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Evidence for phase transition in Cu–O ligands of the ladder material $Sr_{14-x}Ca_xCu_{24}O_{41}$

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Abstract. Measurements of the temperature dependence of the resistance in $Sr_{14-x}Ca_xCu_{24}O_{41}$, a novel cuprate having quasi-one-dimensional, two-leg Cu_2O_3 ladder planes and edge-shared CuO_2 chains, show semiconducting behaviour with a transition to a smaller band gap occurring at temperatures where large surface resistance drops have been observed. At the same temperature changes in the Curie–Weiss dependence of the susceptibility are observed as well as changes of the *g* values of the EPR spectrum of the Cu^{2+} ions in the chains. The effects are suggested to be due to a structural phase transition in the CuO_2 chains possibly resulting from a charge ordering transition in the chains.

1. Introduction

There has been considerable interest in the so-called 'ladder' phases of strontium copper oxide having the general formula $Sr_{n-1}Cu_{n+1}O_{2n}$ because of the prediction that they may be high-temperature superconductors. These materials have parallel planes of copper oxides, but are distinguished from the known copper oxide superconductors by a different arrangement of the coppers and oxygens in planes resembling a ladder-like structure. Theoretical calculations by Dagatto and Rice [1] Rice *et al* [2] and Sigrist *et al* [3] have predicted that these ladder systems should be frustrated antiferromagnets and that materials having $n = 3, 7, \ldots$ lightly doped with holes would have a spin gap and display singlet superconductivity 'on a separate but higher temperature scale'. Materials with even *n* are not predicted to have a spin gap. Several workers [4–6] have synthesized these ladder phases using high-pressure methods and shown, from temperature-dependent susceptibility and NMR measurements, evidence for the existence of a spin gap in $SrCu_2O_3$, but not in $S_2Cu_3O_5$, supporting, in part, the predictions of Rice *et al*. However, to date there has been no report of bulk superconductivity or superconducting fluctuations in these particular ladder phases, perhaps because of the difficulty of achieving the necessary light hole doping under high-pressure synthesis.

Large, highly-reproducible decreases in surface resistance at 9.2 GHz followed by large increases at lower temperature have been observed in the ladder phase $Sr_{14-x}Ca_xCu_{24}O_{41}$ at temperatures as high as 280 K, which are similar to features observed as materials become superconducting [7]. These results were suggested to be associated with superconducting fluctuations followed by a charge density, wave-driven, metal–insulator transition occurring primarily in the surface layers of the grains in the order of the penetration depth of the microwaves [7]. The drop in surface resistance shifted systematically to lower temperature

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with increased calcium content. Under ambient pressure synthesis the maximum calcium content is $x = 10$, however, Uehera *et al* [8] have recently synthesized this material under high pressure with a higher calcium content of $x = 13.6$.

The unit cell of $Sr_{14-x}Ca_xCu_{24}O_{41}$ is orthorhombic and composed of layers of [Sr]–[CuO_2]–[Sr]–[Cu_2O_3]... along the *b*-axis [11]. The CuO_2 layers consist of one-dimensional arrays of edge-shared square CuO_4 ligands. The Cu_2O_3 form two-dimensional planes having the ladder structure corresponding to an $N = 2$ ladder, which has been predicted to have a spin gap and superconductivity. Evidence has been presented from analysis of the temperature dependence of the susceptibility for the opening of a spin gap in this material at lower temperature, but this gap was suggested to occur in the chains rather than the ladder-like planes [9, 10, 12]. The electrical conductivity of the material was attributed to hole mobility in the chains and the ladders were concluded to be magnetically inert [9].

In this paper we report anomalies in the temperature dependence of the resistance and susceptibility as well as changes in the *g* values of the electron paramagnetic resonance (EPR) of the Cu ion in the same temperature region as the surface resistance drops in the same sample, suggesting the existence of a phase transition in the chains, either a structural phase transition and/or a charge ordering transition.

2. Experimental methods

The $Sr_{14-x}Ca_xCu_{24}O_{41}$ phase is synthesized by mixing and grinding stoichiometric amounts of $SrCO_3$, $CaCO_3$ and CuO into fine powders and then pressing the samples into pellets. The pellets, contained in open ceramic boats, are then heated in air at 900 °C for 16 h. The pellets are then slowly cooled, reground and pressed into pellets and re-fired in air at 900 °C for another 16 h. X-ray diffraction of the synthesized sample was used to verify the formation of the $Sr_{14-x}Ca_xCu_{24}O_{41}$ phase by comparison with previously published data [11]. The Ca-containing samples typically have a two-probe resistance at room temperature less than 100 Ω. Samples with no calcium have a higher two-probe resistance, typically 350 Ω.

The surface resistance at 9.2 GHz is measured using a microwave bridge arrangement, which has been previously described in detail [13]. EPR resonance measurements were made using a Varian E-9 EPR spectrometer operating at 9.2 GHz. Four-probe resistance measurements are made in the conventional way with the sample mounted on the cold head of an Advanced Research Systems closed cycle displex dewar. Magnetic susceptibility measurements were made using a George Associates Faraday force magnetometer.

3. Experimental results

Although some of the properties of the surface resistance of the material have been previously reported, they are reproduced here to show that it occurs in the samples in the same temperature region where the other effects are observed and it is also analysed differently than in [7]. Figure 1 is a plot of the surface resistance against temperature in $Sr_{10.8}Ca_{3.24}Cu_{24}O_{41}$ showing that the surface resistance increases with decreasing temperature, indicative of semiconducting behaviour followed by an abrupt drop and rapid increase at lower temperature. Since the surface resistance is proportional to $\rho^{0.5}$, where ρ is the resistivity, the temperature dependence of the surface resistance in a semiconducting material will be given by

$$R_s \sim \exp(\Delta/4kT) \tag{1}$$

A plot of $\ln(R_s)$ against $1/K$ from 270–180 K above the surface resistance drop yields a straight line in accordance with equation (1) as shown on the insert in figure 1. A band gap of 0.2 eV

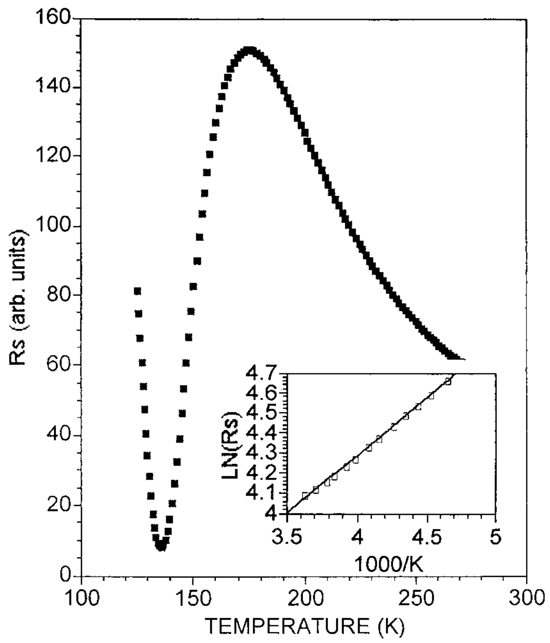

Figure 1. Temperature dependence of the surface resistance in $Sr_{10.8}Ca_{3.24}Cu_{24}O_{41}$.

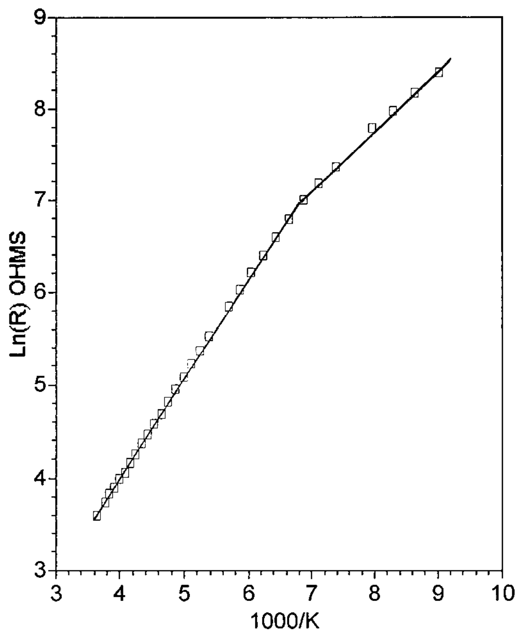

Figure 2. Plot of the logarithm of the bulk resistivity against the reciprocal of absolute temperature in $Sr_{10.8}Ca_{3.24}Cu_{24}O_{41}$.

is obtained from the fit. The temperature dependence of the bulk resistance also indicates semiconducting behaviour. Figure 2 is a plot of the natural logarithm of the resistance against

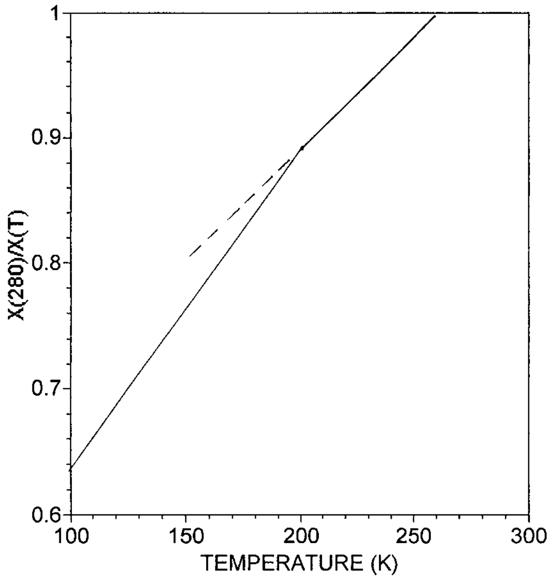

Figure 3. Inverse of susceptibility normalized to value at 270 K against temperature.

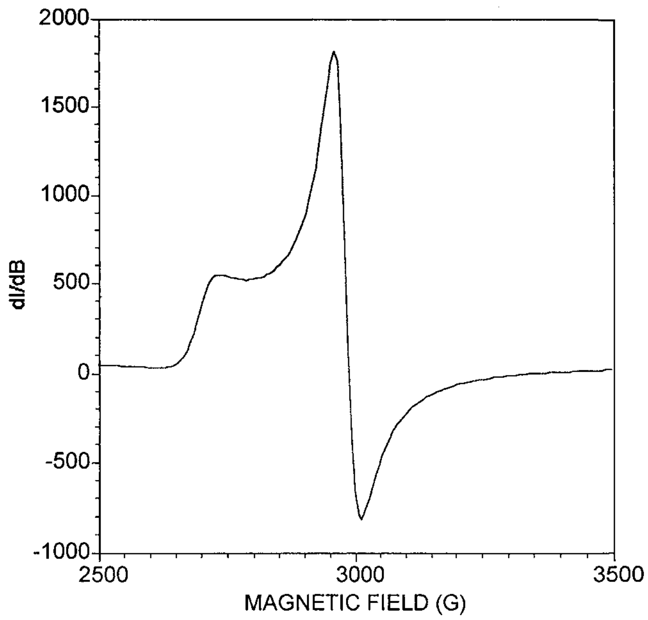

Figure 4. Powder EPR spectrum of the Cu^{2+} ion in as-synthesized samples of $Sr_{10.8}Ca_{3.24}Cu_{24}O_{41}$. The copper ion has an axisymmetric g tensor.

$1/K$ showing the semiconducting behaviour with a transition to a smaller band gap at 143 K; corresponding to the temperature of the minimum of the drop in the surface resistance. Uehara *et al* [14] have also observed a similar change in the slope of ln ρ against $1/K$ in $Sr_{14}Cu_{24}O_{41}$. Above 143 K the band gap is determined to be 0.2 eV, in agreement with that obtained from the temperature dependence of the surface resistance and below 143 K the band gap is 0.08 eV.

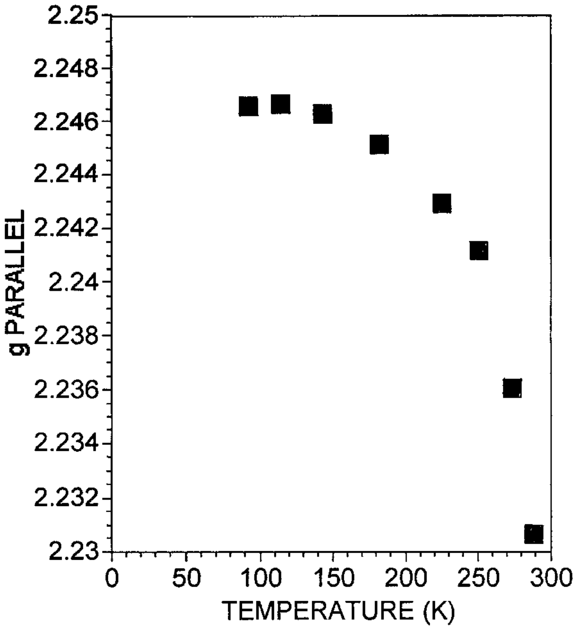

Figure 5. Temperature dependence of the parallel component of the g tensor, $g_{\parallel}$.

Cusps in the bulk resistance, similar to those observed in the surface resistance data, are not observed for materials having a Ca content less than 10, but have been observed in materials with a higher Ca content [8].

A plot of the reciprocal of the susceptibility against temperature, shown in figure 3, yields a straight line consistent with Curie–Weiss behaviour, but displays a small change in slope in the same temperature region where the resistance and surface resistance discontinuities are observed. Figure 4 shows the EPR powder spectrum obtained in the as-synthesized samples of $Sr_{14-x}Ca_xCu_{24}O_{41}$. The spectrum is consistent with that from a Cu^{2+} ion having an axially symmetric g tensor with g values at room temperature of $g_{\parallel} = 2.230$ and $g_{\perp} = 2.045$. Below the transition the symmetry remains axial but the g values change to $g_{\parallel} = 2.247$ and $g_{\perp} = 2.055$. Figure 5 is a plot of the temperature dependence of $g_{\parallel}$ showing a gradual increase as the temperature is lowered, reaching a constant value at a temperature corresponding to the minimum of the surface resistance cusp and break in the log plot of the resistance. It should be noted that the g values are measured by comparing the field position of the Cu signal with that of a DPPH sample which is in the cavity. This insures that the g shifts are not a result of any changes of the frequency of the resonant cavity which might occur because of the larger surface impedance changes. Because the geometry of the copper oxide ligands is different in the ladder planes than in the chains, two EPR spectra having different g values might be expected. However only one spectrum is observed. In fact because the Cu–O distances are not equal as they are in the chains, a spectrum arising from the coppers in the ladders should have an orthorhombic g tensor. The observed axial g tensor suggests the EPR spectrum is arising from the Cu^{2+} in the chains. This conclusion is in agreement with previous analysis of the temperature dependence of the susceptibility by Carter *et al* [9] which showed that the susceptibility only arises from the chains and that the ladder planes are magnetically inert due to the existence of a large spin gap in the ladder planes. In the conventional copper oxide superconductors, the Cu^{2+} ion in the copper–oxygen planes also does not have an EPR signal.

4. Discussion and conclusion

It has been shown that doping of $Sr_{14}Cu_{24}O_{41}$ with calcium introduces holes into the CuO_2 chains and the Cu_2O_3 ladders remain undoped and do not contribute to the susceptibility or conductivity of the material because the spin gap in the ladders is already open below 400 K, i.e. the Cu spins are paired to form singlets and thus do not contribute to the susceptibility of the material [9]. This is also consistent with our observation of only one EPR spectrum having an axisymmetric g tensor. This suggests that the discontinuities in the bulk resistance, susceptibility and changes in g values of the EPR of Cu^{2+} are associated with the CuO_2 chains and not the Cu_2O_3 planes. We have observed similar discontinuities in surface resistance, bulk resistance and susceptibility in materials such as $LiCuO_2$ which only contain edge-shared CuO_2 chains, further supporting this conclusion [15]. The temperature dependence of the resistance shown as a semi-logarithmic plot in figure 2 indicates a transition from a semiconducting state to a semiconducting state having a smaller band gap. In the same temperature region there is a change in the Curie–Weiss dependence of the susceptibility, as indicated by a break in the plot of the reciprocal of the susceptibility against temperature. The g values of the EPR of the Cu^{2+} ion which arise from the copper in the chains are different above and below the transition. A plausible explanation for these effects is a phase transition in the CuO_2 chains; a slight change in the Cu–O bond lengths possibly induced by a charge ordering transition on the chains. It is interesting that similar changes have been observed in Cu–O distances in some high temperature superconductors slightly above T_c [16, 17].

Because the same band gap is obtained from the surface resistance and resistance data above the transition temperature, it is concluded that the surface resistance above the transition temperature is reflecting the bulk behaviour of the sample. However, the very large drop in the surface resistance is not manifested in the bulk resistance in the samples having a low calcium content, indicating that the phenomena giving rise to this effect is occurring in the surface of the grains that are probed by the microwaves and which may have a different oxygen content than the bulk of the sample. This possibility is supported by the fact that the temperature of the surface resistance drops is very sensitive to oxygen and nitrogen annealing [7]. It is interesting that the surface resistance effects occur at the same temperature regions were the other bulk effects are observed. It has previously been suggested that the surface resistance cusp is due to superconducting fluctuations followed by a metal–insulator transition in the surface regions of the material [7]. An alternative, but not unrelated possibility, is that the cusp in the surface resistance or peak in the microwave conductivity is due to the collective mode of a charge density wave. Similar conductivity peaks have been observed as a function of temperature near the transition temperature in materials such as TaS_3 which undergo charge density wave transitions [18]; however, further work is necessary to verify this.

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