Crystal Growth and Physical Properties of T*- Phase SmLa1-xSrxCuO4-d and T-Phase La1.6-xNd 0.4Sr xCuO 4- d

Sutjahja, I.M.

Citation for published version (APA):
Sutjahja, I. M. (2003). Crystal Growth and Physical Properties of T*- Phase SmLa1-xSrxCuO4-d and T-Phase La1.6-xNd 0.4Sr xCuO 4- d

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Chapter 4

Structural instability, superconducting and magnetic properties of T- phase La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_{4.5}$

4.1 General introduction

It has been widely accepted that the undoped precursor of a cuprate superconductor is an antiferromagnetic Mott-insulator, and that superconductivity is induced by appropriate doping with charge carriers. Generally, the kinetic energy of the mobile carriers in the doped system must compete with the superexchange interaction between neighboring Cu spins [1, 2]. Under certain conditions, where the kinetic energy fails to overcome the superexchange interaction, the charge carriers (holes) and spins are inclined to segregate, giving rise to the observed phenomenon of static one-dimensional (1D) phase separation between the holes and spins, commonly known as a static stripe structure, associated with the suppression of superconductivity.

The La$_{2-x-y}$Nd$_y$Sr$_x$CuO$_{4.5}$ compound is a system for which a charge-stripe order induced by a low-temperature structural phase transition has been reported [3-5]. In view of the presence of an incomplete 4$f$-shell of the Nd ions and its coupling with the Cu sublattice, however, the phenomenology is considerably enriched and the physics of this system becomes more complicated [6, 7].

This chapter describes some physical properties of the La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_{4.5}$ ($x = 0, 0.1, 0.125, 0.2$) compounds, covering the temperature- and field-induced structural
phase transformation, the solid vortex-phase in the superconducting state and the magnetism of Nd$^{3+}$ ions. The Sr-free ($x = 0$) La$_{2,4}$Nd$_x$CuO$_{4-\delta}$ compound itself is a Mott insulator that shows long-range antiferromagnetic (AF) ordering of the Cu spins at around room temperature. The Néel temperature ($T_N$) as well as the low-temperature phase transitions depend sensitively on the Nd content ($y$) and oxygen content ($\delta$) in the sample [8, 9]. Low-field magnetization measurements of the Sr-doped ($x \neq 0$) compounds show, on the other hand, that they are bulk superconductors with a critical transition occurring at $T_c \sim 6.5$, 3 and 15 K for $x = 0.1$, 0.125 and 0.2 respectively, in good agreement with the result reported previously by Ichikawa et al. [10].

4.2 Temperature- and field-induced structural transition in La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_{4-\delta}$

Introduction

The structural phase transition in the La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_{4-\delta}$ compound has been intensively studied since the observation of a charge-spin stripe phase in La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_{4-\delta}$, occurring at the same temperature as the low-temperature orthorhombic-tetragonal structural transformation [3-5]. For this particular composition, it has been shown in neutron and x-ray scattering measurements that the charge and magnetic ordering temperatures reach their maximum values, whereas superconductivity is depressed in this composition. This is illustrated in Fig. 4.1, which describes a rich and complete phase diagram of La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_{4-\delta}$, including the different structural phases, the charge-spin-ordering as well as superconducting phases [10]. It has been thought that this low-temperature structural transition, that is stabilized by the Nd substitution, involves a change in the tilting pattern of the CuO$_6$ octahedra. This tilting can serve as a pinning potential for the vertical/horizontal charge stripes, leading to a competition between superconductivity and charge-spin stripe order.
Structural instability, superconducting...

Figure 4.1: The phase diagram of La_{1.6-x}Nd_{0.4}Sr_xCuO_{4+δ}. \( T_{\text{NQR}} \) and \( T_{\text{ch}} \) denote the ‘local’ and ‘global’ charge-ordering temperatures obtained from the nuclear-quadrupole resonance (NQR) and neutron/X-ray diffraction studies, respectively. \( T_m \) and \( T_c \) denote successively the magnetic ordering and superconducting transition temperatures obtained from neutron diffraction studies and susceptibility measurements, respectively. The shaded area indicates the coexistence of LTO and LTT phases [10].

Depending on temperature as well as on hole and rare-earth (Nd) concentrations, four different phases can be identified in the La_{2-x}Nd_{y}Sr_xCuO_{4+δ} system. These are the high-temperature tetragonal (HTT) phase (space group \( I4/mmm \)), the low-temperature orthorhombic (LTO) phase (Bmab), the intermediate second low-temperature orthorhombic (LTO1) or low-temperature less-orthorhombic (LTLO) phase (Pccn) and the low-temperature tetragonal (LTT) phase (\( P4_2/ncm \)) [11, 12]. Within the phenomenological description [13], these phases are characterized in terms of the order parameters \( Q_1 \) and \( Q_2 \), which measure the tilt of the CuO_6 octahedra from the \( [110]_{\text{HTT}} \) and \( [\overline{1}0]_{\text{HTT}} \) axis, respectively. The HTT phase is characterized by \( Q_1 = Q_2 = 0 \), the LTO phase by \( Q_1 \neq 0, Q_2 = 0 \) or vice versa, the LTO1 phase by \( Q_1 \neq 0, Q_2 \neq 0, Q_1 \neq Q_2 \) and the LTT phase by \( |Q_1| = |Q_2| \neq 0 \), as schematically presented in Fig. 4.2.
Figure 4.2: (a) Schematic picture of the CuO$_6$ octahedra tilting, in terms of the order parameters $Q_1$ and $Q_2$. (b) Tilting of the CuO$_6$ octahedron in the HTT, LTO and LTT phases.
In both LTO and LTT phases, the CuO$_6$ octahedrons are tilted with respect to the crystallographic axes by an angle $\Phi < 5^\circ$. The tilt angle $\Phi$ is roughly the same in the LTO and the LTT phases, while the different directions of the tilt produce different buckling patterns of the CuO$_2$ plane. In the LTO phase the tilt axis is parallel to [110]$_{HTT}$, and rotates discontinuously by $\theta = 45^\circ$ towards the [100]$_{HTT}$ direction at the transition into the LTT phase.

The structural phase transition in La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_{4-\delta}$ ($x = 0, 0.1, 0.2$) single crystals reported in this section is the result of a study by means of specific-heat, resistivity, and magnetic susceptibility measurements.

**Experimental**

Single crystals of La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_{4-\delta}$ ($x = 0, 0.1, 0.125, 0.2$) were grown using the travelling-solvent floating-zone (TSFZ) method in a four-mirror furnace. For simplicity, the four samples of La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_{4-\delta}$ are named by Sr-0.00 for $x = 0$, Sr-0.10 for $x = 0.1$, Sr-0.125 for $x = 0.125$, and Sr-0.20 for $x = 0.2$. Samples of various sizes were prepared for different measurements by cutting the as-grown crystal boule in air.

The electrical resistance measurements were carried out by means of the standard four-point method using a low-excitation Linear Research LR-700 ac-resistance bridge. The normal-state magnetic susceptibility measurements were conducted by means of a commercial Quantum Design MPMS-5S magnetometer. The data were taken in the ZFC and FC modes using a scan length of 4 cm. The specific heat was measured using a relaxation method, by means of a commercial Quantum Design PPMS magnetometer. These measurements were performed in the temperature range of 1.6 to 300 K with different temperature steps and in different applied fields. In order to refine the data at temperatures around the structural phase transitions, the measurements have been repeated several times at each of those temperatures.
Results and Discussion

A. Thermal and Transport Properties

The result of zero-field specific-heat measurements for the as-grown Sr-0.00, Sr-0.10 and Sr-0.20 samples are given in Figs. 4.3 (a), 4.4 (a) and 4.5 (a). The data clearly show an anomaly at temperatures around $T_{LT}$: (70 - 85) K, 65 K and 82 K for the Sr-0.00, Sr-0.10 and Sr-0.20 samples, respectively, corresponding to the LTO - LTT (LTO1) structural transformation. These transition temperatures are in good agreement with the phase diagram shown in Fig. 4.1. Apparently, the magnitude of the anomaly decreases monotonically in those samples in the order of Sr-0.10, Sr-0.20, and Sr-0.00. It is to be noted that the structural phase transition in the Sr-0.00 sample revealed by the $c/T$ data in Fig. 4.3 (a) seems to take place in a rather broad temperature range, which might be due to the gradual nature of this transition, as commonly found in samples with an excessive oxygen content [8]. A distinct sign of this transition is, on the other hand, clearly indicated by the specific-heat data presented in Fig. 4.4 (a) for the Sr-0.10 sample.

The enthalpy changes due to this structural transformation, $\Delta H$, can be calculated from the area under the $\Delta c/T$ vs $T$ curve according to the relation $\Delta S = \int (\Delta c/T) dT$, where the integration is taken over the temperature range around the anomaly. With $\Delta c$ representing the specific-heat anomaly extracted from the data after subtraction of the smooth background, we obtained $\Delta H = \Delta S T_{LT} \approx 16.25$ J/mol for Sr-0.10 and $\Delta H \approx 2.36$ J/mol for Sr-0.20. It should be noted that the same analysis could not be done for Sr-0.00 due to the second-order nature of the transition. This second-order (continuous) LTO - LTO1 transformation, which occurs in oxygen excess materials, becomes nearly or distinctly first-order (discontinuous) in the reduced materials [8]. Comparing the resulting $\Delta H$ values with the “universal line” given by Werner et al. [14] as described in Fig. 4.6, we predict the HTT - LTO transition temperature to be in the region of $T_{HT} \approx 450$ K for Sr-0.10 and $T_{HT} \approx 275$ K for Sr-0.20. The latter value is in good agreement with the result from resistivity measurements as will be described in
the following paragraph. This transition, however, could not be detected in our specific-heat measurement.

Figure 4.3: The temperature dependence of (a) heat capacity and (b) magnetic susceptibility of the as-grown Sr-0.00 sample. The arrows indicate the structural phase transition.
Figure 4.4: The temperature dependence of (a) heat capacity, (b) electrical resistivity and (c) magnetic susceptibility of the as-grown Sr-0.10 sample. The arrows indicate the structural phase transition. These susceptibility measurements have been taken in a field of 10 kOe, by which the superconductivity is suppressed.
Figure 4.5: The temperature dependence of (a) heat capacity, (b) electrical resistivity and (c) magnetic susceptibility of the as-grown Sr-0.20 sample. The arrows indicate the structural phase transition.
We now turn our attention to the transport data. The resistivity of the Sr-0.10 sample as shown in the inset of Fig. 4.4 (b) shows a metallic temperature dependence of $\rho_{ab}$ ($d\rho/dT > 0$) at high temperatures. The resistivity changes sharply into a semiconductor-like behavior below the structural transition temperature ($T_{LT} \approx 65$ K), followed by a broad superconducting transition at temperatures below 8 K. The $\rho_a(T)$ curve, on the other hand, shows semiconductor-like behavior in the entire temperature range of the measurement, and a steep upturn below $T_{LT}$ similar to $\rho_{ab}$. The $\rho_{ab}(T)$ curve of the Sr-0.20 sample is clearly dominated by a metallic behavior in the temperature range above 40 K. A subtle low-temperature structural transition around $T_{LT} \approx 82$ K, presumably from LTO to a mixture between LTO and LTT phases, is indicated by a slight upshift in the $\rho_a$ curve below this temperature. In addition to that, the high-temperature $\rho_a(T)$ curve also shows a kink at a temperature around 270 K, in agreement with a previous report by Nakamura et al. [12]. Based on the results of a recent room-temperature XRD analysis [15], we argue that this transition corresponds to the vanishing of the orthorhombicity or orthorhombic strain, resulting in the
orthorhombic crystal structure at lower temperature (< 270 K). We note, however, that the \( \rho_{ab} \) values of our Sr-0.10 and Sr-0.20 samples are smaller than those reported by Ichikawa et al. [10], and probably show some dependence on Nd concentration. Further, the low-temperature upturn of \( \rho_{ab} \), observed in Fig. 4.4 (b) and 4.5 (b) for the present samples, might be related to a tendency for localization of the electronic states as a consequence of the tilting of the CuO\(_6\) octahedra [12].

B. Magnetic properties

Ignoring the in-plane anisotropy, the temperature dependence of the normal-state susceptibility, \( \chi_{ab} = M/H \) (\( H//<100>_{T=300K} \) or \( H//<001>_{T=300K} \)) and \( \chi_c = M/H \) (\( H//<001>_{T=300K} \)), measured in a field of 10 kOe for Sr-0.00, Sr-0.10 and of 50 kOe for Sr-0.20 are shown in Figs. 4.3 (c), 4.4 (c) and 4.5 (c) for the data measured in the ZFC-mode below \( \sim 100 \) K. The complete data are presented in Fig. 4.7 (i).

The magnetization data, shown in these figures, exhibit an anisotropy with \( \chi_c/\chi_{ab} \equiv 1.5 \) at room temperature for all samples, in good agreement with a previous report by Sakita et al. [16]. From these figures, it is clear that there is no appreciable influence of the structural change in the \( \chi_c(T) \) curve. The \( \chi_{ab}(T) \) curves are marked by a discontinuity and hysteretic behavior (between the data taken in the ZFC and FC modes) at around \( T_{LT} \) in Sr-0.10 and Sr-0.20 samples. This seems to be correlated with their specific-heat anomalies, discussed earlier.

For a further analysis of the susceptibility behavior, the data are presented as \( \chi^{-1} vs T \) curves in Fig. 4.7 (ii). It is clear that the \( \chi_c^{-1}(T) \) curves display a Curie-Weiss like behavior, implying that the c-axis components of the Nd spins (\( S_z \)) behave as free spins right through \( T_{LT} \). The \( \chi_{ab}^{-1}(T) \) curves, on the other hand, are consistent with Curie-Weiss behavior only above \( \sim 100 \) K, and become flattened below this temperature as typically found in an antiferromagnet. This change of behavior seems to imply that the in-plane components of the Nd spins (\( S_x \) and \( S_y \)) are more sensitively influenced by the gradual ordering of the Cu spins below \( T_{LT} \). It is interesting to note further, that the inverse susceptibility, \( \chi^{-1}(T) \), in all directions feature practically the
Figure 4.7: The temperature dependence of (i) susceptibility and (ii) inverse susceptibility of (a) Sr-0.00, (b) Sr-0.10 and (c) Sr-0.20 samples, measured in an applied magnetic field parallel (χ_{ab}) and perpendicular (χ_{c}) to the ab-plane. The solid lines are the linear fit to the χ^{-1}(T) data in the temperature range of 100 \leq T \leq 350 \text{ K}.
same slope for $T > 100$ K, irrespective of the magnetic field direction. Below 100 K, however, the curves exhibit the anisotropic crystalline electric field (CEF) effect, which can be taken into account by the following expression,

$$\frac{1}{\chi(T)} = \frac{1}{\chi_{CEF}(T)} + \frac{T - \Theta}{C_{Nd}}$$ (4.1)

where $\Theta$ is the paramagnetic Curie-Weiss temperature, and $C_{Nd} = N\mu_{eff}^2/3k_B$ is a Curie constant of the Nd$^{3+}$ ions with the parameter $N$ denoting the number of Nd$^{3+}$ ions per mole, $\mu_{eff}$ is the effective magnetic moment of the Nd$^{3+}$ ion, while $k_B$ is the Boltzmann constant. The results of a linear fitting of this expression with the $\chi^{-1}(T)$ data in the temperature regime above 100 K are tabulated in Table 4.1. It is seen from this table that the values for the effective moment tend to increase with increasing Sr content, and that they are larger than the free-ion value of $\mu_{eff} = [J(J+1)]^{1/2}g_J\mu_B = 3.62 \mu_B$. These results are comparable with results given in previous reports by Tranquada et al. [5], Sakita et al. [16] and Xu et al. [17].

**Table 4.1:** The values of the effective magnetic moment, $\mu_{eff}$, and the Curie-Weiss temperature, $\Theta$, determined from a linear fit of Eq. (4.1) with $\chi_{ab}$ and $\chi_c$ data in the temperature range of 100 ≤ $T$ ≤ 350 K.

<table>
<thead>
<tr>
<th>La$<em>{1.6-x}$Nd$</em>{0.4}$Sr$<em>x$CuO$</em>{4.5}$</th>
<th>$H$//($ab$)</th>
<th>$H$//c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\mu_{eff,ab}$</td>
<td>$\Theta_{ab}$</td>
</tr>
<tr>
<td>Sr-0.00</td>
<td>3.91</td>
<td>146.61</td>
</tr>
<tr>
<td>Sr-0.10</td>
<td>4.30</td>
<td>225.53</td>
</tr>
<tr>
<td>Sr-0.20</td>
<td>4.46</td>
<td>242.21</td>
</tr>
</tbody>
</table>

The isothermal magnetic-hysteresis loop measurements of the Sr-0.00 sample, as depicted in Fig. 4.8, show that this sample is weakly ferromagnetic at low temperatures, i.e. below 10 K, as a result of the antisymmetric Dzyaloshinskii-Moriya (DM) interaction between the Cu spins [7, 18]. It is to be noted that the onset temperature of this weak ferromagnetic behavior depends on the oxygen content in the...
sample [8]. An onset temperature up to 30 K has been reported by Crawford et al. [8] for a sample with reduced oxygen content.

![Figure 4.8: Isothermal magnetic-hysteresis loop of the Sr-0.00 sample, measured at T = 2 K and 5 K in magnetic field applied along (a) ab-plane and (b) c-axis of the crystal.](image)

The unusual magnetic field effect on the LTO - LTT(LTO1) structural transformation is corroborated by the result of field-dependent specific-heat measurements given in Fig. 4.9 for the Sr-0.10 sample. Our experimental data at a maximum applied field of 90 kOe reveal a shift in the transition temperature ($\Delta T_{LT}$) and a change in the associated entropy jump. We observed further, that the relative shift in temperature of the maximum of the anomaly depends on the field direction (//ab-plane or //c-axis), both in magnitude and sign. Although the precise value of $\Delta T_{LT}$ from our data and that reported by Xu et al. [17] differ, the trend we observe is consistent in that an in-plane field $H//(a,b)$ leads to an increase of $T_{LT}$, while a perpendicular field ($H//c$) tends to reduce $T_{LT}$. Based on the magnetoresistance measurement, they reported that a maximum applied field of 140 kOe yields a shift of $\Delta T_{LT} \sim +0.25$ K for $H//(a,b)$, which changes sign with a slightly smaller value for $H//c$. This behavior constitutes evidence for the coupling between the low-temperature
structural phase transition and the associated spin structure [12, 17]. A Cu spin-reorientation transition followed by weak ferromagnetism at lower temperature, induced by the low-temperature LTO - LTT(LTO1) transition, has also been observed in Sr-free La$_{2-y}$Nd$_y$CuO$_{4+\delta}$ [8, 9].

![Graph showing specific heat anomaly](image)

**Figure 4.9:** The opposing shift of the specific-heat anomaly in the Sr-0.10 sample measured at two different field configurations with an applied field of 90 kOe.

**Conclusion**

In conclusion, we have presented in this study the results of an investigation on the structural phase transformations in La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_{4+\delta}$ ($x = 0, 0.1, 0.2$) single crystals and on related effects in the electrical transport, magnetic and thermal properties of these systems. The transition temperatures of the LTO - LTT(LTO1) structural transformation, determined on the basis of specific-heat, resistivity and magnetic susceptibility measurements are in good agreement with previous reports. It is important to point out in this connection that our experimental results exhibit a consistent occurrence of the structural transition in the three different data sets.
\{\rho(T), \chi(T), \text{and } c(T)\}, measured separately. Further, these signs of the structural transition observed in the \(x = 0.1\) sample are considerably stronger than those found in the \(x = 0.2\) sample, which may be related to the proximity of the \(x = 0.1\) to the "magic number" of \(x = 0.125\). It should be added, that an effect of anisotropy is clearly evidenced in our data, including those parts showing the anomalous phenomena at the structural transition temperatures.

4.3 Solid-vortex states in superconducting La_{1.6-x}Nd_{0.4}Sr_{x}CuO_{4-\delta}

**Introduction**

The complex magnetic phase diagram in the mixed state of the cuprate superconductors has been an interesting subject of study from theoretical as well as experimental points of view. In this state, the structure and characteristics of the vortex system are determined by a competition between elastic, pinning and thermal energies. As a result, the behavior of the corresponding vortex ensemble is represented by a complex function of temperature, magnetic field as well as the degrees of disorder and anisotropy of the system [19]. This behavior is best characterized by the associated phase diagram. We report in this section the \(H - T\) phase diagram of La_{1.6-x}Nd_{0.4}Sr_{x}CuO_{4-\delta} (\(x = 0.1, 0.2\)) single crystals constructed from magnetization data obtained in magnetic field parallel to the \(c\)-axis. A phase diagram determined from the irreversibility line of this system was reported previously for the specific composition of La_{1.45}Nd_{0.4}Sr_{0.15}CuO_{4-\delta} (\(x = 0.15\)) [20]. The present work is undertaken to complement that study and to develop an evolutionary picture of the vortex characteristics with respect to variations of the doping concentration.

**Experiments**

A series of isothermal magnetic-hysteresis measurements was performed by means of a commercial Quantum Design MPMS-5S magnetometer, with the external magnetic field applied parallel to the crystal \(c\)-axis and using a scan length of 4 cm. Each
Structural instability, superconducting...

measurement started after cooling the sample from a temperature above \( T_c \) in zero-field (ZFC - mode) to the pre-determined temperature.

![Graph of temperature-dependent magnetization](image)

**Figure 4.10:** Typical temperature-dependent magnetization of the La\(_{1.5}\)Nd\(_{0.4}\)Sr\(_{0.1}\)CuO\(_{4.8}\) (Sr-0.10), La\(_{1.475}\)Nd\(_{0.4}\)Sr\(_{0.125}\)CuO\(_{4.8}\) (Sr-0.125) \[20\] and La\(_{1.4}\)Nd\(_{0.4}\)Sr\(_{0.2}\)CuO\(_{4.8}\) (Sr-0.20) samples, measured in fields below 10 Oe parallel to the crystal c-axis.

**Results and Discussion**

The temperature-dependent low-field magnetization for the as-grown Sr-0.10, Sr-0.125 and Sr-0.20 crystals are described in Fig. 4.10. This figure indicates the temperatures of the superconducting transition \( (T_c) \) at 6.5 K for Sr-0.10, 3 K for Sr-0.125 and 15 K for Sr-0.20, with \( \Delta T_c \approx 2 \) K for all samples. The Meissner volume fractions estimated from the data after subtracting the paramagnetic background are about 45% for the Sr-0.10 sample, 10% for the Sr-0.125 sample, and less than 5% for the Sr-0.20 sample. Further, the anisotropy parameter estimated from the resistivity measurement at \( T \approx 300 \) K, yields the values \( \gamma \approx 96 \) for Sr-0.10 and \( \gamma \approx 25 \) for Sr-0.20. Combined with the CuO\(_2\) interlayer distance of 13.1 Å \[5\], these \( \gamma \) values lead to
a dimensional crossover field, $H_{2D}$, of about 1300 Oe for Sr-0.10 and 20 kOe for Sr-0.20.

Figure 4.11: Isothermal magnetic-hysteresis loop of the Sr-0.10 crystal measured at various temperatures in the range 2.5 - 4.5 K (a) and 5 - 7 K (b). The penetration field, $H_p$, the second-peak field, $H_{sp}$, and the irreversibility field, $H_{irr}$, are indicated by the arrowheads.
Figure 4.12: (a) Isothermal magnetic-hysteresis loop of the Sr-0.20 crystal measured at various temperatures between 5 and 16 K. The penetration field, $H_p$, and the irreversibility field, $H_{irr}$, are indicated by the arrowheads. (b) Scaling of the $M(H)$ curve with respect to the magnetic field and magnetic moment at the first penetration point ($H_p, M_p$). See text for discussion.

Figures 4.11 and 4.12 present the results of the isothermal magnetization-loop measurement of the two samples. The data for Sr-0.10 reveal the fishtail-like effect in the upper branch of the loop as a peak (indicated by the arrowheads in Fig. 4.11) to the
right of the first peak at a field close to zero. It is interesting to note that this effect also occurs in the same system for other compositions, namely La$_{1.45}$Nd$_{0.4}$Sr$_{0.15}$CuO$_{4.6}$ (Sr-0.15) [20] and La$_{1.475}$Nd$_{0.4}$Sr$_{0.125}$CuO$_{4.6}$ (Sr-0.125) [21]. On the other hand, the same effect is ostensibly absent in the Sr-0.20 sample, see Fig. 4.12 (a). We have, accordingly, identified the penetration field ($H_p$) of the two samples as the field at minimum magnetization in the lower branch, while the second-peak field ($H_{sp}$) of the Sr-0.10 sample is determined from its upper branch curve.

Next, the scaling procedure, introduced previously by Dewhurst et al. [22], is applied to the $M(H)$ curves of Sr-0.20. For this purpose, the magnetization curves at each temperatures are scaled by the magnetic field and magnetic moment at the first penetration point ($H_p,M_p$), as indicated in the figure. The result of this scaling treatment is depicted in Fig. 4.12 (b), which shows a remarkable scaling behavior over the relatively wide temperature range below 10 K in the relatively limited low-field regime. It is interesting to recall in this connection that the scaling behavior in the Bi$_2$Sr$_2$CaCu$_2$O$_8$ [22] and Nd$_{1.85}$Ce$_{0.15}$CuO$_{4.6}$ [23] crystals is also observed in the temperature regime where the second-peak effect does not appear. The associated magnetization curves do not display a symmetry between their two branches due to the diminishing role of bulk pinning. The asymmetric shape of the magnetization curves observed in Fig. 4.12 (a) is in clear contrast to the more symmetric shape displayed by those curves exhibiting the second-peak effect in Fig. 4.11 where the bulk pinning effect is supposed to be dominant.

For comparison of the data with the existing models, the temperature-dependent characteristic fields consisting of $H_{2D}$, $H_p(T)$, $H_{sp}(T)$ and $H_{in}(T)$, determined from the previous figures, are plotted in a semi-logarithmic $H$ - $T$ phase diagram. The resulting phase boundaries, separating the entire solid phase area into a number of distinct regions, are presented in Fig. 4.13 (a) and (b) for the Sr-0.10 and Sr-0.20 samples respectively. Focusing on Fig. 4.13 (a) it is found that the low-temperature penetration field of the Sr-0.10 sample is very well described by the 2D version of the surface barrier model [24] represented by a functional form: $H_p(T) \approx H_c \exp(-T/T_o)$, with $H_c = 540$ Oe and $T_o = 2.7$ K. We find that this function starts to deviate from the data points at higher temperatures ($T > 5.5$ K). In that temperature regime, the data can
Figure 4.13: \( H - T \) phase diagram of (a) Sr-0.10 and (b) Sr-0.20 crystals, showing the temperature dependencies of the penetration field, \( H_p \), the second-peak field, \( H_{sp} \), and the irreversibility field, \( H_{irr} \). The lines are theoretical fits on the basis of existing models. See text for discussions.
better be fitted with a geometrical barrier model [25], leading to a penetration field, $H_p$, having a temperature dependence given by: $H_p(T) = H_p(0) \left(1 - \frac{T}{T_c}\right)$, with $H_p(0) = 250$ Oe and $T_c = 7.8$ K. The second-peak-field data of the Sr-0.10 sample are closely represented by a function of the form: $H_{sp}(T) = H_{sp}(0) \exp(-\alpha T/T_c)$, with $H_{sp}(0) \approx 3$ kOe and $\alpha \approx 5.5$, as reported in previous analyses of a Tl-based single crystal [26, 27] and of (Bi,Pb)$_2$Sr$_2$CaCu$_2$O$_{8-\delta}$ [28] and T'- phase SmLa$_{0.8}$Sr$_{0.2}$CuO$_{4-\delta}$ [29] samples. We observe that the second-peak field in this particular compound disappears at $T > 5.5$ K, well below $T_c$, in conformity with a general trend exhibited by samples with a large electronic anisotropy [29]. The irreversibility line, $H_{ir}(T)$, in the high-temperature ($T \geq 4$ K) and lower-field ($H < H_{2D}$) regions displays an excellent fit to a power-law expression of the form: $H_{ir}(T) = H_{ir}(0) \left(1 - \frac{T}{T_c}\right)^{3.2}$ with $H_{ir}(0) = 3370$ Oe and $T_c = 7.8$ K, confirming the dominance of thermal effects [30, 31]. The data for $H > H_{2D}$ and $T < 4$ K are consistent with an exponential function of the form: $H_{ir}(T) = H_m \exp(k/T)$, with $H_m = 630$ Oe and $k = 3.45$ K. It implies a change in curvature with respect to that of the adjoining curve at lower field as reported also in the case of Bi$_2$Sr$_2$CaCu$_2$O$_8$ [32-36], Tl$_2$Ba$_2$CuO$_{6}$ [26], T'- phase Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ [23], and T'- phase SmLa$_{0.8}$Sr$_{0.2}$CuO$_{4-\delta}$ [29]. Despite the limited amount of data available at $H > H_{2D}$, this result is nonetheless consistent with the quasi-2D Josephson-coupled layered superconductor (JCLS) model with moderate anisotropy [32].

We turn our attention now to Fig. 4.13 (b) which differs obviously from Fig. 4.13 (a) by the absence of the second-peak curve. It is understood that the fishtail effect is, generally, associated with the transition between the ordered vortex quasi-lattice and the disordered (entangled) or less-strongly-pinned vortex-glass states. The absence of this transition in the Sr-0.20 sample is presumably inhibited by a very strong pinning induced by the higher Sr doping level as indicated by the unusually large hysteresis in the normalized magnetization curves. This strong bulk-pinning effect is supposed to prevent the formation of the quasi-vortex-lattice phase. The data of the penetration field for $T < 10$ K are nicely described by the functional form: $H_p(T) \equiv H_c \exp(-T/T_o)$, with $H_c = 15$ kOe and $T_o = 4.4$ K, indicating a
2D surface-barrier character [24]. A distinct deviation from this function is indicated by the data at \( T > 10 \) K, where they are better described by the function: 
\[
H_p(T) \sim H_a (T_c - T)^{3/2}/T
\]
of the quasi-3D version of the surface-barrier model [24], with 
\( H_a = 720 \) Oe and \( T_c = 16.6 \) K. It is important to point out in this connection that the temperature region where the \( M - H \) curves in Fig. 4.12 (b) scale nicely is roughly congruent with the temperature range where the \( H_p(T) \) data are fitted by the 2D surface-barrier model, signifying the effect of decoupled 2D pancake vortices in the lower-temperature region. The irreversibility field of this sample, on the other hand, shows a temperature dependence that can be fitted by a single functional form:
\[
H_{\text{irr}}(T) = H_{\text{irr}}(0) (1 - T/T_c)^{3/2},
\]
in the whole temperature range of measurement (5 - 16 K), with \( H_{\text{irr}}(0) = 70 \) kOe and \( T_c = 17.8 \) K. There is no change in curvature at \( H_{\text{2D}} \), which is in clear contrast to the case of the Sr-0.10 sample. These different behaviors are most likely related to a considerably lower anisotropy \( (\gamma \approx 25) \) of the Sr-0.20 sample compared to that of the Sr-0.10 sample \( (\gamma \approx 96) \).

Conclusion

We have presented in this section the solid-vortex phase diagram of a superconducting La\(_{1.6}\)Nd\(_{0.4}\)Sr\(_x\)CuO\(_{4.5}\) (\( x = 0.1, 0.2 \)) single crystal as constructed from magnetization data for fields parallel to the \( c \)-axis. The magnetization curves of the Sr-0.10 sample reveal the existence of the fishtail-like effect, observed at other compositions of \( x = 0.15 \) and \( x = 0.125 \) as well, but clearly absent in the Sr-0.20 sample. The absence of this effect in the Sr-0.20 sample is attributed to disorder-induced relatively strong pinning in this sample, resulting in a suppression of the vortex-lattice phase. Further analysis of the associated phase diagram of the Sr-0.10 sample shows a sign reversal in the curvature of the irreversibility line at around \( H_{\text{2D}} \), indicating the 2D melting at higher fields. On the other hand, a single irreversibility line is shown to describe the \( H_{\text{irr}}(T) \) data for the Sr-0.20 sample over the entire measurement range, indicating the lack of vortex-line decoupling effects at \( H_{\text{2D}} \) and corroborating the suggested strong pinning-induced reduction of anisotropy in this sample.
4.4 Doping and field effects on the lowest Kramers doublet splitting in $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_{4.5}$

Introduction

The magnetic studies on the $\text{La}_{2-x}\text{Nd}_x\text{Sr}_x\text{CuO}_4$ system have been conducted in this experiment with the expected important role in mind of the electronic energy level scheme in the incomplete 4$f$-shell of the Nd$^{3+}$ ions. The Nd$^{3+}$ ion with the electronic configuration $[\text{Xe}] 5s^2 5p^6 4f^2$ is a Kramers ion [37], with its lowest multiplet specified according to Hund’s rule by $^4I_{9/2}$ corresponding to $J = 9/2$, $S = 3/2$, $L = 6$, and a Landé factor of $g_J = 8/11$. The electronic state of the 4$f$ ion is inevitably affected by the surrounding electric field. As a consequence, the degeneracy of the electronic ground state energy in its isolated state is lifted in the crystal, resulting in a different charge-induced ground state of the 4$f$ subsystem, known as due to the crystalline electric field (CEF) effect [38]. For the special case of the $\text{La}_{2-x}\text{Nd}_x\text{Sr}_x\text{CuO}_4$ crystal, the 10-fold degenerate ground state multiplet $|LSJ\rangle$ of the Nd$^{3+}$ ions is split with respect to $J_z$ into five Kramers doublets under the influence of the CEF effect. An intensive CEF studies for this particular system has been recently reported in Ref. [7].

Due to the strong shielding by the outer 5$s$ and 5$p$ electrons, the CEF effect can, in general, be treated merely as a perturbation to the free-ion 4$f$ state in the formulation of a theoretical model. Additionally, the ionic magnetic moment is also commonly considered to be localized at the lattice site. Further, neutron-scattering experiments have revealed that the lowest excited doublet lies approximately 200 K above the first doublet [6]. Therefore, at temperatures below 30 K, the higher lying doublets are ignored in the study of the energy splitting of the lowest Kramers doublet under the influence of exchange and Zeeman interactions. It is well known that the electronic energy structure will generally affect the electronic specific heat of the system. The study of these doublet-splitting mechanisms reported here is performed by measuring and analyzing the field-dependent specific-heat data at different Sr-doping levels.
Experiments

The specific-heat measurements were carried out using a relaxation method with a commercial Quantum Design PPMS magnetometer. Each data set was collected in the temperature range of 1.6 to 30 K, at different magnetic fields of 0, 50, 70 and 90 kOe applied parallel to the crystal c-axis for the Sr-0.00 and Sr-0.10 samples, while the Sr-0.20 sample was measured only in zero field.

Results and discussion

Figure 4.14 presents the result of specific-heat measurements of the as-grown Sr-0.00, Sr-0.10 and Sr-0.20 single crystalline samples. These data have been corrected from the background contributions associated with sample holder and grease (addenda). As shown by the data in this figure, the low-temperature data are dominated by contributions from the Nd$^{3+}$ ions, featured by a Schottky-type of peak due to the enhanced ordering of the Nd$^{3+}$ magnetic moments at lower temperature as revealed in the magnetic susceptibility measurements described in section 4.2 of this chapter. In particular, the very sharp upturn at temperature below 5 K, as revealed by the zero-field data, clearly indicates the effect of enhanced exchange interactions between the ordered magnetic moments of the Nd ions and those of the Cu sublattice. This peak is shifted to higher temperatures for larger fields. The observation of such a low-temperature Schottky-type of behavior has also been reported before for isostructural T'-phase Nd$_{2-x}$Ce$_x$CuO$_{4-δ}$ [39, 40]. On the other hand, the specific-heat data of other high-$T_c$ systems such as YBa$_2$Cu$_3$O$_{7-δ}$ (YBCO) deviate from this behavior [41], due to the absence of 4f electrons in the system.

Before proceeding with a detailed analysis of the data, let us recall the various physical sources of contributions to the specific heat. The first of these is the lattice effects consisting of Debye and Einstein contributions that both increase monotonically with temperature. At higher temperatures, higher order terms in temperature ($\propto T^5$ and $T^7$), indicating deviations from the low-temperature Debye specific heat, may also have to be considered. The second type of contributions is electronic in nature, consisting of
Figure 4.14: Temperature-dependent specific-heat data for the as-grown (a) Sr-0.00, (b) Sr-0.10 and (c) Sr-0.20 samples. The solid lines are the result of fitting by means of Eq. (4.2).
a linear temperature-dependent electronic contribution as present in normal metals, the Schottky term arising from the Kramers doublet splitting, as well as possible contributions associated with the existence of lines of nodes in the energy gap function expected in a d-wave superconductor [42, 43]. This last contribution is composed of a field- and temperature-dependent term of the form: \( \sim \sqrt{H/T} \) [42] and a zero-field term quadratic in temperature [43]. An additional electronic contribution may arise from the conventional (s-wave) superconducting state as usually indicated by the presence of a large discontinuity at \( T_c \). It should be stressed that contributions to the specific heat related to superconductivity are hardly observable and that among the other contributions, the Schottky effect, if it does exist, may play a dominant role at low temperatures and is the only contribution exhibiting a non-monotonic variation with temperature.

**Table 4.2: Resumé of parameter values resulting from fitting Eq. (4.2) to the specific-heat data for the Sr-0.00, Sr-0.10 and Sr-0.20 samples at different field strengths.**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>( H ) [kOe]</th>
<th>( \Theta_D ) [( \pm 1 ) K]</th>
<th>( T_E ) [( \pm 1 ) K]</th>
<th>( \Delta ) [K]</th>
<th>( \chi^2 ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr-0.00</td>
<td>0</td>
<td>346</td>
<td>83</td>
<td>2.7 ± 0.1</td>
<td>3.70</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>346</td>
<td>82</td>
<td>17.0 ± 0.2</td>
<td>3.24</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>345</td>
<td>83</td>
<td>22.9 ± 0.3</td>
<td>2.80</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>346</td>
<td>83</td>
<td>28.8 ± 0.4</td>
<td>3.32</td>
</tr>
<tr>
<td>Sr-0.10</td>
<td>0</td>
<td>343</td>
<td>95</td>
<td>1.4 ± 0.1</td>
<td>1.91</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>346</td>
<td>93</td>
<td>16.3 ± 0.2</td>
<td>4.07</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>346</td>
<td>93</td>
<td>23.4 ± 0.3</td>
<td>6.62</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>340</td>
<td>100</td>
<td>31.3 ± 0.3</td>
<td>3.63</td>
</tr>
<tr>
<td>Sr-0.20</td>
<td>0</td>
<td>345</td>
<td>95</td>
<td>1.1 ± 0.2</td>
<td>0.64</td>
</tr>
</tbody>
</table>
In our analyses, each data set was individually fitted to a variety of theoretical curves representing different combinations of those contributions with closest resemblance to the \( c/T - T \) data in Fig. 4.14 as well as the related \( c/T - T^2 \) plots. We found that the best fit of these data were achieved by the following expression:

\[
c(H, T) = \beta T^2 + R \left( \frac{T_E}{T} \right)^2 \frac{\exp(T_E/T)}{\left[ \exp(T_E/T) - 1 \right]^2} + R \left( \frac{\Delta(H)}{T} \right)^2 \frac{\exp[\Delta(H)/T]}{\left[ 1 + \exp[\Delta(H)/T] \right]^2}
\]

(4.2)

The first and second terms on the right-hand side represent the Debye \((D)\) and Einstein \((E)\) lattice contributions. The coefficient \( \beta \) is related to the Debye temperature, \( \Theta_D \), through: \( \beta = \left( \frac{12}{5} \pi^4 n k_B (1/\Theta_D) \right)^3 \) (the coefficient \( n \) calculates the number of atom in the system); \( T_E \) is the Einstein temperature. The last term of Eq. (4.2) represents a two-level electronic Schottky \((S)\) contribution, with \( \Delta(H) \) denoting the field-dependent energy separation between the two levels. In the case of a Zeeman interaction and taking into account the possible exchange interaction between the Nd spins and the Cu sublattices, the expression of \( \Delta(H) \) is proportional to the field according to:

\[
\Delta(H) = g \mu_B (H + H_{int})
\]

(4.3)

In this formula, \( g \) is the effective \( g \)-factor along the applied field direction and \( \mu_B \) is the Bohr magneton; \( H_{int} \) is the internal field, resulting from the Cu sublattice and acting on the Nd\(^{3+}\) ion. The results of this fitting for each set of data (at different \( H \), including also the zero-field data) of the Sr-0.00, Sr-0.10 and Sr-0.20 samples are presented as the solid lines in Fig. 4.14. The resulting values for the best-fit parameters are tabulated in Table 4.2. We note that the data is well fitted by Eq. (4.2) as indicated by the corresponding \( \chi^2 \) values listed in the Table. The Debye temperature deduced from this analysis is approximately given by 345 K for all samples, while the Einstein temperature varied from 83 K for the Sr-0.00 sample to 95 K for the Sr-0.10 and Sr-0.20 samples. The value of \( \Theta_D \) is well within the range of values reported for the homologous La\(_{2-x}\)Sr\(_x\)CuO\(_{4+\delta}\) samples [44]. In addition, the behavior of the data in Fig. 4.14 can be readily explained by contributions of each term in Eq. (4.2) to the total...
specific heat as illustrated in Fig. 4.15 for the Sr-0.10 sample at two different field values. The resulting field-dependent $\Delta$ values for each sample are plotted in Fig. 4.16.

![Image of graph showing specific heat vs. temperature for different field values](image)

**Figure 4.15:** Illustration of the behaviors of Debye (D), Einstein (E) and Schottky (S) terms in Eq. (4.2) and the total contribution to the specific heat (solid line).

It is clearly seen that in the absence of an external magnetic field ($H = 0$), $\Delta$ has a non-zero value, which can be attributed to the exchange coupling between the ordered Cu and Nd$^{3+}$ spins. We note that the magnitude of this $\Delta(0)$ value decreases with increasing x, in good agreement with the result deduced from a neutron-scattering study reported by Roepke *et al.* [6]. Particularly for the Sr-0.20 sample, $\Delta(0)$ remains finite as reported in Ref. [6] and observed in a recent spectroscopic measurement.
Figure 4.16: Field-dependent energy splitting, $\Delta(H)$, of (a) Sr-0.00 and (b) Sr-0.10 samples, resulting from the fitting. The solid lines denote the linear fits to the data.

[7, 45]. This is also consistent with the finite value of staggered magnetization deduced from other neutron experiment by Tranquada et al. [4]. Our result has thus corroborated the existing evidence for a magnetic coupling between the rare-earth ion and the Cu sublattice reported for a number of copper oxide superconductors such as T'-phase Nd$_{2-x}$Ce$_x$CuO$_{4.5}$ [46-48], REBa$_2$Cu$_3$O$_{6+y}$ (RE = Nd, Sm) [49, 50], as well as a hybrid system of T' phase SmLa$_{1-x}$Sr$_x$CuO$_{4.5}$ [51]. The excellent linear fit of the data by means of Eq. (4.3) clearly attests to the Zeeman effect, and henceforth yields the values for the g-factor at fields applied along the crystal c-axis, namely $g_\perp = 4.31$ for the Sr-0.00 and $g_\perp = 4.88$ for the Sr-0.10 sample. Further, the values of the internal field deduced from these data are: $H_{int} \approx 9.15$ kOe and 2.70 kOe for the Sr-0.00 and Sr-0.10 sample, respectively. Apparently, introduction of holes into the CuO$_2$ planes by Sr doping reduces the value of $H_{int}$, which is equivalent with a reduction of the Nd-Cu interaction strength. We note furthermore, that this $H_{int}$ value is smaller than the one found in the undoped T'-phase Nd$_2$CuO$_{4.5}$ [46], in which case a value for $H_{int}$ of about 57 kOe has been reported based on an analysis of spectroscopic data.
The electronic Schottky entropy, \( S(T) \), corresponding to the energy cost of splitting the Kramers doublet can be evaluated from the data by integrating

\[
S(T) = \int_0^T \left( c_{Sch}/T' \right) dT',
\]

where \( c_{Sch} \) denotes the electronic Schottky specific heat, which is obtained as a result of subtracting the total heat-capacity by the lattice contributions. The results for the Sr-0.00 and Sr-0.10 samples are presented in Fig. 4.17. It is to be noted that the entropies in the temperature regime ranging from 0 K to the lowest temperature of measurement (~2 K), where no experimental data are available, are extrapolated from the fitted Schottky functions. It is clear from this figure that in both cases the low-temperature entropy decreases invariably with increasing applied magnetic field, with the zero-field entropy rising very rapidly with temperature to the constant value of \( S = R \ln(2) \), which is the theoretical maximum for a two-level system.
Conclusion

In conclusion, we have presented in this study the doping and field effects on the lowest Kramers doublet splitting in the La_{1.6-x}Nd_{0.4}Sr_{x}CuO_{4+delta} single crystals on the basis of specific-heat data. In the absence of an external magnetic field, the splitting of the lowest Kramers doublet of Nd^{3+} ions is due to exchange interactions with the ordered Cu spins. It is shown that its magnitude, as well as the value of the internal field, decreases with increasing Sr content (x) due to the reduction of the Nd-Cu interaction strength. Furthermore, a linear increase of $\Delta$ is shown to occur with increasing external magnetic field applied along the crystal c-axis. Thus, the low-temperature magnetic properties of this La_{1.6-x}Nd_{0.4}Sr_{x}CuO_{4+delta} system depend on the Sr-doping level, which, in turn, influences the oxygen distribution in (and electronic properties of) the CuO_{2} layers.

References

[51] Will be described in Chapter 5 of this thesis.