Low temperature magnetic phases transitions in PrBa$_2$Cu$_3$O$_{6.95}$

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Abstract. We present the results of an experimental study on a polycrystalline sample of PrBa$_2$Cu$_3$O$_{6.95}$ by performing specific heat $C_p(T)$ and susceptibility $\chi(T)$ measurements at low temperature. The Néel temperature $T_N$ of the Pr anomalous antiferromagnetic (AFM) ordering, is confirmed in the $C_p(T)/T$ versus $T$ curve by a large anomaly at 14.0 K. The second critical temperature $T_{cr} \approx 4-5$ K which was already reported is clearly observed in the temperature dependence of specific heat, entropy and susceptibility. Another important result is the rapid increase of susceptibility just below the minimum at $T_{cr}$, which is attributed to the appearance of a weak ferromagnetic ordering along the c axis. The value of the electronic linear term coefficient $\gamma$ from $C_p(T)$ below $T_{cr}$ (80 mJ/mol K$^2$) is much lower than some previously reported values. The $T^3$ specific heat term is fitted for the first time.

1. Introduction

Among all the rare-earth cuprate systems, and especially the REBa$_2$Cu$_3$O$_{6+x}$ (RE = Y or rare earth) family, those with praseodymium became of great interest since most of them were not found to be superconducting [1]. This particular behavior has inspired extensive studies of the physical properties of the PrBa$_2$Cu$_3$O$_{6+x}$ (hereafter PrBCO$_{6+x}$) in order to determine why only Pr suppresses the superconducting state while the other lanthanides exhibit weak magnetic effect [2]. The first temperature dependence of the specific heat $C_p(T)$ and susceptibility $\chi(T)$ performed on PrBCO$_{6+x}$ ($x=0.9$) revealed an anomaly at $T_{N2}=5.2$ K below $T_N=17$ K [3, 4]. This $T_{N2}$ transition is confirmed by neutron diffraction experiments performed on sample with $x=0.93$ by a small anomaly on the (1/2;1/2;1) magnetic Bragg peak at 5 K [5]. An analysis of the thermal properties on PrBCO$_{6+x}$ ($x=0.9$) in term of the Grüneisen parameter yields to the appearance of a sharp increase of this latter below a temperature transition $T_i=5$ K [6]. This work is devoted to the determination of the nature of the transition at 4-5 K which has not been precised until now.

2. Experimental

The specific heat measurements $C_p(T)$, have been made using an ac temperature calorimeter in the 1.4-45 K temperature range. The initial polycrystalline sample (a parallelepiped of 9.04$^L \times 1.81^b \times 2.30^h$ mm de volume geometrique =37.42 mm$^3$; weight=0.11934 g) obtained by the standard ceramic method preparation is an under doped (UN) material with a quadratic crystallographic structure showed by X-ray diffraction. The sample was cut in two parts: one of it was submitted to controlled
oxygen atmosphere. The optimally doped (OP) material obtained by absorbing half a mol of oxygen has an orthorhombic crystallographic structure and grain size in the 10 μm range. The values of the expected oxygen contents are $x=0.95$ and $x=0.44$ respectively for the OP and UN states and we will henceforth refer our sample as PrBCO6+$x$ ($x=0.95$) in this study. The structural analysis details are given by [7]. The susceptibility measurements $\chi(T)=|M/H|(T)$ with $H=0.01$ T, low enough to avoid any nonlinear effect, have been made using a very sensitive vibrating magnetometer in the 1.5-50 K temperature range.

3. Results
We have reported in figure 1 the temperature dependence of $C_p(T)/T$ and $C_p(T)/T^2$ in the 1.4 K–45 K temperature range. A large anomaly is observed in the $C_p(T)/T$ curve and the value of the Néel temperature $T_N$ can be well determined at 14.0 K. In addition to $T_N$, figure 1 shows a small shoulder near a critical temperature labeled as $T_c$$\approx$4-5 K. It corresponds to a change of the concavity in the $C_p(T)/T^2$ curve with a pronounced upturn until 1.4 K. The temperature dependence of $S(T)/T$ and $S(T)/T^2$, where $S(T)$ is the entropy, are shown in figure 2. The Néel temperature $T_N$ is well identified at the same value (14.0 K) in both curves. In addition to $T_N$ and below an inflection point near 10.5 K, we observe a large peak in the $S(T)/T^2$ curve near $T_c$$\approx$4-5 K. It corresponds to a change of the concavity in the $S(T)/T^2$ curve with a pronounced updown until 1.4 K. In a good approximation, the $C_p(T)$ data can be described by the sum of four contributions: $C_p(T)=C_p^{HQ}(T)+C_p^{EL}(T)+C_p^{MR}(T)+C_p^{mr}(T)$.

\[C_p^{HQ}(T) = A. T^2\] is the hyperfine nuclear contribution which could be caused by hyperfine-field and/or electric quadrupolar interactions; $C_p^{EL}(T) = \gamma. T$ is the electronic linear term; $C_p^{MR}(T) = (M+R).T^3$ is the sum of two contributions [8] which are attributed to: the AFM magnon term from the Pr-Pr and Cu-Cu interactions and the harmonic phonon contributions respectively; $C_p^{mr}(T) = (m+r).T^5$ is also the sum of two contributions: the bi-quadratic magnetic exchange term due to the Pr-Cu magnetic coupling [9] and the anharmonic phonon contributions respectively. At these lower temperatures the curve $C_p(T)/T$ versus $T^2$ is fitted with the general formula:

\[
[C_p(T)/T](T^2) = A_c(T_c)^{-3/2}+\gamma (M+R)(T^2)+(m+r)(T^2)^2
\]

The fit is making below the critical temperature $T_c$ in the 1.4 K-2.5 K temperature range. We have reported in figure 3, the fitted curves $C_p(T)/T$ versus $T^2$. The upturn in the $C_p(T)/T$ fit curve which appears at these lower temperatures is associated to nuclear Schottky anomaly. The non linear effects coefficient $(m+r)$ equal to $+10^3$ mJ/mol.K$^2$ are now well observed in our results (Figure 3) and the best values obtained for the different parameters are gathered on table 1.

![Figure 1](image1.png)  **Figure 1.** Temperature dependence of $C_p(T)/T$ and $C_p(T)/T^2$ curves of PrBCO6+$x$ ($x=0.95$).

![Figure 2](image2.png)  **Figure 2.** Temperature dependence of $S(T)/T$ and $S(T)/T^2$ curves of PrBCO6+$x$ ($x=0.95$).
One of the most notable properties of PrBCO$_{6+x}$ system is the electronic linear term coefficient $\gamma$ in the low-temperature region of specific heat $C_p(T)$. Our $\gamma$ value estimated to 80 m J/mol.K$^2$ is too lower in comparison with those reported by some author values [3, 10].

In figure 4, the susceptibility $\chi(T)$ curve is well fitted by a modified Curie-Weiss Law (MCW) $\chi(T) = \chi_0 + C/(T-\theta_p)$ from 25 K to 300 K giving the independent temperature susceptibility $\chi_0=0.00131$ emu/mol, the Curie constant $C=1.13275$ emu K mol$^{-1}$ (with the effective moment of 3.01 $\mu_B$) and the paramagnetic temperature $\theta_p=-7.97$ K. The critical $T_N$ is clearly evident in the divergence of the fit (see insert of figure 4). We show in figure 5 and 6 the temperature dependence of $\chi(T)$ and $\chi(T)\chi_0(T-\theta_p)$ respectively. The minimum in these curves is situated at 4-5 K and corresponds to the above defined critical temperature $T_{cr}$.

Table 1. Comparison of the different coefficients between our results from the fitted curve in figure 3 and fitted values from [3, 10].

|                | A (mJ K mol$^{-1}$) | $\gamma$ (mJ mol$^{-1}$ K$^{-2}$) | M+R (mJ mol$^{-1}$ K$^{-4}$) | $m+r$ (mJ mol$^{-1}$ K$^{-6}$) | Temperature range | $T_N$ (K) |
|----------------|---------------------|-----------------------------------|----------------------------|-----------------------------|------------------|-----------|
| [3] (x=1)      |                     | 114                               |                            |                             | 1.5 K\(\leq T\leq 5\) K | 17.0      |
| [10] (x=0.95)  | 61                  | 102                               | 6.99                       | -                          | 0.3 K\(\leq T\leq 1.5\) K | 17.0      |
| Our results    | 60                  | 80                                | 8.50                       | + 0.001                    | 1.4 K\(\leq T\leq 2.5\) K | 14.0      |

4. Discussion and conclusion

The spontaneous behaviour of a polycrystalline sample of PrBCO$_{6+x}$ (x=0.95) is studied by means of specific heat $C_p(T)$ and susceptibility $\chi(T)$ measurements. From the temperature dependence of $C_p(T)/T$, $C_p(T)/T^2$, $S(T)/T$ and $S(T)/T^2$ in the 1.4 K–45 K temperature range, three magnetic phases are well identified and separated by the two critical temperatures: the Néel temperature $T_N=14.0$ K and the nether been studied before $T_{cr}\approx 4.5$ K. The value of $\gamma$ (80 m J/mol.K$^2$) is reduced in comparison with the overestimated values reported by some author [3, 10]. The $(m+r)$ coefficient (+10$^{-3}$ mJ/mol.K$^6$) of the specific heat $T^4$ term related to the Pr-Cu coupling is fitted for the fist time.
The rapid increase of susceptibility curves just below the minimum at $T_{cr}$ is attributed to the appearance of the weak ferromagnetic order along the c axis [5,11]. The observation of this anomaly at the same critical temperature ($T_{cr}$≈4-5 K) on specific heat and susceptibility measurements performed on our UN polycrystalline sample of PrBCO$_6$+$x$ ($x=0.44$) below the Néel temperature $T_N=9$ K [12] shows that the magnetic effect is not influenced by the state of oxygenation. The occurrence of this magnetic phase transition at 3-4 K in another system like “Pr124” [13] permits us to confirm that this phenomenon is intrinsic to the Pr sublattice. The significance of the work reported here lies in the fact that it proves that $T_{cr}$ is a true magnetic phase transition temperature which is probably associated to the transition from the commensurability to the incommensurability of the anomalous magnetic structure with a doubling of the magnetic periodicity along the c axis [11,14,15].

5. References

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