Crystal Growth and Physical Properties of T*- Phase SmLa1-xSrxCuO4-d and T-Phase La1.6-xNd 0.4Sr xCuO 4- d
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Chapter 5

Magnetic properties of T*-phase SmLa$_{1-x}$Sr$_x$CuO$_{4-\delta}$

5.1 Introduction

The SmLa$_{1-x}$Sr$_x$CuO$_{4-\delta}$ compound, forming the so-called T*-phase, is one of the intensively studied members of the 214 family of cuprate superconductors. Ideally, the crystal structure of this phase, as described in Chapter 2 and in Fig. 5.1, is a hybrid of the T- and T'-phases and is composed of two types of block layers: a fluorite-type layer of Sm$_2$O$_2$ (T'-block) and a rocksalt-type layer of (La,Sr)$_2$O$_{2.5}$ (T-block). Each of them shares similar environments as the T'- and T-blocks of the corresponding T'-phase Sm$_2$CuO$_4$ and T-phase La$_{2-x}$Sr$_x$CuO$_{4.8}$, respectively. We note that the rare-earth Sm ions in the T'- and T'-phase structures occupy the same sites and share the same environment, except for the substitution of the Sm ions by the (La,Sr) group in the T-block of the T'-phase. In other words, the arrangement of the paramagnetic Sm$_2$O$_2$ layers are intervened by non-magnetic rocksalt (La,Sr)$_2$O$_{2.5}$ layers in the T'-phase. This peculiar arrangement is expected to yield different Sm magnetic interactions along the c-axis in SmLa$_{1-x}$Sr$_x$CuO$_{4-\delta}$ compared to those found in Sm$_2$CuO$_4$.

Similar to the doped superconducting T'-phase Sm$_{2-x}$Ce$_x$CuO$_{4-\delta}$, the presence of Sm ions in SmLa$_{1-x}$Sr$_x$CuO$_{4-\delta}$ acts as a probe for the study of various interactions responsible for the superconductivity. In particular, the Sm$^{3+}$ ions in undoped Sm$_2$CuO$_4$ are known to be ordered antiferromagnetically at the rather high temperature of
$T_N = 5.95$ K [1-5], which temperature is reduced by doping with Ce, Th or Y [6]. It is to be noted that such a high Néel temperature is indicative of a strong superexchange interaction, which could produce interesting pair-breaking effects if it is coupled to the superconducting charge carriers [1, 4, 5]. According to Markert et al. [6], the suppression rate of the $T_N$ with Ce$^{4+}$ substitution turns out to be $dT_N/dx = -0.15$ K/at.%, which is twice as large as that of the iso-valent Y$^{3+}$ substitution ($dT_N/dx = -0.07$ K/at.%), which we attribute to the additional electron doping at Ce$^{4+}$ substitution. In addition, the effects of charge carrier doping on the Sm$^{3+}$ ordering can also be investigated by studying the variation of magnetic ordering of Sm ions in the $T^*$- phase SmLa$_{1-x}$Sr$_x$CuO$_{4.5}$ with respect to $x$, in which case we expect additional effects by hole doping.

The Sm ions in Sm$_2$CuO$_4$ are magnetic, being in the valence state $3^+$ (Sm$^{3+}$) with the electronic configuration of [Xe] $5s^2$ $5p^6$ $4f^6$. Its lowest energy multiplet is given, according to Hund’s rule, by $^6H_{5/2}$, corresponding to $J = 5/2$, $S = 5/2$, $L = 5$, and a Landé factor of $g_J = 2/7$. The degeneracy of the $4f$ electronic states of the Sm free-ion
is lifted under the influence of the electric field of the crystal, leading to a new set of levels. These new levels are at least two-fold degenerate, as a consequence of Kramers' theorem [7] for systems with an odd number of 4f electrons. A further lifting of the Kramers degeneracy is only possible by means of additional interactions, such as magnetic interactions with other atoms in the crystal or an external magnetic field. In Sm$_2$CuO$_4$, however, the magnetic moments of the Sm$^{3+}$ ions are aligned along the crystallographic z-axis, which is orthogonal to the Cu spins [4, 8, 9]. Therefore, the presence of an external field is required for the doublet splitting. This behavior is in contrast to the other T'- phase of the Nd$_2$CuO$_4$ compound, where both the magnetic moments of the rare-earth ions Nd and the transition metal Cu ions align in the same x-y plane [10]. It would be important to study the effect of (La,Sr) doping in Sm$_2$CuO$_4$ as well.

In this study, the magnetic properties of the T'- phase SmLa$_{1-x}$Sr$_x$CuO$_{4.6}$ (x = 0.15, 0.20, 0.25) single crystal are investigated by means of its magnetic susceptibility and specific heat, both in the non-superconducting as well as the superconducting state. The data will be analyzed by taking into account the specific crystal structure and will be compared with results obtained for the homologous T'- phase Sm$_2$CuO$_4$ crystal.

5.2 Experimental

In this study, temperature-dependent magnetic susceptibility and specific-heat measurements have been performed on the as-grown T'- phase Sm$_2$CuO$_4$ as well as the as-grown (non-superconducting) and oxidized (superconducting) T'- phase SmLa$_{1-x}$Sr$_x$CuO$_{4.6}$ (x = 0.15, 0.2, 0.25) single-crystalline samples. The sample with x = 0.15 was grown at the University of Tokyo [11]. For simplicity, the SmLa$_{1-x}$Sr$_x$CuO$_4$ samples were coded as Sr(sc/n)-0.15, Sr(sc/n)-0.20 and Sr(sc/n)-0.25 corresponding to x = 0.15, 0.2 and 0.25, respectively. The superconducting (sc) and non-superconducting (n) samples are coded by the sc/n in the parentheses.

The magnetic susceptibility measurements were carried out using a commercial Quantum Design MPMS-5S magnetometer. Each data set was performed in the
zero-field cooled (ZFC) mode, in the temperature range of 1.7 to 350 K. The applied field was 5 kOe for the non-superconducting samples and 50 kOe (the maximum field) for the superconducting sample. In all cases, a scan length of 6 cm was used. The specific-heat measurements for the superconducting samples were performed in Physikalisches Institut, Universität Karlsruhe, by means of a semi-adiabatic method in the temperature range of 2 - 30 K, in zero field and in a field of 140 kOe applied parallel to the crystal c-axis. The specific-heat data for the non-superconducting sample were obtained at the UvA using a relaxation method in the temperature range of 0.3 - 10 K without an external magnetic field.

5.3 The magnetic susceptibility data and their analysis

The typical temperature-dependent magnetic susceptibilities per mole Sm$^{3+}$ ions are shown in Figs. 5.2 - 5.4 for T'- phase Sm$_2$CuO$_4$ as well as for the T'- phase Sr(n)-0.20 and Sr(sc)-0.20 samples. For Sm$_2$CuO$_4$, the susceptibility exhibits a significant anisotropy in the whole temperature range of the measurement. At temperatures below about 50 K, the in-plane ($\chi_\parallel$) and the out-of-plane ($\chi_\perp$) susceptibility corresponding to the external magnetic field applied parallel and perpendicular to the CuO$_2$ layers (ab-plane), show a pronounced difference in their variation with temperature as it decreases below $T_N \approx 6$ K. While $\chi_\perp$ rises sharply with temperature starting from 1.7 K, there is a much more gradual rise for $\chi$. This preferential behavior indicates that a spontaneous ordering of the Sm magnetic moments takes place along the c-axis that is perpendicular to the Cu spins, in good agreement with previous reports on the neutron scattering studies [4, 8, 9].

In contrast to the T'- phase Sm$_2$CuO$_4$, the anisotropic behavior of the temperature-dependent susceptibility in the T'- phase Sr(n)-0.20 sample, shown in Fig. 5.3, is remarkably less pronounced, and becomes better observable only at temperature well above $\sim 100$ K, with the $\chi_\perp$ curve lying above the $\chi$ curve in the whole temperature range. As shown in the inset of Fig. 5.3, the ab-plane inverse susceptibility ($\chi_\parallel^{-1}$) curve is deviates positively from the calculated curve with
Magnetic properties of $T^\prime$-phase Sm$_{1-x}$Sr$_x$CuO$_{4+\delta}$

**Figure 5.2:** Temperature-dependent susceptibility of a $T^\prime$-phase Sm$_2$CuO$_4$ single crystalline sample measured in a magnetic field of 5 kOe, applied parallel ($\chi_{//}$) and perpendicular ($\chi_{\perp}$) to the CuO$_2$ planes. The inset shows details of the low-temperature data below 10 K.

**Figure 5.3:** Temperature-dependent susceptibility of non-superconducting $T^\prime$-phase SmLa$_{0.8}$Sr$_{0.2}$CuO$_{4+\delta}$ (Sr(n)-0.20) measured in a magnetic field of 5 kOe, applied parallel ($\chi_{//}$) and perpendicular ($\chi_{\perp}$) to the CuO$_2$ planes. The inset shows the inverse susceptibility; the solid lines are the result of fitting the low-temperature data (1.7 $\leq$ T $\leq$ 100 K) to Eq. (5.1).
Figure 5.4: Temperature-dependent susceptibility of superconducting $T^*$-phase SmLa$_{0.8}$Sr$_{0.2}$CuO$_{4.8}$ (Sr(sc)-0.20) measured in a magnetic field of 50 kOe applied perpendicular ($\chi_\perp$) to the CuO$_2$ planes. The inset shows the low-temperature data ($T \leq 40$ K), showing a cusp around 2 K.

parameter values deduced from a fit of the data below 100 K to Eq. (5.1). This is similar to results previously reported on polycrystalline oxide SmLa$_{0.8}$Sr$_{0.2}$CuO$_{4.8}$ [12] and oxy-chloride CaSmCuO$_3$Cl samples [13]. We note further that no magnetic ordering of the Sm ions is observed at $T \geq 1.7$ K. However, the susceptibility of the Sr(sc)-0.20 superconducting sample ($T_c^{on} \sim 24$ K) as depicted in Fig. 5.4 shows a cusp around 2 K. The specific-heat measurement, however, do not show an anomaly at 2 K, as we will discuss in the next section. Therefore, instead of assigning this feature to the antiferromagnetic ordering of Sm ions, we argue that this is a manifestation of the diamagnetic contribution at entering the superconducting state. Apparently this transition overwhelms the eventual magnetic ordering of the Sm ions at temperature below $T_c$.

It has been known that for Sm$^{3+}$ ions, the close proximity of the $J$ multiplets, which is due to the weaker spin-orbit splitting, causes a mixture/hybridization of the matrix elements between the lowest $J$ and the next higher $J$ multiplets. Ignoring any
crystalline electric field (CEF) effect, the data in the low-temperature regime are then fitted by means of a Curie-Weiss law incorporating an additional temperature independent Van Vleck term corresponding to a coupling between the $J = 5/2$ ground-state multiplet and the $J = 7/2$ excited multiplet at an average energy of $\Delta E$ as expressed by [2, 14]:

$$
\chi(T) = N_A \left[ \frac{\mu_{\text{eff}}^2}{3k_B(T-\Theta)} + \frac{20\mu_B^2}{7k_B\Delta E} \right]
$$

where $N_A$ is the Avogadro number, $\mu_{\text{eff}}$ is the effective magnetic moment of the Sm ions in the crystal (expressed in terms of Bohr magneton, $\mu_B$), and $\Theta$ is the Curie-Weiss temperature. The resulting $\mu_{\text{eff}}$, $\Theta$ and $\Delta E$ values for the T'- phase Sm$_2$CuO$_4$ and the T' - phase Sr(n)-0.20, Sr(n)-0.25 and Sr(sc)-0.20 samples are tabulated in Table 5.1.

**Table 5.1:** The effective magnetic moment, $\mu_{\text{eff}}$, the Curie-Weiss temperature, $\Theta$, and the average energy separation between the $J = 5/2$ ground-state multiplet and the $J = 7/2$ excited multiplet, $\Delta E$, of the T' - phase Sm$_2$CuO$_4$ and the T'- phase Sr(n)-0.20, Sr(n)-0.25 and Sr(sc)-0.20 samples. Note: the temperature ranges for the fitting are different for each samples considered.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$H/ (ab)$</th>
<th>$H/ (ab)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\mu_{\text{eff}}/|\mu_B|$</td>
<td>$\Theta/|K|$</td>
</tr>
<tr>
<td>Sm$_2$CuO$_4$</td>
<td>7.5 - 70 K</td>
<td>0.363</td>
</tr>
<tr>
<td>Sr(n)-0.20</td>
<td>1.7 - 100 K</td>
<td>0.311</td>
</tr>
<tr>
<td>Sr(n)-0.25</td>
<td>1.7 - 100 K</td>
<td>0.314</td>
</tr>
<tr>
<td>Sr(sc)-0.20</td>
<td>3 - 40 K</td>
<td>-</td>
</tr>
</tbody>
</table>

This table shows that the c-axis effective magnetic moment of the Sm ions in the T' - phase Sm$_2$CuO$_4$ ($\mu_{\text{eff}}/ = 0.838 \mu_B$) is closer to the free-ion value of 0.845 $\mu_B$ than the values reported previously [2, 4, 8, 9]. On the other hand, a considerably smaller value is obtained for the $ab$-plane configuration, i.e., $\mu_{\text{eff}}/ = 0.363 \mu_B$, which is well within the range of typical values for $\mu_{\text{eff}}$ of 0.33 $\mu_B$ [Ref. 2] and 0.37 $\mu_B$ [Refs. 4, 8, 9].


reported from magnetic susceptibility and neutron diffraction measurements, respectively. This result confirms a dominant influence of the Sm magnetic moments along the crystal c-axis described previously. The anisotropic magnetic properties of the $T'$- phase $\text{Sm}_2\text{CuO}_4$ is also revealed by the values of $\Theta$ and $\Delta E$. The relatively large negative value $\Theta_\perp \approx -19$ K, compared to $\Theta = -1.654$ K is believed to be related to the relatively large inter-Sm-antiferromagnetic coupling ($J_{\text{Sm-Sm}}$) along the crystal c-axis. On the other hand, the relatively small $\Delta E = 405$ K and $\Delta E_\perp = 1187$ K compared to $\Delta E \approx 1500$ K for the free-ion might be indicative of the importance of a CEF effect.

For the $T'$- phase $\text{SmLa}_{1-x}\text{Sr}_x\text{CuO}_4$ on the other hand, the effective magnetic moment values, both in the $ab$-plane and parallel to the crystal c-axis, are considerably smaller than the free-ion value. The values corresponding to $H//c$ are slightly larger than those corresponding to $H//ab$-plane. They display slight increases with the Sr content. A reduced value of $\mu_{\text{eff}}$ is found in the superconducting sample as compared to the as-grown sample. We note that the values of $\Theta$ and $\Delta E$ are relatively insensitive to the applied field direction, consistent with the isotropic behavior of $\chi_\parallel$ and $\chi_\perp$ pointed out earlier. Furthermore, the relatively small values of $\Theta (|\Theta| \approx 1.5 - 2.6$ K) implies a relatively small antiferromagnetic correlation between the Sm magnetic moments, consistent with the absence of Sm ordering in our experiment above 1.7 K, as alluded before. It is important to note that the average energy separations $\Delta E \approx 800 - 1100$ K are smaller than those of the free-ion value ($\Delta E \approx 1500$ K), signifying the importance of CEF effects in this system. It is also interesting to mention at this point that the values of $\mu_{\text{eff}}$, $\Theta$ and $\Delta E$ derived from our data for the $\text{SmLa}_{1-x}\text{Sr}_x\text{CuO}_{4.6}$ compounds are comparable with the values $\mu_{\text{eff}} = 0.38$ $\mu_B$, $\Theta = -5.3$ K and $\Delta E = 790$ K reported by Fuller et al. [13] for the oxy-chloride $T'$- phase compound $\text{CaSmCuO}_3\text{Cl}$. We have found, in addition, that the calculated magnetic susceptibility of the Sm$^{3+}$ ions by means of Eq. (5.1) and using the free-ion values for the magnetic parameters is larger than the measured value by a factor of $\sim 2$ at $T = 50$ K. A similar observation has been reported by Ikegawa et al. [12] from a polycrystalline $\text{SmLa}_{0.4}\text{Sr}_{0.2}\text{CuO}_{4.6}$ sample. Such a discrepancy might arise from a mixed-valence state of the Sm ions, or an as yet unknown interaction between the Sm
magnetic moments and the charge carriers [15]. We recall that the mixed-valence state of Sm ions has been suggested previously in the SmBa$_2$Cu$_3$O$_{7.6}$ compound [16, 17] based on the result of neutron scattering experiments.

Finally, it is interesting to discuss the reduction of the Néel temperature in T'-phase SmLa$_{1.5}$Sr$_x$CuO$_{4.6}$ compounds from $T_N = 5.95$ K in T'-phase Sm$_2$CuO$_4$ to values for $T_N$ below 1.7 K in terms of the superexchange interaction, which is known to prevail in the T'-phase compounds [1, 4, 5]. It has been known that the main structural difference between the T'- phase Sm$_2$CuO$_4$ and T'-phase SmLa$_{1.5}$Sr$_x$CuO$_{4.6}$ is the insertion of the non-magnetic (La,Sr)$_2$O$_{2.6}$ layers along the $c$-direction (the same direction that the Sm$^{3+}$ spins are ordered in Sm$_2$CuO$_4$) without any difference along the $ab$-directions. The presence of this La-O rocksalt layer might disrupt the magnetic interactions along the $c$-direction, confining the superexchange interaction to the two-dimensional (2D) network in the CuO$_2$ plane. Meanwhile, the holes resulting from both oxygen doping as well as divalent Sr substitution of the trivalent (La,Sm) introduce additional disorder in the Cu-O sheet, which, in turn, disturb the superexchange interaction and reduce the Néel temperature to below 1.7 K.

5.4 The specific-heat data and their analysis

The temperature-dependent specific heat of the T'- phase Sm$_2$CuO$_4$ and T'- phase SmLa$_{1.5}$Sr$_x$CuO$_{4.6}$ samples with different $x$ values are separately shown in Figs. 5.5 - 5.8. The data for Sm$_2$CuO$_4$ reveal a sharp $\lambda$-type of anomaly with a peak occurring at its Néel temperature of $T_N = 5.95$ K ($H = 0$). This peak is ascribed to the three-dimensional (3D) antiferromagnetic ordering of the Sm spins, in good agreement with the magnetic susceptibility data (Fig. 5.2). We note that the specific-heat anomaly of Sm$_2$CuO$_4$ is only slightly suppressed by an applied field and that the effect of an anisotropic antiferromagnetic exchange is weak. One observes a shift of the specific-heat peak from 5.95 K to 5.90 K ($\Delta T_N = 0.05$ K) in a magnetic field of 80 kOe applied parallel ($H//c$) and perpendicular ($H//ab$) to the crystal $c$-axis. Similar effects were reported by Holubar et al. [18] for a polycrystalline Sm$_2$CuO$_4$ sample, for which a
considerably larger shift of about 0.14 K was observed in an applied field of 110 kOe, along with a larger reduction of the specific-heat peak.

![Temperature-dependent specific heat of T'-phase Sm$_2$CuO$_4$, in zero field (□) and in a magnetic field of 80 kOe, applied parallel (o) and perpendicular (△) to the crystal c-axis (from N.T. Hien, Ref. [19]).](image)

**Figure 5.5:** Temperature-dependent specific heat of T'-phase Sm$_2$CuO$_4$, in zero field (□) and in a magnetic field of 80 kOe, applied parallel (o) and perpendicular (△) to the crystal c-axis (from N.T. Hien, Ref. [19]).

The specific-heat data of the superconducting T'-phase SmLa$_{1-x}$Sr$_x$CuO$_{4.8}$: Sr(sc)-0.15 and Sr(sc)-0.20 samples, as well as those of the non-superconducting Sr(n)-0.20 sample are shown in Figs. 5.6 - 5.8. The electrical resistivity and low-field magnetization data have already established that the Sr(sc)-0.15 and Sr(sc)-0.20 samples are superconducting with $T_c = 23$ and 16 K, respectively [11, 20]. However, no specific-heat jump associated with the superconducting transition is indicated in Figs. 5.6 and 5.7. Additionally, instead of a sharp $\lambda$-type of peak, signifying a long-range antiferromagnetic ordering, the peaks shown in these figures are broad and “bell-shaped”, characterizing an electronic Schottky anomaly that arises from CEF splitting of the Sm–4$f$ electronic energy levels. Upon application of an external magnetic field of 140 kOe parallel to the crystal c-axis,
Magnetic properties of T'-phase SmLa$_{1-x}$Sr$_x$CuO$_{4.5}$

Figure 5.6: (a) Temperature-dependent specific heat of a superconducting T'-phase Sr(sc)-0.15 sample, in zero field (□) and in a magnetic field of 140 kOe (○) applied parallel to the crystal c-axis. Note that the scales used here are different from those employed in Fig. 5.5. (b) The c/T vs $T^2$ plot of the same data.

The temperature $T_m$ corresponding to the maxima is slightly shifted to lower temperature ($\Delta T_m \approx 0.05$ K) with a slight increase of the peak height. We note that the behavior of this field-dependent specific-heat data resemble those of the antiferromagnetic ordering or a Kondo effect due to dilution of the magnetic Sm$^{3+}$ ions by the non-magnetic La$^{3+}$ ions.

As shown in Fig. 5.1, the Sm ions in the T'-type Sm$_2$O$_2$ block layers of the T'-phase SmLa$_{1-x}$Sr$_x$CuO$_{4.5}$ are coordinated by approximately a cubic oxygen environment in a fluorite-like arrangement. According to Hund’s rules, the ground state of this Sm ion has a total angular momentum of $J = 5/2$ which is split into $2J + 1 = 6$ energy levels by the CEF effect. As a first approximation, due to the lack of crystal-field studies on this T'-phase compound, the energy-level scheme employed to fit the specific-heat data is adopted from the T'-phase Sm$_2$CuO$_4$ analysis by Strach et al. [21] based on the result of Raman scattering measurements. In this scheme, three doublets are assigned to energy levels of
Figure 5.7: (a) Temperature-dependent specific heat of a superconducting T*-phase Sr(sc)-0.20 sample, in zero field (□) and in a magnetic field of 140 kOe (○) applied parallel to the crystal c-axis. Note that the scales used here are different from those employed in Fig. 5.5. (b) The c/T vs T^2 plot of the same data.

(0, 108 cm\(^{-1}\) \(\sim\) 155 K), and 221 cm\(^{-1}\) \(\sim\) 318 K). However, the most important phenomenon is the splitting of the Kramers doublet(s) in the absence of an external magnetic field, which is presumably due to the exchange interaction between the Sm ions and the ordered Cu spins. Application of an external magnetic field is, therefore, expected to result in a Zeeman splitting of the doubly degenerate energy levels. The scenario is schematically illustrated in Fig. 5.9. It is to be noted that the real splitting of the higher-energy doublets might be different from this simple picture. It will be shown, nonetheless, that these excited levels (with energy above \(\sim\) 100 K) have a negligible effect on the low-temperature fitting.

In addition to the linear-electronic (as expressed by \(\gamma T\)) and lattice (Debye and Einstein modes) terms, the electronic Schottky contribution to the specific heat can be expressed on the basis of the above model as follows:
Magnetic properties of T'-phase SmLa_{1-x}Sr_xCuO_{4.6}  

Figure 5.8: (a) Temperature-dependent specific heat of a non-superconducting T'-phase Sr(n)-0.20 sample, in zero field. Note: The vertical scale is different from those of Fig. 5.5. (b) The same data plotted in the c/T vs T^2 curve.

\[ c_{Sch}(H,T) = \frac{nR}{2T^2} \sum_{i=0}^{n} \sum_{j=0}^{n} (E_i - E_j)^2 \exp \left( -\frac{E_i + E_j}{T} \right) \sum_{i=0}^{n} \sum_{j=0}^{n} \exp \left( -\frac{E_i + E_j}{T} \right) \]  

(5.2)

with \( E_0 = \Delta_0 - \Delta/2, E_1 = \Delta_0 + \Delta/2, E_2 = \Delta_1 - \Delta/2, E_3 = \Delta_1 + \Delta/2, E_4 = \Delta_2 - \Delta/2, \) and \( E_5 = \Delta_2 + \Delta/2. \) \( \Delta_0, \Delta_1, \) and \( \Delta_2 \) represent the crystal-field energy levels of the Sm^{3+} ions in Sm_2CuO_4, which are assumed to be the same as those of SmLa_{1-x}Sr_xCuO_{4.6} in the absence of exchange and/or Zeeman interaction. The constant \( R = 8.314 \text{ J/mol.K} \) is the universal gas constant, while \( \Delta \) represents a common value of the Kramers doublet splitting due to those interactions. The factor \( n \) indicates the fraction of magnetic Sm ions involved in the excitation, in order to take into account the possibility of its mixed-valence state in this T'-phase compound. This possibility has been suggested by the magnetic susceptibility data as described previously. More clearly, \( n = 1 \) if all the Sm ions are magnetic, being in the valence state of Sm^{3+}. It is to be noted
Fig. 5.9: A model of the electronic energy-level scheme of Sm$^{4+}$ ions in $T^*$-phase $SmLa_{1.3}Sr_2CuO_{4+\delta}$; the ground state $J = 5/2$ multiplet is shown, in the absence and presence of exchange and/or Zeeman interaction. See text for details.

at this point, that a possible low-temperature quadratic electronic term ($\sim \alpha T^2$), which is expected to occur in zero field of a $d$-wave superconductor with lines of nodes in the gap function [22], has been neglected in this fitting due to the relatively overwhelming contribution of electronic Schottky term at low temperature. The analyses of the data were performed by individual fitting of each data set to Eq. (5.2). It is worth noting that Eq. (5.2) reduces to the well-known two-level Schottky function given by

$$c_{Sch}(H, T) = nR \left(\frac{\Delta}{T}\right)^2 \frac{\exp(\Delta/T)}{[1 + \exp(\Delta/T)]^2}$$

which is valid when only the splitting of the lowest Kramers doublet is considered.
Fig. 5.10 describes the result of individual fitting of the specific-heat data of a superconducting T*-phase Sr(sc)-0.15 sample. The broken lines represent the individual contributions associated with the linear-electronic (L), lattice Debye (D), lattice Einstein (E), and the electronic Schottky contribution (S), as labeled. The best fit of these data yields the following values for the parameters: $\gamma(0) \approx 3.0 \text{ mJ/mol.K}^2$, $n \approx 0.76$ and $\Delta = (4.38 \pm 0.03) \text{ K}$ for $H = 0$, while $\gamma(140 \text{ kOe}) \approx 25.0 \text{ mJ/mol.K}^2$, $n \approx 0.81$ and $\Delta = (4.44 \pm 0.01) \text{ K}$ for $H = 140 \text{ kOe}$. It was found that $\Theta_D = 332 \text{ K}$ and $T_c \approx 100 \text{ K}$ for both data sets. We note that the resulting $\gamma(0)$ value deduced from this fitting is comparable with the homologous T-phase La$_{2-x}$M$_x$CuO$_{4.8}$ ($M = \text{Sr, Ca}$) [23], while an inaccurate large $\gamma$ value for $H = 140 \text{ kOe}$ is apparently due to the presence of the rare-earth Sm ions. Besides, the occurrence of a mixed-valence state of the Sm ions is also revealed by the value of $n$ which differs from 1. Further, a non-zero value of $\Delta$ in $H = 0$, $\Delta = 4.38 \text{ K}$, clearly signifies a splitting of the Kramers doublet in the absence
Figure 5.11: The temperature dependence of the Schottky contribution to the specific heat. The solid lines are the fitted Schottky curve according to Eq. (5.2), and its extrapolation in the lower temperature regime.

of an external magnetic field. This gap value slightly increases upon the application of an external magnetic field of $H = 140$ kOe parallel to the $c$-axis, resulting in an enlarged value of $4.44$ K for $\Delta$. It is important to mention at this point that the Zeeman splitting energy of this $T^*$-phase Sr(sc)-0.15 sample is smaller than that of the $T'$-phase Sm$_2$CuO$_4$ for the same $H$ value, in which case the values of $3.3$ cm$^{-1}$ (4.75 K) and $5.5$ cm$^{-1}$ (7.92 K) have been theoretically predicted for fields applied in the $ab$-plane and parallel to the $c$-axis direction, respectively [24].

The excess specific heat associated with the resulting electronic Schottky contribution, $c_{Sch}(T)$, obtained after subtracting the total specific-heat data by the linear-electronic and lattice terms, is shown in Fig. 5.11, along with the fitted lines and its extrapolation in the lower temperature regime below $\sim 1.6$ K, where experimental data are not available. It turns out that the high-field data can be fitted very well by the theoretical curves, whereas the fit is not as good for the zero-field data.
Figure 5.12: Temperature-dependent electronic Schottky entropy, $S(T)$. The horizontal dashed lines are the theoretically expected values of $S = nR \ln(2)$. See text for discussion.

The electronic Schottky entropy, $S(T)$, obtained by numerical calculation of $S(T) = \int_0^T \frac{c_{Sch}}{T'}dT'$ is displayed in Fig. 5.12. In order to reduce the uncertainty in calculating this value, the entropy in the lower temperature regime below $\sim 1.6$ K was calculated from the extrapolated fitting lines. As shown in this figure, the calculated total entropy at $T \approx 20$ K are reasonably close to the theoretical values of $S = nR \ln(2)$ shown by the horizontal dashed lines, corresponding to a doublet ground state with $nR$ - Sm ions participating in the excitation. In the figure the different values of $nR$ for $H = 0$ and $H = 140$ kOe are indicated. The field-dependent value of $n$ may have a significant physical origin, which requires additional data for its clarification. It is clear from the figure that the experimental values of $S$ in the low temperature regime for both cases are much closer to the theoretical value given by $S = nR \ln(2)$ than that given by $S = nR \ln(6)$. The unavoidable implication of this evidence is that the higher energy doublets associated with $(2J + 1) = 6$ are not playing a significant role in that temperature regime. This conclusion holds even when another set of crystal-field levels
of 0.175 and 242 cm\(^{-1}\), adopted by Nekvasil [25], is used in the fitting. However, above 20 K, these contributions become noticeable.

Regarding the splitting of the Kramers doublet in T\(^{-}\) phase Sm\(_{1-x}\)Sr\(_x\)CuO\(_{4+\delta}\) in the absence of an external magnetic field, we tentatively ascribe this phenomenon to the superexchange interaction between the Sm–4\(f\) electrons with the neighboring Cu spins, in analogy with the case of Nd–CuO\(_4\) [26-28]. This situation is in contrast to that found in T\(^{-}\) phase Sm\(_2\)CuO\(_4\), in which case there is no indication for a coupling between the Sm magnetic moments and the Cu spins due to the orthogonal arrangement of their moments [4, 8, 9]. Thus, the observed differences in magnetic behaviors between the T\(^{-}\) phase Sm\(_{1-x}\)Sr\(_x\)CuO\(_{4+\delta}\) and T\(^{-}\) phase Sm\(_2\)CuO\(_4\) (in particular for the nature of Sm-Cu interaction) is likely to come from the different local environments around the magnetic Sm\(^{3+}\) ions. As a final note, we stress that further 'microscopic' measurements, such as optical and neutron diffraction, are still needed in order to probe more detailed magnetic properties of the T\(^{-}\) phase Sm\(_{1-x}\)Sr\(_x\)CuO\(_{4+\delta}\), and for a further theoretical study of the underlying physical mechanisms.

References

Magnetic properties of T-phase SmLa$_{1-x}$Sr$_x$CuO$_{4-δ}$


