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INFLUENCE OF FLUORINATION ON THE TRANSPORT PROPERTIES OF $La_{1.85-y}Sr_{0.15}Nd_yCuO_4$ NEAR THE LOW-TEMPERATURE STRUCTURAL TRANSITION.

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The influence of fluorination on thermal conductivity, specific heat, magnetic susceptibility, electrical resistivity and thermoelectric power of $La_{1.85-y}Sr_{0.15}Nd_yCuO_4$ has been investigated. The temperature variation of the thermal conductivity of the untreated samples with Nd exhibits a change in slope just below the low-temperature structural transition (LTO--->LTT), which could be associated with strong phonon-electron interactions. The specific heat of the y = 0.2 unfluorinated sample presents a jump near 50 K confirming the structural transition. Below 10 K, the specific heat of the two y = 0.8 samples (unfluorinated or fluorinated) shows an important increase with decreasing temperature, presumably associated with some type of magnetic ordering in the Nd^{3+} ions. In addition to an increase of T_c, the fluorination process suppress the anomalies observed in the thermal conductivity.

1. Introduction.

The low temperature structural transition from an orthorhombic phase stable at intermediate temperatures (LTO) to a low-temperature tetragonal structure (LTT) was first observed by Axe et al. in $La_{1.875}Ba_{0.125}CuO_4$ [1]. These authors also associated this transition to the previously observed decrease of the superconducting transition temperature [2]. Below the phase transition temperature, the Seebeck coefficient was found to exhibit a sharp drop and even to become negative, while the thermal conductivity was found to increase with decreasing temperature [3, 4]. These results indicated an important correlation between phonons and charge carriers. However, it was found that all these anomalies disappeared after a fluorination treatment, which also lead to an increase of the superconducting transition temperature [4]. It was then assumed that the fluorination treatment leads to the disappearance of the low temperature structural transition [4].

Subsequent work has shown the occurrence of a similar low temperature structural transition in the $La_{2-x-y}Sr_xNd_yCuO_4$ system [5]. Indeed in these compounds, a (LTO-->LTT) phase transition occurs for $y \geq 0.18$. The transition temperature increases from 40 K to 80 K with increasing Nd concentration. Subsequently, the superconducting transition temperature decreases and the bulk superconductivity disappears around y = 0.4 [6,7]. It seems then that the decrease or the disappearance of the superconducting properties could be associated to the low temperature structural transition. Recently, it was reported that a fluorine-gas treatment extends the bulk superconducting behaviour to all compositions with $0 \leq y \leq 1$ with a critical temperature decreasing linearly with the increase in Nd concentration from 40 K for y = 0 to 11 K for y = 1.0 [6].

We report here on the influence of the low temperature structural transition and the effect of fluorination on the transport properties.

2. Experimental procedure.

The $La_{1.85-y}Sr_{0.15}Nd_yCuO_4$ compounds were prepared by thoroughly mixing appropriate amounts of La_2O_3, Nd_2O_3, CuO and $SrCO_3$ powders each 99.9 % pure. The mixtures were preheated three times in alumina boats at 950°C in air, with intermediate grinding. The samples were then pressed into pellets and sintered under a flow of oxygen gas at 1150°C during 146 hours, with five intermediate grindings [7]. The fluorination treatments were carried out under 9 bar of pure F_2 gas for 72 hours at 150°C. The resulting products were all

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characterized by X-ray powder diffraction using a Guinier Camera (CuK_α radiation) and their composition and chemical homogeneity were thoroughly checked by microprobe analysis [6, 8]. The fluorine presence was also checked by weight uptake [8].

The thermal conductivity, electrical resistivity and thermoelectric power measurements were carried out using a previously described four probe steady state technique [4]. The influence of the radiative heat transfer between the sample and its environment was carefully taken into account. The specific heat was measured using a thermal relaxation technique [9].

3. Results and discussion.

3.1. *Effect of Nd substitution.*

The substitution of Nd for La for $y \geq 0.2$ leads to the presence of a minimum in the temperature variation of the electrical resistivity at a temperature that corresponds to the low temperature structural transition. We may observe in Figure 1 that the electrical resistance of the untreated samples first decreases with decreasing temperature, reaches a minimum, then increases. After reaching a maximum the electrical resistivity decreases again with further decrease in temperature to reach values close to zero for y = 0.2.

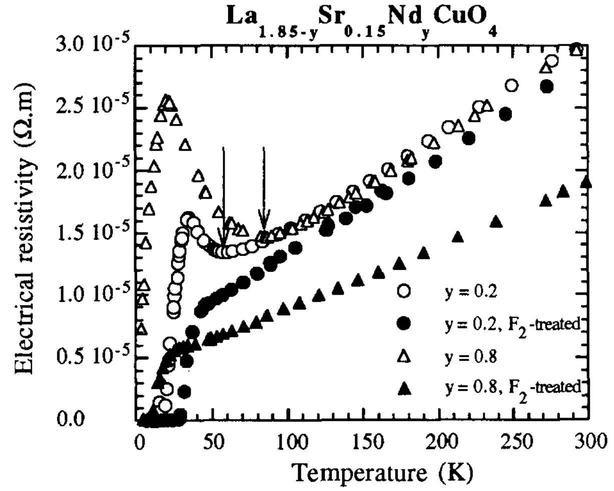

Figure1: Temperature dependence of the electrical resistivity of untreated or F_2-gas treated $La_{1.85-y}Sr_{0.15}Nd_yCuO_4$ samples (y = 0.2 and 0.8). In the unfluorinated samples, the temperature of the observed minimum increases with increasing Nd concentration.

The thermoelectric power of the $La_{1.85}Sr_{0.15}CuO_4$ sample first increases with decreasing temperature (Fig. 2), then after reaching a maximum, around 120 K, it decreases slowly first with decreasing temperature, then decreases more rapidly when the temperature is close to that of the superconducting transition. The substitution of Nd for La leads to a slight decrease of the thermoelectric power for sample with y = 0.8. However, in the temperature range where the MTO phase is stable, the temperature dependence of the thermoelectric power compares well to that measured for the sample without Nd. When decreasing the temperature below that of the structural transition, the thermoelectric power of these compounds decreases more rapidly than that of the sample without Nd (see inset Fig. 2).

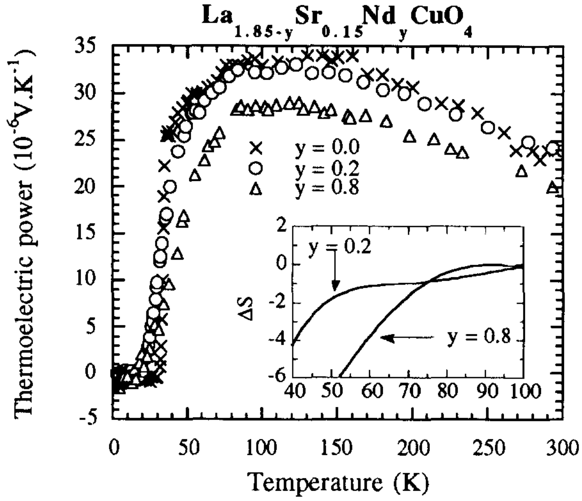

Figure 2: Temperature dependence of the thermoelectric power of samples of the $La_{1.85-y}Sr_{0.15}Nd_yCuO_4$ system, with y = 0.0, 0.2 and 0.8. The inset shows the difference between the thermoelectric power of the y = 0.2 and 0.8 samples and that of the y = 0.0 sample reported to the difference at 120 K $[(S(T)_{y \neq 0} - S(T)_{y=0}) - (S(120\ K)_{y \neq 0} - S(120\ K)_{y=0}]$.

The thermal conductivity of the untreated samples presents a peculiar behaviour at the temperature at the phase transition temperature (Fig. 3). Indeed, while the thermal conductivity decreases with decreasing temperature starting from 300 K, we observe a change in the slope at a temperature that corresponds to that of the low temperature structural transition (50-90 K range). Below this temperature, the thermal conductivity increases with decreasing temperature and, after reaching a maximum, decreases with further decrease in temperature. If the lattice thermal conductivity is dominant and primarily limited by phonon-electron scattering, a decrease of the density of charge carriers would lead to an increase in the thermal conductivity, since it reduces the frequencies of phonon-electron interactions. Also, a decrease in the density of charge carriers naturally leads to an increase in the electrical resistivity. This is exactly what is observed. Indeed, the observed minima in the temperature dependence of the thermal conductivity and of the electrical resistivity occur at the same temperature. This favours the hypothesis of a lattice thermal conductivity mainly limited by charge carrier scattering, as it seems to be the case in the parent compound, i.e. La_2CuO_4 [4].

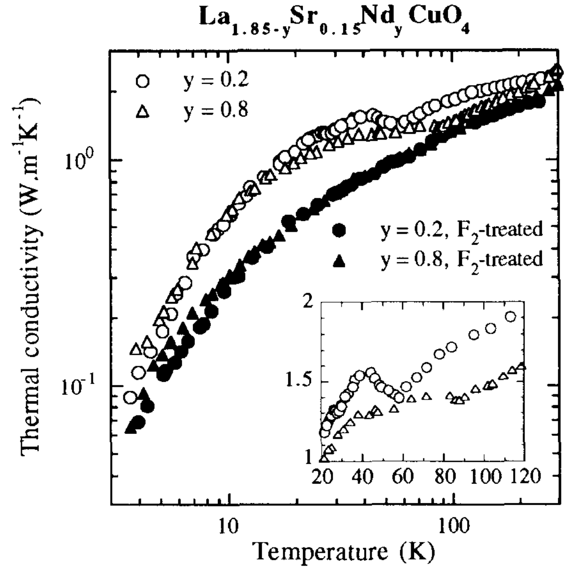

Figure 3: Temperature dependence of the thermal conductivity of untreated and of F_2-gas treated $La_{1.85-y}Sr_{0.15}Nd_yCuO_4$ (with y = 0.2 and 0.8). The inset shows the temperature dependence of the thermal conductivity of the unfluorinated samples around the temperature of the LTT phase.

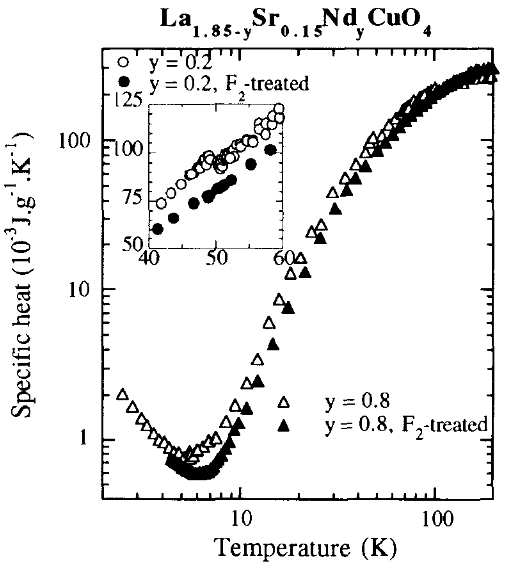

Figure 4: Temperature dependence of the specific heat of untreated and F_2-treated $La_{1.05}Sr_{0.15}Nd_{0.8}CuO_4$. The inset show the influence of F_2-treatment on C_p anomaly at the LTO-LTT structural transition for y = 0.2 samples.

The y = 0.2 sample presents an additional change in slope at the superconducting transition (around 27 K) (Fig. 3). Since the phonons are not scattered by the fraction of electrons which are in the superconducting state, the small increase observed at this temperature could then be attributed to the decrease of the phonon-electron scattering at the superconducting transition [10]. These observations confirm the presence of a strong electron-phonon scattering in this compound.

The occurrence of the low temperature structural transition is clearly apparent around 50 K in the specific heat data of the unfluorinated $La_{1.65}Sr_{0.15}Nd_{0.2}CuO_4$ (see inset of Figure. 4). No linear term was detected in the heat capacity of this sample at low temperature. Below 6 K, the specific heat of the y = 0.8 samples exhibits an important increase with decreasing temperature that seems to correspond to a Schottky anomaly and could presumably be associated with some type of magnetic ordering of the Nd^{3+} ions as it is the case for the Nd_2CuO_4 compound [11].

3.2 *Influence of fluorine treatment*

Contrary to the untreated samples, there is a clear trend in the dependence of the electrical resistivity of the fluorinated samples on Nd content in the form of a slight decrease with increasing Nd concentration (Fig. 1). The fluorine treatment leads also to a more pronounced decrease of the thermoelectric power of the y = 0.8 sample than in the case of the y = 0.2 sample (Fig. 5). The thermoelectric power depends on two parameters: the Fermi energy and the scattering parameter. The latter depends only on the nature of the scattering mechanism, i.e. phonons, static defects,... but not on the efficiency of the scattering process, i.e. on the magnitude of the relaxation time itself. On the other hand, the electrical resistivity depends also on the Fermi energy. However, it also depends directly on the magnitude of the relaxation time. Thus, for a given dominant scattering mechanism, the thermoelectric power and electrical resistivity are related only through their dependence on the Fermi energy, which is directly related to the carrier density. Thus, a parallel variation of both coefficients should be attributed to a variation of the charge carriers densities. Here we observe only a small decrease in the electrical resistivity while the thermoelectric power decreases drastically. It seems then difficult to attribute the important decrease in the thermoelectric power solely to an increase in the number of the majority charge carriers, since in that case the magnitude of the effect on both properties should have been comparable. Another possible explanation could be based on the existence of two kinds of charge carriers [12]. If holes and electrons coexist, the thermoelectric power depends on the number and the mobility of the different charge carriers. In that case, if the fluorine presence modifies the ratio between the electron and hole conductivities in favor of electrons, the thermoelectric power could decrease, while the electrical resistivity could be less modified. It would mean that the simultaneous presence of Nd and F increases the number of minority carriers, i.e. electrons.

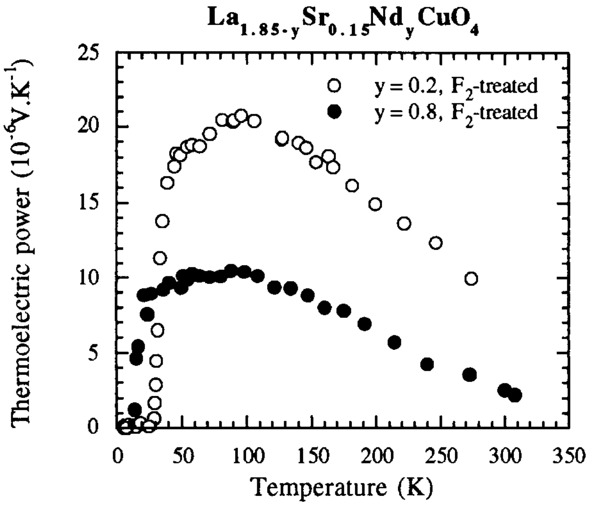

Figure 5: Temperature dependence of the thermoelectric power of $La_{1.85-y}Sr_{0.15}Nd_yCuO_4$ samples treated with F_2-gas (y = 0.2 and 0.8).

After fluorination, the anomalies in the thermal conductivity observed at the occurrence of the LTT phase disappear. We observe a monotonous decrease of the thermal conductivity with decreasing temperature. The same observations could be made for the specific heat. The intercalation of fluorine in the structure decreases the mismatch between the [(La, Nd, Sr)O] layers and the (CuO_2) layer and therefore seems to suppress the LTT phase.

4. Conclusions.

We have studied the influence of fluorination on the thermal conductivity, specific heat, electrical resistivity and thermoelectric power of $La_{1.85-y}Sr_{0.15}Nd_yCuO_4$ compounds which are known to undergo a transition to a (LTT) phase for y greater than 0.18. We have observed in the transport properties of the non fluorinated sample, the existence of anomalies at a temperature that corresponds to the apparition of the LTT phase. The F_2-gas treatment leads to the occurrence of bulk superconductivity in all studied samples, and suppresses the anomalies observed in the transport properties. These results suggest that the fluorination may suppress the low-temperature structural transition. Neutron diffraction are in progress at Los Alamos National Laboratory (U.S.A.) to verify this assumption.

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