Calorimetric studies on the magnetic order of $Pb_2Sr_2TbCu_3O_{8+\delta}$

C. R. Shih and T. H. Meen
Department of Physics, National Sun Yat-Sen University, Kaohsiung, Taiwan 80424, Republic of China
and Institute of Electrical Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan 80424, Republic of China

Y. C. Chen
Institute of Electrical Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan 80424, Republic of China

H. D. Yang
Department of Physics, National Sun Yat-Sen University, Kaohsiung, Taiwan 80424, Republic of China
(Received 22 April 1994)

The magnetic-field dependence of the specific-heat measurements on $Pb_2Sr_2TbCu_3O_{8+\delta}$ with $0.5\ K < T < 30\ K$, are reported in order to study the magnetic order in this compound. Anomalies in the specific heat $C(T)$ of $Pb_2Sr_2TbCu_3O_{8+\delta}$ are observed at $T_{N1} \sim 5.3$ K and $T_{N2} \sim 2.4$ K, which are related to two antiferromagnetic transitions in the Tb sublattice. While the anomaly seen in the specific heat as well as in the magnetic susceptibility at $T_{N1} \sim 5.3$ K is suppressed, the peak position is unaffected with increasing magnetic fields. On the other hand, the anomaly at $T_{N2} \sim 2.4$ K is quickly suppressed by a low field. The entropy change associated with the magnetic transitions deduced from the specific heat of $Pb_2Sr_2TbCu_3O_{8+\delta}$ by subtracting the data from $Pb_2Sr_2YCu_3O_{8+\delta}$ up to $T=12$ K is about 5.8 J/mol K ($\sim R \ln 2$), indicative of a doublet ground state for Tb in the crystalline electric fields. In addition, the magnetic specific heat far below the transitions has the form $C_M(T) = AT^2 + B/T^2$, suggesting contributions from two-dimensional magnon and nuclear Schottky, respectively. These results are discussed in comparison to those of related compounds, such as $RBa_2Cu_3O_7$ and $Pb_2Sr_2RCu_3O_{8+\delta}$.

Since the high-T_c superconductor $La_{2-x}Ba_xCuO_4$ was discovered,[1] many other high-T_c superconductors with modified perovskite structures have been found. Almost all these copper oxide high-T_c superconductors have a similar fundamental structure consisting of conducting CuO_2 plane layers and intercalated layers known as the charge reservoir. These insulating compounds become metallic and superconducting by the way of charge transfer from the reservoir to the CuO_2 plane layers and the T_c depends on the hole concentration in the CuO_2 plane. Recently Cava *et al.*[2] and Subramanian *et al.*[3] reported the existence of bulk superconductivity in $Pb_2Sr_2(R,Ca)Cu_3O_{8+\delta}$ (R = rare earth) and the crystal structure of these compounds is orthorhombic. The samples without Ca doping are insulators but become superconducting with partial Ca substitution for the rare earths.[3] As for $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$, it shows a variation of T_c in x with a maximum of $T_c \sim 70$ K for $x = 0.5$.[4] This series has received a great deal of attention because of its closely related structure to that of $RBa_2Cu_3O_{7-\delta}$ (R = rare earths) except that the CuO chain is replaced by the PbO-CuO_δ-PbO triple-layered block.[5] Chaillout *et al.* deduced from single-crystal neutron diffraction that the charge transfer takes place from (Y,Ca) layers to the CuO_2 layers in $Pb_2Sr_2(Y,Ca)Cu_3O_{8+\delta}$ with respect to the route mentioned above, such as in $YBa_2Cu_3O_{6+\delta}$ the charge transfer from the chain Cu to the planar ones.[6] It should be pointed that single-phase $TbBa_2Cu_3O_{7-\delta}$ cannot be synthesized with the traditional solid-state-reaction methods because of the existence of stable impurity phases of $TbBaO_3$ and $BaCuO_2$,[7] while $Pb_2Sr_2TbCu_3O_{8+\delta}$ is one of the very few Tb-containing cuprates. Preliminary results[8,9] have indicated that the magnetic ordering temperature (T_N) for $Pb_2Sr_2TbCu_3O_{8+\delta}$ is about 5.5 K, which is lower than that of $PrBa_2Cu_3O_{7-\delta}$ ($T_N \sim 17$ K) (Ref. 10) and $Pb_2Sr_2PrCu_3O_{8+\delta}$ ($T_N \sim 8.5$ K) (Ref. 8) but higher than that of other corresponding magnetic rare-earth cuprates, such as $GdBa_2Cu_3O_{7-\delta}$ ($T_N \sim 2.2$ K) (Ref. 11) and $Pb_2Sr_2GdCu_3O_{8+\delta}$ ($T_N \sim 2.4$ K).[8] Therefore, it is worthwhile to investigate the magnetic order of Tb in $Pb_2Sr_2TbCu_3O_{8+\delta}$ and compare the similarities and differences with Pr, Gd, and other rare-earth-based cuprates. In this paper we report the results of the specific-heat and magnetic-susceptibility measurements on $Pb_2Sr_2TbCu_3O_{8+\delta}$ and compare the results to the related compounds $RBa_2Cu_3O_{7-\delta}$ and $Pb_2Sr_2RCu_3O_{8+\delta}$.

The details of sample preparation, characterization, and dc magnetic-susceptibility measurements were described elsewhere.[8] Ac magnetic-susceptibility data were taken in a low frequency (~ 20 Hz) and at a low field (~ 2 Oe) on a powder sample. The specific heat of pieces (~ 5 mg) cut from the samples was measured in the range of 0.5–12 K with a ^{3}He relaxation calorimeter using the heat-pulse technique[12] at fields of 0, 2, and 4 T. The samples were attached to a sapphire chip, which has two separated silicon films deposited on it to serve as the heater and thermometer. The Si-film thermometer was calibrated against a calibrated germanium thermometer. For measurements in magnetic fields, a calibrated capacitance sensor was used to calibrate the thermometer. For each point of the specific-heat measurements, a small heat power was introduced to the chip and the thermal relaxation was measured and analyzed to obtain the

specific heat of the samples.

Figure 1 shows the low-temperature specific heat for $Pb_2Sr_2YCu_3O_{8+\delta}$ without magnetic field and $Pb_2Sr_2TbCu_3O_{8+\delta}$ with fields of 0, 2, and 4 T. The shape of the specific heat for $Pb_2Sr_2TbCu_3O_{8+\delta}$ is more similar to the Gd-containing cuprates than to the Pr-containing ones. In zero field, the specific heat of $Pb_2Sr_2TbCu_3O_{8+\delta}$ decreases parallel with that of $Pb_2Sr_2YCu_3O_{8+\delta}$ down to 8 K and then starts to deviate from the smooth curve. The clear λ-like specific heat is formed with a sharp peak at 5.3 K marked by T_{N1}. The anomaly at 5.3 K in the specific heat for $Pb_2Sr_2TbCu_3O_{8+\delta}$ corresponding to the Tb antiferromagnetic order is consistent with the previous magnetic-susceptibility study.[8] With decreasing temperature there is another peak at 2.4 K marked by T_{N2} whose magnitude is much smaller than that at 5.3 K. This compound does not contain Ba constituent and no extra peak in the x-ray-diffraction pattern is detected within our instrument resolution. Thus, it reduces the possibility that the magnetic transition at 2.4 K is due to impurity phases (such as $TbBaO_3$). It is noted that the anomaly at 2.4 K can be reproduced in samples from different batches and is also evidenced by the ac susceptibility measurement with a 2-Oe magnetic field as shown in the inset of Fig. 2. Therefore, this anomaly may be attributed to another antiferromagnetic ordering structure in analogy with the observation in the intermetallic ternary compound $Tb_2Fe_3Si_5$.[13] It is noted that the anomaly at 2.4 K is totally suppressed by field of 2 T in specific heat (Fig. 1) or not seen in the dc magnetic susceptibility (Fig. 2). This suggests that the anomaly at 2.4 K may be associated with a weak magnetic order such as spin reorientation or short-range magnetic order, which can be easily destroyed by applying a large magnetic field. The specific heat above the ordering temperature increased with field is similar to $PrBa_2Cu_3O_{7-\delta}$ (Ref. 14), but is different from $DyBa_2Cu_3O_{7-\delta}$ in which the specific heat above ordering temperature is suppressed with field.[15] The ordering temperature T_{N1} at 5.3 K shows little change with field both in specific heat (Fig. 1) and dc magnetic-susceptibility data (Fig. 2). This is similar to the magnetic-susceptibility results for $PrBa_2Cu_3O_{7-\delta}$

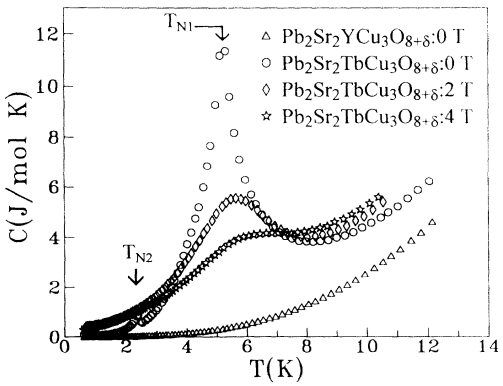

FIG. 1. The low-temperature specific heat of $Pb_2Sr_2TbCu_3O_{8+\delta}$ with fields of 0, 2, and 4 T. The data of $Pb_2Sr_2YCu_3O_{8+\delta}$ in zero field are also included as the background.

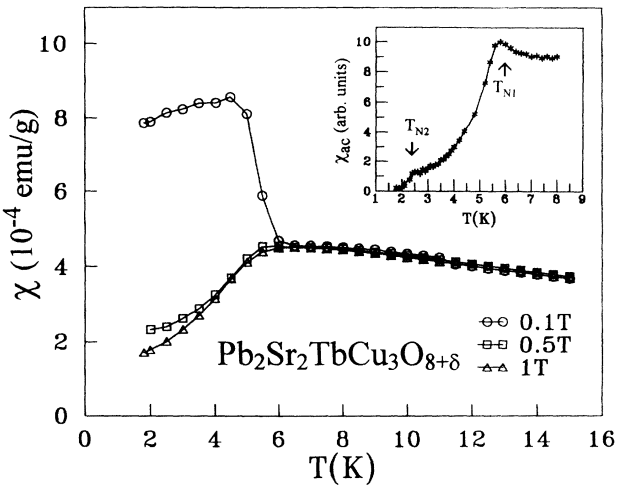

FIG. 2. The low-temperature magnetic susceptibility of $Pb_2Sr_2TbCu_3O_{8+\delta}$ with applied fields of $H=0.1$, 0.5, and 1 T. The inset shows the ac magnetic-susceptibility data under magnetic field of 2 Oe.

(Ref. 10) and $Pb_2Sr_2PrCu_3O_{8+\delta}$ (Ref. 16) but dissimilar for $DyBa_2Cu_3O_{7-\delta}$ (Ref. 15) and $GdBa_2Cu_3O_{7-\delta}$ (Ref. 17) in which the T_N is lowered by the applied fields.

Figure 3 shows the magnetic specific heat C_M of $Pb_2Sr_2TbCu_3O_{8+\delta}$ by subtracting the specific heat of $Pb_2Sr_2YCu_3O_{8+\delta}$ as the background assuming the same lattice and electronic contributions to specific heat for these two compounds. The magnetic entropy change, estimated from $\Delta S_M(T)=\int C_M(T)/TdT$, up to 12 K is about 5.8 J/mol K, which is close to R ln2 (5.76 J/mol K), suggesting a doublet ground state. A previous susceptibility measurement[8] showed that μ_{eff} of $Pb_2Sr_2TbCu_3O_{8+\delta}$ is about $10.04\mu_B$, close to $9.72\mu_B$, indicative of Tb^{+3}. In comparison the entropy change for $PrBa_2Cu_3O_{7-\delta}$ is about 5 J/mol K, which is smaller than the expected entropy change due to the ordering of a crystalline electric-field doublet ground state. This has been used to argue for the mixed valence for the Pr

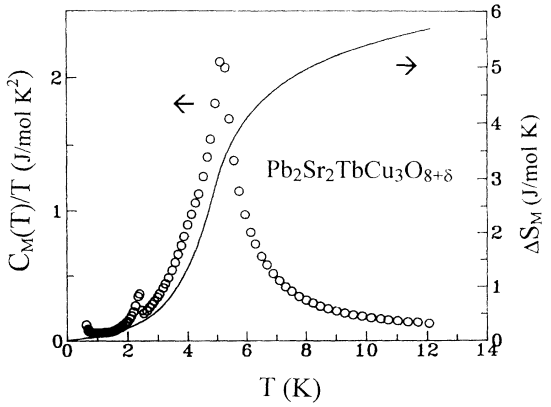

FIG. 3. The magnetic contribution to the specific heat $C_M(T)$, where $C_M(T)=C(Pb_2Sr_2TbCu_3O_{8+\delta})-C(Pb_2Sr_2YCu_3O_{8+\delta})$ and entropy $S_M(T)$ (solid line) for $Pb_2Sr_2TbCu_3O_{8+\delta}$.

TABLE I. The magnetic ordering temperature (T_N), effective moment (μ_{eff}), and magnetic entropy change (ΔS) for $Pb_2Sr_2RCu_3O_{8+\delta}$ (2213) with R = Pr, Gd, and Tb and for $RBa_2Cu_3O_{7-\delta}$ (1237) with R = Pr and Gd. The calculated effective moments of free trivalent ions for Pr, Gd, and Tb are also included for comparison.

Compound	T_N (K)	$\mu_{eff}(\mu_B)$	$\mu_{eff}(\mu_B)$ calculated free ion	ΔS(J/mol K)	Ref.
Pr-1237	17	2.7		$\sim 0.87R$ ln2	19,25
Gd-1237	2.2	7.5		$\sim R$ ln8	11,26
Pr-2213	8.5	3.1	Pr^{+3}:3.58		8
Gd-2213	2.4	7.8	Gd^{+3}:7.94	$\sim R$ ln8	8,22
Tb-2213	5.3	10.04	Tb^{+3}:9.72	$\sim R$ ln2	8, this work

state.[18] The μ_{eff} and entropy change for other related compounds are listed in Table I for comparison. The upturn in C_M/T below 0.9 K (Fig. 3) is associated with a nuclear Schottky anomaly similar to the observation in many other cuprates.[19] In the temperature range far below transition at T_{N1} the magnetic contribution to specific heat can be described by a power law $C_M = AT^2 + B/T^2$, where the first term is a characteristic of two-dimensional (2D) magnons and the second term is the property of nuclear Schottky anomaly. Figure 4 shows the fitting results as well as the values of A and B for $Pb_2Sr_2TbCu_3O_{8+\delta}$ with fields of 0, 2, and 4 T. In curve 4(a), the data can be fit only in the temperature range of 0.6–1.8 K and the fitting curve starts to deviate from the data points above 1.8 K due to the anomaly at T_{N2}. In curves 4(b) and (c), the anomaly at T_{N2} is suppressed by magnetic fields and the data points can be fit up to 5.1 and 4.2 K, respectively. Apart from the zero-field data, the A decreases with fields suggesting that

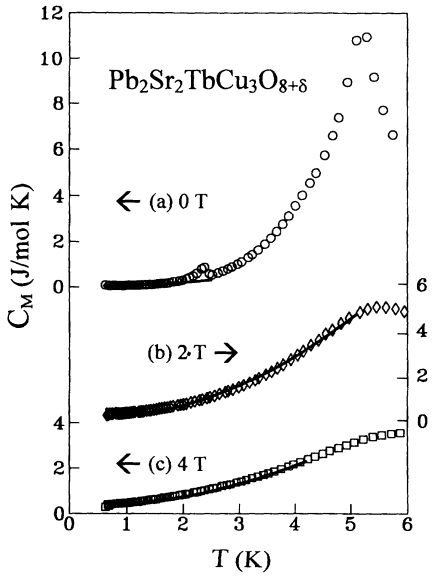

FIG. 4. The fitting of magnetic specific-heat data C_M to power law $AT^2 + B/T^2$ (solid lines) with magnetic fields of (a) 0, (b) 2, and (c) 4 T. The fitting parameters A and B with magnetic fields of 0, 2, and 4 T are equal to 49.9 mJ/mol K^3 and 10.7 mJ K/mol; 184.1 mJ/mol K^3 and 232.5 mJ K/mol; and 157.8 mJ/mol K^3 and 298.3 mJ K/mol, respectively.

the magnetic order is antiferromagnetic in nature; while the B increases with fields confirming the existence of the nuclear Schottky effect. These results are consistent with the neutron-diffraction study that the antiferromagnetic order of Tb in $Pb_2Sr_2TbCu_3O_{8+\delta}$ is a 2D dominant process with the nearest-neighbor spins in the basal plane antiparallel.[9]

The magnetic ordering temperatures for $GdBa_2Cu_3O_{7-\delta}$, $PrBa_2Cu_3O_{7-\delta}$, $Pb_2Sr_2GdCu_3O_{8+\delta}$, and $Pb_2Sr_2PrCu_3O_{8+\delta}$ are summarized in Table I. The suppression of T_N for $Pb_2Sr_2PrCu_3O_{8+\delta}$ in comparison to that for $PrBa_2Cu_3O_{7-\delta}$ may be due to the PbO-CuO_δ-PbO block causing a longer Pr-Pr distance along the c axis than that for $PrBa_2Cu_3O_{7-\delta}$. In $PrBa_2Cu_3O_{7-\delta}$, this shorter Pr-Pr distance permits one to mediate magnetic correlation along c axis, forming the 3D magnetic ordered structure for the Pr ions.[19,20] For $GdBa_2Cu_3O_{7-\delta}$, a 3D ordering process has been determined by neutron-diffraction experiments;[21] while for $Pb_2Sr_2GdCu_3O_{8+\delta}$, the long Gd-Gd distance along the c axis compared to that in the basal plane describes the effective 2D characteristic.[22] The invariance of T_N for Gd-containing compounds may be ascribed to a dipole-dipole coupling mechanism for these two compounds.[22,23] The dipole-dipole exchange interaction for $Pb_2Sr_2TbCu_3O_{8+\delta}$ can be roughly estimated with the formula $U_{d-d} \sim 4\mu^2(1/r_1^3 - 1/r_2^3)$, where $\mu = 10.04\mu_B$, $r_1 = 3.84$ Å, the nearest-neighbor distance and $r_2 = \sqrt{2}r_1 = 5.43$ Å is the second-nearest-neighbor distance. A value of 0.25 meV is obtained corresponding to 2.9 K, which is smaller than the experimentally observed magnetic ordering temperature 5.3 K. Thus, the dipole-dipole exchange interaction seems not to be the main source for Tb-Tb coupling. Also the semiconducting characteristic of $Pb_2Sr_2TbCu_3O_{8+\delta}$ suggests that there are not enough conduction electrons to mediate the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. It should be noted that a magnetic transition is also observed at $T_N \sim 5.5$ K in the superconducting ($T_C \sim 35$ K) Tb-containing cuprate $TbSr_2(Cu_{2.7}Mo_{0.3})O_{7-\delta}$.[24] This insensitivity of ordering temperature to electrical conductivity also suggests that the RKKY mechanism is unlikely for these Tb-containing cuprates. Finally, a complicated superexchange interaction could be involved in the magnetic order of Tb in $Pb_2Sr_2TbCu_3O_{8+\delta}$. The Pr ion in these Pr-, Gd-, and Tb-based compounds has the smallest effective

moment, its magnetic ordering temperature is the highest. Although Tb ion has the largest effective moment, its magnetic ordering temperature is lower than that for $Pb_2Sr_2PrCu_3O_{8+\delta}$, but higher than that for $Pb_2Sr_2GdCu_3O_{8+\delta}$. The inconsistency between the magnetic ordering temperature and effective moment may be due to an individually anisotropic magnetic coupling mechanism and/or a special route of charge transfer. At this point, the theoretical study may be helpful for clarifying their relationships.

In summary, the antiferromagnetic order of Tb in $Pb_2Sr_2TbCu_3O_{8+\delta}$ at $T_{N1}\sim 5.3$ K observed by specific-heat measurements is consistent with the magnetic-susceptibility results which is higher than that of $Pb_2Sr_2GdCu_3O_{8+\delta}$ at $T_N\sim 2.3$ K and lower than that of $Pb_2Sr_2PrCu_3O_{8+\delta}$ at $T_N\sim 8.5$ K. The magnitude of the specific-heat anomaly is suppressed with magnetic field, while the field has only little effect on T_{N1}. There is another smaller anomaly at $T_{N2}\sim 2.4$ K which may be due to a weak magnetic order or spin reorientation, which is suppressed easily by a magnetic field. The entropy associated with magnetic transitions is about R ln2, suggestive of a doublet ground state for Tb. The magnetic contribution to the specific heat well below the ordering temperature can be described by $C_M(T)=AT^2+B/T^2$, which is consistent with the observation of the 2D spin structure by neutron-diffraction experiments. A complicated superexchange interaction is proposed for the magnetic order of Tb in $Pb_2Sr_2TbCu_3O_{8+\delta}$.

We are grateful to Professor W. H. Lee for ac magnetic-susceptibility measurement and Professor W.-H. Li for helpful discussion. This research was supported by the National Science Council, R. O. C. under Contract No. NSC 83-0212-M-110-028.

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