Studies on Li-doped $Ca_{0.85}Sr_{0.15}CuO_2$: the prototype of cuprate family of oxide superconductors

B LAKSHMI BRINDA, U V VARADARAJU and G V SUBBA RAO

Materials Science Research Centre, Indian Institute of Technology, Madras 600 036, India

Abstract. The layer-type compound, $Ca_{0.85}Sr_{0.15}CuO_2$, which is the prototype of the cuprate family of high T_c oxide superconductors is an electronic insulator, and has a low ordered moment at 300 K indicating that Cu^{2+} ions are highly correlated. Doping with lithium (up to $x = 0.15$) decreases the room temperature resistivity drastically (from 10^3 ohm·cm to 0·6 ohm·cm) but metallic behaviour is not induced below 300 K. The magnetic moment on Cu^{2+} remains low but our studies did not show any antiferromagnetic ordering below 300 K in any of the Li-doped phases.

Keywords. Layered copper compounds; Li doping; high temperature superconductors.

1. Introduction

The compound, $Ca_{0.85}Sr_{0.15}CuO_2$ with the layer structure (Siegrist *et al* 1988) is interesting for the following reasons: (i) It is the prototype of the high T_c copper oxide superconductors (HTSC) of the Bi and Tl families, viz. $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ and $Tl_mBa_2Ca_{n-1}Cu_nO_{2n+2+m}$ $m = 1, 2$; $n = 1, 2, 3$ (Rao 1988a, b; Rao and Raveau 1989; Ramakrishnan and Rao 1989). The $(Ca_{0.85}Sr_{0.15})$ plane does not contain any oxygens and the CuO_2 planes are all well-defined (figure 1). (ii) It is an insulator (semiconductor) similar to the parent HTSC phases, viz. $Bi_2Sr_2YCu_2O_{8.5}$, $TlBa_2YCu_2O_7$ and $YBa_2Cu_3O_6$ (Ganguli *et al* 1989; Hervieu *et al* 1988; Torardi *et al* 1987). (iii) The Cu^{2+} has a magnetic moment, despite a low value of 0·5 μB and the compound orders antiferromagnetically with a fairly high Néel temperature $(T_N = 537 \pm 5K)$ (Vaknin *et al* 1989). This behaviour is analogous to the parent HTSC insulating phases which order antiferromagnetically at high temperature. Hence a detailed understanding of the properties of the prototype compound, $Ca_{0.85}Sr_{0.15}CuO_2$, can help in elucidating the mechanism of HTSC in the mixed copper oxides. It is to be noted that pure $CaCuO_2$ does not have a layer structure and incorporation of Sr at the Ca-site is essential to stabilize the desired layer structure.

In the present work we have attempted to introduce charge carriers by doping with monovalent Li ions at the Ca-site. In this process mixed valence can be created at the Cu site (Cu^{2+}/Cu^{3+}) and hopping of holes resulting in improved conductivity. In the ideal case, we may expect a metallic behaviour similar to $La_{2-x}Sr_xCuO_4$. We present the X-ray, magnetic susceptibility and resistivity data for the phases, $Li_x(Ca_{0.85}Sr_{0.15})_{1-x}CuO_2$ $(x = 0 - 0.15)$.

2. Experimental

Compounds were prepared in polycrystalline form by the high temperature solid-state reaction of high purity $CaCO_3$ (Cerac, 99·99%), $SrCO_3$ (Cerac, 99·99%), CuO (Cerac,
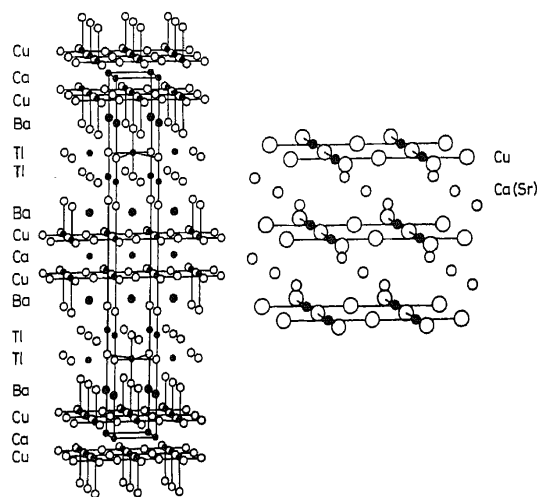
Figure 1. Structures of $Tl_2Ba_2Ca_1Cu_2O_8$ and $Ca_{0.85}Sr_{0.15}CuO_2$.

99.9%), Li_2CO_3 (Cerac, 99.99%) in stoichiometric amounts. The mixture was calcined at 910°C for 24 h and cooled, reground and heated at 920°C for 24 h. The black powder was pelletized (WC-lined stainless steel die and plungers; 8 mm dia, 1–2 mm thick; 3 tons/cm² pressure) and again heated in air at 930°C for 24 h and cooled. The Li-doped samples were prepared in the range of $0 \leqslant x \leqslant 0.25$ in steps of 0.05.

The phase formation was tested by X-ray diffraction (XRD) using a Phillips, PW-1140 unit (CuKα-rad; Ni- filter; 40 kV; 20 mA). Lattice parameters were obtained by LSQ fitting of the high angle (*hkl*) lines. Electrical resistivity was measured on sintered pellets by four-probe Van der Pauw technique using a closed cycle He refrigerator (CTI cryogenics, USA; model 21C) in the range 150–300 K. Metallic indium contacts on the pellets were provided using an ultrasonic soldering iron. Magnetic susceptibility data were collected using the SQUID magnetometer (Quantum Design model 1822 MPMS, USA) in the range 4·2–350 K.

3. Results and discussion

3.1 *Structure and stability*

The compounds are black in colour and stable. The XRD patterns of the pure compound (figure 2) $Ca_{0.85}Sr_{0.15}CuO_2$ indicated a single-phase formation and the lines could be indexed on the basis of tetragonal unit cell with space group $P4/mmm$. The LSQ fitted lattice parameters given in table 1 are in very good agreement with those reported by Siegrist *et al* (1988). The XRD patterns of $Li_x(Ca_{0.85}Sr_{0.15})_{1-x}CuO_2$ are similar to that of the pure phase up to $x = 0.15$ indicating single phase nature (figure 2 and table 1). Li doping decreases the a and c values. For $0.2 \leqslant x \leqslant 0.25$ impurity lines of CuO and Ca_2CuO_3 were seen in addition to those of
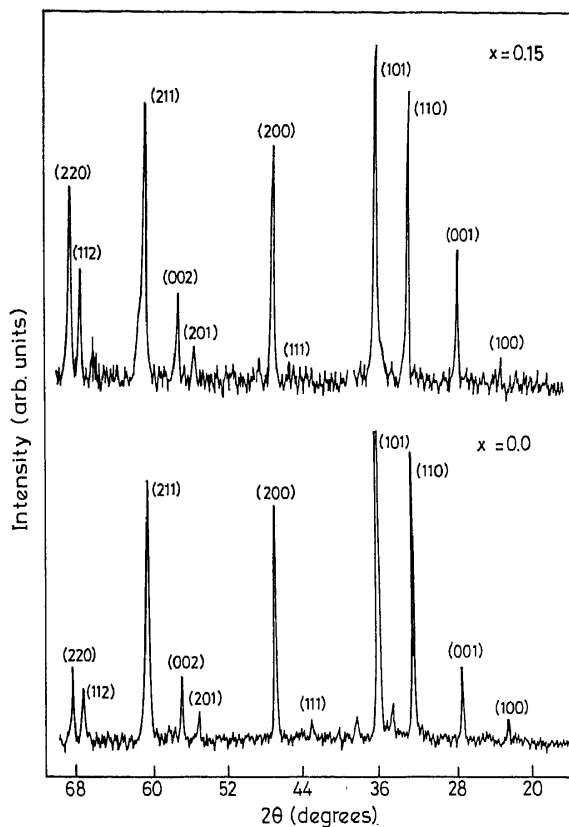
Figure 2. X-ray diffraction patterns of $Li_x(Ca_{0.85}Sr_{0.15})_{1-x}CuO_2$. x values are shown.

Table 1. Structure and property data on the $Li_x(Ca_{0.85}Sr_{0.15})_{1-x}CuO_2$ system

Composition	Tetragonal lattice param.		Resistivity, Ω cm		E_a(eV)	p_{eff} B.M
	a(Å)	c(Å)	$\rho_{300\,K}$	$\rho_{150\,K}$		
$x = 0$	3·88	3·23	3×10^3	—	—	0·1
	(3·86)*	(3·20)*				(0·5)*
$x = 0·05$	3·88	3·23	2·15	25·18	0·1 (300–210 K)	0·15
					0·06 (210–150 K)	
$x = 0·1$	3·87	3.22	0·78	15·37	0·08 (300–150 K)	0·21
$x = 0·15$	3·87	3.22	0·55	21·60	0·1 (300–150 K)	0·15

*Values in parenthesis are from Siegrist *et al* (1988) and Vaknin *et al* (1989).

$Ca_{0.85}Sr_{0.15}CuO_2$. For $x > 0.25$ the XRD patterns are complex and could not be indexed.

Substitution at the calcium site by Mg^{2+}, Ba^{2+}, Y^{3+}, La^{3+} and Ce^{4+}, at the copper site by Fe^{2+} and Ni^{2+}, and at the oxygen site by F^- was tried by the solid-state reaction method but did not yield single-phase materials.

3.2 *Electrical properties*

The pure phase $Ca_{0.85}Sr_{0.15}CuO_2$ is found to be an insulator with a room temperature resistivity $(\rho_{300K}) \sim 10^3 \, \Omega \, cm$ (table 1) as observed by Siegrist *et al.* As expected resistivity decreases with increasing Li content (table 1). Drastic decrease occurs for x as small as 0·05. Much smaller decrease in $\rho_{300\,K}$ occurs for further increase in x. However, all compounds showed only semiconducting behaviour below room temperature and no metallicity was noted (figure 3). Measurements were restricted to the range of 150–300 K due to the high resistivity of the samples below 150 K. No measurements could be carried out on the pure $Ca_{0.85}Sr_{0.15}CuO_2$ phase below room temperature again due to high resistance.

The activation energy (E_a) was calculated from the slope of the Arrhenius plot of $\log \sigma$ vs $1000/T$ where $\sigma = 1/\rho \, ohm^{-1} cm^{-1}$. The E_a values are low (0·06–0·1 eV) for the Li-containing phases (table 1). For the $x = 0.05$ sample we notice a break in the $\log \sigma$ vs $1/T$ plot at 210 K, the significance of which is not clear to us at present.

3.3 *Susceptibility measurements*

The molar susceptibility vs temperature plots for the pure and lithium-doped phases are shown in figure 4. Our value of χ_M for pure compound, viz. 1.3×10^{-5} emu/mole at 300 K is smaller than the value of 4×10^{-5} emu/mole reported by Vaknin *et al* (1989). However, the χ-T dependence in the range of 50–300 K is the same in both measurements. The rise in χ_M below 50 K is due to the small amounts of magnetic impurities. For Li-doped compounds, the $\chi_{M,300K}$ values are large by an order of magnitude compared to the pure sample. The χ-T dependence in the range 140–300 K is more or less temperature-independent and χ_M increases below 140 K. The data for
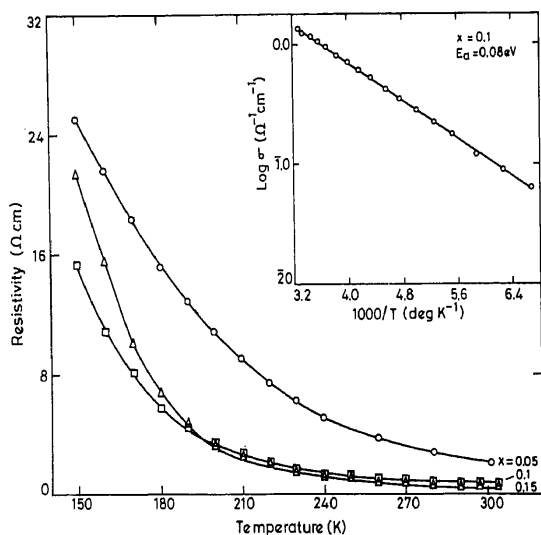

Figure 3. Resistivity plots of $Li_x(Ca_{0.85}Sr_{0.15})_{1-x}CuO_2$. x values are shown. Inset is the Arrhenius plot to get activation energy.
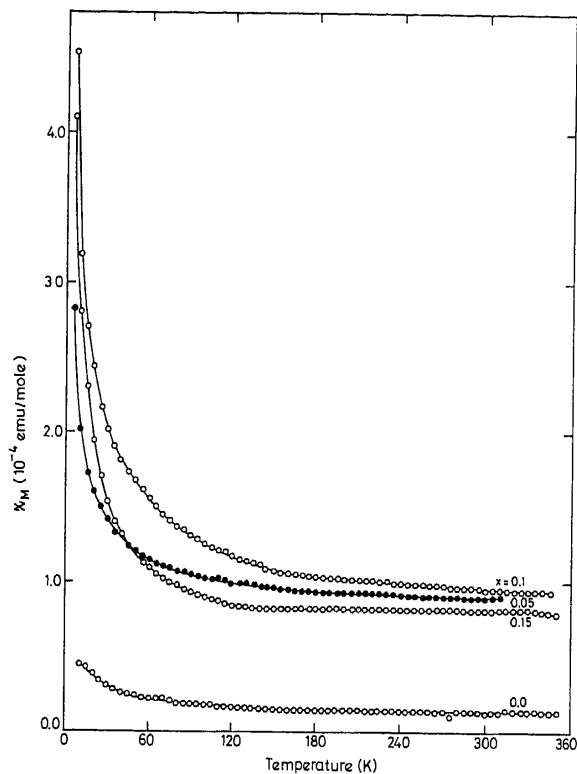
Figure 4. Magnetic susceptibility vs temperature plots for $Li_x(Ca_{0.85}Sr_{0.15})_{1-x}CuO_2$. x values are shown.

the pure and Li-doped ($x = 0.05, 0.1$) phases were fit to a modified Curie Weiss law: $\chi = \chi_0 + C/(T - \theta)$ where χ_0 is temperature-independent susceptibility (a sum of core diamagnetic and Van Vleck contribution), C the Curie constant and θ the Curie-Weiss temperature.

The effective magnetic moment p_{eff} was calculated from the molar C using the equation $p_{eff} = 2.83\, C^{1/2}$. The values of p_{eff} are listed in table 1. The value for the pure phase is $0.1\, \mu_B$. This is smaller than the value of $0.51 \pm 0.05\, \mu_B/Cu$ ion reported by Vaknin *et al* (1989) from their neutron diffraction data. We find that the p_{eff} slightly increases for Li-doped compounds (table 1 and figure 4).

It is known that in the $La_{2-x}Sr_xCuO_4$ system, with increase in x, the $\rho_{300\,K}$ decreases due to the introduction of Cu^{3+} ions, and a change from semiconductor-to-metallic behaviour occurs for $x > 0.05$ and superconductivity for $x \geqslant 0.15$. Simultaneously, the antiferromagnetic T_N decreases with increasing x. In the present case of $Li_x(Ca_{0.85}Sr_{0.15})_{1-x}CuO_2$, we expect a decrease in $\rho_{300\,K}$ with increase in x as is indeed observed. However, no metallicity is induced. We also expect a decrease in T_N with increase in x. However, we do not see any magnetic ordering, within the limits of our measurement, in the doped samples in the range 4.2–300 K. More careful studies including heat capacity data may throw light on this aspect.

4. Conclusions

Present studies show that the tetragonal layer type compound $Ca_{0.85}Sr_{0.15}CuO_2$ is a semiconductor with $\rho_{300\,K} \approx 10^3\,\Omega\,cm$ and is paramagnetic with $p_{eff} = 0.1\,\mu_B$ due to the highly correlated nature of the $Cu^{2+} - 3d$ spins. Lithium can be doped to the extent of 0.15 and produces a drastic decrease in the resistivity of the compound. However, no metallic behaviour is noted below 300 K. The p_{eff} remains small in the Li-doped phases but no evidence for antiferromagnetic ordering is seen below 300 K in any of the doped phases.

Acknowledgements

References

Ganguli A K, Nagarajan R, Nanjundaswamy K S and Rao C N R 1989 *Mater. Res. Bull.* **24** 103
Hervieu M, Maignan A, Martin C, Michel C, Provost J and Raveau B 1988 *J. Solid State Chem.* **75** 212
Ramakrishnan T V and Rao C N R 1989 *J. Phys. Chem.* **93** 4414
Rao C N R (ed.) 1988a in *Chemistry of oxide superconductors* (Oxford: Blackwell Sci. Publ.)
Rao C N R (ed.) 1988b in *Chemical and structural aspects of high temperature superconductors*, (Singapore: World Scientific)
Rao C N R and Raveau B 1989 *Acc. Chem. Res.* **22** 106
Siegrist T, Zahurak S M, Murphy D W and Roth R S 1988 *Nature (London)* **334** 231
Torardi C C, Mc Carron E M, Bierstedt P E and Sleight A W 1987 *Solid State Commun.* **64** 497
Vaknin D, Caignol E, Davies P K, Fischer J E, Johnston D C and Goshorn D P 1989 *Phys. Rev.* **B39** 9122