Electrical Instability in CuO_{1-x}: Possible Correlations with the CuO-based High Temperature Superconductors

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Physical properties of stoichiometric and non stoichiometric CuO are reported. The electrical conductivity has been measured on CuO pellets, sintered with the usual procedure for the preparation of Y–Ba–Cu–O superconductors and then deoxygenated under a nitrogen flow. It is shown that oxygen deficient CuO pellets present abrupt and large resistivity drops as the temperature decreases below 230–200 K. Possible correlations between the electrical instability of oxygen deficient CuO and the high temperature superconductivity problem are discussed.

Key words: Cupric oxide, Superconductors, Electrical conductivity.

The discovery of copper oxide based superconductors with high transition temperatures (HTSCs) gave rise to a large variety of problems. In particular, the main problem concerning the electronic structure of copper oxides (CuO, Cu_2O) is the localized or itinerant nature of the Cu 3d valence electrons [1]. After the early efforts to explain the high temperature superconductors in terms of one electron band calculations, nowadays there is strong evidence that such an approach is not really adequate. These materials are better understood as Mott-Hubbard insulators where the 3d valence electrons are localized while the oxygen holes are itinerant. In this framework a deeper kowledge of the physical properties of the Cu–O bond in different structural combinations, in particular in the copper oxides, could give some clue to the understanding of the HTSC problem.

Cu_2O is a diamagnetic insulator with an energy gap $Eg = 2.17$ eV [2] and a filled d shell. Its electronic properties are well described in the framework of band calculations [3]. The crystal structure of Cu_2O is highly symmetric with six atoms per cell: oxygens form a b.c.c. lattice while the copper atoms are on the vertices of a tetrahedron around each oxygen atom. The copper atoms are linearly coordinated with oxygens [4].

The crystal structure of CuO is in the monoclinic space group C2/c with four formula units per unit cell [5]. Each atom has four nearest neighbors of the other kind; oxygens are at the center of a distorted copper tetrahedron; copper atoms are at the center of an oxygen rectangle. The distortion from a regular octahedron, generally explained as a consequence of the Jahn-Teller effect, is very large, the Cu–O out of plane distance being 0.82 Å or about 42% greater than the in plane distance. Moreover, the thermal motion of copper atoms has a large component perpendicular to the plane formed by the coordinated oxygen atoms.

CuO has an open d shell (3 d^9). X-ray photoelectric spectroscopy (XPS) has shown the presence of strong correlation effects as proved by the existence of Cu core line satellites. CuO belongs to the class of charge transfer Mott insulators, the energy transfer integral between a 3d metal state and a 2p anion state becoming lower than the d–d Coulomb interaction. The ground state properties are well described by assuming a mixing between the d^9 and d^{10} L (where L indicates a hole in the otherwise filled 2p oxygen state) configurations. Evidence of the fluctuating character

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of the Cu–O bond has recently been obtained from an XPS study by two of us [6].

Heat capacity data proved that CuO undergoes two magnetic transitions at about 213 and 230 K [7]. Neutron scattering measurements [8–10] have clarified the origin of the heat capacity anomalies: an incommensurate antiferromagnetic structure forms between 213 and 230 K. Below 213 K a commensurate antiferromagnetic order is observed. The volume of the magnetic unit cell is double that of the unit cell. The ordered moment is 0.38 μB per Cu [9], significantly smaller than expected for a one-spin only Cu^{2+} ion. Magnetic susceptibility measurements [11] showed a somewhat unusual behavior: the susceptibility continues to increase above the Néel temperature (T_N) and reaches a maximum only at 540 K. It has been suggested that this maximum is due to diffuse magnetic scattering originating from one-dimensional correlations along the Cu–O chains [9]. A new set of heat capacity measurements [12] supports the quasi one-dimensional nature of the magnetic interaction in CuO, with Cu^{2+} chains more than 70% ordered at T_N and with an intrachain coupling constant $J/k = 460$ K. This exchange coupling is close to the values reported for La_2CuO_4 and $YBa_2Cu_3O_{7-x}$. It has been suggested that CuO could be a resonating valence bond (RVB) quantum spin liquid as proposed for the oxide superconductors [12].

In the framework of a systematic investigation of the resistivity behavior as a function of the oxygen content in stoichiometric and non stoichiometric CuO, the aim of this paper is to report a preliminary account of the electric properties of cupric oxide. It will be shown that non stoichiometric CuO sintered pellets present sudden resistivity drops as the temperature falls to 230–200 K. Finally, a discussion based on the possible influence of grain boundaries on the electrical properties is given.

Experimental

The samples were prepared by sintering pure CuO powder (Aldrich, 99.999%) 9 h at 950 °C and annealing for 10 h at 500 °C in an oxygen flow (50 ml min^{-1}), i.e., following the same procedure as employed by Reeves et al. [13] for HTSCs. The first prepared pellets were supposed to be stoichiometric, and their stoichiometry was not checked. Thermogravimetric analysis carried out on subsequent samples showed a Cu : O ratio of 1 : 1 within the experimental sensitivity. No contaminants were found. X-ray diffraction (XRD) indicated that the samples were fully crystallized in the monoclinic phase with cell parameters $a = 4.681(5)$ Å, $b = 3.422(5)$ Å, $c = 5.122(5)$ Å, $\beta = 99.810°$.

Resistivity measurements were performed in a closed two stage helium cryostat (Air Products) both on cooling and heating, at scan speeds of 1 and 2 K min^{-1}, respectively, in the range 10–300 K. A calibrated silicon diode was used to measure the temperature. The temperature stability was better than 0.1 K. Electrical contacts were achieved by fastening copper leads with silver paint. The standard dc four probes method was adopted, with a programmable current source (Keithley 220) in the range 50 μA to 10 mA and a microvoltmeter. For higher resistivity measurements (> 10 MΩ) an ohmmeter (Keithley 616) in the two probes configuration was employed.

The magnetic susceptibility was measured by means of a magnetometer consisting of a Faraday balance system working in the temperature range 80–280 K, with a magnetic field of 5000 G, under helium ($p = 700$ Torr).

The CuO reduction was carried out by a thermogravimetric technique, using a Du Pont 951 TG Analyzer connected with a 1090 Thermal Analyzer: the samples (weight range: 60–80 mg) were exposed to a pure nitrogen flow (about 30 ml min^{-1}) and heated at different rates (5–20 °C min^{-1}) from room temperature up to 840–940 °C. After the oxygen loss, no mass change was detected on cooling the samples under nitrogen. The reduced samples, examined by optical microscopy, showed two dispersed phases. The grey-black one was assigned to CuO and the red one to cuprous oxide. XRD analysis confirmed this attribution.

Results and Discussion

In previous literature, resistivity measurements by several research groups are reported. It was observed that the grain boundaries in pellets formed from CuO powder, as well as phase boundaries in CuO foils obtained by oxidation of Cu, make it difficult to obtain reproducible resistivity values [14]. In particular, Bobleter and Fessler [15] studied the electrical behavior of a CuO foil in the range 200–800 °C both in air and under vacuum, finding a significant difference between the two series of data. Their measurements in air can be fitted by two exponential equations below and above 600 °C, whereas the curve recorded under

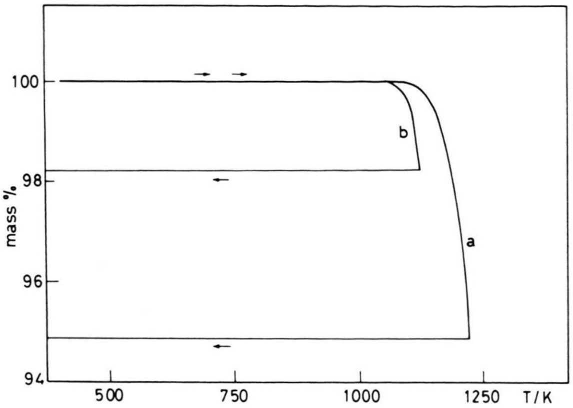

Fig. 1. Thermogravimetric curves of CuO samples, heated in a pure nitrogen flow: a) Ip4, b) Ip3.

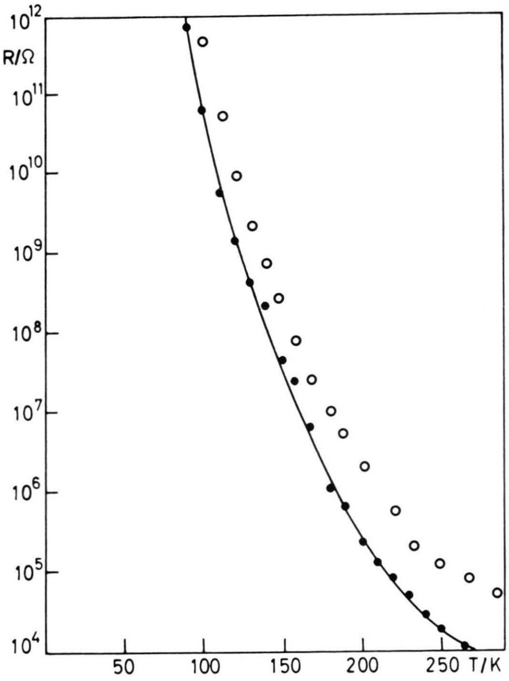

Fig. 2. Temperature dependence of the resistance of a sintered CuO pellet in oxygen (●), and of an original CuO pellet under vacuum (○).

Table 1. Parameters of reduced CuO samples.

Sample	Mass loss %	Oxygen loss %	Scan rate °C/min	T_{max} °C
Ip2	0.4	2.0	10	880
Ip3	1.8	9.0	5	840
Ip4	5.2	25.9	20	940

vacuum could not be described by a suitable expression.

In the present work, preliminary measurements of resistivity at subambient temperatures on sintered CuO pellets – the stoichiometry of which had not been checked – brought out remarkable anomalies in the form of sharp resistivity drops, in the temperature range in which the magnetic transitions occur (200 to 230 K). These phenomena seemd to be dependent on the thermal history of the samples and the environmental conditions, thus suggesting possible correlations with the oxygen stoichiometry.

It was therefore decided to compare the electrical properties of stoichiometric CuO with those of CuO_{1-x} samples ($0 < x < 0.26$). Such samples, cut from the original stoichiometric one in form of pellets, were reduced (by the method outlined above) under different operational conditions in order to obtain different oxygen contents. In Table 1 the characteristic parameters of the examined samples are reported. As an example, in Fig. 1 the thermogravimetric curves of two of these samples, corresponding to oxygen losses of 9.0 and 25.9%, are illustrated.

The dependence of the resistivity on the oxygen stoichiometry can be summarized as follows:

i) The bulk resistivity ϱ of stoichiometric CuO has an activated character: $\varrho = \varrho_0 \exp(E_a/kT)$, where the activation energy, E_a, is about 1 eV. The high value of E_a is partly due to the intergrain barriers, as proved by the strong frequency dependence of the resistivity. This was shown by means of ac measurements performed at room temperature. The dc measurements always gave resistivity values by two orders of magnitude larger than those obtained in the audiofrequency ac region. Such a behavior can be expected if one takes into account the polycrystalline nature of the samples. On cooling in an oxygen atmosphere, the dc resistance increased from 10^4 Ω at room temperature to 10^{12} Ω at 90 K and was even larger at lower temperatures (90–10 K), where it exceeds the input impedance of the electrometer (10^{12} Ω). One can conclude that stoichiometric CuO in these conditions behaves like a typical semiconductor. The same behavior was observed on cooling under vacuum a pellet of the original powder as supplied by Aldrich. In Fig. 2, a plot of R vs. T for both sintered and original CuO in the low temperature range is presented.

Heat capacity measurements, carried out by means of differential scanning calorimetry on CuO, in the range 200–360 K, were in good agreement with the

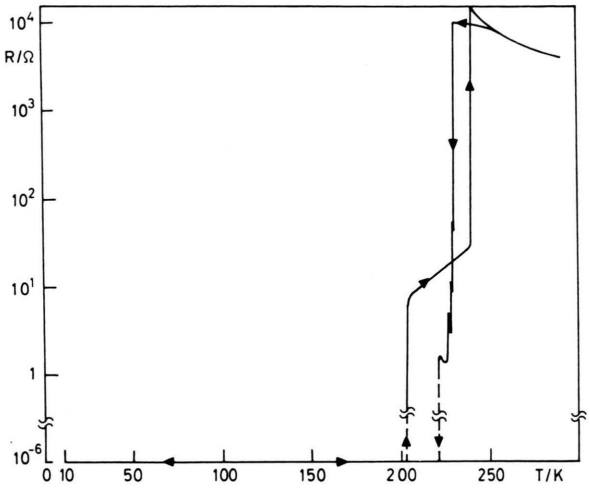

Fig. 3. Resistance vs. temperature for the $CuO_{1-0.26}$ sample.

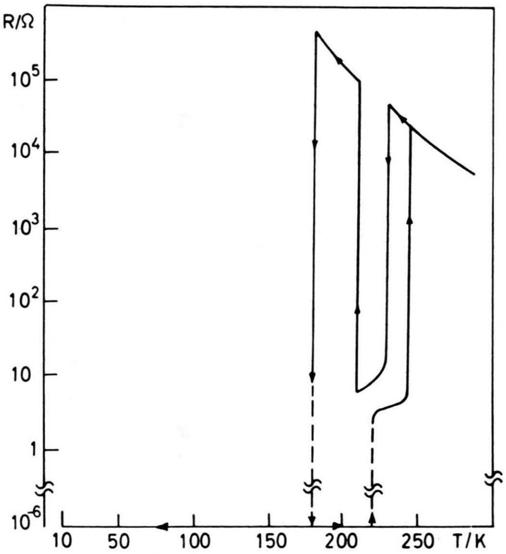

Fig. 4. Resistance vs. temperature for the $CuO_{1-0.09}$ sample.

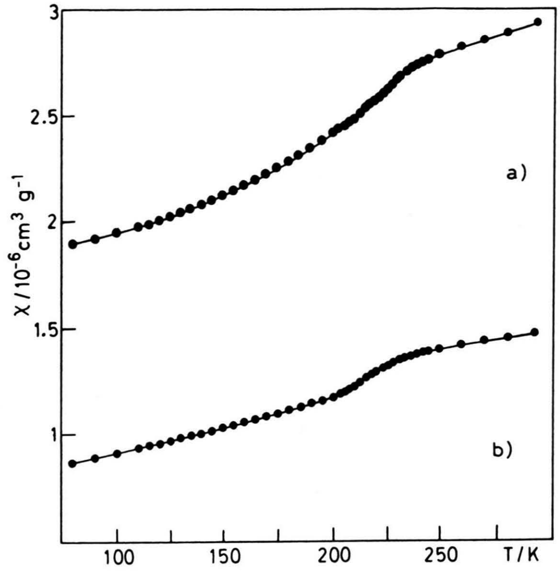

Fig. 5. Magnetic susceptibility (χ) vs. temperature for: a) CuO, b) $CuO_{1-0.26}$.

data available in the literature [7], confirming the above mentioned phase transitions in the range 210 to 230 K. As reported below, magnetic susceptibility measurements also agreed with previously published data [7, 11].

ii) In slightly reduced samples ($x < 0.02$) the resistivity had again a semiconductive character, but sudden instabilities, of about two orders of magnitude, were observed below 230 K.

iii) Sharp resistivity drops, more than 11 orders of magnitude (below the sensitivity limit of the instrument, i.e. 10^{-6} Ω) were always displayed by all the samples with lower oxygen content, viz., for $0.09 < x < 0.26$. In Figs. 3 and 4, the resistance vs. temperature curves of the samples with $x = 0.26$ and 0.09, respectively, are reported. The former sample, after a sudden drop at 230 K, did not show any measurable resistance down to 10 K and recovered a high value of resistance at about 230 K upon reheating. A similar behavior was presented by the sample with $x = 0.09$, but for the fact that two instabilities were apparent (Figure 4). In other samples of the mentioned compositions, the temperatures at which the resistivity changes abruptly were always found in the 180–230 K range. No measurable resistivity was detected below these temperatures. The above behavior was reproducible in subsequent thermal cycles of resistivity measurements under vacuum between 300 and 10 K on a given sample. However, somewhat different temperatures associated with the resistivity changes, possibly due to hysteresis, were found in some cases.

As for the magnetic susceptibility data recorded on these samples, a relatively intense field of 5000 G was used to bring out the different behavior of the two oxides. In Fig. 5, the data are plotted vs. T for samples of CuO (a) and $CuO_{1-0.26}$ (b). The slope step in curve (a) between 230 and 210 K corresponds to the paramagnetic-antiferromagnetic transitions in agreement with [7]. In curve (b) the changes in slope associated with the same transition, are better defined. Curve (b) is shifted toward lower values of the susceptibility, due to the lower amount of Cu^{2+} ($3d^9$) in the $CuO_{1-0.26}$ sample with respect to stoichiometric CuO.

It can be argued that the resistance drops can not be assigned to the presence of metallic copper. In fact, due to the geometry of the samples, the lower limit of the sample resistance, in the present measurements, was $2 \cdot 10^{-6}$ Ω, which corresponds to a resistivity of less than $2 \cdot 10^{-6}$ Ω cm. Since the resistivity of copper at 200 K is of the order of $1 \cdot 10^{-6}$ Ω cm, in order to explain the above results one should assume that the CuO_{1-x} samples have been nearly completely reduced to metallic copper. Such a reduction was never achieved in the present experimental conditions; actually, neither XRD nor XPS measurements could detect any copper in the studied samples.

On the other hand XRD showed the existence of two different phases: Cu_2O and CuO; both of them are known to have semiconductor character when undoped. The existence of the CuO phase in the reduced samples has been confirmed by NMR measurements [16].

One might suppose that the resistivity instabilities could arise from a small quantity of intergrain or interlayer phase displaying superconductive character. Should some percolation path be activated, this could explain the resistance drops. The interlayer (CuO–Cu_2O) phase is probably formed by reduced CuO, electron doped by the oxygen vacancies present in the CuO_4 chains.

In a more general framework, all copper oxide-based HTSCs so far discovered have Cu–O layers with apical oxygens, forming two dimensional arrays of Cu–O pyramids. The charge carriers are holes, introduced by doping the parent compounds, which are antiferromagnetic insulators as a consequence of strongly correlated Cu 3d electrons. However, a new class of recently discovered superconducting cuprates $L_{2-y}Ce_yCuO_{4-x}$ (L = Pr, Nd, and Sm) [17], is composed of two-dimensional sheets of planar square coordinated CuO_4, i.e., with no apical oxygens. These new compounds, in contrast with the previous ones, are considered to be electron doped like the oxygen reduced CuO system.

In particular, the fact that high-T_c superconductivity is observed in CuO_4 layered cuprates with both kinds of charge carriers, provides a support to the hypothesis that the resistance fluctuations observed in CuO_{1-x} could have a superconductor character. This is in agreement with several theories proposed for the mechanisms of HTSC that foresee the pairing of oxygen 2p holes mediated either by charge fluctuations, as already observed in stoichiometric CuO [6], or by spin fluctuations.

An important point of the reported experiments concerns the site of the doping charge carriers which might be located within the CuO chains, having therefore a Cu 3d character. It can be also imagined that in the CuO_{1-x} system the number of charge carriers needed to produce superconductive effects could have a threshold value, at least high enough to destroy the structural and/or magnetic order of the insulator phase, thus allowing the insulator-superconductor transition.

In conclusion, it has been proved that in the sub-stoichiometric CuO_{1-x} oxides, for $0.09 < x < 0.26$, electrical anomalies systematically occur, giving rise to dramatic resistivity changes around 200–230 K. Much more work is needed to gain a deeper understanding of these facts. Different preparation methods under carefully controlled conditions, as well as different investigation techniques can be employed to shed light on the electrical behavior of copper oxides.

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