Observation of Pr and Gd ordering in the 2212-type compounds
\((\text{Pb}_{0.5}\text{Cu}_{0.5})_2(\text{Ba}_{0.5}\text{Sr}_{0.5})_2\text{RCu}_2\text{O}_8\) \((R = \text{Pr}, \text{Gd})\)

C. L. Yang, J. H. Shieh, Y. Y. Hsu, and H. C. Ku

Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China

J. C. Ho

Department of Physics and National Institute for Aviation Research, Wichita State University, Wichita, Kansas 67260

(Received 20 March 1995; revised manuscript received 19 April 1995)

Magnetic and calorimetric measurements have been made to reveal a Pr ordering in the \((\text{Pb}_{0.5}\text{Cu}_{0.5})_2(\text{Ba}_{0.5}\text{Sr}_{0.5})_2\text{PrCu}_2\text{O}_8\) compound which has the \((\text{Pb},\text{Cu})\)-2212-type tetragonal structure with lattice parameters \(a = 3.878(3)\) Å and \(c = 27.594(9)\) Å. The transition occurs at a relatively high \(T_c(\text{Pr})\) of 9 K. In comparison, isostructural \((\text{Pb}_{0.5}\text{Cu}_{0.5})_2(\text{Ba}_{0.5}\text{Sr}_{0.5})_2\text{GdCu}_2\text{O}_8\) exhibits a \(T_c(\text{Gd})\) of only 2.2 K. The magnetic entropy associated with the Pr ordering has a lower limit value equivalent to about 20% of \(R\ln 3\) expected for Pr\(^{3+}\) with a quasitriplet ground state, suggesting a more three-dimensional-like process. These results represent the observation of anomalous Pr ordering in the 2212-type cuprate and a complete demonstration of such effects in all two-CuO\(_2\)-layer \(m=2\) \((m = 1, 2, 3)\) systems.

I. INTRODUCTION

The anomalously high antiferromagnetic Pr ordering temperature of 17 K for \(\text{PrBa}_2\text{Cu}_3\text{O}_7\) with the two-CuO\(_2\)-layer 123-type structure, which is the only nonsuperconducting member of the 90-K \(\text{RBa}_2\text{Cu}_3\text{O}_7\) system \((R = \text{Y} \text{or a rare earth})\), has been the focus of extensive research ever since the discovery of high-\(T_c\) superconductor.\(^1\)\(^–\)\(^6\) With further oxygen deficiency, \(T_N(\text{Pr})\) decreases to 10 K in \(\text{PrBa}_2\text{Cu}_3\text{O}_6\).\(^5\)\(^,\)\(^7\) In comparison, other magnetic rare-earth compounds have a maximum \(T_N(R)\) of 2.2 K in \(\text{GdBa}_2\text{Cu}_3\text{O}_7\).\(^8\)\(^,\)\(^9\) Meanwhile, Pr substitution leads to \(T_c\) suppression from above 90 K in \((\text{R}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_7\).\(^3\)\(^–\)\(^5\) For higher Pr concentration, superconductivity is totally quenched, and Pr magnetic ordering begins to set in.

From the structural viewpoint, the 123-type \(\text{PrBa}_2\text{Cu}_3\text{O}_7\) system can be reclassified as 1212C or 1212-type two-CuO\(_2\)-layer system,\(^10\) in analogous with \(\text{Tl}-1212\) \(\text{Tl}(\text{Ba},\text{Sr})\text{PrCu}_2\text{O}_7\).\(^11\)\(^–\)\(^15\) \((\text{Pb},\text{Cu})\)-1212 \((\text{Pb},\text{Cu})\text{Sr}_{2}\text{PrCu}_2\text{O}_7\)\(^13\) and \(\text{Hg}-1212\) \(\text{HgSr}_2\text{PrCu}_2\text{O}_7\) compounds.\(^16\) They also exhibit the common feature of having relatively high \(T_N(\text{Pr})\) values ranging from 4 to 8 K. Similar Pr anomalies with \(T_N(\text{Pr})\) of 6–14 K were reported recently for a new \((\text{Pb},\text{Cu})\)-3212-type two-CuO\(_2\)-layer system \((\text{Pb},\text{Cu})\text{Sr}_{2}\text{PrCu}_2\text{O}_8\) or commonly written as \(2213\) \(\text{Pb}_{1/2}\text{Sr}_{1/2}\text{PrCu}_2\text{O}_8\).\(^16\)\(^–\)\(^18\) Since in high-\(T_c\) cuprates a total replacement of Ca between the CuO\(_2\) layers can be achieved only in the two-CuO\(_2\)-layer \(m=2\) \((m = 1, 2, 3)\) structures, questions arise as to whether the anomalous Pr effect occurs when \(m = 2\). Particularly, no Pr ordering was observed down to 1.6 K in the Bi-2212 compound \(\text{Bi}_2\text{Sr}_2\text{PrCu}_2\text{O}_8\).\(^19\) Therefore, this work was carried out by synthesizing and characterizing a new \((\text{Pb},\text{Cu})\)-2212 compound \((\text{Pb}_{0.5}\text{Cu}_{0.5})_2(\text{Ba}_{0.5}\text{Sr}_{0.5})_2\text{PrCu}_2\text{O}_8\). Two other compounds with Pr substituted by Y or Gd formed the basis for comparison.

II. EXPERIMENTS

Samples with the nominal composition \((\text{Pb}_{0.5}\text{Cu}_{0.5})_2(\text{Ba}_{0.5}\text{Sr}_{0.5})_2\text{RCu}_2\text{O}_8\) \((R = \text{Pr}, \text{Gd}, \text{Y})\) were prepared by two-state solid-state reaction techniques. High-purity \(\text{BaCO}_3\), \(\text{SrCO}_3\), \(\text{R}_2\text{O}_3\), and \(\text{CuO}\) powders with the ratio \(\text{Ba:Sr:R:Cu} = 1:1:1:3\) were well mixed first, ground and calcined at 920 °C in air with intermediate grinding. The precursor \(\text{BaSrRCu}_2\text{O}_8\) powders were then mixed with the appropriate amount of \(\text{PbO}\) and heated at 730 °C in air for 24 h. The reacted powders were pressed into pellets and sintered at 825–830 °C in flowing \(\text{Ar}\) for 3 days, then quenched in liquid nitrogen.

Crystallographic data were obtained with a Rigaku RotaFlex 18 kW rotating anode powder x-ray diffractometer using Cu \(K_\alpha\) radiation with a scanning rate of 1° in 2θ per minute. A Lazy-Pulverix-PC program was employed for phase identification and lattice parameter calculation. ac electrical resistivity (16 Hz) was measured by the standard four-probe method in a RMC Cryosystems closed-cycle refrigerator. Magnetic susceptibility \(\chi(T)\) and magnetic hysteresis \(M(H)\) measurements were carried out with a Quantum Design MPMS superconducting quantum interference devices (SQUID) magnetometer down to 2 K in an applied field from 50 G to 5 T. Low-temperature specific-heat measurements were made with an adiabatic calorimeter\(^14\) for \(R = \text{Pr}\) and Gd or a relaxation calorimeter\(^11\) for \(R = \text{Y}\).

III. RESULTS AND DISCUSSION

The powder x-ray-diffraction pattern of the \((\text{Pb}_{0.5}\text{Cu}_{0.5})_2(\text{Ba}_{0.5}\text{Sr}_{0.5})_2\text{PrCu}_2\text{O}_8\) sample is shown in Fig. 1. The diffraction lines can be well indexed with the
OBSERVATION OF Pr AND Gd ORDERING IN THE 2212-... 10453

tetragonal \((\text{Pb}_{0.5}\text{Cu}_{0.5})_2(\text{Ba}_{0.5}\text{Sr}_{0.5})_2\text{PrCu}_2\text{O}_8\) (Pr2212) sample.

The isosstructural Gd2212 sample \((\text{Pb}_{0.5}\text{Cu}_{0.5})_2(\text{Ba}_{0.5}\text{Sr}_{0.5})_2\text{GdCu}_2\text{O}_8\) shows smaller lattice parameter of \(a = 3.854(3)\ \text{Å}, c = 27.457(9)\ \text{Å}\) and \(V = 407.8(4)\ \text{Å}^3\) while the lattice parameters, of the prototype compound Y2212 \((\text{Pb}_{0.5}\text{Cu}_{0.5})_2(\text{Ba}_{0.5}\text{Sr}_{0.5})_2\text{YCu}_2\text{O}_8\) are \(a = 3.830(3)\ \text{Å}, c = 27.450(9)\ \text{Å}\), and \(V = 402.7(4)\ \text{Å}^3\). The unit-cell volumes \(V\) for these three typical samples

FIG. 2. Tetragonal unit-cell volume \(V\) of the \((\text{Pb}_{0.5}\text{Cu}_{0.5})_2(\text{Ba}_{0.5}\text{Sr}_{0.5})_2\text{RCu}_2\text{O}_8\) (R2212) compounds vs rare-earth \(R^{3+}\) ionic radius \((R = \text{Pr, Gd, Y})\) and \(\text{Pr}^{4+}\) ionic radius.

FIG. 3. Temperature dependence of logarithmic electrical resistivity \(\ln(\rho)\) of R2212 \((R = \text{Pr, Gd, Y})\). Solid lines are guides to the eyes only.

\((\text{Pb}_{0.5}\text{Cu}_{0.5})_2(\text{Ba}_{0.5}\text{Sr}_{0.5})_2\text{RCu}_2\text{O}_8\) \((R2212; R = \text{Pr, Gd, Y})\) in Fig. 2 follow a linear dependence with the \(R^{3+}\) ionic radius, indicating a predominantly \(R^{3+}\) character in Pr2212. The deviation of the \(\text{Pr}^{4+}\) point from this simple relation is apparent. The conclusion is consistent with those for all other Pr-containing two-CuO2-layer \(m212\)-type compounds \((m = 1, 3)\).

All these samples are insulators or semiconductors based on the electrical resistivity data. As shown in Fig. 3, the temperature dependence of the logarithmic electrical resistivity \(\ln(\rho)\) of the Pr2212 sample shows a resistivity of 746 \(\Omega\) cm at room temperature which rises to 9.96 k\(\Omega\) cm at 200 K. For the isostructural Y2212 sample, a lower room-temperature resistivity of 6.26 \(\Omega\) cm was observed, which rises to 36.2 \(\Omega\) cm at 200 K.

The temperature dependence of the molar magnetic susceptibilities \(\chi_m\) in a 1-T applied field is shown in Fig. 4. The small fluctuation observed around room temperature indicates a possible \(\text{Cu}^{2+}\) magnetic ordering around or above room temperature. The relatively high applied field of 1 T is used in order to suppress the possible magnetic coupling between the \(\text{Cu}^{2+}\) and \(\text{Pr}^{4+}\) moments. The figure inset shows a simple \(\chi_m = C/(T + \theta_p)\) Curie-
Weiss fit which yields a negative paramagnetic intercept $\theta_p = -10$ K and an effective magnetic moment of $3.22 \mu_B$ per Pr if the small Cu$^{2+}$ moment is neglected. The effective moment again is closer to that of the free Pr$^{3+}$ ion ($3.58 \mu_B$) rather than the Pr$^{4+}$ ion ($2.54 \mu_B$). Indeed, most experimental evidence of Pr-containing high-$T_c$ cuprates imply a Pr$^{3+}$ state. The negative paramagnetic intercept and the low-temperature deviation from the Curie-Weiss fit indicate the occurrence of a long-range antiferromagnetic Pr ordering. The $T_N(\text{Pr})$ of 9 K was obtained from the minimum in the temperature derivative of molar magnetic susceptibility $d\chi_m/dT$ in Fig. 5, with the onset of deviation from the Curie-Weiss fit (dashed line) below 15 K. The field dependence of magnetization $M(H)$ measurements indicates the occurrence of nonlinear magnetic hysteresis below 15 K. As shown in Fig. 6, an apparent magnetic hysteresis with a small remnant magnetization difference $\Delta M(0 G) = M^+(0) - M^-(0)$ of 0.03 emu/g was observed at $T_N(\text{Pr})$ of 9 K. At 5 K, $\Delta M(0 G)$ increased to 0.47 emu/g.

For the isostructural magnetic compound Gd2212, the low-temperature molar magnetic susceptibility $\chi_m$ in Fig. 7 shows a lower $T_N(\text{Gd})$ of 2.3 K. A simple $\chi_m = C/(T+\theta_p)$ Curie-Weiss fit yields a negative paramagnetic intercept $\theta_p = -2.31$ K and an effective magnetic moment of 8.06 $\mu_B$ per Gd if the small Cu$^{2+}$ moment is again neglected. The observed effective moment of $8.06 \mu_B$/Gd is close to the free-ion Gd$^{3+}$ value of 7.98 $\mu_B$.

Pr and Gd magnetic transitions are clearly corroborated by low-temperature specific-heat data $C(T)$ as shown in Fig. 8 for R2212 ($R = \text{Pr}, \text{Gd}$), along with the data of nonmagnetic Y2212 for comparison. A distinct but broad magnetic transition prevails in Pr2212 at $T_N(\text{Pr}) = 9$ K with an onset around 10–11 K. This transition temperature is anomalously higher than $T_N(\text{Gd})$ of 2.2 K for isostructural Gd2212 with a well-defined $\lambda$-type transition. No transition was observed for Y2212. It is possible that the $T_N(\text{Pr}) = 9$ K represents the true three-dimensional (3D), or quasi-two-dimensional (quasi-2D) long-range magnetic ordering, above which, the broad onset of 11–15 K observed from calorimetric and mag-

FIG. 5. Low-temperature differential molar magnetic susceptibility $d\chi_m/dT$ for Pr2212 sample in applied field of 1 T.

FIG. 6. Field dependence of the magnetization $M(H)$ at 5 and 9 K.

FIG. 7. Temperature dependence of the molar magnetic susceptibility $\chi_m$ of Gd2212.

FIG. 8. Temperature dependence of specific heat $C(T)$ for R2212 ($R = \text{Pr}, \text{Gd}, \text{Y}$).
magnetic measurements is due to the 2D ordering effect.\textsuperscript{11,12,17,18}

With the data plotted in Fig. 9 as $C/T$ versus $T^2$, the Pr anomaly is shown to be superimposed on a $\beta T^3$ lattice contribution as well as an additional term roughly linear with temperature. The estimated Debye temperature $\theta_D$ as derived from $\beta$ is 220 K for Pr2212 and 260 K for Y2212. The linear term coefficient $\gamma = 0.31$ J/mol K\textsuperscript{2} in Pr2212 is much larger than the corresponding value of 0.016 J/mol K\textsuperscript{2} for Y2212, which is also insulating. Such a sizable linear term in specific heat is one of the most pronounced characters of the Pr-containing two-CuO\textsubscript{2} layer $m$212 compounds ($m = 1, 2, 3$).\textsuperscript{1,5,11,13,14,16,17} However, since these compounds are either insulators or semiconductors, the large linear term is apparently not related to the standard conduction electron contribution. By considering the crystal field splitting of the Pr\textsuperscript{3+} ions\textsuperscript{23} and the small $\gamma$ value of nonmagnetic Y2212, this linear term may represent the extended tails of the high-temperature Schottky term. Another issue which remains to be solved is the $C(T)$ behavior below $T_N$(Pr) where, as shown in Fig. 6, the lowest-temperature data are already below the linear extrapolation. It is possible that the large linear term coefficient may gradually diminish as the temperature decreases, or simply be quenched as soon as the Pr ordering takes place. Without these questions answered, one can only estimate the lower limit of magnetic entropy $S_m$ for Pr2212 by integrating $C_m/T$ ($C_m = C - \gamma T - \beta T^3$) with respect to $T$ between 3 and 10 K as shown in Fig. 10. A value of 1.37 J/mol K thus obtained is equal to 15% of $R \ln 3$ expected for the complete ordering of Pr\textsuperscript{3+} with a quasitriplet ground state.\textsuperscript{23} A better $S_m$ value of 20% $R \ln 3$ can be derived between 2.5 and 10 K if an arbitrary straight baseline between 10 and 0 K is used as shown in Fig. 10. Simply integrating $C/T$ with respect to $T$ between 2.5 and 10 K gives a high value of 51% $R \ln 3$.

Similar analysis resulted in only 13% of $R \ln 3$ for the 2D-like 3212-type compounds (Pb\textsubscript{0.5}Cu\textsubscript{0.5}Sr\textsubscript{3}PrCu\textsubscript{2}O\textsubscript{8} (3212 with $R = $ Pr, Gd, or Y) were synthesized. Pr ordering in Pr2212 was observed through low-temperature magnetic and calorimetric measurements. The $T_N$(Pr) of 9 K is much higher than $T_N$(Gd) = 2.2 K, while Y2212 shows no magnetic transition. The specific heat has an exceeding large linear term which is common to most of the Pr-containing cuprates. Along with earlier reports on 1212- and 3212-type compounds, the new results complete the demonstration of anomalous Pr ordering in all two-CuO\textsubscript{2}-layer $m$212 ($m = 1, 2, 3$) systems. Finally, judging from the magnetic entropy, the Pr-ordering appears to be a more 3D-like process.

IV. CONCLUSION

Three 2212-type compounds (Pb\textsubscript{0.5}Cu\textsubscript{0.5}Sr\textsubscript{3}PrCu\textsubscript{2}O\textsubscript{8} (R2212 with $R = $ Pr, Gd, or Y) were synthesized. Pr ordering in Pr2212 was observed through low-temperature magnetic and calorimetric measurements. The $T_N$(Pr) of 9 K is much higher than $T_N$(Gd) = 2.2 K, while Y2212 shows no magnetic transition. The specific heat has an exceeding large linear term which is common to most of the Pr-containing cuprates. Along with earlier reports on 1212- and 3212-type compounds, the new results complete the demonstration of anomalous Pr ordering in all two-CuO\textsubscript{2}-layer $m$212 ($m = 1, 2, 3$) systems. Finally, judging from the magnetic entropy, the Pr-ordering appears to be a more 3D-like process.

ACKNOWLEDGMENTS

We thank S.H. Lin of the Academia Sinica for technical support in relaxation calorimeter measurements. This work was supported by the National Science Council of Republic of China under Contract Nos. NSC-84-2112-M007-003 and 038.