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Anomalous Pr ordering in $HgSr_2PrCu_2O_{6+\delta}$ and the systematic variation of T_N(Pr) for the Hg-1212-type systems

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Structural, magnetic, and calorimetric studies have been made to reveal an anomalous Pr antiferromagnetic ordering at T_N(Pr) of 6 K in $HgSr_2PrCu_2O_{6+\delta}$. This compound has the Hg-1212-type tetragonal structure with lattice parameters $a=3.8532$ Å and $c=12.1199$ Å. X-ray Rietveld refinement yields a Pr-O bond length d(Pr-O) of 2.492 Å between Pr and oxygen in the adjacent CuO_2 layers and an O-Pr-O bond angle of 101.3°. The low-temperature magnetic entropy associated with the Pr ordering is only about 10% of $R\ln3$ expected for Pr^{3+} with a quasitriplet ground state, suggesting a more two-dimensional-like ordering process. This result supports the earlier observation of a systematic dependence of T_N(Pr) on Pr-O bond length in various $M(Ba,Sr)_2PrCu_2O_y$ ($M=$Cu, Hg, Tl, Pb) 1212-type Pr compounds. This in turn points to the importance of a superexchange magnetic coupling mechanism.

I. INTRODUCTION

The orthorhombic $PrBa_2Cu_3O_7$ compounds with an anomalously high Pr antiferromagnetic ordering temperature T_N(Pr) of 17 K is the only nonsuperconducting member of the $RBa_2Cu_3O_7$ system ($R=$Y or a rare earth).[1–6] With further oxygen deficiency, T_N(Pr) decreases to 10 K in tetragonal $PrBa_2Cu_3O_6$.[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 ordering begins to set in. Since Pr is one of the lightest elements of the rare-earth series, its $4f$ wave functions are more extended and the anomalously high T_N(Pr) observed indicates the importance of the quasi-two-dimensional (quasi-2D) Pr-O-Pr superexchange magnetic coupling mechanism through the strong hybridization between the Pr $4f$ and the eight O $2p_\pi$ orbitals in the adjacent two-CuO_2 layers.[6] The proposed T_c suppression by either hole filling or hole localization is presumably a consequence of the orbital hybridization.

From the structural viewpoint, the 123-type $PrBa_2Cu_3O_{7-y}$ system can be recategorized as either the Cu-1212C type (C stands for chain) for orthorhombic $[Cu]Ba_2PrCu_2O_7$ (space group $Pmmm$) or Cu-1212 $TlBa_2CaCu_2O_{7-\delta}$ type for tetragonal $[Cu]Ba_2PrCu_2O_6$ (space group $P4/mmm$),[10] in analogy with other two-CuO_2-layer Pr compounds in the Tl-1212 $Tl(Ba,Sr)_2PrCu_2O_{7-\delta}$ system[11–15] and (Pb,Cu)-1212 $(Pb,Cu)Sr_2PrCu_2O_{7-\delta}$.[13] They also exhibit the common feature of having anomalously high T_N(Pr) values ranging from 4 to 8 K. The anomalous T_N(Pr) in all Pr-containing 1212 compounds again demonstrates the importance of the Pr-O-Pr superexchange coupling mechanism.

Recently, a 1212 system with the $HgBa_2CaCu_2O_{6+\delta}$-type structure was reported.[16,17] From previous experience, if the Ca site can be completely occupied by Pr, a Pr-1212 compound with anomalous T_N(Pr) is expected. However, with the composition $HgBa_2PrCu_2O_{6+\delta}$, the Hg-1212-type phase is unstable.[18] A simultaneous substitution of Ba by Sr is necessary to stabilize the Hg-1212 phase.

II. EXPERIMENTS

Mercury samples with the nominal composition $HgSr_2PrCu_2O_{6+\delta}$ were prepared by two-stage solid-state reaction techniques. High-purity $SrCO_3$, Pr_2O_3, and CuO powders with the ratio Sr:Pr:Cu$=2:1:2$ were well mixed first, ground, and calcined at 900 °C in air with intermediate grinding. The precursor $Sr_2PrCu_2O_x$ powders were then mixed with an appropriate amount of HgO powder (~30% excess), pressed into pellets, sealed in a 2-mm-thick-wall quartz tube in vacuum, and reacted at 1000 °C in vacuum for 8 h, then quenched in liquid nitrogen.

Crystallographic data were obtained with a Rigaku RTP5000 18 kW rotating-anode powder x-ray diffractometer using Ni-filtered Cu $K\alpha$ radiation. A LAZY-PULVERIX-PC program was employed for preliminary phase identification and lattice parameter calculation. Structure refinement was performed with a Rietveld analysis DBWS-9006-PC program.[19] The x-ray intensity data were collected by a scan over an angle range of $20°<2\theta<130°$ in increments of 0.02°.

Magnetic susceptibility measurements were carried out with a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer from 2 to 300 K

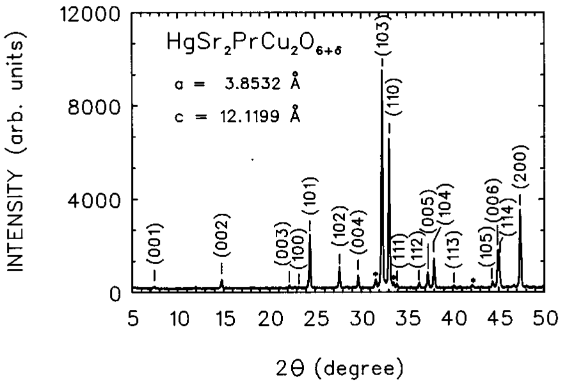

FIG. 1. Powder x-ray diffraction pattern of Hg-1212 sample with the nominal composition of $HgSr_2PrCu_2O_{6+\delta}$. Minor peaks due to unreacted precursor/impurities are indicated by asterisks.

in an applied magnetic field of 1 T. Low-temperature specific heat measurements were made with an adiabatic calorimeter from 2 to 15 K. The sample was thermally anchored to a copper block containing a germanium thermometer and a Manganin wire heater, for which measurements were made separately for addenda correction.

III. RESULTS AND DISCUSSION

The powder x-ray diffraction pattern of the Hg-1212 sample $HgSr_2PrCu_2O_{6+\delta}$ is shown in Fig. 1. Except for small amounts of unreacted precursor/impurities due to low HgO decomposition temperature and very high mercury vapor pressure, all diffraction lines can be well indexed with the tetragonal $HgBa_2CaCu_2O_{6+\delta}$-type structure[10,16,17] having the lattice parameters $a=3.8532(3)$ Å and $c=12.1199(5)$ Å and a unit-cell volume V of 179.95(1) Å^3.

The temperature dependence of the molar magnetic susceptibilities χ_m for $HgSr_2PrCu_2O_{6+\delta}$ in a 1 T applied magnetic field is shown in Fig. 2. A small fluctuation was observed around room temperature, indicating a possible magnetic Cu^{2+} ordering near 300 K or above. 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 inset shows a simple Curie-Weiss fit, $\chi_m = C^*/(T+\theta_p)$ with negative paramagnetic intercept $\theta_p = -13$ K. An effective magnetic moment of $3.31\mu_B$ per Pr can be derived from the Curie constant C^* if the small Cu^{2+} moment is neglected. As in many other Pr-containing cuprates, this effective moment again is closer to that of the free Pr^{3+} ion ($3.58\mu_B$) rather than that of the Pr^{4+} ion ($2.54\mu_B$). Indeed, most experimental results on such compounds imply a Pr^{3+} state. The negative paramagnetic intercept and the low-temperature deviation from the Curie-Weiss fit indicate the occurrence of long-range antiferromagnetic Pr ordering. A T_N(Pr) value of 6 K was identified from the minimum in the temperature derivative of the molar magnetic susceptibility $d\chi_m/dT$ as shown in Fig. 3.

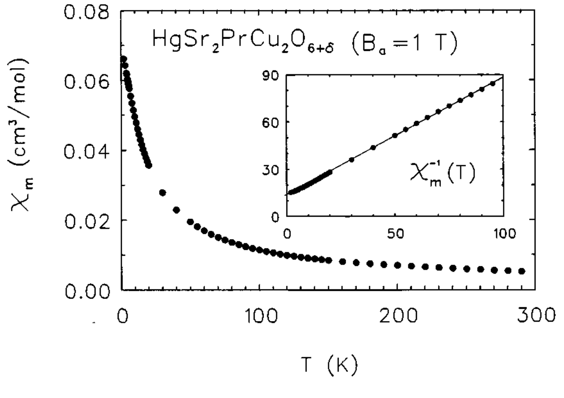

FIG. 2. Temperature dependence of molar magnetic susceptibility $\chi_m(T)$ and low-temperature inverse molar magnetic susceptibility χ_m^{-1} (inset).

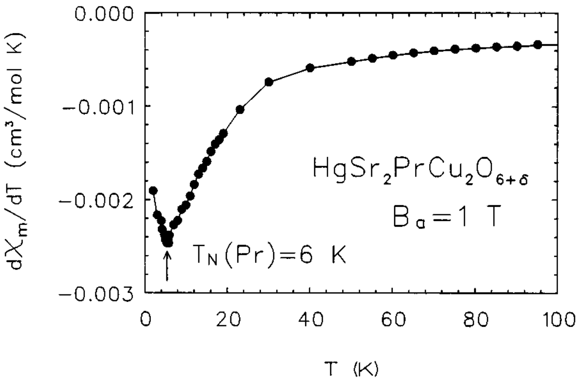

FIG. 3. Low-temperature differential molar magnetic susceptibility $d\chi_m/dT$ reveals T_N(Pr)=6 K.

The magnetic transition of $HgSr_2PrCu_2O_{6+\delta}$ is clearly corroborated by low-temperature specific heat data $C(T)$ as shown in Fig. 4. A distinct but broad magnetic transition prevails at T_N(Pr)=6 K with very high onset around 11 K. The broad transition indicates that a truly three-dimensional (3D) or quasi-two-dimensional (quasi-2D) long-range magnetic ordering is represented by the T_N(K)=6 K, while the 2D ordering effect persists up to the onset near 11 K.[11,12,20,21] When the data are plotted in Fig. 5 as C/T versus T^2, the Pr-induced anomaly is shown to be superimposed on a βT^3 lattice contribution term with an equivalent Debye temperature $\theta_D = 240$ K as well as an additional term roughly linear

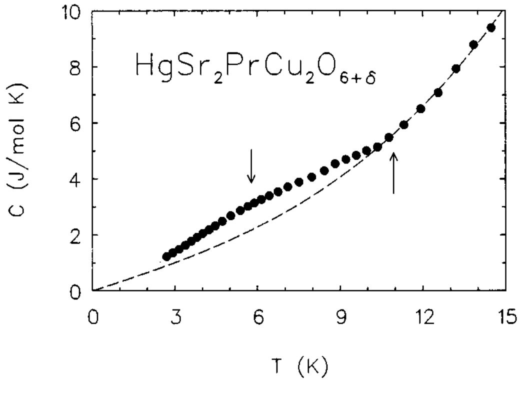

FIG. 4. Temperature dependence of specific heat $C(T)$ with baseline representing $C_n = \gamma T + \beta T^3 = 0.33T + 0.0016T^3$.

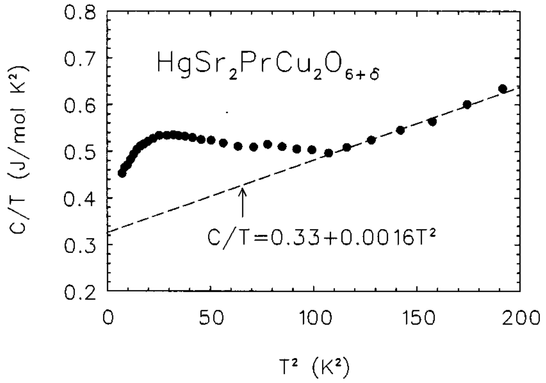

FIG. 5. C/T versus T^2 with the linear fit representing $C_n/T=\gamma+\beta T^2=0.33+0.0016T^2$.

with temperature. The linear term has a coefficient $\gamma\approx0.33$ J/mol K^2 which is quite large. Such a sizable linear term in the specific heat is one of the most pronounced features of the Pr-containing two-CuO_2-layer $m212$ compounds ($m=1,2,3$).[1,5,11,13,14,20,22] However, since these compounds are either insulators or semiconductors, the large linear term is probably not related to the standard conduction-electron contribution. By considering the crystal-field splitting of the Pr^{3+} ions,[23] this linear term may represent the extended tail of high-temperature Schottky terms. Another issue remains to be solved is the $C(T)$ behavior below T_N(Pr). 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 magnetic entropy S_m(Pr) of $HgSr_2PrCu_2O_{6+\delta}$ by integrating C_m/T with respect to T between 2 and 11 K, where $C_m=C-C_n$ with $C_n=\gamma T-\beta T^3$. A value of 0.86 J/mol K thus obtained is equal to 9.5% of $R\ln3$ expected for the complete ordering of Pr^{3+} with a quasitriplet ground state.[23] A similar analysis resulted in 13% of $R\ln3$ for the quasi-2D 3212-type compound $(Pb_2Cu)Sr_2PrCu_2O_{8+\delta}$ with a short magnetic correlation length of 20 Å along the c axis from neutron diffraction studies.[20,21] In contrast, neutron data indicate a more 3D-like Pr ordering in the Tl-1212 compound $TlBa_2PrCu_2O_{7-\delta}$ with a magnetic entropy of 31% $R\ln3$.[11,12] Accordingly, it seems reasonable to categorize the Pr ordering in Hg-1212 $HgSr_2PrCu_2O_{6+\delta}$ as a more 2D-like process. Confirmation awaits detailed neutron diffraction studies.

The anomalously high T_N(Pr) in Hg-1212 indicates the importance of the quasi-2D Pr-O-Pr superexchange magnetic coupling through the strong hybridization between the Pr $4f$ and the eight O $2p_\pi$ orbitals in the adjacent CuO_2 layers.[6] This degrees of hybridization can be readily reflected in the Pr-O bond length, which can be accurately derived from the Rietveld analysis. An x-ray Rietveld refinement on a powder sample was accordingly carried out based on the $HgBa_2CaCu_2O_{6+\delta}$-type Hg-1212 structure with the tetragonal space group $P4/mmm$; the Ba $(2h)$ site is occupied by Sr and the Ca $(1d)$ site by Pr. All minor impurity lines in the diffraction pattern were artifically removed during the refinement process. The refined atomic positions with refinement factors $R_p=4.06\%$ and $R_{wp}=5.98\%$ for step intensities are listed in Table I, where x, y, and z are the fractional coordinates, $B_{\rm iso}$ is the equivalent thermal parameter, and the numbers in parentheses are the estimated standard deviations (ESD's). Similarly to the isostructural compound $HgBa_2CaCu_2O_{6+\delta}$, the O(3) $(1c)$ site is only partially occupied (we set $\delta\sim0$ during the refinement). Due to the high Hg volatility and the observation of minor precursor Pr-Sr-O impurity phases, the constraint refinement at the last stage of the Rietveld analysis reveals partial Cu substitution on the Hg site. The solubility parameter of 0.272 or a refined composition of $(Hg_{0.728}Cu_{0.272})Sr_2PrCu_2O_{6+\delta}$ was obtained with the reliability index of $R_p=4.06\%$. Several calculated interatomic distances and angles are listed in Table II. The refine bond length d(Pr-O) between Pr and O(1) in the adjacent two-CuO_2 layers is 2.492 Å and the O(1)-Pr-O(1) bond angle is 101.3°.

The d(Pr-O) value for the present Hg-1212 $HgSr_2PrCu_2O_{6+\delta}$ sample with $T_N(\mathrm{Pr})=6$ K is shorter than 2.514 Å for Tl-1212(Sr) $TlSr_2PrCu_2O_{7-\delta}$ with $T_N=4$ K or 2.499 Å for (Pb,Cu)-1212(Sr) $(Pb_{0.6}Cu_{0.4})Sr_2PrCu_2O_{7-\delta}$ with $T_N=5.6$ K, but is longer than 2.478 Å for Tl-1212(Ba) $TlBa_2PrCu_2O_{7-\delta}$ with $T_N=8$ K.[13,14] This regularity propels us to study the systematic variation of T_N(Pr) for all reported $M(Ba,Sr)_2PrCu_2O_y$ ($M=$ Cu, Hg, Tl, or Pb) 1212-type compounds as a function of the Pr-O bond length as shown in Fig. 6. Note that for the orthorhombic $T_N(\mathrm{Pr})=17$ K 1237(Ba) $PrBa_2Cu_3O_7$ (Cu-1212C), instead of a single Pr-O bond length, there are two Pr-O bond lengths of 2.443

TABLE I. Refined structure parameters for $(Hg_{0.728}Cu_{0.272})Sr_2PrCu_2O_{6+\delta}$ obtained from powder x-ray Rietveld analysis [space group $P4/mmm$, $Z=1$; tetragonal lattice parameters $a=3.8532(3)$ Å and $c=12.1199(5)$ Å]. $R_p=4.06\%$ and $R_{wp}=5.98\%$.

Atom	Site	x	y	z	$B_{\rm iso}$ (Å^2)	Occupancy
Hg	1a	0	0	0	1.47(3)	0.728(6)
Cu(1)	1a	0	0	0	1.47(3)	0.272(6)
Sr	2h	1/2	1/2	0.2084(1)	1.04(4)	1
Pr	1d	1/2	1/2	1/2	1.47(3)	1
Cu(2)	2g	0	0	0.3556(2)	0.77(5)	1
O(1)	4i	0	1/2	0.370(1)	1.5(1)	1
O(2)	2g	0	0	0.173(1)	4.5(4)	1
O(3)	1c	1/2	1/2	0		$\delta\sim0$

TABLE II. Some selected interatomic distances (Å) and angles (deg) for $(Hg_{0.728}Cu_{0.272})Sr_2PrCu_2O_{6+\delta}$. n is the number of equivalent bonds.

Bond	Distance (Å)	n
Hg/Cu(1)-O(2)	2.092(9)	2
Sr-O(1)	2.744(5)	4
Sr-O(2)	2.759(2)	4
Pr-O(1)	2.492(5)	8
Cu(2)-O(1)	1.934(1)	4
Cu(2)-O(2)	2.218(9)	1
Cu(2)-Cu(2)	3.500(3)	(intersheet)
Bond	**Angle (deg)**	n
O(1)-Pr-O(1)	101.3(2)	4
O(1)-Cu(2)-O(1)	169.9(3)	2

and 2.460 Å, respectively.[24] For the oxygen-depleted tetragonal 1236(Ba) $PrBa_2Cu_3O_6$ (Cu-1212) compound, a single long Pr-O bond length of 2.472 Å with lower T_N(Pr) of 10 K was observed.[7] Clearly, T_N(Pr) decreases montonically with increasing Pr-O bond length which reflects the degree of Pr $4f$–O $2p_\pi$ orbital hybridization or the strength of Pr-O-Pr superexchange coupling. Meanwhile, an effective coupling occurs between Cu and Pr moments through oxygen $2p_\pi/2p_\sigma$ as revealed by preliminary neutron and NMR studies on the Tl-1212 Tl(Ba,Sr)$_2$PrCu$_2$O$_{7-\delta}$ system.[25] This competition should be taken into account before a final conclusion can be reached.

IV. CONCLUSION

The Hg-1212 compound $HgSr_2PrCu_2O_{6+\delta}$ was synthesized with an anomalously high Pr ordering observed at $T_N(\mathrm{Pr})=6$ K with a broad transition onset from 11 K. The specific heat has an exceedingly large linear term, which is common to most Pr-containing cuprates. Along with earlier reports on other Pr-1212 M(Ba,Sr)$_2$PrCu$_2$O$_y$ (M=Cu, Hg, Tl, or Pb) compounds, this Pr sample further demonstrates the anomalous Pr-ordering behavior in the two-CuO$_2$-layer $m212$ systems ($m=1, 2, 3$). Finally, judging from the very low magnetic entropy, the Pr ordering in this Hg-1212 compound appears to be a more 2D-like process.

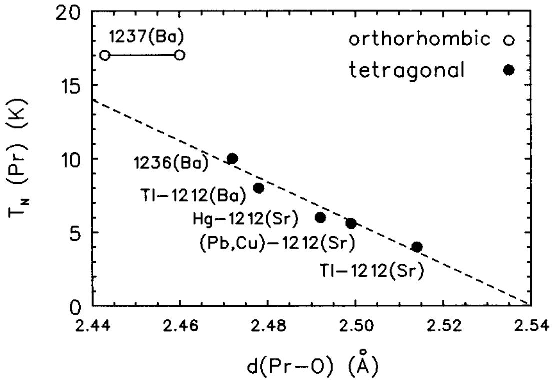

FIG. 6. T_N(Pr) versus Pr-O distance in various M(Ba,Sr)$_2$PrCu$_2$O$_y$ (M=Cu, Hg, Tl, or Pb) 1212-type compounds. The dashed line is a guide to the eyes only.

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[1] L. Soderholm, K. Zhang, D. G. Hinks, M. A. Beno, J. D. Jorgensen, C. U. Segre, and I. K. Schuller, Nature **328**, 604 (1978).

[2] J. K. Liang, X. T. Tu, 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. Rodriguez, F. F. Owen, R. L. Hitterman, and J. D. Jorgensen, *Crystal Structure of the High-T_c Superconducting Copper-Oxides* (Elsevier, Amsterdam, 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] A. Schilling, M. Cantoni, J. D. Guo, and H. R. Ott, Nature **363**, 56 (1993).

[17] L. Gao, Z. J. Huang, R. L. Meng, J. G. Lin, F. Chen. L. Beauvais, Y. Y. Xue, and C. W. Chu, Physica C **213**, 261 (1993).

[18] H. C. Ku, S. G. Chiou, C. C. Lai, and Y. B. You, Physica C **235**, 923 (1994).

[19] D. B. Wiles and R. A. Young, J. Appl. Crystallogr. **14**, 149 (1981).

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

[21] 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).

[22] C. L. Yang, J. H. Sheih, Y. Y. Hsu, H. C. Ku, and J. C. Ho, Phys. Rev. B (to be published).

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

[24] M. E. Lopez-Morales, D. Rios-Jara, J. Taguena, R. Escudero, S. Laplaca, A. Bezinge, V. Y. Lee, E. M. Engler, and P. Grant, Phys. Rev. B **41**, 6655 (1990).

[25] K. Kumagai, W. H. Li, and H. C. Ku (unpublished).