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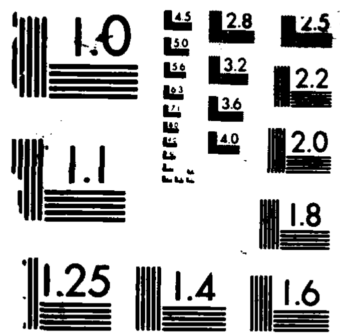

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STUDY OF THE OXIDATION STATE OF COPPER IN $La_{1.8}Sr_{.2}CuO_4$

by

Y-C. Zhang, J-H. Liu, K. Dwight, P. H. Rieger and A. Wold

Prepared for publication
in
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Brown University
Chemistry Department
Providence, Rhode Island 02912

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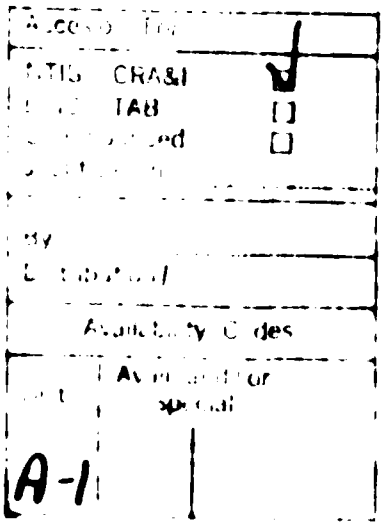

STUDY OF THE OXIDATION STATE OF COPPER IN $La_{1.8}Sr_{.2}CuO_4$

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Samples of $La_{1.8}Sr_{.2}CuO_4$ were prepared by decomposition of the nitrates. From magnetic susceptibility, temperature programmed reduction and ESR measurements it is concluded that the Cu(II) has most probably disproportionated to Cu(I), Cu(III).

Introduction

In the last few months the compound $La_{1.8}Sr_{.2}CuO_4$ has received much attention in the literature because of its high temperature superconducting transition. This compound was reported to have a superconducting transition at 36K (1-4). X-ray data from both powder diffraction and single crystals indicated that this compound has an undistorted tetragonal K_2NiF_4 type structure (1,2,5). A single crystal study has indicated that the compound crystallizes in the space group of I4/mmm (5). The coordination geometry around the copper atoms is a tetragonally elongated octahedron with four short copper-oxygen bonds d[Cu-O(1)] = 1.90Å, and two long bonds d[Cu-O(2)] = 2.41Å. The high temperature superconducting transition has been attributed to the existence of mixed oxidation states of copper in the structure (1,3), but the valence and valence distribution of copper in the compound have not been determined. The oxidation state of copper in $Ba_2YCu_3O_x$ has a crucial effect on the superconducting transition of the compound as demonstrated by a recent, careful study (6). Therefore, the determination of copper valence in $La_{1.8}Sr_{.2}CuO_4$ could be a key for the understanding of the superconducting mechanism of the compound. It is the purpose of this work to study the oxidation state of copper in the $La_{1.8}Sr_{.2}CuO_4$ structure.

Experimental

Samples of La_2CuO_4 and $La_{1.8}Sr_{.2}CuO_4$ were prepared by codecomposition of the corresponding nitrates. The starting compounds were high purity copper metal (Matthey S. 50250), La_2O_3 (Lindsay #528 99.999%), and $SrCO_3$ (Matthey 2H118, 99.999%). The copper was prereduced in 85%Ar/15%H_2 at 450°C for 6 hours. The La_2O_3 was heated at 800°C for 8 hours to drive off adsorbed CO_2 and water. The molecular weight of the $SrCO_3$ was analyzed as 147.6 by thermogravimetric analysis. A mixture of 254.2 mg copper metal, 1172.9 mg La_2O_3 and 118.1 mg $SrCO_3$ was dissolved in 6 ml of concentrated nitric acid to convert all of the initial compounds to nitrates. The solution was dried at 150°C for 12 hours and then predecomposed at 500°C for 4 hours. The sample was ground and heated at 970°C for 120 hours. During the heating the sample was taken out and ground 4 times. Finally, the sample was quenched to room temperature by taking it out of the furnace at

the elevated temperature. The sample of pure La_2CuO_4 was prepared by the same procedure.

Characterization of products

X-ray powder diffraction patterns of the samples were obtained using a Philips diffractometer and monochromated high intensity $CuK\alpha_1$ radiation (λ = 1.5405Å). The diffraction patterns were taken in the range $12° < 2\theta < 75°$ with a scan rate of 1° 2θ/min and a chart speed of 30 in/hr.

Temperature programmed reduction of $La_{1.8}Sr_{.2}CuO_4$ was carried out using a Cahn System 113 thermal balance. The sample was purged in a stream of 85%Ar/15%H_2 for 2 hours. Then the temperature was increased to 990°C at a rate of 50°/hr. The flow rate of the gas mixture was 60 ml/min.

Magnetic susceptibility measurements were carried out using a Faraday Balance (7) from 77 to 300K with a field strength of 10.4kOe. Honda-Owen (field dependency) measurements were carried out at both 77 and 296K.

Electron spin resonance spectra of $La_{1.8}Sr_{.2}CuO_4$ and La_2CuO_4 were recorded using a Bruker ER220D Spectrometer at room temperature. The frequency was ν_0 = 9.464 GHz, the microwave power was 200 mW, and the field modulation amplitude was 1 Gauss.

Results and Discussion

The x-ray powder diffraction patterns of La_2CuO_4 and $La_{1.8}Sr_{.2}CuO_4$ are given in Fig. 1(a) and (b). La_2CuO_4 shows a single phase which can be indexed on the basis of a distorted K_2NiF_4 type structure. The data obtained is consistent with those of orthorhombic La_2CuO_4 reported by J. M. Longo (8). $La_{1.8}Sr_{.2}CuO_4$ was also prepared as a single phase and could be indexed on the basis of an undistorted tetragonal K_2NiF_4 type structure. The tetragonal phase is the superconducting phase with a transition reported to be about 36K (1-3).

The average oxidation state of copper in the $La_{1.8}Sr_{.2}CuO_4$ was determined from the TPR results shown in Fig. 2. X-ray diffraction confirmed that that $La_{1.8}Sr_{.2}CuO_4$ decomposed completely during the reduction, the detectable reduction products being La_2O_3 and metallic copper (Fig. 1(c)). The reduction proceeded

according to the following equation:

$$10La_{1.8}Sr_{.2}CuO_{(2.9+0.5x)} + 5xH_2 \rightarrow$$

$$9La_2O_3 + 2SrO + 10Cu + 5xH_2O$$

where x is the average oxidation state of the copper ions. From the ratio of final and initial weights the average valence of the copper ions was determined as 2.00(±.04). There are several possibilities consistent with these results. The copper could remain all Cu^{2+}, disproportionate to Cu^{+} and Cu^{3+}, or be a mixture of all three valencies. In order to help determine the most probable oxidation state, an Electron Spin Resonance study was carried out.

In the La_2CuO_4 structure, the Cu ion has an elongated octahedral coordination with respect to oxygen (3,8). The lengths of the four short planar Cu-O bonds are 1.90Å, and the two long Cu-O bonds along the +z and -z direction are 2.43Å. Hence, the copper is actually in a square planar coordination with respect to oxygen. Wang et al. have reported that $La_{1.85}Sr_{.15}CuO_4$ has a tetragonal K_2NiF_4 structure with space group I4/mmm. The four short [Cu-O(1)] bonds and the two long [Cu-O(2)] bonds are 1.90Å and 2.41Å, respectively (5). They found that copper ions were also in a tetragonally distorted octahedral site. The copper ions in $La_{1.85}Sr_{.15}CuO_4$ are also primarily square planar coordinated with respect to oxygen. Since there is an apparent structural similarity of Cu in the two compounds, Cu^{2+} in La_2CuO_4 can be used as a standard (9) for the ESR study of $La_{1.8}Sr_{.2}CuO_4$.

The electron spin resonance spectrum of La_2CuO_4 (ν_o = 9.464GHz, room temperature) is shown in Fig. 3(a). The spectrum can be interpreted with

$g_{\parallel} = 2.310\pm0.002$, $g_{\perp} = 2.062\pm0.002$, $A_{\parallel} = (132\pm2)\times10^{-4}cm^{-1}$, and $A_{\perp} = (21\pm2)\times10^{-4}cm^{-1}$.

Such parameters are typical of Cu(II) in a square planar or tetragonally distorted octahedral site. ESR spectra of $La_{1.8}Sr_{.2}CuO_4$ show a feature with the same g-value as the perpendicular features seen in the La_2CuO_4 spectrum. However, the size of this resonance decreases with sample purification and appears to be due to a trace of the La_2CuO_4 phase. The

spectrum of one such sample, shown in Fig. 3(b) (same experimental conditions as the spectrum of Fig. 3(a)) has an intensity about 1% that of pure La_2CuO_4. This fact means that only about 1% of the copper atoms in the $La_{1.8}Sr_{.2}CuO_4$ heated at 970°C for 120 hours are in the Cu(II) state. Considering that copper in $La_{1.8}Sr_{.2}CuO_4$ has an average valence of 2.0, it is proposed that the copper has disproportionated into Cu(I) and Cu(III). Cu(II) is generally the most stable copper ion; therefore, the disproportionation is a unique characteristic of $La_{1.8}Sr_{.2}CuO_4$. This unique property is probably related to the observed superconductivity at high temperature.

The magnetic susceptibility of $La_{1.8}Sr_{.2}CuO_4$ is plotted against temperature in Fig. 4. The absence of any temperature dependence demonstrates Pauli paramagnetism over the temperature range from 77 to 300 K. Cu(II) $3d^9$ electrons are usually localized and characterized by Curie-Weiss behavior; such results were obtained by Ganguly and Rao for La_2CuO_4 (10). Since the Pauli-paramagnetic behavior of $La_{1.8}Sr_{.2}CuO_4$ is consistent with delocalized electrons, this would also indicate a high probability for the existence of Cu(I) Cu(III) formed as a result of disproportionation of Cu(II).

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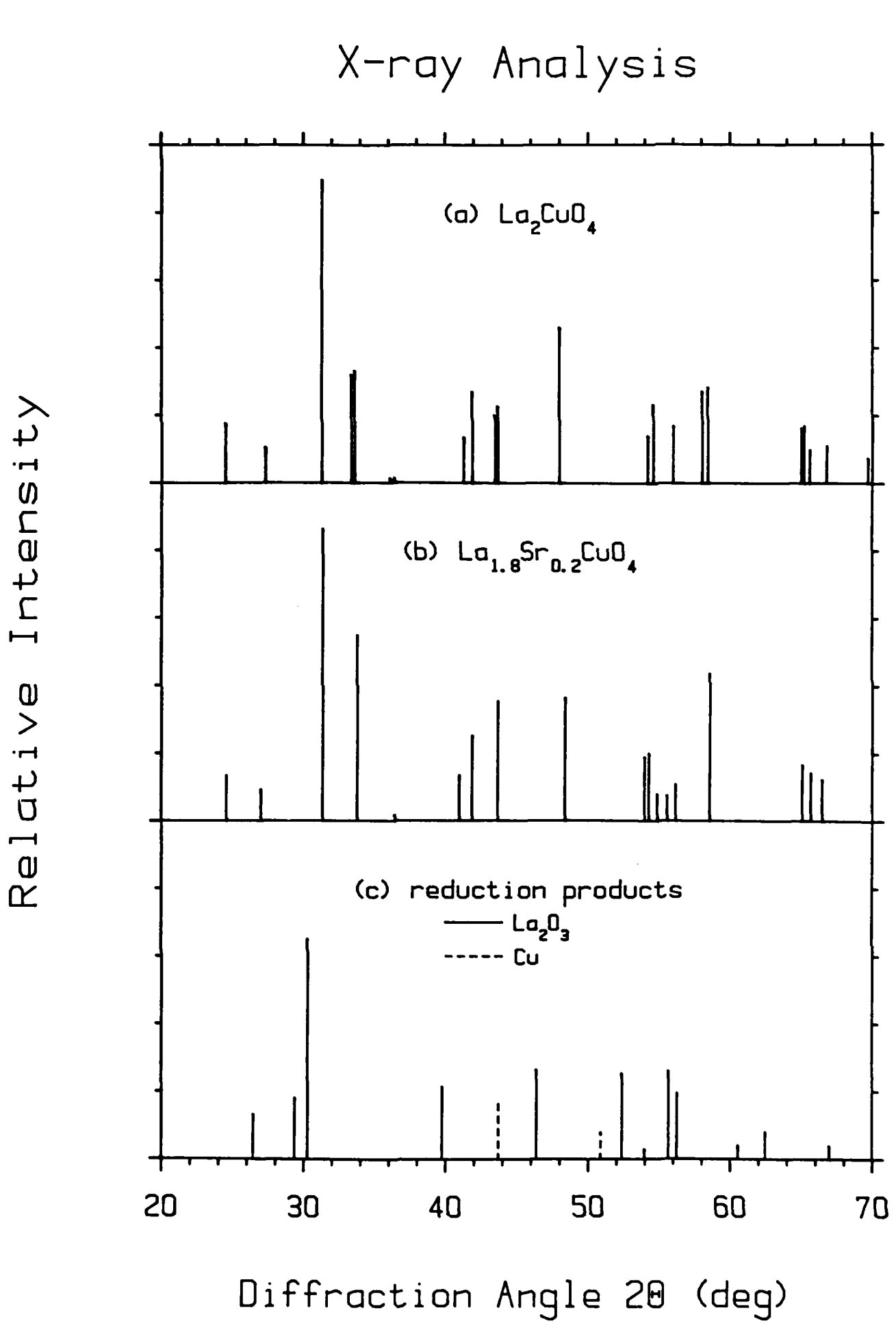
Figure Captions

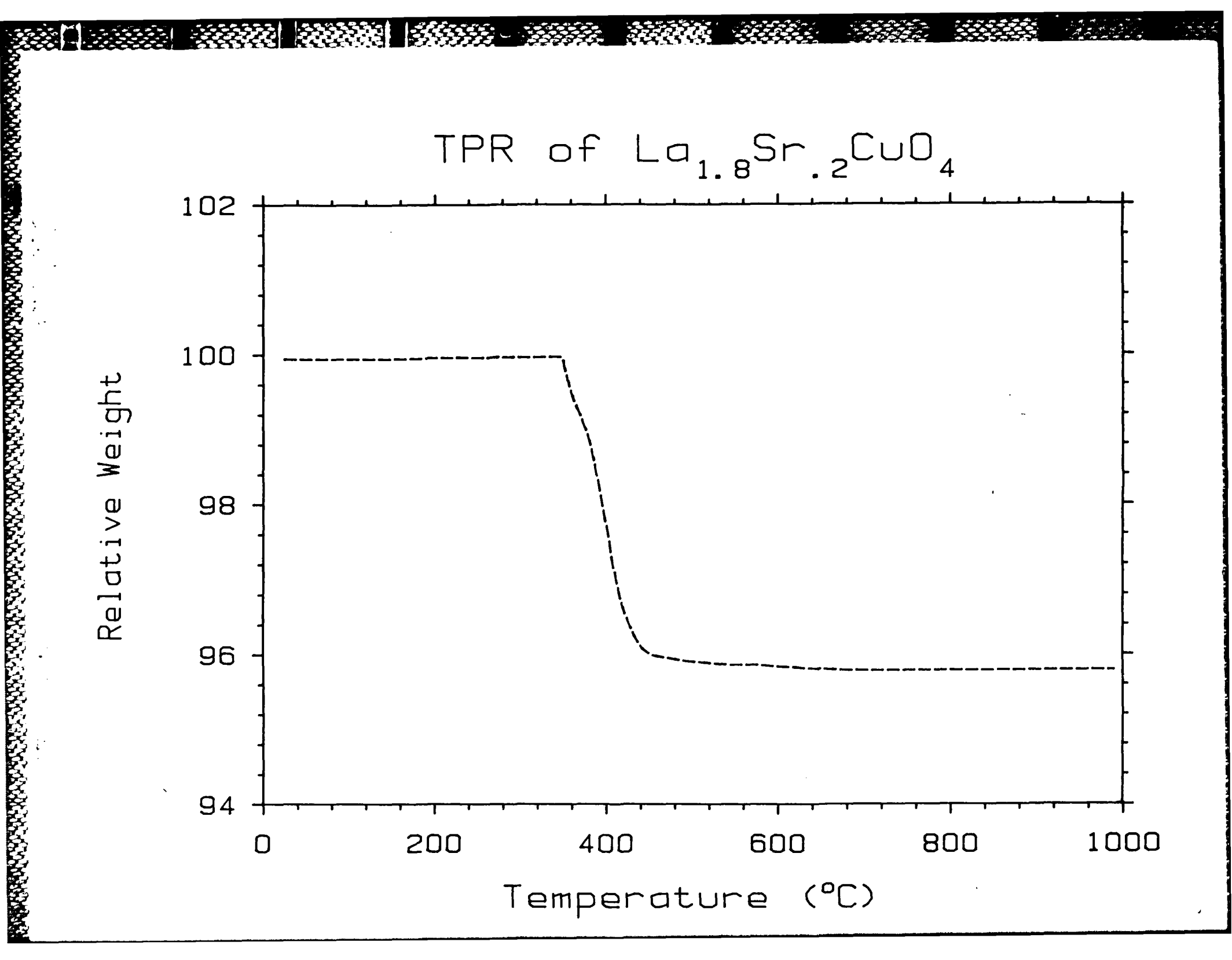
Fig. 1. X-ray diffraction patterns of (a) La_2CuO_4, (b) $La_{1.8}Sr_{.2}CuO_4$, (c) reduction products of $La_{1.8}Sr_{.2}CuO_4$.

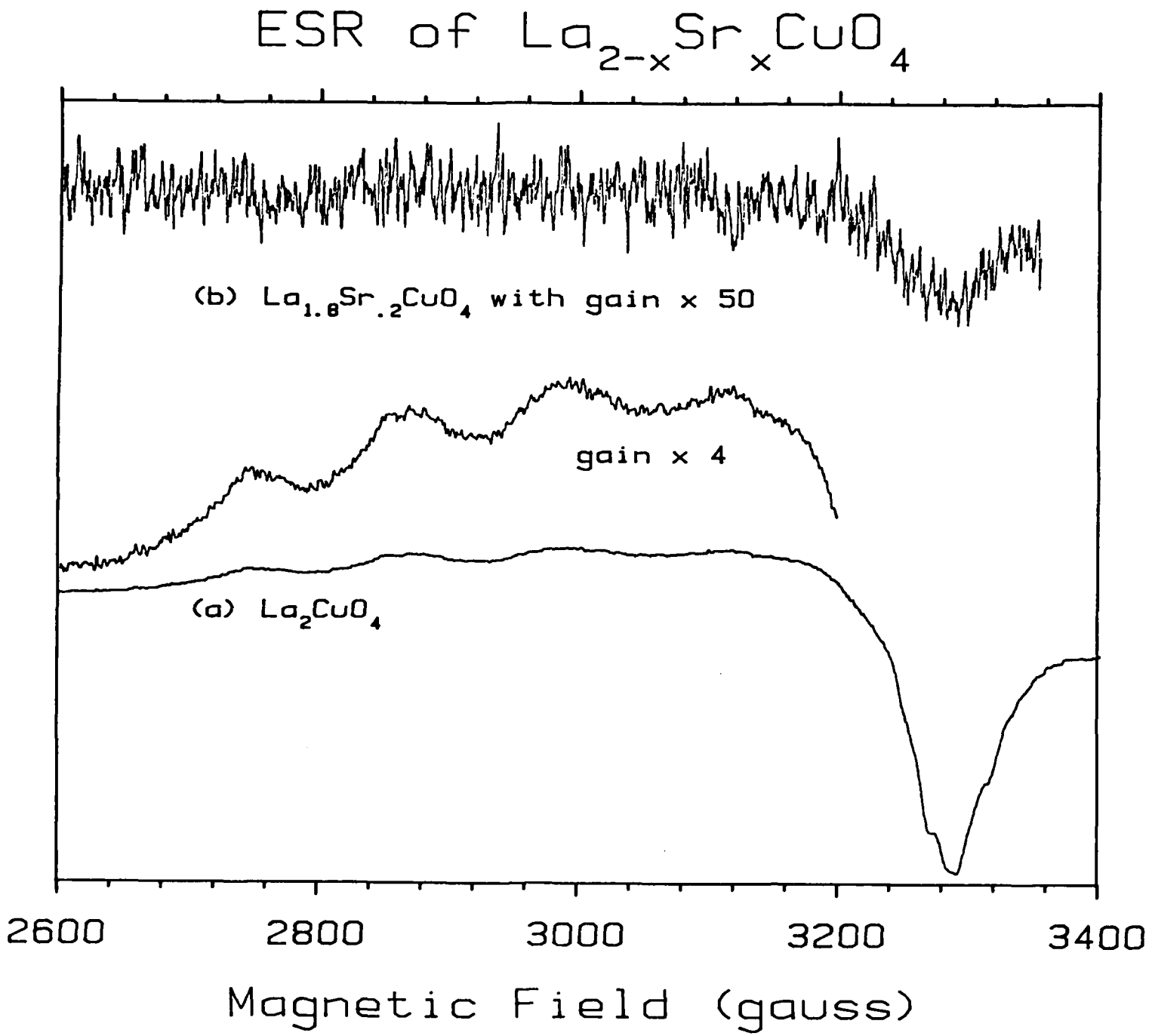
Fig. 2. Temperature programmed reduction profile of $La_{1.8}Sr_{.2}CuO_4$ in 85%Ar/15%H_2.

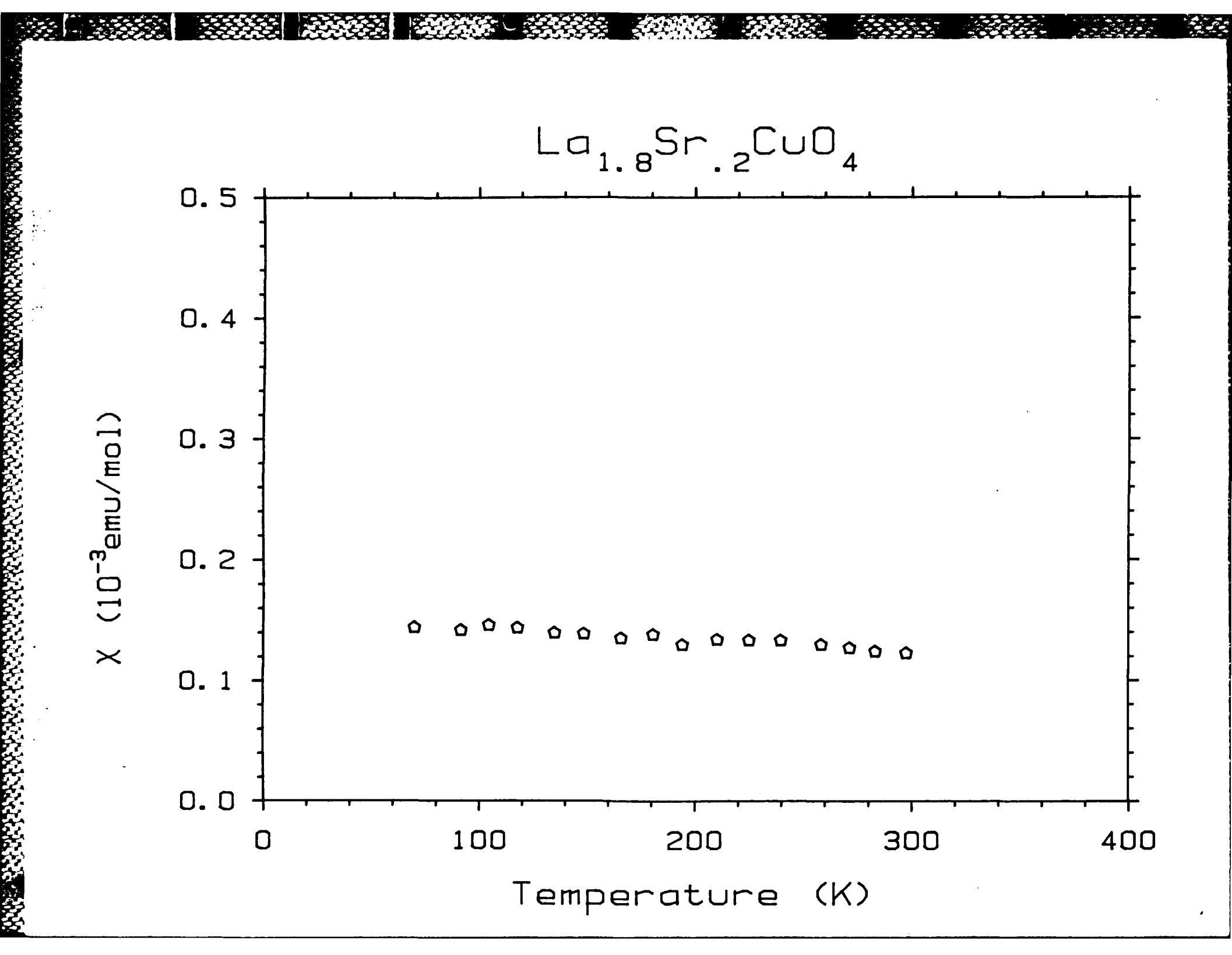
Fig. 3. X-band ESR spectra of (a) La_2CuO_4 and (b) $La_{1.8}Sr_{.2}CuO_4$. (Microwave power, 200 mW, field modulation amplitude, 1 Gauss.)

Fig. 4. Temperature dependence of the magnetic susceptibility of $La_{1.8}Sr_{.2}CuO_4$.


X-ray Analysis
(a) La_2CuO_4
(b) $La_{1.8}Sr_{0.2}CuO_4$
(c) reduction products
La_2O_3
Cu
Relative Intensity
20
30
40
50
60
70
Diffraction Angle 2θ (deg)


TPR of La1.8Sr.2CuO4
Relative Weight
102
100
98
96
94
0
200
400
600
800
1000
Temperature (°C)


ESR of $La_{2-x}Sr_xCuO_4$
(b) $La_{1.8}Sr_{.2}CuO_4$ with gain x 50
gain x 4
(a) La_2CuO_4
2600
2800
3000
3200
3400
Magnetic Field (gauss)


La1.8Sr.2CuO4
0.5
0.4
0.3
0.2
0.1
0.0
χ (10-3emu/mol)
0
100
200
300
400
Temperature (K)

END

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