Observation of Charge Stripes in Cupric Oxide

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One of the present intensive concerns about the high-temperature superconductors is whether charge stripes are a key to superconductivity. Here we report observation of charge stripes in the simplest copper oxide, CuO, by real-space images obtained by electron microscopy. Charge-ordered domains and normal-lattice domains exist alternatively in the vapor-grown single crystal of CuO. Since CuO consists of the Cu-O bonding, which is a basic material feature for high-T_c cuprates, the discovery of charge stripes in this basic compound has important implications for discussing the mechanism of superconductivity in complex cuprates.

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Strong spin-charge orbital coupling is coming to be viewed as an essential property of transition metal oxides that is responsible for their versatile properties. By doping antiferromagnetic insulators of transition metal oxides of a perovskite structure with charge carriers, phenomena such as colossal magnetoresistance and high-temperature superconductivity can be produced. At low dopings, charge ordering and phase separation are well developed. The doped charge carriers localize in the lattice to form stripes in manganese oxide ($La_{1-x}Ca_xMnO_3$) [1–3], and there is indirect evidence of the existence of spin-charge stripes in copper oxides (cuprates) of nonsuperconducting La_{2-x-y}-$Nd_ySr_xCuO_4$ and even superconducting $La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_{7-y}$, and $Bi_2Sr_2CaCu_2O_8$ [4–7]. Tranquada *et al.* suggested by neutron scattering that stripes of magnetic order alternate with stripes rich with electrical charges. More directly, Bianconi *et al.* proved by extended x-ray-absorption fine structure that in $Bi_2Sr_2CaCu_2O_8$ and $La_{1.85}Sr_{0.15}CuO_4$ the 1D modulation is formed by alternating stripes with distorted lattice and undistorted lattice [8]. The latest theories of high-temperature superconductivity take account of one-dimensional spin-charge density modulations (charge stripes) in the two-dimensional CuO_2 planes [9–14]. Therefore, whether the spin-charge stripe is an intrinsic property of copper oxides is of great interest.

Aimed at revealing a basic property of copper oxides (cuprates), which are often complicated by their complex compositions and inhomogeneity, we investigated cupric oxide, which has a simple structure and yet retains antiferromagnetic order. The merit of CuO is that it consists of only the Cu-O bonding, which is a basic material feature for high-T_c cuprates. The monoclinic CuO is unique among the 3*d* monoxides in departing considerably from a simple NaCl structure with a large distortion brought about by the Jahn-Teller effect [15,16]. The structure can be viewed as ribbons running along 110 and 1-10, respectively, or be considered as being composed of Cu-O zigzag chains running along the 101 and 10-1 directions. The former is similar to planar-coordinated Cu as in $YBa_2Cu_3O_7$ and the latter can be compared with the ladder-structure superconductors that are composed of parallel one-dimensional chains of copper and oxygen atoms [17,18]. CuO is shown to undergo long-range antiferromagnetic transition at $T_{N1} = 230$ K followed by an incommensurate to commensurate transition with spin reorientation at $T_{N2} = 213$ K, and strong short-range AF interactions well above T_N [19–28]. The amplitude of the calorimetric transition is small, the entropy loss below T_N is only 31% of $R\ln 2$, and the short-range order contribution above T_N is large. CuO usually showed semiconductive property due to holes naturally introduced by a slight nonstoichiometry of CuO_{1+x}. DeSisto *et al.* showed that polycrystalline CuO could contain a microquantity of Cu^{3+}, i.e., slightly rich with charges (holes), due to excess oxidation with a maximum x of 0.007 [29]. We have developed a vapor-growth method to grow clean and high quality single crystal CuO, and found electric and magnetic anomalies in hole-doped CuO [30]. Recently we found that the short-range AF is due to a strong $d_{x^2-y^2}$ orbital antiferromagnetism coupling. Further, we have found that the charges in CuO_{1+x} become ordered with the short-range magnetic ordering in CuO. This paper reports direct observation of charge stripes and one-dimensional charge transport in CuO.

For the present study clean single crystals were grown from vapor phase by modifying the chemical vapor transport (CVT) technique we have previously reported [30]. The CVT method is used because CuO decomposes into Cu_2O and O_2 before melting; thus a usual melt growth method would require a flux, which causes contamination. High purity powder of CuO (99.99%) and I_2 (99.9%) were sealed in vacuum into a quartz tube with 5 mg per cm^3 of iodine as the transport gas, then put into a two-zone electric furnace and heated for 1–2 months with the starting material end kept at 1223 K and the growth end at 1173 K. Single crystals obtained at the lower temperature end were then annealed in flowing oxygen atmosphere at 673 K for 3 days to enhance the homogeneity of the oxygen content. Lattice parameters were investigated with a four-circle x-ray diffractometer. Electron diffraction as well as a real-space image of the single crystal was investigated by the use of high-voltage electron microscopy after the usual Ar ion milling. Electric transport properties for the crystallographic a, b, c directions were measured, respectively, by a two-probe dc method with double shielding using three single crystals cut from a well-grown, large single crystal of 1 cm^3 and mechanically polished to produce two parallel sides for electrodes. For the high-resistance measurement, a ferroelectric system of Radiant RT6000HVA was used. The electrodes for the measurement were formed by cold sputtering gold onto the two polished smooth surfaces and silver plates were pressed onto the electrodes by spring to obtain Ohmic contact at all temperatures. The resistivity was deduced from the slope of the voltage-current plot.

The cell parameters a, b, c, and β at 293 K were determined by four-circle x-ray diffraction to be 4.6894A, 3.4222A, 5.1299A, 99.591°, respectively, which are consistent with the structure determined by Asbrink and Norrby [16]. An example of electron diffraction patterns observed at ambient temperature is shown in Fig. 1 (left) where weak spots can be seen in addition to the fundamental spots of CuO. The weak spots have two shapes, one related to the other in a mirror along (001), which is more clearly seen in the picture shown on the right. The weak spots suggest a nonrectangular superlattice with two variants as are illustrated by the solid and dotted lines in Fig. 2(a). The 001 spot is forbidden in the CuO lattice but appears due to the effect of double reflection of the 021 spot. Actually, however, the weak 001 spot remained at diffraction conditions when the double reflection was eliminated. The superlattice was not observed with x-ray diffractions including the very strong synchrotron x ray at Spring-8, BL02B2. The absence of the superlattice reflections in the x-ray patterns is an indication that a difference in charge density, rather than the existence of atom displacement or vacancies, is involved. As shown by previous studies by DeSisto *et al.* [29] and Zheng *et al.* [30], CuO contains a microquantity of Cu^{+3}, which explains p-type conductance in this insulator. A long-period ordering of such a small quantity of charges would account for the weak superlattice reflection, which is too feeble to be detected by the less sensitive x-ray diffraction, while electron diffraction is much more sensitive to such a difference [31]. The dark-field image of Fig. 1 shows two kinds of areas with different contrast. Bright chains of 5 nm in diameter, 10–100 nm in length are running along the [01-2] direction in one area and less-bright chains in the neighboring area; by choosing the adjacent superlattice spot the two areas turned to an opposite contrast of brightness. Figure 2 shows a key diagram of the electron diffraction pattern along [100] and a two-dimensional model of the superlattice consisting of charge (Cu^{3+}) ordering. The two variants in Fig. 2 can qualitatively explain the observed extra spots and the dark-field image suggesting that the chains in Fig. 1 are charge-ordered domains.

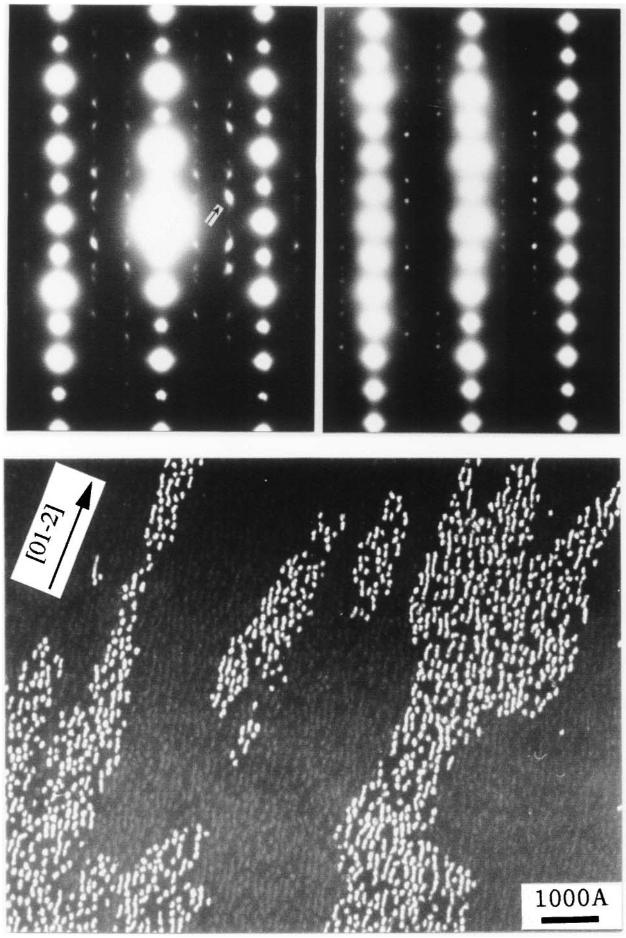

FIG. 1. Electron diffraction pattern taken along [100] and dark-field image taken with the weak spot indicated by an arrow in the pattern.

The dark-field image shows that the charge-ordered domains (bright stripes in the bright sections and less bright ones in the adjoining sections in the lower panel of Fig. 1) and normal $\mathrm{Cu}^{2+}\mathrm{O}$ sections (background) exist alternatively. The boundaries of the charge-ordered domains are slightly zigzagged with small discontinuities but are well oriented along [01-2]. Connecting the bright and darker domains, we can see that the charge-ordered domains and normal lattices are oriented in an alternative order at a spacing of about 5 nm with the charges forming stripes in the antiferromagnetically (here short-range AF) ordered $\mathrm{Cu}^{2+}\mathrm{O}$ lattice. Comparing with the report of Bianconi *et al.* that the 1D modulation of charge stripes in high-T_c cuprates is formed by alternating stripes of several nm with distorted lattice and undistorted lattice [8], it is seen that the one-dimensional distribution of charge-ordered domains analogous to the charge stripes in the manganese

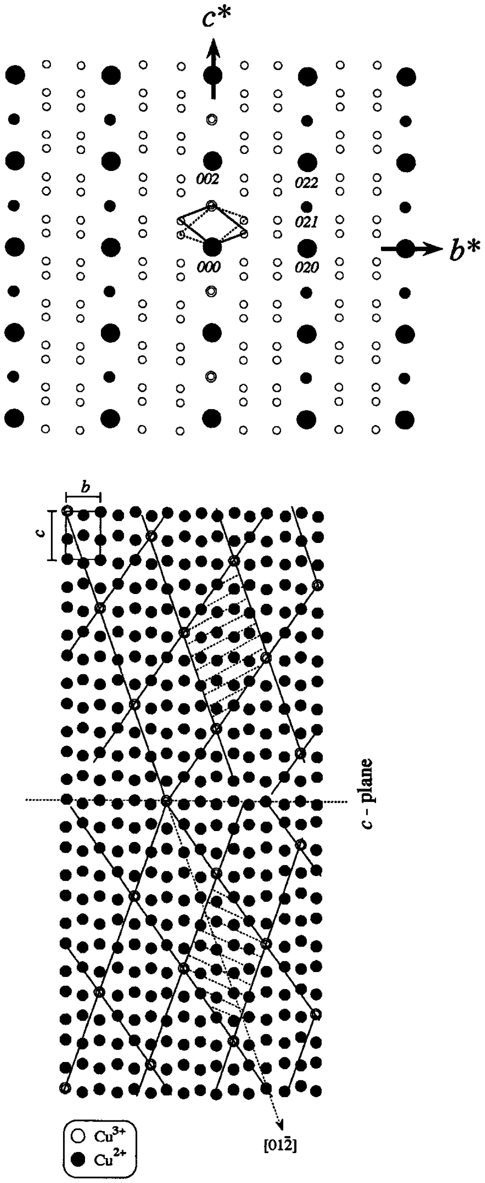

FIG. 2. Key diagram of electron diffraction pattern in Fig. 1 (●: fundamental reflection; ○: superlattice reflection; ◎: superlattice reflection + double reflection) and two variants of the superlattice projected on the (100) plane. The two variants are twinned with a common c plane.

oxides and cuprates are discovered and directly observed in the real-space image in CuO.

Evidence of one-dimensional charge transport in CuO is found in the anisotropy of resistivity for the single crystal. Figure 3 shows the resistivities (ρ's) along the three lattice axes at temperatures ranging from 300 to 100 K. In the whole temperature range, $\rho_{\parallel a}$ and $\rho_{\parallel b}$ are nearly identical while $\rho_{\parallel c}$ is more than 1 order of magnitude lower than $\rho_{\parallel a}$ and $\rho_{\parallel b}$, which clearly proves the anisotropic charge transport is consistent with the real-space image where the charge stripes run along the direction close to the c axis. The relatively high resistance of $\rho_{\parallel c}$ as compared to a

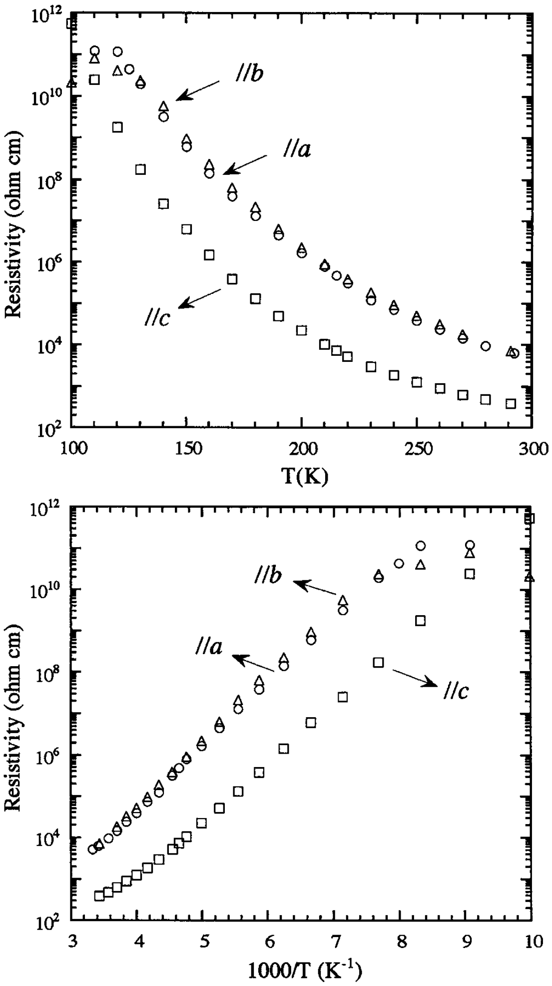

FIG. 3. Temperature dependence of electrical resistivity ρ along a, b, c axes showing anisotropic charge transport consistent with the charge stripes.

value considered for the charge stripes is attributed to discontinuities in the zigzagged stripes.

In summary, quasi-one-dimensional (zigzagged) charge stripes were found in a simpler copper oxide, CuO. This is thought to be analogous to the case of spin-charge stripes whose presence has been directly viewed in a manganese oxide and indirectly evidenced in high-temperature cuprate superconductors. The most significant result of the present work, by the observation of spin-charge ordering in the simplest copper oxide of CuO, is the suggestion that low-dimensional spin-charge ordering is an intrinsic property of the Cu-O bonded structure. This is of high interest as viewed in the ladder-structured high-temperature superconductors where doping into this much simpler structure produces superconductivity as in other complex-structured cuprates. This discovery may contribute to understanding the mechanism of superconductivity in high-temperature superconductors.

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