Characterization of $\text{La}_{1-x}\text{Sr}_{1+x}\text{Cu}_{5-x}\text{Fe}_x\text{O}_{12+\delta}$ ($0 \leq x \leq 1.0$) by dc electrical conductivity, magnetic susceptibility and EPR measurements

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Abstract. The DC electrical resistivity results of $\text{La}_{1-x}\text{Sr}_{1+x}\text{Cu}_{5-x}\text{Fe}_x\text{O}_{12+\delta}$ ($0 \leq x \leq 1.0$) showed that for S1 ($x = 0$) and S2 ($x = 0.25$) the temperature coefficient of resistivity (TCR), $\text{d}\rho/\text{d}T$, is positive and slightly increases with increasing temperature in the range 20–270 K. This shows the metallic nature of S1 and S2. For the samples S3 ($x = 0.5$) and S4 ($x = 0.75$), TCR slightly increases in the range 20–270 K, with change in sign from negative to positive at ~ 80 K and ~ 130 K, respectively. These results show the metal–insulator type transition in S3 and S4. For the sample S5 ($x = 1.0$), the TCR is negative and gradually increases in the range 20–270 K, which shows its semiconductor-like behaviour. The activation energy for S5 is found to be 0.21×10^{-2} eV. Furthermore, the DC resistivity results of S1–S5 in the range 350–660 K are in conformity with the low temperature results. The very weak temperature dependence of magnetic susceptibility results of S1–S3 show Pauli-paramagnetic behaviour in the range 77 K–400 K, while S4 and S5 exhibit Pauli-paramagnetic behaviour in the range 77–850 K. Long-range antiferromagnetic interaction is observed in S5 ($x = 1.0$) below $T_c \sim 100$ K. The room temperature EPR lineshapes gradually improve from metallic S1 ($x = 0$) to semiconductor-like S5 ($x = 1.0$). Negative g -shift is observed in the samples S2–S5 with increasing trend in g_{iso} -values of 1.880 in S2 to 1.961 in S5. However, the g_{iso} -value for S1 could not be observed due to very poor lineshape.

Keywords. Electron paramagnetic resonance; magnetic susceptibility; dc electrical resistivity; cuprates.

1. Introduction

The oxygen deficient perovskites (Michel *et al* 1985, 1987) can exist as superconductors (Bednorz and Müller 1985; Rao *et al* 1987; Torrance *et al* 1988), as metallic non-superconducting compounds like $(\text{La}_{1-x}\text{Sr}_x)_8\text{Cu}_8\text{O}_{20}$ ($0.16 \leq x \leq 0.24$) (Er-Rakho *et al* 1988), $(\text{La}_{1-x}\text{Sr}_x)_8\text{Cu}_8\text{O}_{20-\epsilon}$ ($x = 0.1666, 0.2, 0.2381, 0.25$) (Otzschi *et al* 1992), $(\text{La}_{1-x}\text{Sr}_x)_8\text{Cu}_4\text{O}_{16}$ ($x = 0.1429$) (Otzschi and Ueda 1992) and as semiconductor-like as in $(\text{La}_{1-x}\text{Sr}_x)_8\text{Cu}_8\text{O}_{16+\delta}$ ($x = 0.70$ – 0.80) (Otzschi *et al* 1993) depending on their composition and structures. Considering the wide application potentialities of these perovskites as superconducting to semiconducting materials, it is worth investigating these materials to understand their structure and physical properties. In this paper, we report our investigations on characterizing $\text{La}_{1-x}\text{Sr}_{1+x}\text{Cu}_{5-x}\text{Fe}_x\text{O}_{12+\delta}$ ($0 \leq x \leq 1.0$) by DC electrical conductivity measurements, magnetic susceptibility measurements and electron paramagnetic resonance (EPR) spectroscopy.

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2. Experimental

The samples were prepared by solid state reaction. The appropriate mixtures of dried La_2O_3 , CuO and Fe_2O_3 were heated in platinum crucibles at 1173 K for 6 h followed by heating the samples at 1273 K for 24 h, in air atmosphere. The compositions of the samples are shown in table 1.

The bars from the powdered samples were prepared at 104 daN pressure by a hydraulic press and sintered at 1273 K for 18 h. The bars were then polished on emery papers and accurate dimensions were taken. The DC electrical resistivity measurements of the bars were carried out by four-probe method in the range 20–270 K at 1K interval in air atmosphere and in the range 350–660K at 5K interval in 250 mbar He atmosphere. The magnetic susceptibility of the samples were measured using a Setaram Faraday balance in an external magnetic field of 0.3T in the temperature range 77–850 K and further for the sample S5 in the range 4.2–300 K. Finely powdered samples were used to record the EPR spectra of the samples. The X-band EPR spectra at 300 K were recorded on a Bruker spectrometer system (Model ER 200D) fitted with a double cavity TE_{110} . In all the cases, 100 kHz magnetic field modulation was used. The measured g -values were calibrated with respect to the Bruker strong pitch ($g = 2.0028$).

3. Results and discussion

In the above series, $\text{La}_{4-x}\text{Sr}_{1+x}\text{Cu}_{5-x}\text{Fe}_x\text{O}_{12+\delta}$, the samples were prepared in the range $0 \leq x \leq 3.5$ using the preparation procedures mentioned above. Interestingly samples in the range $0 \leq x \leq 1.0$ form tetragonal phase, whereas in the range $1.2 \leq x \leq 2.0$, mixed tetragonal and cubic phases and in the range $2.5 \leq x \leq 3.5$, the cubic phase are formed. In this paper, our study is restricted to the samples in the tetragonal phase in the range $0 \leq x \leq 1.0$. The oxygen contents in the samples S1–S5 were determined by DTA and TG analyses as discussed elsewhere (Das 1993).

In figure 1a, we present our observed DC electrical resistivity versus temperature plots in the range 20–270 K of samples S1–S5 (table 1). The plots show that in the samples S1 ($x = 0$) and S2 ($x = 0.25$), the temperature coefficient of resistivity (TCR), $d\rho/dT$ is positive and slightly increases with increasing temperature in the range 20–270 K. This behaviour can be characterized by the following equation for the specific conductivity σ , of metals or metallic conductors (West 1986a)

$$\sigma = \sum_i n_i e_i \mu_i, \quad (1)$$

Table 1. Compositions of the samples studied in the series $\text{La}_{4-x}\text{Sr}_{1+x}\text{Cu}_{5-x}\text{Fe}_x\text{O}_{12+\delta}$ ($0 \leq x \leq 1.0$).

Sample	Compositional formula	x
S1	$\text{La}_4\text{SrCu}_5\text{O}_{12+0.43}$	0
S2	$\text{La}_{3.75}\text{Sr}_{1.25}\text{Cu}_{4.75}\text{Fe}_{0.25}\text{O}_{12+0.24}$	0.25
S3	$\text{La}_{3.5}\text{Sr}_{1.5}\text{Cu}_{4.5}\text{Fe}_{0.5}\text{O}_{12+0.21}$	0.5
S4	$\text{La}_{3.25}\text{Sr}_{1.75}\text{Cu}_{4.25}\text{Fe}_{0.75}\text{O}_{12+0.17}$	0.75
S5	$\text{La}_3\text{Sr}_2\text{Cu}_4\text{FeO}_{12+0.10}$	1.0

Figure 1. **a.** DC electrical resistivity, $\rho(\Omega\text{cm})$ vs $T(\text{K})$ in the temperature range of 20–270 K of samples S1 ($x = 0$), S2 ($x = 0.25$), S3 ($x = 0.5$), S4 ($x = 0.75$) and S5 ($x = 1.0$) (table 1) and **b.** DC electrical resistivity, $\rho(\Omega\text{cm})$ vs $T(\text{K})$ in the temperature range of 350–660 K of samples S1 ($x = 0$), S2 ($x = 0.25$), S3 ($x = 0.5$), S4 ($x = 0.75$) and S5 ($x = 1.0$) (table 1). I indicates increasing and D indicates decreasing temperatures.

where $\sigma = 1/\rho$ and n_i is the charge carrier concentration with charge e_i and mobility μ_i . The above results show that S1 and S2 exhibit metallic behaviour. In the cases of the samples S3 ($x = 0.5$) and S4 ($x = 0.75$), the plots (figure 1a) show that at low temperature the TCR ($d\rho/dT$) is negative and increases in magnitude with increasing temperature until the change in sign of the TCR occurs. Above the transition temperature, in each case of S3 and S4, the TCR is positive and slightly increases in magnitude up to 270 K. The change in sign in TCR ($d\rho/dT$) through minima is ~ 80 K for S3 and ~ 130 K for S4. Such behaviour is well known in metallic alloy and metallic glasses containing d-elements, but is rather rare in metallic (or insulating) oxides or perovskites. Four main effects can account for such a minimum in the ρ versus temperature plots as pointed out by Howson and Gallagher (1988). The first one is the well known Kondo effect (Ashcroft and Mermin 1976). We think that if some magnetic Cu^{3+} or

Cu^{2+} and/or Fe^{4+} or Fe^{3+} ions were responsible for Kondo effect, it would be at least present in the samples S1 + S4, since S1 contains mixed valence Cu^{3+} and Cu^{2+} as discussed by Er-Rakho *et al* (1988). Also our Mössbauer study (Das 1993) of a Fe containing sample with $x = 3.0$, having cubic phase, revealed that 72% Fe^{3+} and 28% Fe^{4+} ions are formed in the lattice. The other effects are: scattering from two-level states but it seems only applicable to glasses and amorphous materials (Howson and Gallagher 1988), and quantum interference effect. Elastic collision with small relaxation times may give rise to quantum interferences which increase the resistivity at low temperature where they are expected to be the main scattering mechanism (Mott 1991). Quantum interferences are destroyed by inelastic scattering so that, as T increases phonon scattering leads to decreased resistivity. However, at higher temperatures normal inelastic phonon scattering becomes the predominant mechanism and the usual increase of ρ versus temperature is observed. The fourth effect which can give rise to a decrease of ρ with increasing temperature in a metallic system results from long-range electron-electron interactions (Altschuler and Aronov 1979). Such long-range interaction appears to be feasible in the systems studied. Er-Rakho *et al* (1988) reported the structure of the Fe free compound S1 ($x = 0$). The structure is built of corner-sharing CuO_6 octahedra, CuO_5 pyramids and CuO_4 square planar groups forming hexagonal tunnels in which are located the La^{3+} and Sr^{2+} ions. Furthermore, we discussed elsewhere (Das 1993) from the Rietveld analysis of the X-ray powder diffraction results of the Fe incorporated sample S5 ($x = 1.0$) that Fe and Cu are statistically distributed in the MO_6 ($M = \text{Cu}$ or Fe) octahedra. Thus long-range interaction of electrons occurs through superexchange (West 1986b) of electrons between Cu or Fe 3d orbitals via corner-shared p-orbitals of oxygen. The above third and fourth effects are expected to occur near the metal-insulator transition and lead to electronic localization (Howson and Gallagher 1988; Mott 1991). Another origin for a tendency to localization even applicable in an impurity-free or defect free crystal is the possibility of a strong electron-phonon interaction which can eventually lead to formation of polaron (Rao and Gopalakrishnan 1986).

Again, for the sample S5 ($x = 1.0$) (figure 1a) the temperature coefficient of resistivity ($d\rho/dT$) is negative within the temperature range of 20–270 K and gradually increases in magnitude from 20 K to 270 K. This result shows the semiconductor-like behaviour in S5 ($x = 1.0$) in the range 20 to 270 K. Using the Arrhenius relation as under

$$\rho = \rho_0^{E/kT}, \quad (2)$$

we calculate the activation energy, E , to be 0.2×10^{-2} eV. As expected the sample S5 exhibiting semiconductor-like behaviour has extremely low DC activation energy.

From figure 1a, it is also interesting to note that the resistivities of the samples increase gradually from S1 ($x = 0$) to S4 ($x = 0.75$) with increasing Fe content at all temperatures in the range 20–270 K. This result shows that the presence of Fe ions in the matrix increases the resistivities of the samples. Furthermore, the increasing trend in resistivity depends on the concentration of the Fe ions present in the matrix.

In figure 1b, we report our observed DC electrical resistivity, ρ versus temperature plots in the range 250–650 K, of the samples S1–S5 (table 1). In the plots, I indicates resistivity with increasing temperature and D indicates resistivity with decreasing temperature. As in the cases for the low temperature resistivity behaviour in the range 20–270 K, in the high temperature range 350–360 K also, the TCR, ($d\rho/dT$), is positive

in the I and D cases for the samples S3 and S4. Furthermore, the value of TCR ($d\rho/dT$) gradually increases from 20 K to 270 K, in the cases of increasing, I and decreasing, D temperatures for S1–S4 (table 1) in the above particular cases. This is in agreement with our low temperature results as discussed earlier. However, in the cases of samples S3 and S4, the resistivity behaviour with increasing, I, temperature is rather complex. In these cases, the TCR, ($d\rho/dT$) changes sign from positive to negative, ~ 500 K, and then again at ~ 660 K from negative to positive. It is interesting to mention here that for the samples S3 ($x = 0.5$) and S4 ($x = 0.75$) in the low temperature case (figure 1a), the resistivities are measured with increasing temperature. In these cases also, change in the sign of TCR ($d\rho/dT$) from negative to positive occur at ~ 80 K for S3 and ~ 130 K for S4. This shows the complex resistivity behaviour of S3 and S4 with increasing temperature in both the temperature ranges studied. However, in the cases of decreasing temperature for S3 and S4, the TCR does not change sign in both the cases, and from the difference in the ρ versus T plots for increasing and decreasing temperature cases, we infer that for increasing temperature for S3 and S4 (figures 1a and b) the temperatures at which TCR changes sign, an irreversible phase transition occurs. In the case of the sample S5 ($x = 1.0$) (figure 1b), the TCR ($d\rho/dT$), is negative and increases in magnitude slightly from 350 K to 650 K, for both increasing I, and decreasing D, cases. This result shows the semiconductor-like behaviour of the sample in the temperature range 350 K–660 K, and is in agreement with low temperature result of S5 ($x = 1.0$) in the range 20–270 K, as discussed earlier.

The thermal variation of $1/\chi$, the inverse magnetic susceptibility of the samples are shown in figure 2a. In the cases of samples S4 ($x = 0.75$) and S5 ($x = 1.0$) the experimental points were fitted with the usual Curie–Weiss law,

$$\chi_M = \frac{C_M}{T - \theta} + \text{TIP}, \quad (3)$$

and the values of the Curie constant, C_M , and TIP parameters are shown in table 2 along with the g_{iso} -values of the samples S1–S5 (table 1). The g_{iso} -values of the samples will be discussed later. The table shows that values of the Curie constant, C_M are fairly low. However, these values could not be ascribed to a particular metal ion, since the samples S4 and S5 contain mixed valence Cu and Fe ions.

The observed TIP values are much larger than the Van Vleck term, which may be approximately estimated as $70\text{--}80 \times 10^{-6} \text{ emu mol}^{-1}$ (Figgis 1961). The larger part of this TIP value we ascribe due to the Pauli paramagnetic behaviour of the compounds. Pauli type paramagnetism in such cuprates is also discussed by Otzchi and Ueda (1992) and Otzchi *et al* (1992, 1993).

In samples S1–S3 (figure 2a) the temperature variations of inverse susceptibility, $1/\chi$, show rather complex behaviour. From 77 K to ~ 400 K the weak temperature dependence of the magnetic susceptibility of the samples S1–S3 shows the Pauli paramagnetic behaviour in the above temperature range. However, above ~ 400 K in the above samples steep increase in $1/\chi$ value is observed. It is interesting to note that this steep increase in $1/\chi$ values have decreasing trend from S1 ($x = 0$) to S3 ($x = 0.50$) through S2 ($x = 0.25$).

Figure 2b shows the inverse susceptibility, $1/\chi$, versus $T(\text{K})$ plot of S5 ($x = 1.0$) (table 1) in the temperature range 4.2–300 K. The weak temperature dependence of the magnetic susceptibility shows the Pauli paramagnetic behaviour of S5 ($x = 1.0$) in the

Figure 2. Inverse susceptibility, $1/\chi$, vs T (K) in the temperature range of 77–850 K of samples S1 ($x=0$), S2 ($x=0.25$), S3 ($x=0.50$), S4 ($x=0.75$), S5 ($x=1.0$) (table 1) and **b.** inverse susceptibility, $1/\chi$, vs T (K) in the temperature range of 42–300 K of $\text{La}_3\text{Sr}_2\text{Cu}_4\text{FeO}_{12+0.1}$ ($x=1.0$) (table 1).

temperature range ~ 100 – 300 K as discussed above in figure 2a also. However, the sharp decrease in $1/\chi$ value below 100 K up to 4.2 K shows the long range antiferromagnetic coupling at lower temperature with Curie temperature $T_c \sim 100$ K.

Our results on EPR studies will be discussed now. In figure 3 we present our observed EPR spectra of samples S1 ($x=0$) to S5 ($x=1.0$) at room temperature. We know from our DC electrical resistivity results as discussed earlier that S1 and S2 are metallic; S3 and S4 exhibit transition from semiconductor-like to metallic at ~ 80 K and ~ 130 K, respectively, whereas S5 is semiconductor-like. This behaviour is reflected in the nature of the gradually improved EPR lineshapes of the samples from S1 ($x=0$) to S5 ($x=1.0$). The extremely weak lineshape in S1 ($x=0$) shows the presence of

Table 2. Curie constant, C_M , and TIP of samples S4 ($x = 0.75$) and S5 ($x = 1.0$) and g_{iso} -values of the samples (table 1) in the series $\text{La}_{4-x}\text{Sr}_{1+x}\text{Cu}_{5-x}\text{Fe}_x\text{O}_{12+\delta}$ ($0 \leq x \leq 1.0$).

Sample	x	C_M (emu K ⁻¹ mol ⁻¹)	TIP ($\times 10^{-5}$ emu mol ⁻¹)	g_{iso} -value
S1	0	...	...	(1.981) ^a
S2	0.25	...	...	1.880
S3	0.5	...	...	1.944
S4	0.75	0.11	215	1.954
S5	1.0	0.15	158	1.961

^a anomalous g_{iso} -values of 1.981 for S1 is discussed in the text.

Figure 3. EPR spectra of the samples in the series $\text{La}_{4-x}\text{Sr}_{1+x}\text{Cu}_{5-x}\text{Fe}_x\text{O}_{12+\delta}$ recorded at room temperature: (a) S1 ($x = 0$), (b) S2 ($x = 0.25$), (c) S3 ($x = 0.5$), (d) S4 ($x = 0.75$) and (e) S5 ($x = 1.0$) (table 1).

highly delocalized electrons in the lattice due to its metallic behaviour, whereas in S5 ($x = 1.0$), due to its semiconductor-like behaviour the electrons are less delocalized in the lattice and as a result, comparatively improved EPR lineshape is observed. Furthermore, table 2 for g_{iso} -values shows negative g -shift for all the samples. This shows positive nature of the spin-orbit coupling constant. However, such values cannot be ascribed to any particular paramagnetic ion, since all the samples contain more than one paramagnetic ions.

Furthermore, it is known from literature (Er-Rakho *et al* 1988) that the sample S1 ($x = 0$) has mixed valence of Cu^{2+} and Cu^{3+} ions. Both the Cu^{2+} and Cu^{3+} ions have negative values of spin-orbit coupling constant (Abragam and Bleaney 1970). Thus a g_{iso} -value of 1.981 with negative g -shift is an anomalous nature observed for S1. It appears plausible that because of the metallic nature of S1 a very broad and undetectable EPR signal (Ziman 1964) results and the very weak signal at the middle could be

due to impurity present in the sample. However, with the gradual increase in g_{iso} -value of 1.880 in S2 ($x = 0.25$) to 1.961 in S5 ($x = 1.0$), we ascribe to the gradual change in the net crystal field effect on Cu and Fe ions present in the matrices.

4. Conclusion

From our above studies the DC electrical resistivity results in the range 20–270 K show that S1 ($x = 0$) and S2 ($x = 0.25$) exhibit metallic behaviour, while S3 ($x = 0.50$) and S4 ($x = 0.75$) exhibit metal-insulator type transition at ~ 80 K and ~ 130 K, respectively. The sample S5 ($x = 1.0$) exhibits semiconductor-like behaviour in the range 20–270 K. Furthermore, the DC resistivity results in the range 350–650 K are also in conformity with the low temperature results. The magnetic susceptibility results show that S1–S3, show Pauli-paramagnetic behaviour in the range 77 K to ~ 400 K, while S4 and S5 exhibit Pauli-paramagnetic behaviour in the range 77–850 K. In the case of S5 ($x = 1.0$), long-range antiferromagnetic interaction is observed at lower temperature with $T_c \sim 100$ K. The EPR lineshapes improve gradually in the samples from metallic ($x = 0$) to semiconductor-like ($x = 1.0$). Negative g -shift is observed in the case of the samples S2–S5. However, for S1, the g_{iso} -value could not be observed due to very poor lineshape.

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