Observation of Pr and Gd ordering in the 2212-type compounds $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2RCu_2O_8$ ($R = Pr,Gd$)

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

Magnetic and calorimetric measurements have been made to reveal a Pr ordering in the $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2PrCu_2O_8$ compound which has the (Pb,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 $T_N(Pr)$ of 9 K. In comparison, isostructural $(Pb_{0.5}Cu_{0.5})_2 (Ba_{0.5}Sr_{0.5})_2GdCu_2O_8$ exhibits a $T_N(Gd)$ of only 2.2 K. The magnetic entropy associated with the Pr ordering has a lower limit value equivalent to about 20% of $R\ln3$ 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 $m212$ ($m = 1,2,3$) systems.

I. INTRODUCTION

The anomalously high antiferromagnetic Pr ordering temperature of 17 K for $PrBa_2Cu_3O_7$ with the two-CuO_2-layer 123-type structure, which is the only nonsuperconducting member of the 90-K $RBa_2Cu_3O_7$ system ($R = Y$ or a rare earth), has been the focus of extensive research every since the discovery of high-T_c superconductor.[1-6] With further oxygen deficiency, $T_N(Pr)$ decreases to 10 K in $PrBa_2Cu_3O_6$.[5,7] In comparison, other magnetic rare-earth compounds have a maximum $T_N(R)$ of 2.2 K in $GdBa_2Cu_3O_7$.[8,9] Meanwhile, Pr substitution leads to T_c suppression from above 90 K in $(R_{1-x}Pr_x)Ba_2Cu_3O_7$.[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 $PrBa_2Cu_3O_{7-y}$ system can be recategorized as 1212C or 1212-type two-CuO_2-layer system,[10] in analogous with Tl-1212 $Tl(Ba,Sr)_2PrCu_2O_7$,[11-15] (Pb,Cu)-1212 $(Pb,Cu)Sr_2PrCu_2O_7$,[13] and Hg-1212 $HgSr_2PrCu_2O_7$ compounds.[16] They also exhibit the common feature of having relatively high $T_N(Pr)$ values ranging from 4 to 8 K. Similar Pr anomalies with $T_N(Pr)$ of 6–14 K were reported recently for a new (Pb,Cu)-3212-type[10] two-Cu_2O-layer system $(Pr_2Cu)(Ba,Sr)_2PrCu_2O_8$ or commonly written as 2213 $Pb_2(Ba,Sr)_2PrCu_3O_8$.[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 $m212$-type ($m = 1,2,3$) 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 $Bi_2Sr_2PrCu_2O_8$.[19] Therefore, this work was carried out by synthesizing and characterizing a new (Pb,Cu)-2212 compound $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2PrCu_2O_8$. Two other compounds with Pr substituted by Y or Gd formed the basis for comparison.

II. EXPERIMENTS

Samples with the nominal composition $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2R Cu_2O_8$ ($R 2212; R = Pr,Gd,Y$) were prepared by two-state solid-state reaction techniques. High-purity $BaCO_3$, $SrCO_3$, R_2O_3, and CuO powders with the ratio $Ba:Sr:R:Cu = 1:1:1:3$ were well mixed first, ground and calcined at 920 °C in air with intermediate grinding. The precursor $BaSrRCu_3O_x$ powers were then mixed with the appropriate amount of 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 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_α 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 $R = Pr$ and Gd or a relaxation calorimeter[11] for $R = Y$.

III. RESULTS AND DISCUSSION

The powder x-ray-diffraction pattern of the $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2PrCu_2O_8$ sample is shown in Fig. 1. The diffraction lines can be well indexed with the

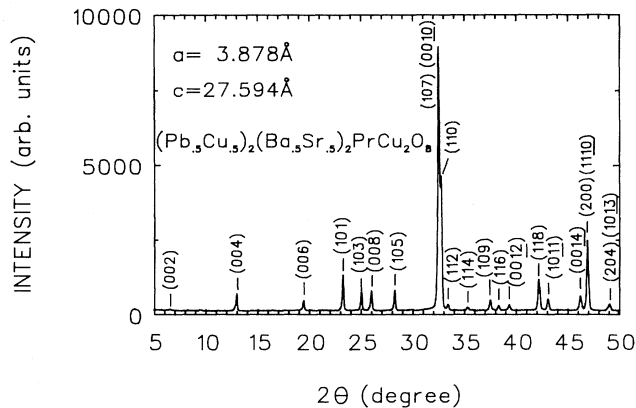FIG. 1. Powder x-ray-diffraction pattern of (Pb,Cu)-2212 tetragonal $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2PrCu_2O_8$ (Pr2212) sample.

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

tetragonal $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2YCu_2O_8$-type (Refs. 20 and 21) or $Tl_2Ba_2CaCu_2O_8$-type 2212 structure[10] having lattice parameters $a = 3.878(3)$ Å, $c = 27.594(9)$ Å and a unit-cell volume $V = 415.0(4)$ Å^3. No impurity phases were detected. This (Pb,Cu)-2212 tetragonal structure with space group $I4/mmm$ (Ref. 10) is very similar to the pseudotetragonal Bi-2212-type structure of $Bi_2Sr_2PrCu_2O_8$ ($a_t = 3.870$ Å $\approx b_t = 3.871$ Å, $c = 30.34$ Å) with the orthorhombic space group $Fmmm$,[22] where two BiO planes are replaced by two (Pb,Cu)O planes. The only structural discrepancy is caused by the strong structural modulation along the orthorhombic b_o axis in Bi-2212, which is absent in the tetragonal (Pb,Cu)-2212.

The isostructural Gd2212 sample $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2GdCu_2O_8$ shows smaller lattice parameter of $a = 3.854(3)$ Å, $c = 27.457(9)$ Å and $V = 407.8(4)$ Å^3 while the lattice parameters, of the prototype compound Y2212 $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2YCu_2O_8$ are $a = 3.830(3)$ Å, $c = 27.450(9)$ Å, and $V = 402.7(4)$ Å^3. The unit-cell volumes V for these three typical samples

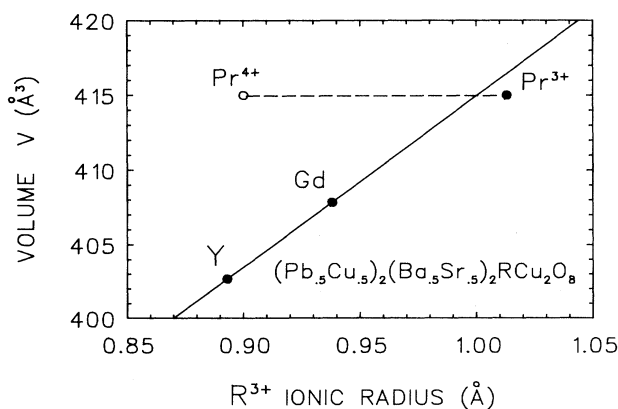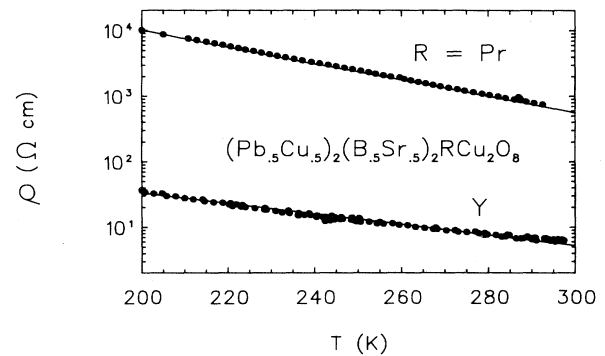$(Pb_{0.5}Cu_{0.5})_2$ $(Ba_{0.5}Sr_{0.5})_2R$ Cu_2O_8 (R2212; R = Pr, Gd, Y) in Fig. 2 follow a linear dependence with the R^{3+} ionic radius, indicating a predominantly Pr^{3+} character in Pr2212. The deviation of the Pr^{4+} point from this simple relation is apparent. The conclusion is consistent with those for all other Pr-containing two-CuO$_2$-layer m212-type compounds ($m = 1,3$).[5,11,15-17]

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 $\ln\rho(T)$ of the Pr2212 sample shows a resistivity of 746 Ω cm at room temperature which rises to 9.96 kΩ cm at 200 K. For the isostructural Y2212 sample, a lower room-temperature resistivity of 6.26 Ω cm was observed, which rises to 36.2 Ω cm at 200 K.

The temperature dependence of the molar magnetic susceptibilities χ_m in a 1-T applied field is shown in Fig. 4. The small fluctuation observed around room temperature indicates a possible 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 Cu^{2+} and Pr^{3+} moments. The figure inset shows a simple $\chi_m = C/(T + \theta_p)$ Curie-
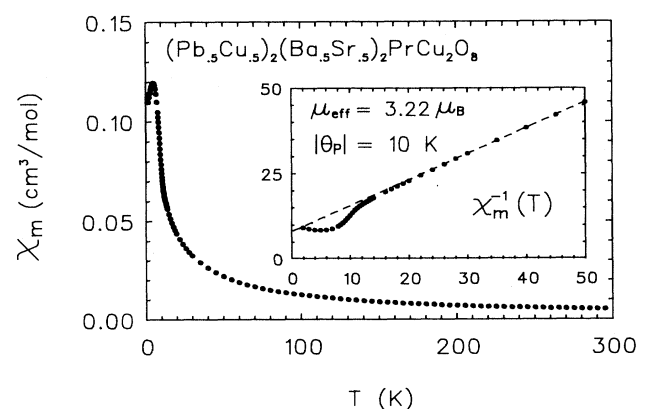

FIG. 2. Tetragonal unit-cell volume V of the $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2R$ Cu_2O_8 (R2212) compounds vs rare-earth R^{3+} ionic radius (R = Pr, Gd, Y) and Pr^{4+} ionic radius.

FIG. 4. Temperature dependence of molar magnetic susceptibility χ_m and low-temperature inverse molar magnetic susceptibility χ_m^{-1} (inset) of Pr2212.
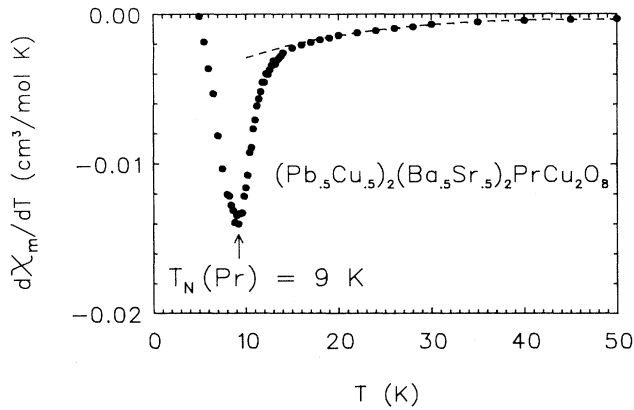
FIG. 5. Low-temperature differential molar magnetic suscep-tibility $d\chi_m/dT$ for Pr2212 sample in applied field of 1 T.

FIG. 7. Temperature dependence of the molar magnetic sus-ceptibility χ_m of Gd2212.

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 cu-prates imply a Pr^{3+} state. The negative paramagnetic in-tercept and the low-temperature deviation from the Curie-Weiss fit indicate the occurrence of a long-range antiferromagnetic Pr ordering. The $T_N(Pr)$ of 9 K was obtained from the minimum in the temperature deriva-tive 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 mag-netization $M(H)$ 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 $\Delta M(0G) = M^+(0)$ $-M^-(0)$ of 0.03 emu/g was observed at $T_N(Pr)$ of 9 K. At 5 K, $\Delta M(0$ G) increased to 0.47 emu/g.
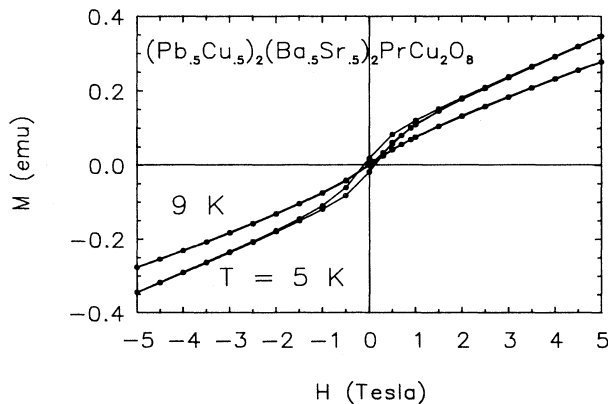
For the isostructural magnetic compound Gd2212, the low-temperature molar magnetic susceptibility χ_m in Fig. 7 shows a lower $T_N(Gd)$ of 2.3 K. A simple χ_m $=C/(T+\theta_p)$ Curie-Weiss fit yields a negative paramag-netic intercept $\theta_p = -2.31$ K and an effective magnetic moment of 8.06 μ_B 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 corroborat-ed by low-temperature specific-heat data $C(T)$ as shown in Fig. 8 for R 2212 ($R = Pr, Gd$), along with the data of nonmagnetic Y2212 for comparison. A distinct but broad magnetic transition prevails in Pr2212 at $T_N(Pr) = 9$ K with an onset around 10–11 K. This tran-sition temperature is anomalously higher than $T_N(Gd)$ of 2.2 K for isostructural Gd2212 with a well-defined λ-type transition. No transition was observed for Y2212. It is possible that the $T_N(Pr) = 9$ 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-
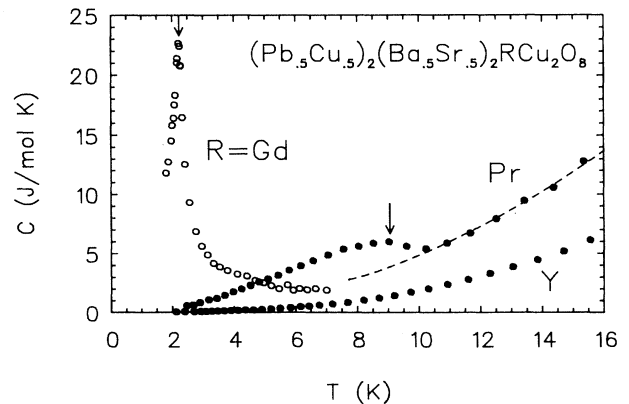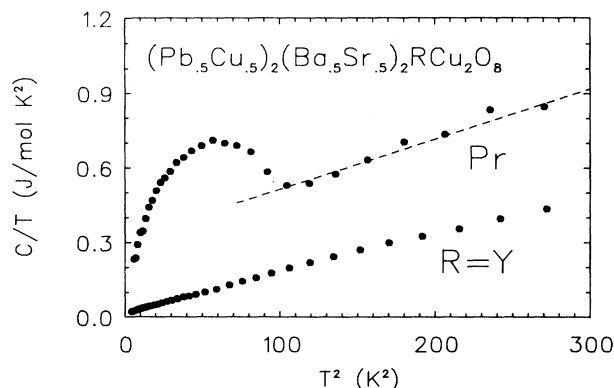

FIG. 6. Field dependence of the magnetization $M(H)$ at 5 and 9 K.

FIG. 8. Temperature dependence of specific heat $C(T)$ for R 2212 ($R = Pr$, Gd, Y).

FIG. 9. C/T vs T^2 for $R\,2212$ (R =Pr, Y).

netic measurements is due to the 2D ordering effect.[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 βT^3 lattice contribution as well as an additional term roughly linear with temperature. The estimated Debye temperature θ_D as derived from β is 220 K for Pr2212 and 260 K for Y2212. The linear term coefficient $\gamma \approx 0.31$ J/mol K^2 in Pr2212 is much larger than the corresponding value of 0.016 J/mol K^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$_2$-layer $m212$ compounds ($m = 1,2,3$).[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^{3+} ions[23] and the small γ 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 $T_N(\text{Pr})$ 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 ln3 expected for the complete ordering of Pr^{3+} with a quasitriplet ground state.[23] A better S_m value of 20% R ln3 can be derived between 2.5 and 10 K if an arbitrary straight base line 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 ln3.

Similar analysis resulted in only 13% of R ln3 for the 2D-like 3212-type compound (Pb$_2$Cu)Sr$_2$PrCu$_2$O$_8$ with a short magnetic correlation length of 20 Å along the c axis from the neutron-diffraction studies.[17,18] On the contrary, neutron data indicate a 3D-like Tl-1212 compound TlBa$_2$PrCu$_2$O$_7$ with a magnetic entropy of 31% R ln3.[11,12] Accordingly, it seems reasonable to categorize
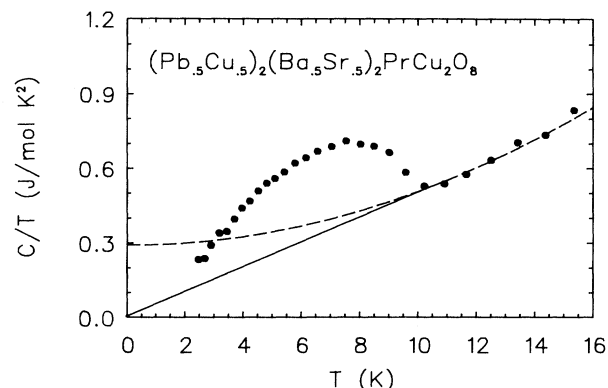
FIG. 10. C/T vs T of Pr2212 for magnetic entropy S_m estimation. The dashed line is the extrapolation of the $\gamma T + \beta T^3$ term from above $T_N(\text{Pr})$. The solid line is an arbitrary straight base line between 10 and 0 K.

the Pr ordering in Pr2212 as a more 3D-like process. Confirmation awaits detailed neutron-diffraction studies.

Since Pr is one of the lightest elements of the rare-earth series, its $4f$ wave function should be more extended. The anomalously high $T_N(\text{Pr})$ in Pr2212 indicates the importance of the quasi-2D Pr-O-Pr superexchange mechanism through the strong hybridization between the Pr $4f$ and the eight O $2p_\pi$ orbitals in the adjacent CuO$_2$ layers.[6] This degree of hybridization can be readily reflected in the Pr-O bond length.[14-16] As a consequence, the Pr ordering temperature $T_N(\text{Pr})$ for the $m212$ ($m = 1,3$) systems decreases monotonically with increasing Pr-O bond length.[5,14-16] The reason that no $T_N(\text{Pr})$ can be observed down to 1.6 K for orthorhombic Pr2212 compound Bi$_2$Sr$_2$PrCu$_2$O$_8$ (Ref. 19) is probably due to the longer Pr-O bond length which is caused by the long c-axis lattice parameter of 30.34 Å and a strong structural modulation.[22]

IV. CONCLUSION

Three 2212-type compounds (Pb$_{0.5}$Cu$_{0.5}$)$_2$(Ba$_{0.5}$Sr$_{0.5}$)$_2$R Cu$_2$O$_8$ ($R\,2212$ with R =Pr, Gd, or Y) were synthesized. Pr ordering in Pr2212 was observed through low-temperature magnetic and calorimetric measurements. The $T_N(\text{Pr})$ of 9 K is much higher than $T_N(\text{Gd})=2.2$ 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$_2$-layer $m212$ ($m = 1,2,3$) systems. Finally, judging from the magnetic entropy, the Pr-ordering appears to be a more 3D-like process.

ACKNOWLEDGMENTS

[1] L. Soderholm, K. Zhang, D. G. Hinks, M. A. Beno, J. D. Jorgensen, C. U. Segre, and I. K. Schuller, Nature **328**, 604 (1987).

[2] J. K. Liang, X. T. Xu, S. S. Xie, G. H. Rao, X. Y. Shao, and Z. G. Duan, Z. Phys. B **69**, 137 (1987).

[3] Y. Dalichaouch, M. S. Torikachvili, E. A. Early, B. W. Lee, C. L. Seaman, K. N. Yang, H. Zhou, and M. B. Maple, Solid State Commun. **65**, 1001 (1988).

[4] H. C. Ku, C. C. Chen, and S. W. Hsu, Int. J. Mod. Phys. B **2**, 1411 (1988).

[5] H. B. Radousky, J. Mater. Res. **7**, 1917 (1992), and references cited therein.

[6] R. Fehrenbacher and T. M. Rice, Phys. Rev. Lett. **70**, 3471 (1993).

[7] S. Uma, T. Sarkar, M. Seshasayee, G. Rangarajan, C. R. V. Rao, and C. Subramanian, Solid State Commun. **87**, 289 (1993).

[8] J. C. Ho, P. H. Hor, R. L. Meng, C. W. Chu, and C. Y. Huang, Solid State Commun. **63**, 711 (1987).

[9] J. W. Lynn, in *High Temperature Superconductivity,* edited by J. W. Lynn (Springer-Verlag, Berlin, 1990), Chap. 8, p. 268, and references cited therein.

[10] H. Shaked, P. M. Keane, J. C. Rodriquez, F. F. Owen, R. L. Hitterman, and J. D. Jorgensen, *Crystal Structure of the High-T_c Superconducting Copper-Oxides* (Elsevier Science, British Vancouver, 1994).

[11] C. C. Lai, B. S. Chiou, Y. Y. Chen, J. C. Ho, and H. C. Ku, Physica C **202**, 104 (1992).

[12] W. T. Hsieh, K. J. Chang, W. H. Li, K. C. Lee, J. W. Lynn, C. C. Lai, and H. C. Ku, Phys. Rev. B **49**, 12 200 (1994).

[13] H. C. Ku, C. C. Lai, J. H. Shieh, J. W. Liou, C. Y. Wu, and J. C. Ho, Physica B **194-196**, 213 (1994).

[14] C. C. Lai, T. J. Lee, H. K. Fun, H. C. Ku, and J. C. Ho, Phys. Rev. B **50**, 4092 (1994).

[15] H. K. Fun, P. Yang, C. C. Lai, H. C. Ku, and T. J. Lee, Physica C **223**, 267 (1994).

[16] H. C. Ku, J. H. Shieh, C. C. Lai, C. S. Chiou, J. W. Liou, and J. C. Ho (unpublished).

[17] J. H. Shieh, H. C. Ku, and J. C. Ho, Phys. Rev. B **50**, 3288 (1994).

[18] W. T. Hsieh, W. H. Li, K. C. Lee, J. W. Lynn, J. H. Shieh, and H. C. Ku, J. Appl. Phys. **76**, 7124 (1994).

[19] Y. Gao, P. Pernambuco-Wise, J. E. Crow, J. O'Reilly, N. Spencer, H. Chen, and R. E. Salomon, Phys. Rev. B **45**, 7346 (1992).

[20] T. Rouillon, R. Petoux, D. Groult, C. Michel, M. Hervieu, T. Provost, and B. Raveau, J. Solid State Chem. **78**, 322 (1989).

[21] A. Tokiwa, T. Oku, M. Nagoshi, M. Kikuchi, K. Hiraga, and Y. Syono, Physica C **161**, 459 (1989).

[22] R. M. Hazen, C. T. Prewitt, R. J. Angel, N. L. Ross, L. W. Finger, C. G. Hadidiacos, D. R. Veblen, P. J. Heaney, P. H. Hor, R. L. Meng, Y. Y. Sun, Y. Q. Wang, Y. Y. Xue, Z. J. Huang, L. Gao, J. Bechtold, and C. W. Chu, Phys. Rev. Lett. **60**, 1174 (1988).

[23] L. Soderholm, C. K. Loong, G. L. Goodman, and B. D. Dabrowski, Phys. Rev. B **43**, 7923 (1991).