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Carrier Characteristics in Copper-Doped WO_3 from Conductivity, Hall Voltage, and Thermal E.m.f. Studies[1]

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Single crystals of $Cu_{0.076}WO_3$, $Cu_{0.094}WO_3$, and $Co_{0.95}WO_{3+\delta}$ have been prepared by thermal decomposition of $CuWO_4$ and WO_3. Potential-probe resistivity measurements in the range 120 to 770°K. indicate complex semiconducting behavior. $Cu_{0.094}WO_3$, which is orthorhombic, shows three linear segments in the log ρ *vs.* $1/T$ dependence, the apparent activation energies being 0.05 e.v. below 170°K., 0.4 e.v. between 170 and 220°K., and 0.45 e.v. above 500°K. Between 220 and 500°K., behavior is "metallic." $Cu_{0.95}WO_{3+\delta}$, which is triclinic, shows no metallic region but has two linear segments with activation energy 0.10 e.v. below 700°K. and 0.15 e.v. above. Measurements of the Hall voltage and of the thermoelectric power indicate that carriers are electrons. At 300°K., representative carrier densities are 5×10^{18}, 15×10^{18}, and 1×10^{18} electrons/cc. with mobilities 6, 10, and 0.4 cm.^{2}/v. sec. for $Cu_{0.076}WO_3$, $Cu_{0.094}WO_3$, and $Cu_{0.95}WO_{3+\delta}$, respectively. Thermal e.m.f. values fall in the range -220 to -300 μv./deg. Results are interpreted in terms of a conduction band model with destruction of the band below room temperature due to a probable ferroelectric transition in the host lattice. Excess oxygen acceptor centers of appreciable ionization energy apparently are present in small concentration in the low-copper materials and in large concentration in the high-copper material.

In contrast to the alkali metal tungsten bronzes,[2] M_xWO_3 $(0 < x < 1)$, which are typically metallic[3] under normal conditions, the copper analog has been reported[4] to behave as a semiconductor. In the temperature range $-160°$ to $+80°$ the specific resistivity ρ as measured on single crystals of $Cu_{0.77}WO_3$ was observed to follow an exponential dependence on inverse temperature with an activation energy of 0.15 e.v. The implication was that, unlike the alkali tungsten bronzes[5] in which the alkali metal M is completely ionized to M^+ and e^-, the charge carriers in copper-doped WO_3 seem to be bound to localized trapping centers. Attempts by Hall voltage measurements to determine the fraction of carriers excited to the conduction band were unsuccessful; because of lack of sensitivity it was feasible only to set a lower limit at 5×10^{17} charge carriers/cc. with no conclusion possible as to the sign of the carrier.[4] In this investigation, we have undertaken solid state studies of Cu_xWO_3, including Hall voltage determination and thermoelectric power studies, in order to identify the nature of the carriers, their concentration, and their mobility.

Experimental

Preparation.—Single crystals of Cu_xWO_3 and of $Cu_xWO_{3+\delta}$ were prepared both by electrolytic and thermal decomposition of $CuWO_4$–WO_3 mixtures. As was found[6] in the preparation of Ag_xWO_3, the electrolytic method was the less satisfactory in producing crystals of sufficient size for convenient mounting of electrical probes. (It is probable that electrolysis of molten $CuWO_4$–WO_3 mixtures does not produce the ultimate product by direct electrode reaction, since variation of electrolysis conditions brought about no noticeable effect on the quality or amount of product and the current–voltage "polarization curves" on extrapolation to zero current gave a "decomposition potential" of zero.) In the thermal method, which was the one most successfully used in this research, temperature control was the most critical factor, the best crystals being obtained by 24-hr. heats of the reaction mixture at 950–1000° under argon flow followed by programed cooling at 0.5° per min. to 400°.

Differences in copper content were produced by firing $CuWO_4$ and WO_3, prepared as previously described,[4] in molar ratios of 1:0, 3:1, or 2:1. The stoichiometry of the reaction is uncertain but there was observed on firing weight loss attributable to oxygen evolution and formation of CuO and Cu_2O in varying amounts besides the desired product Cu_xWO_3. A possible equation is

$$CuWO_4 \longrightarrow Cu_xWO_3 + yCuO + \frac{1-x-y}{2}Cu_2O + \frac{1-y+x}{4}O_2$$

(Differential thermal analysis using Al_2O_3 as standard showed a rather broad endothermic peak between 950 and 980°, which was irreversible and disappeared on equilibra-

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[1] This research was sponsored by the U. S. Office of Scientific Research under Contract No. AF 49 (638)-191 and was supported in part by Advanced Research Projects Agency.

[2] See for example the review by R. P. Ozerov, *Uspekhi Khimii*, **24**, 951 (1955).

[3] E. J. Huibregtse, D. B. Barker, and G. C. Danielson, *Phys. Rev.*, **84**, 142 (1951); B. W. Brown and E. Banks, *ibid.*, **84**, 609 (1951); L. D. Ellerbeck, H. R. Shanks, P. H. Sidles, and G. C. Danielson, *J. Chem. Phys.*, **35**, 298 (1961).

[4] L. E. Conroy and M. J. Sienko, *J. Am. Chem. Soc.*, **79**, 4048 (1957).

[5] M. J. Sienko, *ibid.*, **81**, 5556 (1959).

[6] M. J. Sienko and B. R. Mazumder, *ibid.*, **82**, 3508 (1960).

tion or on repeated thermal cycling.) When possible, well formed single crystals of Cu_xWO_3 were picked out of the product mass before leaching. Otherwise, unreacted material and undesired products were separated by the following sequence of operations: 5% NaOH at 70° overnight, concentrated HCl and H_2O washes, 5% NaOH at 70° for 1 to 2 hr., concentrated HCl and H_2O washes, 48% HF for two days, 12 *M* HCl, 5% NaOH washes. The residual product generally consisted of a mixture of black, shiny, somewhat brittle orthorhombic and triclinic crystals, which had to be separated manually. The triclinic crystals, which were more numerous the higher the $CuWO_4$-to-WO_3 ratio, proved on analysis to be high in copper; the orthorhombic, low.

Chemical Analysis.—Products were brought into solution by fusion with a 3:1 (by weight) mixture of $NaNO_3$ and Na_2CO_3, followed by treatment with H_2O. After addition of NH_3 and NH_4Cl, copper was determined by electrodeposition on platinum.[7] Tungsten was determined by adding HNO_3 and cinchonine hydrochloride to the remaining solution.[8] The precipitated H_2WO_4 was ignited at 800° and weighed as WO_3.

For the orthorhombic crystals, a range of copper contents was possible; those crystals selected for study corresponded to 0.076 or 0.094 copper atom per tungsten. For the triclinic crystals, only the copper content 0.95 per tungsten was observed. The precision in the copper determination is believed to be 1% of the copper content; in tungsten, about 5%. These numbers also are believed to reflect the relative accuracies of the two determinations, the tungsten analysis being notoriously difficult to reproduce. Oxygen content, calculated by difference, amounted to 3.0 ± 0.1 oxygen atoms per tungsten for the low-copper materials (orthorhombic) and 3.6 ± 0.4 oxygen atoms per tungsten for the high-copper materials (triclinic). The lower limit of the oxygen range is the more probable, since the errors in the tungsten analysis most likely would be to make the W analysis too low and, therefore, the oxygen results too high. It is believed that the low-copper materials contain very close to three oxygen atoms per tungsten, as is true for the alkali tungsten bronzes, but that the high-copper material contains considerable oxygen excess over that required for simple Cu_xWO_3 stoichiometry. In the remainder of this paper we refer to the latter as $Cu_xWO_{3+\delta}$; the former, Cu_xWO_3. Direct analysis for oxygen was attempted several times using sulfur vapor as reducing agent[9] to form SO_2, but even the blank results were difficult to reproduce.

X-Ray Studies.—Powder photographs taken with copper $K\alpha$ radiation and a 114-mm. camera showed lines corresponding to interplanar spacings as calculated from the lattice parameters previously reported by Conroy and Sienko.[4] For randomly selected powder samples both sets of lines appeared, corresponding within a few hundredths Å. to the orthorhombic $Cu_{0.26}WO_3$ spacings and the triclinic $Cu_{0.77}WO_3$ spacings. The single crystals used for the electrical measurements, however, gave on grinding only one set of powder lines corresponding either to the triclinic set for $Cu_{0.95}WO_{3+\delta}$ or to the orthorhombic set for $Cu_{0.076}WO_3$ and $Cu_{0.094}WO_3$; 15° oscillation and zero layer Weissenberg photographs confirmed these results.

Electrical Resistivity Measurements.—Single crystals, selected for regularity of external geometry, were clamped between spring-loaded copper rods or Chromel-A strips and the resistivity measured by the potential probe method.[10] Nine crystals of composition $Cu_{0.076}WO_3$, three of $Cu_{0.094}WO_3$, and eleven of $Cu_{0.95}WO_{3+\delta}$ were investigated, each at several temperatures and some over the entire range. Results were independent of whether the potential-sensing probes were spring-loaded against the side of the crystal or sputtered on by condenser discharge. Because of the large investment in time required for mounting the crystals, circuits and crystal holders were designed to measure resistivity and thermoelectric power or resistivity and Hall voltages simultaneously. Figure 1 shows on the left the complete assembly used for measuring resistivity or thermoelectric power; on the right, there is a magnified view of the relative placing of the crystal, the heater coil, and the two copper–constantan thermocouples. With no heating current through the nichrome coil but with a standard-resistance-monitored conductivity current *I* through one copper rod into the crystal to the other copper rod, the resistance *R* of the crystal could be measured from the *IR* drop as determined potentiometrically between the copper lead of the upper thermocouple and the copper lead of the lower thermocouple. For thermoelectric measurements, current could be passed through

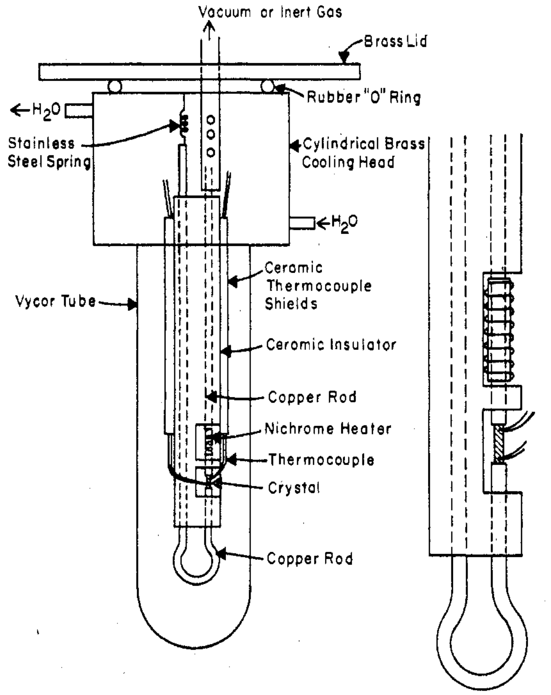

Fig. 1.—Crystal holder for resistivity and thermoelectric power.

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(7) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1942, 9th ed., p. 68.

(8) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Analysis," The Macmillan Co., New York, N. Y., 1953, 3rd ed., p. 695; A. Claeys, *Anal. Chim. Acta*, **17**, 360 (1957).

(9) F. T. Eggertsen and R. M. Roberts, *Anal. Chem.*, **22**, 924, (1950).

(10) See, for example, A. F. Ioffe, "Physics of Semiconductors," Academic Press, Inc., New York, N. Y., 1960, p. 329.

the nichrome coil to heat the copper rod pressing against one end of the crystal, the copper rod pressing against the other end of the crystal serving as a heat sink.

Figure 2 shows the crystal holder primarily designed for the Hall measurements but used to get data on resistivity as well. The crystal is shown with its end pressed against the flat face of a copper rod by the large-loop Chromel-A strip, which provided spring-loading and served to conduct the conductivity current I into the crystal. The IR drop was measured potentiometrically between the two small-loop Chromel-A strips pressed against the long narrow side of the crystal.

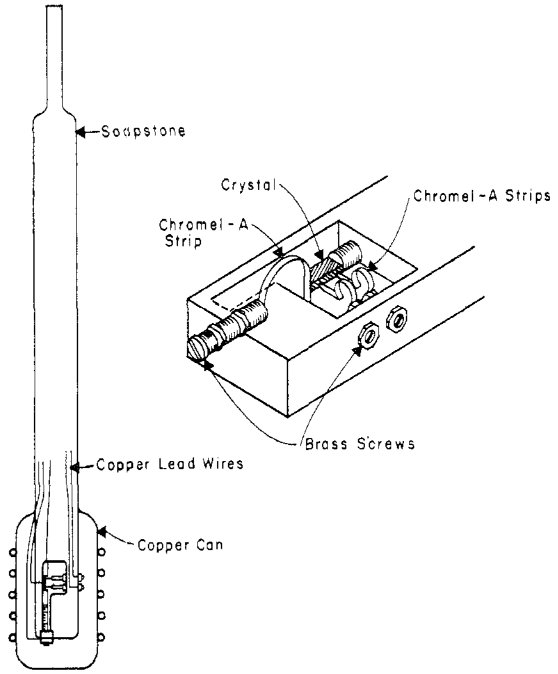

Fig. 2.—Crystal holder for resistivity and Hall effect.

For converting measured resistances to specific resistivities, the crystal cross-section and the potential probe separation were measured with a low power microscope fitted with a calibrated eyepiece. Figure 3 gives sample curves of crystal resistivity as a function of temperature for specific crystals that were followed over the entire temperature range. For a given crystal in a given mounting results on heating and cooling generally were reproducible to 1%; for different crystals of the same composition or for the same crystal in different holders, within 20%. (Occasionally, after repeated heating and cooling cycles, contact resistances increased to the point where galvanometer sensitivity was poor, in which case a discharge pulse from a condenser had to be passed through the contact in order to restore reproducibility. With some crystals, resistivity curves were observed to shift to larger resistivity on repeated thermal cycling; however, in all cases the curve shape was preserved.)

Hall Voltage.—For measurement of the Hall voltage the crystal holder shown in Fig. 2 was inserted in the gap of a 4-in. electromagnet, so arranged that the magnetic field was perpendicular to the current passed through the crystal and the Hall voltage generated. Magnetic fields of 6700 and 7200 gauss were used, with homogeneity over the sample volume better than 0.1 gauss as monitored by proton n.m.r. For temperatures below 25°, dry nitrogen was passed through a copper coil immersed in a liquid nitrogen bath, through a straight-bore condenser with its outer jacket evacuated to give the necessary insulation, and into a small dewar which enclosed the crystal holder. Temperature was varied by adjusting the nitrogen flow rate and was constant to 5° over the 30–45 min. required to make resistance and Hall voltage measurements. Above room temperature, a copper can wound with nichrome wire and fixed to the soapstone holder by a bayonet lock served as the heater.

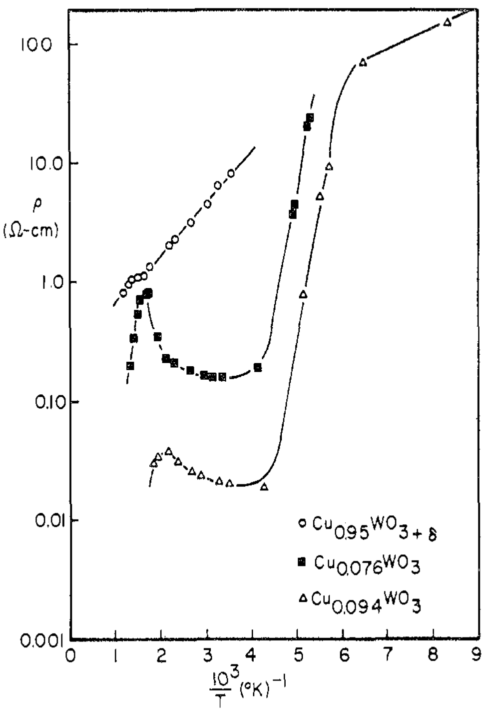

Fig. 3.—Log resistivity *vs.* $1/T$.

Because of the great difficulties encountered in locating the Hall probes on an equipotential plane before any magnetic field is imposed on the crystal, a "virtual" equipotential plane is established by placing two Hall probes on one side of the crystal and tuning a misalignment potentiometer between them so that its center tap is at the same potential as the Hall probe located on the opposite side of the crystal. The mismatch created when the magnetic field was energized was measured with a Leeds and Northrup Type K-3 potentiometer (0.1-μv. sensitivity) using a galvanometer of sensitivity 8×10^{-5} μamp./mm. Both the crystal current and the magnetic field were periodically reversed for all settings. The temperature range was severely limited on the high and the low ends by a sharp drop in signal-to-noise ratio, even when thin disks of indium or gold were inserted between the current leads and the crystal to improve contact.

Hall coefficients were calculated from

$$R_H = \frac{V_H t \, 10^8}{fIH}$$

where R_H is the Hall constant in cm.^{3}/coulomb, V_H is the observed Hall voltage in volts, t is the crystal thickness in cm. perpendicular to I and H, I is the current in amperes,

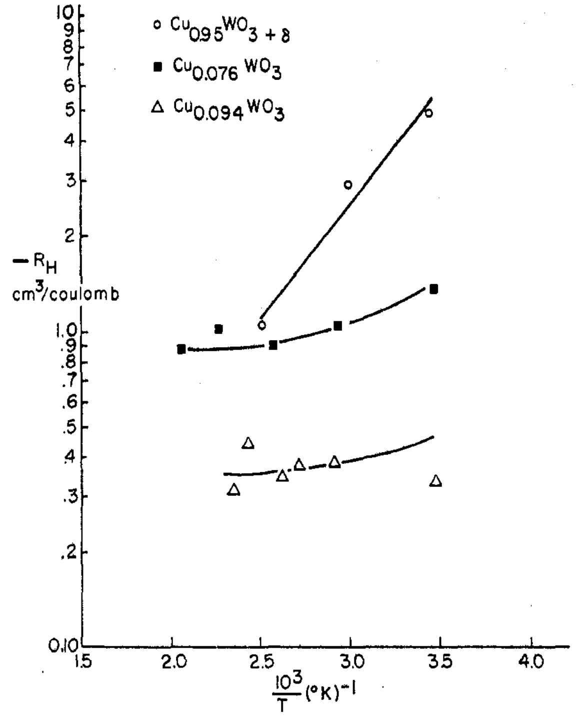

Fig. 4.—Hall coefficient *vs.* $1/T$.

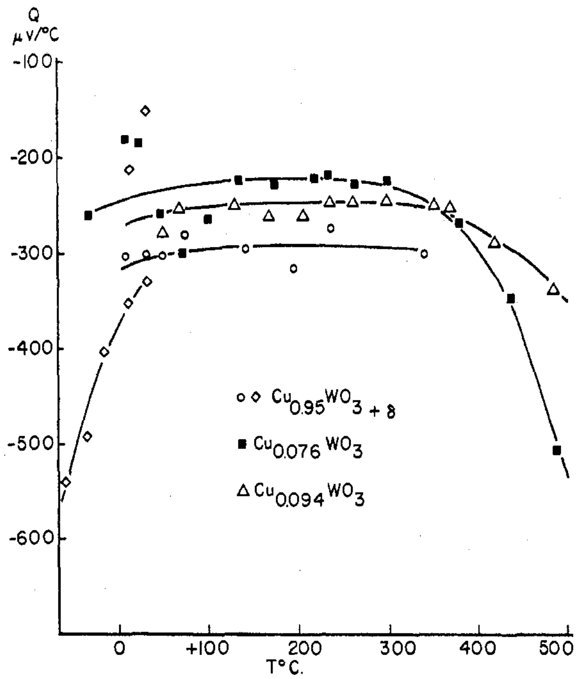

Fig. 5.—Thermoelectric power *vs.* temperature.

H is the magnetic field in gauss, and f is a "shorting out" factor[11] which depends on the length-to-width ratio of the crystal. From the sign of the experimental voltage, R_H was found to be negative indicating electron current carriers. Representative values of $-R_H$ are shown in Fig. 4. The accuracy is believed to be within 20%. The plotted points represent measurements on the crystals for which resistivity values are given in Fig. 3.

Carrier concentrations were calculated from

$$n = \frac{r}{-R_H e}$$

where n is the number of electrons per cc., e is the electronic charge, and r is the scattering factor, taken here to be $3\pi/8$ because as seen below lattice scattering seems to be the dominant mode.

Thermoelectric Power.—The thermoelectric power, or Seebeck coefficient, Q is defined as the thermal gradient of the thermally generated e.m.f.

$$Q = \frac{\Delta V}{\Delta T}$$

Here ΔV is the e.m.f. generated in the crystal when there is a thermal difference ΔT between the hot and cold ends. ΔT was measured with the crystal holder shown in Fig. 1 as the difference between the readings of two copper–constantan thermocouples, spot-welded to the two ends of the crystal. ΔV was determined directly as the potential difference between the copper leads of the two thermocouples. Q was determined from the slope of the plot ΔV *vs.* ΔT for values of ΔT ranging from 1 to 10°. Following the usual convention of defining Q as positive for a junction A/B when positive current flows from A to B at the hot junction, it was found experimentally that Q for Cu_xWO_3/Cu is negative. This finding is consistent with n-type semiconduction and confirms the Hall voltage indication that the current carriers in Cu_xWO_3 are electrons. Figure 5 shows how the thermoelectric power of Cu_xWO_3 referred to copper was observed to vary with the temperature for representative crystals. The scatter is quite large but the drop-off in Q below 0° and above 400° was reproduced with several crystals.

In a thermoelectric power experiment the energy transferred from one junction to the other is equal to the potential energy barrier overcome by the carriers, $E_c - E_F$, plus the kinetic energy transferred from the hot junction to the cold.

$$QT = \frac{(E_c - E_F) + 2kT}{e}$$

E_c is the energy at the bottom of the conduction band, E_F is the Fermi energy, k is Boltzmann's constant, and e is the electronic charge. Since Q is known from experiment, $E_c - E_F$ can be calculated and used to estimate the effective mass m^* of the carriers.[12] In a "spherical" band, the density of carriers is given by

$$n = 2\left[\frac{2\pi m^* kT}{h^2}\right]^{3/2} e^{\frac{E_F - E_c}{kT}}$$

Using the Hall measurements to get n, assuming positive carriers are negligible, we calculate effective masses as given in Table I. Table I also gives representative values of the other significant parameters that characterize the materials investigated in this work.

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(11) K. Lark-Horovitz and V. A. Johnson (Ed.), "Methods of Experimental Physics," Vol. 6B, Academic Press, New York, N. Y., 1959, p. 149.

(12) V. A. Johnson and K. Lark-Horovitz, *Phys. Rev.*, **92**, 226 (1953).

TABLE I

CARRIER DENSITY n, MOBILITY μ, AND EFFECTIVE MASS m^* IN COPPER-DOPED WO_3

	n (e^-/cc.)	μ (cm.²/v.-sec.)	m^* (g.)
	At 298°K.		
$Cu_{0.95}WO_{3+\delta}$	1×10^{18}	0.4	4×10^{-28}
$Cu_{0.076}WO_3$	5×10^{18}	6	5×10^{-28}
$Cu_{0.094}WO_3$	15×10^{18}	10	12×10^{-28}
	At 373°K.		
$Cu_{0.95}WO_{3+\delta}$	4×10^{18}	0.3	6×10^{-28}
$Cu_{0.076}WO_3$	7×10^{18}	4	4×10^{-28}
$Cu_{0.094}WO_3$	18×10^{18}	8	5×10^{-28}
	At 423°K.		
$Cu_{0.95}WO_{3+\delta}$	8×10^{18}	0.2	7×10^{-28}
$Cu_{0.076}WO_3$	7×10^{18}	4	4×10^{-28}
$Cu_{0.094}WO_3$	19×10^{18}	7	9×10^{-28}

Discussion

The electrical conductivity results illustrated in Fig. 3 indicate that the change in crystal structure from orthorhombic to triclinic that accompanies increasing copper content and increasing oxygen-to-tungsten ratio is accompanied by a sufficiently drastic change in carrier characteristics that separate models are called for in their description. In the following discussion, therefore, we separate the problem into consideration of (a) low-copper, orthorhombic Cu_xWO_3 and (b) high-copper, triclinic $Cu_xWO_{3+\delta}$.

(a) **Low-Copper, Orthorhombic Cu_xWO_3.**—In a single fluid model, the specific conductivity σ can be represented as $ne\mu$, where n is the concentration of carriers, e is their charge, and μ is their mobility. From the Hall measurements at room temperature we deduce that n is 5×10^{18} electrons/cc. in $Cu_{0.076}WO_3$ and 1.5×10^{19} e^-/cc. in $Cu_{0.094}WO_3$; from stoichiometry and the observed densities of these materials, we calculate there are, respectively, 1.5×10^{21} and 1.8×10^{21} copper atoms/cc. If it is assumed that copper in Cu_xWO_3 acts as a donor center then the fraction of copper atoms ionized would have to be less than 1%. Furthermore, it would seem that the free electrons so produced move in the same conduction band as in the alkali tungsten bronzes. The carrier mobility, calculated from the observed conductivity σ and the carrier density n, is 6 cm.²/v.-sec. in $Cu_{0.076}WO_3$ and 10 cm.²/v.-sec. in $Cu_{0.094}WO_3$. These values are not very different from the 6.1–9.3 cm.²/v.-sec. observed for $Li_{0.4}WO_3$ and 16 cm.²/v.-sec. for $Na_{0.7}WO_3$.[13] The conduction band in the alkali bronzes is believed to arise mainly from overlap of $5d_\epsilon$ orbitals of the tungsten; it is believed that the same d-band also is operative in the copper-doped WO_3.

However, there is a problem in attempting to account for the three straight-line portions of the log ρ *vs.* $1/T$ curve shown in Fig. 3 for $Cu_{0.094}WO_3$ by assigning them to donor excitation processes. Conventional semiconductor theory would account for the shape of this curve by postulating three donor centers—*e.g.*, Cu^0, Cu^+, O^{2-}—having excitation energies E_1, E_2, and E_3 (counting from low temperature to high) corresponding to a dependence of the form

$$\sigma = \sigma_1 e^{-E_1/kT} + \sigma_2 e^{-E_2/kT} + \sigma_3 e^{-E_3/kT}$$

where σ_1, σ_2, and σ_3 are constants related to the number of donor centers available. To account for the observed slopes of Fig. 3, E_1, E_2, and E_3 would have to be 0.50, 0.4, and 0.45 e.v., respectively, but with these as excitation energies there is no reasonable choice possible for the number of donor centers of each type. Specifically, at 170°K., where the first break in the log ρ *vs.* $1/T$ curve occurs, kT is equal to 0.015 e.v. and $e^{-E_1/kT}$ is approximately 2000 times as large as $e^{-E_2/kT}$. Thus, the conductance contribution by the second term would be negligible until well after the first term excitation had been exhausted, unless the donor centers of type 2 were many orders of magnitude more numerous than donor centers of type 1. A similar difficulty is encountered at 500°K., where the second break in the log ρ *vs.* $1/T$ curve occurs. Excitation out of donor center type 2 would need to be completely exhausted to account for the turn-up in the log ρ *vs.* $1/T$ curve. (This turn-up resembles a typical "exhaustion" region where the number of carriers remains constant with increasing temperature but carrier mobility drops due to increased scattering by polar modes of the crystal.) However, if donor center type 2 is of energy 0.4 e.v., it cannot be exhausted when kT has only reached the value appropriate at 500°K., namely 0.05 e.v. Furthermore, the sharp rise in conductivity that sets in above 500°K. can occur only if donor centers of type 3 are even more numerous than donor centers of type 2. Estimating very approximately, we require at least 10^{20}, 10^{23}, and 10^{24} centers, respectively, of excitation energy 0.05, 0.4, and 0.45 e.v.—obviously impossible if such centers are to be derived from the stoichiometrically available 10^{21}

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[13] M. J. Sienko and T. B. N. Truong, *J. Am. Chem. Soc.*, **83**, 3939 (1961).

copper atoms or 10^{22} oxygen atoms/cc.

For $Cu_{0.076}WO_3$ there is a similar difficulty in accounting for the steeply increasing conductivity between 200 and 250°K., the "metallic" region around room temperature, and the second steeply increasing conductivity that sets in at 600°K. The slope of the 200–250°K. portion corresponds to 0.33 e.v.; that above 600°K., 0.45 e.v. Again, the 0.33 e.v. center cannot be depopulated by 250°K. nor can the 0.45 e.v. center take over in contributing carriers unless there are at least 10^{24} of them. The latter figure is inconsistent with the 10^{21} copper atoms or 10^{22} oxygen atoms present/cc.

A further reason for believing that the log ρ *vs.* $1/T$ curve is not explainable by a simple donor-center theory is provided by the magnetic properties of Cu_xWO_3. The magnetic susceptibility of $Cu_{0.26}WO_3$ has been reported[4] as $+34 \times 10^{-6}$/g.-formula. Although some three times as concentrated in copper, $Cu_{0.26}WO_3$ has the same orthorhombic structure as the $Cu_{0.076}WO_3$ and $Cu_{0.094}WO_3$ here under discussion, so probably it can be used to imply something about the magnetic situation in the latter materials. Applying diamagnetic corrections of -21×10^{-6}/mole for the host WO_3[14] and -12×10^{-6}/mole for the copper ions,[15] we calculate the equivalent of 0.18 mole of spins/mole of copper in Cu_xWO_2. Because Cu^0 and Cu^{++} both are paramagnetic with one spin whereas Cu^+ is diamagnetic, the observed magnetic susceptibility could be interpreted as 18% Cu^0, 82% Cu^+, 0% Cu^{++} or 0% Cu^0, 82% Cu^+, 18% Cu^{++}, or any combination of Cu^0 and Cu^{++} totaling 18%. However, none of these possibilities is satisfactory, since the 82% Cu^+ implies that most of the copper atoms have ionized. As a result there would be approximately 10^{21} electrons/cc. to be accounted for whereas the Hall voltage indicates there are only 10^{18}/cc. in the conduction band. Trapping of the electrons to give Cu^-, as suggested previously,[4] is possible, but donor excitation from Cu^- would be expected to require less energy than excitation from Cu^0 or Cu^+. As indicated above, the higher energy donor centers need to be the more numerous in order to account for the observed conductivity curve, so Cu^- could not be present in sufficient concentrations to be of much use.

Electron spin resonance studies[16] also suggest that a simple donor-center model of Cu^0 in WO_3 is not satisfactory for Cu_xWO_3. Comparison of the absorption signal of powdered, single crystals of $Cu_{0.076}WO_3$ with the signal from $MnSO_4$ indicates approximately 10^{20} spins/cc. On the basis of signal strength, these spins could be due to Cu^0 or Cu^{++}. However, the *g*-factor for the center of the absorption line is 2.24, which is more suggestive of Cu^{++} than of Cu^0. For Cu^0 the *g*-factor might be expected to be very close to 2.00 since the state of Cu^0 is presumably $^1S_0$.

Because of the problems in expressing the conductivity–temperature data as a function of electron excitations into a conduction band alone, we are led to postulate that the steep rise in conductivity observed in the range 200–250°K. is not due to an exponential increase in the number of carriers but to a large increase in carrier mobility brought about by a phase change in the host crystal. Specifically, we suggest that the structure change which gives rise to the ferroelectric-to-antiferroelectric transition[17] observed in pure WO_3 at approximately 220°K. also occurs in copper-doped WO_3. (In $Ag_{0.04}WO_3$ an even more spectacular change in conductivity occurs at about 220–280°K., probably due to the same kind of structure change in the host.)[18]

The fact that the Hall voltage in $Cu_{0.076}WO_3$ and $Cu_{0.094}WO_3$ is not changing much with temperature near 300°K. indicates that the number of carriers is essentially constant near room temperature. Still, as the temperature drops below room temperature there should be an increase in conductivity because lattice scattering would be expected to decrease. We can estimate what the mobility would be at 170°K. *if no structure change occurs* assuming that the mobility is defined by lattice vibrations and follows the dependence

$$\mu = \text{constant } (e^{\theta/T} - 1)$$

where θ is the Debye temperature of the lattice.[19] Thermal studies on the sodium tungsten bronzes suggest that the value appropriate for the Debye cut-off is 500°K.[20] Since at room temperature μ for the electrons in $Cu_{0.094}WO_3$ is 10 cm.²/v. sec., we expect at 170°K. it would be about 40

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(14) L. E. Conroy and M. J. Sienko, *J. Am. Chem. Soc.*, **74**, 3520 (1952).

(15) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 2nd ed., 1956, p. 74.

(16) J. L. Ragle, private communication.

(17) B. T. Matthias and E. A. Wood, *Phys. Rev.*, **84**, 1255 (1951); K. Hirakawa, *J. Phys. Soc. Japan*, **7**, 331 (1952); see also Werner Känzig, "Solid State Physics," Vol. 4, Academic Press, Inc., New York, N. Y., 1947, p. 141.

(18) L. E. Conroy, private communication.

(19) J. Yahia and H. P. R. Frederikse, *Phys. Rev.*, **123**, 1257 (1961).

(20) R. W. Vest, M. Griffel, and J. F. Smith, *J. Chem. Phys.*, **28**, 293 (1958).

cm.^{2}/v. sec. However, the specific resistivity of $Cu_{0.094}WO_3$ at 170°K. is about 60 ohm-cm.—some 6000 times the 0.01 ohm-cm. anticipated by extrapolating the room temperature behavior to 170°K. If we assume that the carrier density remains constant through the transition, then we have to conclude that the mobility has dropped to 0.007 cm.^{2}/v. sec.

Mobilities of this order of magnitude are too low to be ascribed to conduction through a band of finite width. Rather they resemble the mobility values found in conduction by "hopping" processes, as for example in Fe_2O_3 or NiO.[21] Furthermore, if the low temperature portion of the log ρ *vs.* $1/T$ curve for $Cu_{0.094}WO_3$ corresponds to conductance *via* such a "hopping" mechanism then the slope of the curve is ascribable not to an excitation energy for raising carriers into a conduction band but to an activation energy associated with the hopping process. In the simplest picture, this activation energy can be taken as a polarization energy associated with distortion of the local crystal environment as an electron "hops" from one localized center to another.[22]

What might be the nature of the structure change that can produce such a 6000-fold change in mobility? If we idealize the atomic arrangement in $Cu_{0.094}WO_3$ as a simple cubic array similar to that existing in the perovskite-type sodium tungsten bronzes, we would have a unit cell consisting of W atoms at the cube corners and O atoms in the middle of the cube edges. The copper atoms would be distributed at random amongst the centers of the cubes so as to occupy 9.4% of them. Above the transition temperature, there would be no net electric moment, so each W atom would have to be symmetrically placed with respect to its octahedral cage of surrounding oxygen atoms. However, if as in pure WO_3, Cu_xWO_3 goes over to a ferroelectric state below 220°K., there would have to be a net, collective displacement of the tungsten atoms away from the centers of the oxygen octahedra. This would be necessary to produce a spontaneous electric polarization such as characterizes the ferroelectric state. With a reduction in symmetry of the unit cell, it is probable that the overlap of $5d_\epsilon$ orbitals of the W atoms would be reduced—in fact, the overlap might vanish, particularly when one considers interaction with the p orbitals of the near oxygen atoms. If the orbitals do not overlap, banding would not occur and conduction would have to occur by a hopping mechanism rather than through Bloch waves.

A major assumption of the above discussion is that the number of carriers remains essentially constant in going through the transition. Normally, this assumption could be tested by Hall voltage measurement at low temperatures to determine the carrier density. However, we did not see any Hall voltage over the noise below room temperature. This actually may be one of the strongest arguments for the above model, since there is considerable reason for believing that conduction by a "hopping" process mechanism does not lead to an appreciable Hall effect.[23]

Still, the above model is oversimplified since it does not explain why the number of carriers in the "exhaustion" region above room temperature should be limited to 1.5×10^{19} whereas there are 1.8×10^{21} copper atoms potentially able to furnish electrons. A possible answer is suggested by the magnetic susceptibility and e.s.r. results. The magnetic spins, which on the basis of their g-factor are probably Cu^{++}, number about 3.6×10^{20}, corresponding to 7.2×10^{20} electrons released from copper atoms. The rest of the stoichiometric copper must have gone to Cu^+. Of the total density of electrons released, only 1.5×10^{19} are available in the conduction band at room temperature. The rest must be trapped on an acceptor center with fairly high ionization energy. A possible candidate for this center is oxygen excess. We would need only 0.0016 g.-atom of oxygen/cc., about 1.8% in excess over that required for 3:1 stoichiometry of O:W. Unfortunately, this is too small for our analytical methods to detect.

In summary, the shape of the resistivity-temperature curve of $Cu_{0.094}WO_3$ is attributed to the following processes occurring progressively as the temperature is raised: (a) "hopping" of electrons from one site to an adjacent one, the site probably being the cage of tungsten atoms around a Cu^+ ion; (b) a phase change characterized by a small displacement of tungsten atoms, leading to overlap of trap sites and hence band formation; (c) a decrease in band conductivity due to thermal excitation of lattice vibrations—the so-called

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(21) F. J. Morin, *Phys. Rev.*, **83**, 1005 (1951); *Bell System Tech. J.*, **37**, 1047 (1958).

(22) R. R. Heikes and W. D. Johnston, *J. Chem. Phys.*, **26**, 582 (1957).

(23) See, for example, the discussion after "Session B: Theory I" of the 1958 International Conference on Semiconductors, *J. Phys. and Chem. Solids*, **8**, 50 (1959).

"exhaustion" region; (d) a sharp rise in band conductivity due to a significant excitation of additional carriers, either from Cu^+ or possibly from oxygen atoms.

(b) **High-Copper, Triclinic $Cu_xWO_{3+\delta}$.**—The picture here is simpler since the resistivity *vs.* $1/T$ curves for these specimens consist of two straight-line portions, without any visible evidence of the up-turning hook that signals the onset of the "exhaustion" region in the low-copper materials. The simplest model would call for two donor centers of appreciable but differing excitation energies. The low temperature portion would correspond to an activation energy of 0.10 ± 0.05 e.v., which value is to be compared to the 0.15 e.v. previously reported for $Cu_{0.77}WO_3$; the high temperature portion, to an activation energy of 0.15 ± 0.05 e.v. The number of carriers as deduced from the Hall experiments is considerably less, and the carrier mobility is smaller than in the low-copper material. The low carrier mobility—0.4 cm.^{2}/v. sec. at room temperature—is not low enough to warrant unambiguous assignment to "hopping" conduction; it more likely is due to the rather low symmetry of the host structure. The fact that by 423°K. the mobility has decreased to 0.2 cm.^{2}/v. sec. suggests that lattice scattering is still the dominant mechanism of resistivity. The effective mass of the carriers is surprisingly close to the rest mass of the electron (m^* varies from 0.3 m_0 at 298°K. to 0.8 m_0 at 423°K.), though the calculation based on thermoelectric power has to be considered as rather unreliable because the band form is probably not simply spherical.

The Hall measurements indicate at 298°K. there are about 10^{18} electron carriers/cc., which is to be compared to the 1.6×10^{22} copper atoms/cc. calculated from the stoichiometry and the density. The spin-resonance studies,[16] however, indicate there are present about 10^{22} spins/cc. with a g-factor of 2.18, strongly implying that practically all of the copper atoms are in a doubly ionized state. To account for this low number of carriers but a large number of ionized copper atoms it is necessary to assume there are fairly deep traps for removing electrons from the conduction band. If these traps are excess oxygen atoms, we need about 4×10^{21} oxygen atoms/cc. This corresponds to $Cu_{0.95}WO_{3.2}$, in substantial agreement with the oxygen excess indicated by the chemical analysis.

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Phthalocyaninoaluminum Compounds[1]

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A group of phthalocyaninoaluminum compounds has been prepared and studied in which organo- and organosiloxy groups have been bonded to the central aluminum atom. These compounds illustrate some types of groups that can replace the simple inorganic groups which ordinarily are attached to the metal. One of these compounds, $PcAlOSi(C_6H_5)_3$, contains an AlOSi backbone which is not easily hydrolyzed.[2]

The phthalocyaninoaluminum compounds are complexes in which two of the primary valencies of the coördinated aluminum atom are taken up by the dibasic, quadridentate, planar phthalocyanino ligand and the third by other groups (Cl^-, Br^-, OH^-, etc.).[3,4] Because of the nature of the phthalocyanino ligand, it is probable that the arrangement of the ligand atoms surrounding the aluminum atom is square pyramidal and that the aluminum atom lies near or in the plane formed by the nitrogen atoms (Fig. 1).

This suggests that in some cases the aluminum atom is coördinated in a square pyramidal fashion.

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[2] Pc = $C_{32}H_{16}N_8$, the phthalocyanino ring.

[3] P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1719 (1936).

[4] M. E. Kenney, *J. Inorg. & Nuclear Chem.*, **11**, 167 (1959).