen prepared under a low oxygen pressure is

stoichiometric, however cooling in vacuo is necessary for homogeneity. 3) 10^{-7} to 10^{-6} ohm $^{-1}$ cm $^{-1}$.

Borg, R.: Can you tell us the pressure dependence which you found for the diffusion of oxygen? How does it compare with what might be expected from theoretical considerations?

O'Keefe, M.: The diffusion coefficient depends on the 1/2 power of oxygen pressure. This is consistent with diffusion by uncharged oxygen atoms. This is stated in the manuscript submitted for the Proceedings.

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Equilibria among Defects in Group III-V Crystals Containing Group IV Substituents*

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When a Group IV element dissolves substitutionally in a Group III-V semiconductor, it may enter either of two sites, or both. The sublattice distribution ratio for Sn in Ga sites to Sn in Sb sites in the crystal GaSb under certain equilibrium conditions has been calculated. Covalent bond energies, monatomic vapor pressures of the elements of the host crystal, and strain energies make the chief contribution to establishing this ratio. A less precise calculation is given for all III-V compounds and Group IV elements of practical interest.

In conjunction with the intrinsic, donor, and acceptor ionization constants, and an ion-pair dissociation constant, the sublattice distribution constant may be used to predict the approximate electrical properties of GaSb brought to equilibrium with a liquid external phase containing Sn, Ga, and Sb.

Relations governing the concentrations of defects, foreign atoms, and charge carriers in a solid may be derived from the Law of Mass Action, provided the charge carrier concentrations are such that classical statistics are obeyed, and provided that the solid is in equilibrium with its environment. Kröger and Vink¹⁾ have described in detail the applications of the Law of Mass Action to many situations of interest, and have generalized the treatment to cover all common types of defect and foreign-atom interaction. It is clear from the method of Kröger and Vink that equilibrium with the phase external

to the solid must be established in order that concentrations may be subsequently calculated from equilibrium constants.

There are few crystals for which sufficient data exist so that equilibrium calculations may be tested over a wide range of compositions or pressures of the external phase. CdS and Cu₂O have been discussed in some detail^{2), 3)}, and Reiss, Fuller, and Morin⁴⁾ have studied the interactions between ionized donors and acceptors in elemental semiconductors.

This report is an account of the application of thermodynamic and structural calculations in deducing probable values for the equilibrium constants governing the electrical properties of the Group III-V compounds containing foreign atoms of Group IV.

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