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High-pressure electrical conductivity measurements in the copper oxides

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We have measured the temperature-dependent electrical conductivity of Cu_2O at pressures up to 500 kbar and of CuO up to 700 kbar. The high-pressure phase of Cu_2O has a resistive thermal activation energy of a few meV and localization behavior below 7 K. No phase transitions were observed in CuO at pressures and temperatures up to 700 kbar and 3000 K, but its thermal activation energy decreases linearly with pressure and extrapolates to zero at about 1 Mbar.

I. INTRODUCTION

All known superconductors with critical temperatures above 40 K have in common a structure based on square-planar-coordinated Cu-O sheets. This fact has generated great interest in the behavior of carriers in the Cu-O planes, which are believed to be responsible for superconductivity, and also in electronic interactions in the simple copper oxides. In this paper we report for the first time the temperature- and pressure-dependent electrical properties of the high-pressure phase of Cu_2O, and estimate the pressure at which the electrical properties and perhaps the structure of CuO will change.

Two phases of copper oxide are known to be stable at room temperature and pressure. Cu_2O is a reddish semiconductor with a cubic structure (space group $O_h^4 = Pn3m$) and a band gap at ambient pressure of about 2.1 eV. It has been shown to transform into a hexagonal structure at 100 kbar and then into a $CdCl_2$-type structure at pressures above 130 kbar.[1] The electrical properties at atmospheric pressure are sensitive to factors such as thermal history, oxygen defect levels, and photomemory effects.[2] This makes the intrinsic properties difficult to measure, but it has been suggested[2] that near-stoichiometric Cu_2O is a defect semiconductor with *p*-type conductivity from excess oxygen. CuO is a black semiconductor with a monoclinic structure (space group $C\,2/c$).[3] At ambient pressure, the spins on the copper atoms order helically below 231 K and antiferromagnetically below 212.5 K.[4] CuO is reported to have an indirect optical band gap with a value of 1.4 eV,[5] but electrical conductivity measurements[6] have found thermal activation energies ranging from 0.13 to 0.6 eV.

The experiments reported here were performed on high-purity single-crystal Cu_2O samples grown[7] with the Czochralski technique in an arc-image furnace. The optical properties, including the nonradiative recombination rate, were measured[8] in these bulk crystals and were consistent with what is expected from low-impurity concentrations. The CuO crystals were grown as described in Ref. 9, with a melt of CuO (99.99%), MoO_3 (99.7%), V_2O_5 (99.99%), and K_2CO_3 (99.999%) in a platinum crucible. The crystals had melt inclusions, but fragments from crushed crystals appeared to be single phase and showed sharp polarized peaks in the Raman spectra. These peaks were in good agreement with Raman spectra from single crystals of CuO that we obtained from Chaminade and Nganga at the Laboratorie de Chimie du Solide du CNRS in Talence, France.

Our high-pressure electrical conductivity measurements were performed in a gasketed diamond anvil cell (DAC) as described by Erskine *et al.*,[10] using copper wires in a quasi-four-probe configuration and a mixture of vacuum grease and $CaSO_4$ as the pressure medium. Electrical contacts were made by placing the sample on top of the wires and relying on pressure to make good contacts. Resistance measurements represent an average over a finite volume of the sample, and are therefore subject to pressure inhomogeneities; this effect was minimized by using small samples (linear dimensions ≈ 100 μm) and by placing the wires less than 50 μm apart. Estimates of the absolute resistivities are only approximate because of uncertainties in the sample geometries. Pressures were determined by the ruby fluorescence technique using several ruby chips placed around the sample. At a given anvil load, the pressure variation over the set of ruby chips was typically 5–10%; the pressure inhomogeneity across the sample was expected to be somewhat less. The pressure increased by about 5% when the cell was cooled from room temperature to 100 K. This influenced the linear terms in the resistance versus temperature curves, but the effect on the calculated activation energies was negligible. Below 100 K there was no observed change in pressure with temperature.

II. RESULTS

A. Cu_2O

High-pressure electrical conductivity measurements were performed on seven Cu_2O samples taken from the same bulk crystal, with consistent results. The resistance versus temperature curves were fitted to the Arrhenius equation

$$R = R_\infty \exp(\Delta E / kT) ;$$

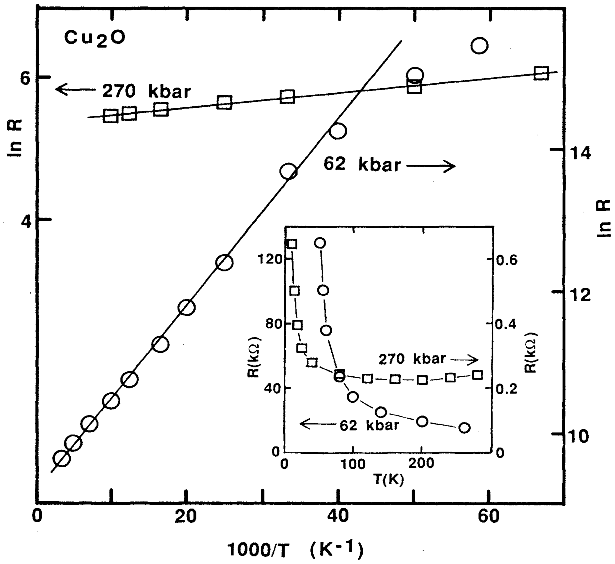

FIG. 1. Resistance vs temperature curves for Cu_2O at 62 kbar (cubic structure) and at 270 kbar ($CdCl_2$ structure).

here ΔE is the thermal activation energy of the resistance, and is not necessarily related to the optical band gap. Activated behavior is typically found between 10 and 100 K. Resistance versus temperature data taken at two different pressures are shown in Fig. 1. The pressure dependences of ΔE and R_∞ are shown in Fig. 2. Abrupt changes in both $d(\Delta E)/dP$ and $d(R_\infty)/dP$ occurred at 100 kbar, perhaps corresponding to the phase transition observed in Ref. 1. Hysteretic behavior was observed in both ΔE and R_∞, with the change in slope occurring at about 70 kbar on depressurization. Data from the second pressurization cycle reproduced the data from the first cycle at pressures above 50 kbar. As shown in Fig. 2, there was little change in ΔE at pressures above 100 kbar; between 300 and 500 kbar there was only a slight decrease in ΔE, from 0.5 to 0.4 meV, in spite of a decrease in the resistance of nearly one order of magnitude.

Below 10 K, the resistance of Cu_2O above 100 kbar cannot be characterized by a single activation energy. The low-temperature resistance data at 270 kbar can be fitted to the form

$$R = R_\infty \exp[(T_0/T)^{1/4}] ,$$

as shown in Fig. 3, with $R_\infty = 250\ \Omega$ and $T_0 = 9.38$ K. The ac resistance was measured at 4.2 and 1.6 K at 270 kbar, and was found to be independent of frequency up to 150 kHz. At 470 kbar, data were taken down to only 5 K, but if we fit the points between 7 and 5 K, we can set an upper limit of $T_0 \approx 10^{-3}$ K and $R_\infty \approx 17\ \Omega$ ($\rho_\infty \approx 0.05\ \Omega$ cm).

After depressurization, the color of the Cu_2O samples had changed to a darker red. Inspection under an optical microscope showed that the bulk of the samples still had the original color, but there was also a fine network of black lines that were probably caused by mechanical deformation. This indicated that any bulk phase transitions that occurred were reversible with pressure.

B. CuO

Figure 4 shows both the electrical resistance and the thermal activation energy for six CuO samples. During

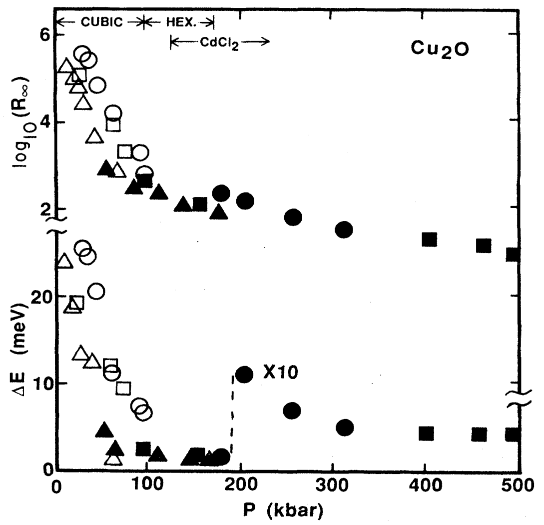

FIG. 2. $\log_{10}R_\infty$ and ΔE vs pressure for Cu_2O, for two representative samples. Open symbols represent one sample and solid symbols represent the other. Circles indicate data from the first pressurization, triangles for the first depressurization, and squares for the second pressurization. The structural phases shown at the top of the figure are from Ref. 1.

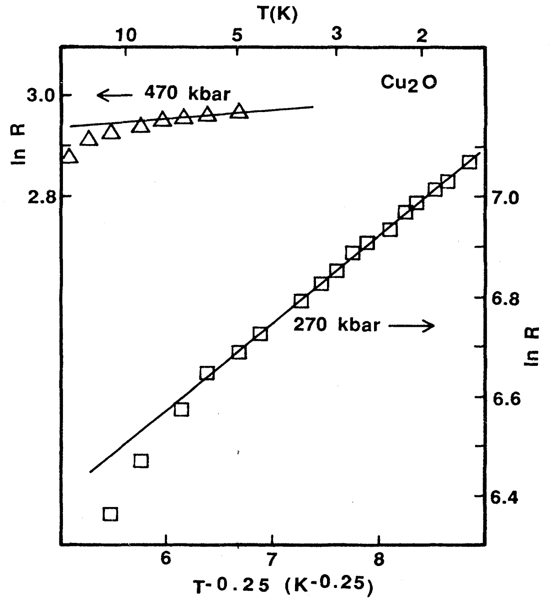

FIG. 3. Low-temperature resistance of Cu_2O at 270 and 470 kbar, showing localization behavior with a hopping energy that decreases rapidly with pressure.

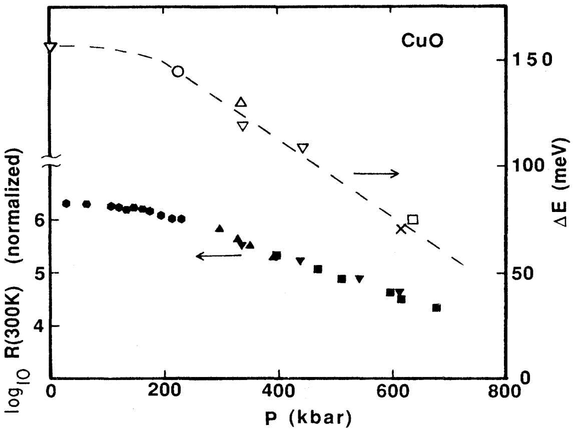

FIG. 4. $\log_{10}R$ and ΔE vs pressure for CuO. Each sample is indicated with a different symbol.

the initial pressurization, there were irreversible drops in resistance that we attribute to the formation of electrical contacts. The resistance was reversible with pressure after the initial pressurization cycle. The resistivity decreased smoothly by over two orders of magnitude to a value of about 50 Ω cm as the pressure was increased to 680 kbar, with no indication of any phase transitions. The activation energy decreased linearly with pressure between 220 and 630 kbar at a rate of about 0.18 meV/kbar. If this pressure coefficient remains constant at higher pressures, the resistive activation energy of CuO will vanish at about 1 Mbar.

We attempted to induce a phase transition in CuO by heating the sample under high pressure. A sample was pressurized to about 600 kbar, and the side of the sample that was pressed against the diamond face was heated with a cw Nd:YAG laser focused to approximately 10 μm, using a configuration described in Ref. 11. The spot was scanned across the sample and produced temperatures that ranged between 1300 and 3000 K, depending on the laser output and on the spot location. The initial sample resistance of 3.5 kΩ was essentially unchanged by the heating process.

III. DISCUSSION

A. Cu_2O

Cu_2O decomposes irreversibly to CuO and Cu metal at combined temperatures and pressures above 100 kbar and 500 °C.[12] One study found[13] an irreversible chemical decomposition above 150 kbar at room temperature, while a more recent study[1] found no decomposition at room temperature up to at least 240 kbar. The reversibility of the electrical and optical properties of our samples with pressure cycling rules out a simple phase separation of Cu_2O up to 500 kbar at room temperature.

The optical gap of Cu_2O was recently reported[14] to *increase* with pressure up to 85 kbar. An earlier study[15] found that the resistance of Cu_2O also increased slightly with pressure, becoming 5% higher at a nominal pressure of 90 kbar. This is in contrast to our finding that the activation energy of the resistivity in Cu_2O decreases with pressure in the same pressure range. As the conductivity of Cu_2O at ambient pressure is known to change by up to 10 orders of magnitude with changes in oxygen concentration,[2] it is possible that dR/dP is also sample dependent. The electrical properties of our Cu_2O samples at pressures below 100 kbar appear to be dominated by defect levels which are probably sensitive to the preparation history and the mechanical deformation of the samples. The electrical properties at higher pressures might also be influenced by sample-dependent defect levels.

The high-pressure phase of Cu_2O displays metallic behavior at temperature above 100 K, with a resistance that increases linearly with temperature, but it is not a simple metal because the resistance diverges as $T \rightarrow 0$, with a low-temperature resistance behavior of $\exp[(T_0/T)^{1/4}]$ that is characteristic of variable-range hopping.[16] The approximate sample conductance of 30 $\Omega^{-1}\,\mathrm{cm}^{-1}$ at 500 kbar is only about a factor of 10 below the Mott "minimum" metallic conductivity;[16] the exponential increase of the conductance with pressure and the rapid drop of the T_0 parameter between 270 and 470 kbar both suggest that at higher pressures, perhaps less than 1 Mbar, Cu_2O will show more conventional metallic behavior throughout the entire temperature range. Variable-range hopping behavior is common in both the planar Cu-O (Ref. 17) and the cubic (Ba,K)BiO_3 superconductors,[18] suggesting perhaps a similar conduction mechanism, but the experimental data in high-pressure Cu_2O are also consistent with a highly doped small gap semiconductor or disordered metal, with the doping or disorder due to grain boundary dislocation and/or stress. It would be interesting to test any similarities between the superconducting oxides and Cu_2O by introducing additional carriers into Cu_2O via doping to try to induce superconductivity in the high-pressure phase.

B. CuO

The thermal activation energy of the resistance of CuO is 0.15 eV at ambient pressure, much less than the actual band gap of 1.4 eV, which demonstrates that the conductivity is extrinsic in this material. We are presumably observing an impurity level whose binding energy decreases under pressure, as in the case of Cu_2O. If the binding energy continues to decrease linearly with pressure above 680 kbar, the electronic properties and perhaps the structure of CuO will show a transition at about 1 Mbar when the activation energy of the resistance vanishes.

A previous high-pressure electrical experiment[19] in CuO found that the resistance dropped slowly with increasing pressure up to a nominal pressure of 480 kbar, in qualitative agreement with our results. A direct comparison with this experiment is not possible because of the unreliability of the older pressure scales. Thermal activation energies were not determined in the earlier experiment. No phase transitions were observed at room temperature at any pressure, or at temperatures up to 419 K at 17 kbar. A discontinuous resistance drop of four orders of magnitude was observed at 383 K at a nominal pressure of 187 kbar, and at 360 K at a nominal pressure of 462 kbar, but no attempt was made to determine the nature of the transition or to rule out a reaction between the sample and the AgCl pressure medium. The latter explanation seems likely in light of our inability to induce a phase transition at temperatures up to 3000 K.

IV. SUMMARY

We have measured for the first time the electrical conductivity properties of the high-pressure phase of Cu_2O, finding a thermally activated resistance of a few meV and evidence of localization behavior below 7 K. We estimate that Cu_2O should become a conventional metal at less than 1 Mbar. CuO has no phase transitions up to 700 kbar and 3000 K, but has a thermal activation energy that decreases with pressure and extrapolates to zero at 1 Mbar, suggesting that a change will occur in the electrical behavior at this pressure.

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