

Magnetic ordering of Pr and Cu in $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-y}$

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Neutron-scattering measurements have been performed to study the magnetic ordering of Pr and Cu in semiconducting $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-y}$. This compound has a nuclear structure which is similar to that of $\text{YBa}_2\text{Cu}_3\text{O}_7$ but with the CuO-chain layers fully replaced by TlO layers. At low temperatures the magnetic diffraction pattern reveals magnetic Bragg peaks of the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ type, which are associated with the antiferromagnetic ordering of the Pr moments. The magnetic structure consists of nearest-neighbor spins along all three crystallographic directions being antiparallel. The spin direction is along the c axis, with a saturated moment of $1.05\mu_B$. The temperature dependence of the intensity of these reflections indicates a Néel temperature $T_N \approx 8$ K, which is about half that observed in the related $\text{PrBa}_2\text{Cu}_3\text{O}_7$ system. A second set of magnetic reflections, of the $\{\frac{1}{2}\frac{1}{2}1\}$ type, are also observed, and these are associated with the Cu magnetic sublattice. This magnetic structure is identical to the "plane ordering" observed in the related 1:2:3 system, where the nearest-neighbor Cu spins are again antiparallel. The spin direction is in the tetragonal ab plane, with a saturated ordered moment of $0.59\mu_B$. The temperature dependence indicates a Néel temperature of ≈ 370 K for the Cu spins.

I. INTRODUCTION

As far as the atomic arrangement is concerned, the high- T_c class of layered perovskite oxides contain almost identical CuO_2 layers. A wide variety of physical phenomena may then be obtained by inserting different types and numbers of other layers between them: High- T_c superconductivity, high- T_N antiferromagnetism, metal-insulator phase transition, superconductor-antiferromagnet phase transition, suppression of superconductivity, coexistence of superconductivity and antiferromagnetism, two-dimensional (2D) magnetic order, 3D magnetic order, mixed valent behavior, and heavy fermion behavior, for example. Many of these properties are then affected by introducing particular atoms onto particular sites. Among them, introducing Pr atoms onto the rare-earth sites of the $\mathcal{R}\text{Ba}_2\text{Cu}_3\text{O}_7$ (\mathcal{R} 1:2:3:7) compounds not only suppresses superconductivity¹ but also gives rise to a very high (in comparison to the other rare earths) antiferromagnetic ordering temperature of $T_N \approx 17$ K for the Pr spins.² It is now generally believed that the hybridization of the Pr wave function at the Fermi level^{3,4} is responsible for the suppression of superconductivity in Pr 1:2:3:7, and the Pr ions are strongly coupled² through the copper-oxygen layers between them which then makes the Pr spins have a T_N which is more than two orders of magnitude higher than expected by

purely dipolar interactions.

Various experiments indicate that both the CuO_2 -plane and the CuO-chain layers in $\text{PrBa}_2\text{Cu}_3\text{O}_{6+x}$ (Pr 1:2:3:6+x) might affect the Pr magnetism. A replacement of the Cu atoms in the CuO_2 -plane layers by Fe, Co, or Ga atoms effectively reduces⁵ the T_N of Pr, while a 15 at. % replacement of the Cu atoms in the CuO-chain layers by Zn atoms alters⁶ the spin structure of Pr. Moreover, a full replacement of the CuO-chain layers by NbO_2 octahedra⁷ or a reduction of the oxygen content in the CuO-chain layers^{8,9} results in a reduction of T_N for Pr. Even more dramatically, reducing the oxygen content in the CuO-chain layers from Nd 1:2:3:7 to Nd 1:2:3:6 not only increases the T_N of Nd by a factor of 3 but also changes the type of the magnetic correlations between Nd spins from 3D long-range order to 2D short-range order, to 3D short-range order, and then returning to 3D long-range order.^{10,11} A removal of the CuO-chain layers may help reduce some complexities related to the Pr magnetism. One candidate compound is the single-Tl-layer system $\text{TlBa}_2\text{PrCu}_2\text{O}_7$ (Pr 1:2:1:2:7), in which the CuO-chain layers have been fully replaced by TlO layers but with the oxygen now located at the center of the unit cell rather than being along one edge.¹² This system is the semiconducting version of the 85-K superconductor $\text{TlBa}_2\text{CaCu}_2\text{O}_7$. The Pr ions in Pr 1:2:1:2:7 have been observed to order at 8 K via susceptibility and specific-heat measurements.¹³ Specific-heat data also show a sizable

linear term that is comparable to that found in heavy fermion systems.¹⁴ On the other hand, the antiferromagnetism of the Cu spins in Y 1:2:1:2:7 has also been observed via neutron-diffraction measurements,¹⁵ and the results show that the Cu spins have a Néel temperature which is above 350 K.

In this paper we report neutron-diffraction measurements on the semiconducting, tetragonal $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-y}$ compound. We have observed 3D long-range antiferromagnetic order of the Pr spins, with a Néel temperature $T_N \approx 8$ K, and a low-temperature saturated moment $\langle \mu_z \rangle = 1.05\mu_B$, and with the spins directed along the c axis. In comparison with the Pr ordering in Pr 1:2:3:7, the full replacement of the CuO-chain layers by TlO layers does not alter the spin structure of Pr but reduces its ordering temperature by a factor of 2 while enhancing its saturated moment by a factor of 1.5. In addition, we have also observed the antiferromagnetic ordering of the Cu spins with an ordering temperature of ≈ 370 K, a saturated moment $\langle \mu_z \rangle = 0.59\mu_B$, and with the spin direction lying in the tetragonal ab plane. This Cu ordering in the present $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-y}$ compound is the same as the CuO_2 -plane ordering observed in the Nd 1:2:3:6+ x (Refs. 16 and 17), Y 1:2:3:6+ x (Ref. 18), and Pr 1:2:3:6+ x (Ref. 19) compounds. Finally, we have noted a small superlattice distortion of the chemical unit cell, which doubles it along all three directions. A similar distortion has been observed in the related material Y 1:2:1:2:7.¹⁵

II. EXPERIMENTAL RESULTS

The polycrystalline samples were prepared by standard solid-state reaction techniques, starting from mixing and grinding appropriate quantities of high-purity powders of Pr_6O_{11} , BaO_2 , CuO , and Tl_2O_3 , followed by pressing the mixture into pellets and wrapping them in gold foils. After firing at 870°C for 10 h in flowing oxygen, the reaction products were then slowly cooled to room temperature. Both x-ray and neutron diffraction were used to characterize the sample. The structure of the tetragonal Pr 1:2:1:2:7 is very similar to that of orthorhombic Pr 1:2:3:7. Its crystal structure can be obtained from that of the Pr 1:2:3:7 by simply replacing each CuO-chain layer by a TlO layer, but with the O now located at the center of each Tl square. This can be emphasized if we write the chemical formula of $\text{TlBa}_2\text{PrCu}_2\text{O}_7$ as $\text{PrBa}_2(\text{TlCu}_2)\text{O}_7$. The replacement of the CuO-chain layers by TlO layers also makes the unit cell along the c axis somewhat larger while the ab plane remains basically unaltered. The lattice parameters that we obtained for Pr 1:2:1:2:7 at room temperature are $a = b = 3.910(1)$ Å and $c = 12.53(1)$ Å. The tetragonal crystal structure of Pr 1:2:1:2:7 is expected, since the oxygen atoms in the TlO layers are now located at the center of the unit cell rather than being along one edge. For comparison we note that the lattice parameters² for Pr 1:2:3:7 at room temperature are $a = 3.879$, $b = 3.913$, and $c = 11.715$ Å.

Neutron-diffraction measurements were performed at the Research Reactor at the U.S. National Institute of Standards and Technology. The data were collected us-

ing the BT-9 triple-axis spectrometer which was operated in double-axis mode. A pyrolytic graphite PG(002) crystal was used as the monochromator to extract neutrons of energy 14.8 meV (2.351 Å). A PG filter was also placed after the monochromator position to suppress higher-order wavelength contaminations, and no $\lambda/2$ or $\lambda/4$ contaminations were found in the incident beam. The angular collimations used were $40'$ before the monochromator, and $48'-48'$ before and after the sample, respectively. The sample was mounted in a cylindrical aluminum can filled with helium exchange gas to facilitate thermal conduction at low temperatures. A pumped ^4He cryostat was used to cool the sample, and the lowest temperature obtained was 1.36 K. For each temperature change, sufficient time was given for allowing the sample to reach thermal equilibrium.

At a temperature well above any magnetic ordering temperature, the spins of the unpaired electrons scatter neutrons incoherently, and the magnetic scattering hence appears as paramagnetic "background" in a neutron powder-diffraction pattern. As a result, only the nuclear coherent scattering will appear as Bragg peaks in the diffraction pattern. When magnetic correlations develop, as the temperature of the system is reduced, the magnetic scattering develops into magnetic peaks, which become Bragg peaks below the ordering temperature. A diffraction pattern taken at low temperatures then consists not only of nuclear but also magnetic Bragg peaks. In the situation where there is no significant structural distortion, which is usually the case for these low-temperature magnetic phase transitions, it is then only the magnetic contribution to the scattering that will survive a procedure of subtracting the diffraction pattern taken at high temperature from one taken well below the ordering temperature.²⁰ The basic spin configuration can then be determined from the angular positions of the magnetic Bragg peaks, while the spin direction can be obtained by a detailed comparison between the observed magnetic intensities. The absolute value of the magnetic moment of the ordered ions in the system can also be determined by comparing the intensities of the magnetic peaks to the (known) nuclear Bragg intensities.²⁰

III. RESULTS

Figure 1(a) shows a portion of the diffraction pattern observed at the lowest temperature of $T = 1.36$ K. Based on the tetragonal nuclear unit cell, the peaks at $2\theta = 25.27^\circ$, 26.85° , and 30.07° may be indexed as the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$, $\{\frac{1}{2}\frac{1}{2}1\}$, and $\{\frac{1}{2}\frac{1}{2}\frac{3}{2}\}$ Bragg reflections, respectively. As the temperature was increased to $T = 16$ K, the intensities of the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ and $\{\frac{1}{2}\frac{1}{2}\frac{3}{2}\}$ peaks clearly decreased strongly, and we will see that this is well above the Néel temperature of the Pr ordering. Nevertheless, the peaks have not disappeared, and this extra intensity remains up to 300 K (the highest temperature at which measurements were made). We associate this scattering with a superlattice distortion, which has also been observed¹⁵ in Y 1:2:1:2:7. The $\{\frac{1}{2}\frac{1}{2}1\}$ reflection shown in Fig. 1(b), on the other hand, does not change intensity between 1.36 and 16 K. We have measured the $\{\frac{1}{2}\frac{1}{2}1\}$ peak up to 420

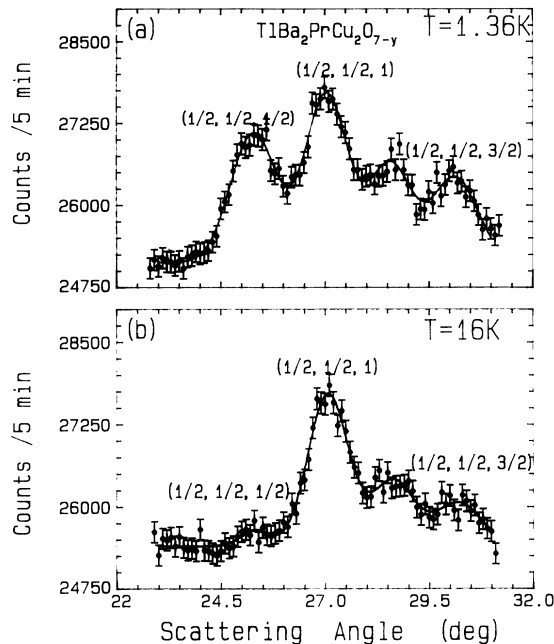


FIG. 1. A portion of the diffraction pattern observed in $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-y}$ at (a) $T = 1.36$ K and (b) $T = 16$ K. The indices shown are based on the tetragonal nuclear unit cell. The solid lines are fits to the Gaussian instrumental resolution function. The intensity of the $\{\frac{1}{2}\frac{1}{2}1\}$ reflection remains the same at these two temperatures, while that of the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ and $\{\frac{1}{2}\frac{1}{2}\frac{3}{2}\}$ reflections clearly decreased as the temperature was increased. The peak at $2\theta = 28.35^\circ$ does not change significantly with temperature, and is due to impurity scattering.

K, and the data show that the intensity of this peak begins to noticeably decrease for temperatures above 225 K, and has dropped to background intensity at 390 K. From these data we obtain an ordering temperature for the Cu spins of ≈ 370 K. The intensity of the peak at $2\theta = 28.35^\circ$ does not change significantly with temperature, and is due to impurity scattering; this impurity peak has an intensity which is less than 1% of the most intense sample reflection.

A. Cu ordering

In the \mathcal{R} 1:2:3:6+x compounds, there are three copper-oxygen layers per nuclear unit cell. Two of those layers are the so-called “CuO₂-plane” layers in which there are O ions between the Cu ions in both the a and b axes. The third layer is the so-called “CuO-chain” layer in which there are O ions between the Cu ions only along the b axis and the oxygen content in this layer can be easily changed. The Cu magnetism for both the CuO₂-plane and the CuO-chain layers have proven to be very sensitive to the oxygen content x in the CuO-chain layers.^{16–19,21} In the small x regime, where the compounds are semiconducting, the Cu spins in the CuO₂-plane layers order as high as $T_N \approx 525$ K. For the high-temperature phase,^{16–18} where the Cu spins in the CuO-chain layers are already completely disordered but the Cu spins in the CuO-plane layers remain ordered, the

nearest-neighbor Cu spins of the CuO₂-plane layers are aligned antiparallel along all three crystallographic directions.

In the present $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-y}$ compound, where the CuO-chain layers have been fully replaced by nonmagnetic TlO layers, there are only two copper-oxygen layers per nuclear unit cell. If the Cu spins that are aligned antiparallel along all three crystallographic directions as in the 1:2:3 system, then we anticipate magnetic Bragg reflections of the $\{m/2, n/2, l\}$ type, where m and n are odd integers and l is an integer. The $\{\frac{1}{2}\frac{1}{2}1\}$ peak that we observed in $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-y}$ hence originates from Cu ordering. The temperature dependence of this peak is shown in Fig. 2, which reveals a typical order parameter for powder samples. The data indicate an ordering temperature of $T_N \approx 370$ K for the Cu ions. This ordering temperature of Cu spins is consistent with those found in Y 1:2:1:2:7,¹⁵ PrBa₂NbCu₂O₈ (Pr 1:2:1:2:8),⁷ and NdBa₂NbCu₂O₈ (Nd 1:2:1:2:8).⁷ By comparing the intensity of the $\{\frac{1}{2}\frac{1}{2}1\}$ reflection to the nuclear Bragg peaks, we obtain a saturated ordered moment of $\langle \mu_z \rangle = 0.59 \pm 0.06 \mu_B$ for the Cu ions at $T = 1.36$ K, with the spin direction in the ab plane. This value of the ordered moment is less than the $0.8 \mu_B$ observed for Nd 1:2:3:6+x (Ref. 16) and Pr 1:2:3:6+x (Ref. 19).

The proposed spin structure of the Cu ions in $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-y}$ is shown in Fig. 3(a), where we have used the coordinate system with the Tl atoms located at the origin. The Cu spins alternate along all three crystallographic directions with the moments lying in the tetragonal ab plane. The specific direction of the moment within the ab plane cannot be determined from our powder sample measurements, since the different domains of our powder sample were assumed to be equally populated,²² and the information on this direction is lost when a domain average is taken. In Fig. 3(a) we have

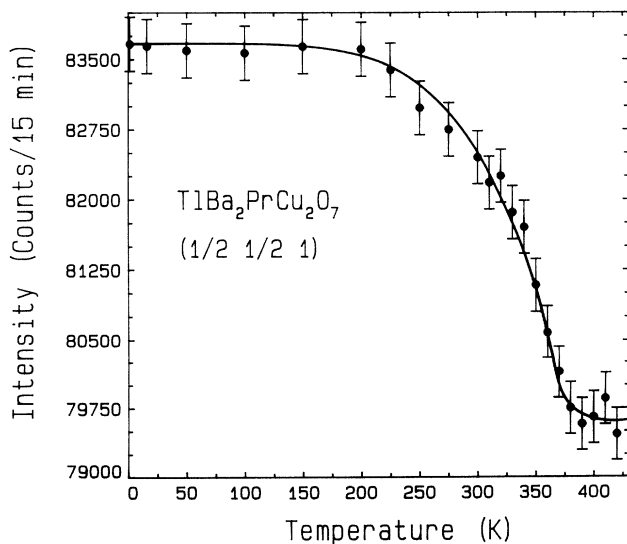


FIG. 2. Temperature dependence of the $\{\frac{1}{2}\frac{1}{2}1\}$ peak intensity. The data reveal a typical order parameter, and show an ordering temperature of $T_N \approx 370$ K for the Cu ions. The solid curve is a guide to the eye.

(a) Cu ordering (b) Pr ordering

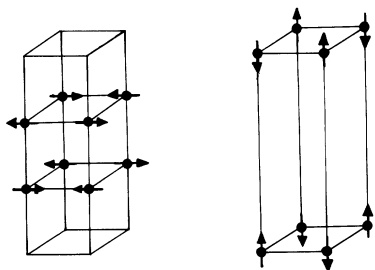


FIG. 3. The spin configurations of the (a) Cu and (b) Pr ions in $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-y}$. Both the Cu and Pr spins alternate along all three crystallographic directions. The moment direction of the Pr is along the c axis, while that of the Cu lies in the tetragonal ab plane. The specific direction of the Cu moment within the ab plane cannot be determined from our measurements, and we have simply chosen it to be along the a axis for clarity.

simply chosen the moment direction of the Cu spins to be along the a axis for clarity. The same Cu ordering structure has also been observed⁷ in Pr 1:2:1:2:8 and Nd 1:2:1:2:8, where the CuO-chain layers have been fully replaced by nonmagnetic NbO_2 layers. We note that the crystal structure of Pr 1:2:1:2:8 and Nd 1:2:1:2:8 is similar to but not quite the same as that of Pr 1:2:1:2:7. In the former, the CuO-chain layers are fully replaced by NbO_2 layers with the same Nb-O octahedra as that of Cu-O in the CuO_2 -plane layers. In the latter, the CuO-chain layers are also fully replaced by TlO layers but with the O now located at the center rather than being along one edge.

B. Pr ordering

Figure 4 shows the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ peak intensity as a function of temperature, where we observe a variation with temperature that is typical of a magnetic phase transition in a powder, with a Néel temperature $T_N \approx 8$ K. This scattering originates from the Pr ordering, and the ordering temperature observed agrees well with the specific-heat and magnetic-susceptibility data.¹³ As noted above in Fig. 1(b), however, there is still some scattering at the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ and $\{\frac{1}{2}\frac{1}{2}\frac{3}{2}\}$ positions above T_N . We note that the intensity ratio between the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ and the $\{\frac{1}{2}\frac{1}{2}\frac{3}{2}\}$ peaks at $T=16$ K is quite different from that at $T=1.36$ K; the observed integrated intensities for the two peaks are in the ratio of $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}:\{\frac{1}{2}\frac{1}{2}\frac{3}{2}\}=1.51(9):1$ and $0.22(7):1$ at $T=1.36$ K and $T=16$ K, respectively. This difference in intensity ratio suggests that the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ type of reflections in these two temperature regimes have different origins. We have measured the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ and $\{\frac{1}{2}\frac{1}{2}\frac{3}{2}\}$ peaks up to room temperature, and within experimental error no variation with temperature was noted. Thus this extra scattering cannot be associated with the Pr or Cu magnetism. We hence believe that these small extra peaks at high temperatures are due to a small modulation of the nuclear unit cell along all three crystal-

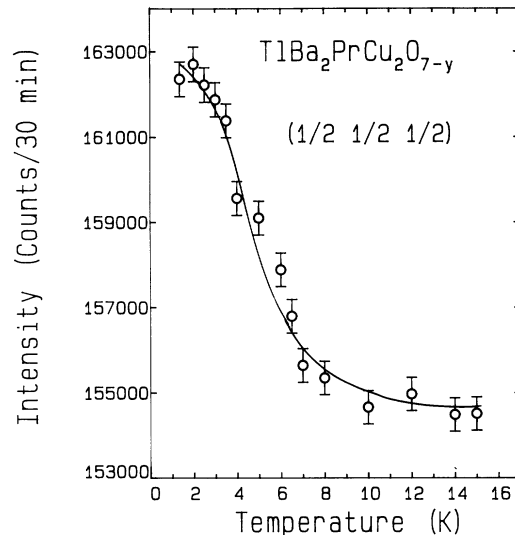


FIG. 4. Temperature dependence of the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ peak intensity, showing the variation of the square of the staggered magnetization with temperature. The data reveal a typical order parameter with a Néel temperature of $T_N \approx 8$ K, which is a factor of 2 smaller than the ordering temperature of Pr observed in $\text{PrBa}_2\text{Cu}_3\text{O}_7$. The solid curve is a guide to the eye.

lographic directions. The same observations and conclusions have also been reached by neutron studies on the Y 1:2:1:2:7 compound.¹⁵

Having established that these extra peaks are temperature independent, we can then use the subtraction procedure to isolate the magnetic scattering of the Pr ions. The difference between the diffraction patterns taken at $T=1.36$ K and $T=16$ K are shown in Fig. 5, where the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ and $\{\frac{1}{2}\frac{1}{2}\frac{3}{2}\}$ peaks are the magnetic intensities that develop at low temperatures. We note that the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$

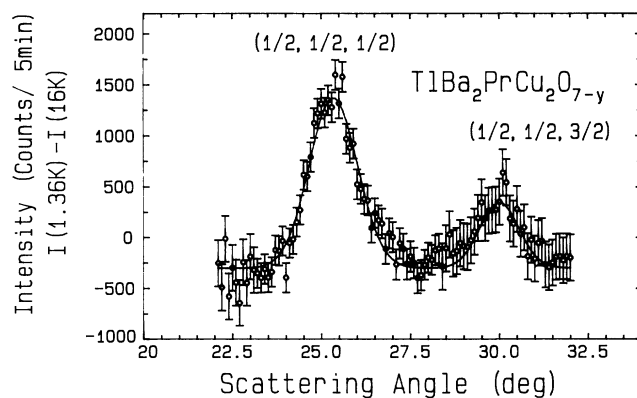


FIG. 5. Magnetic intensities observed in $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-y}$ at $T=1.36$ K. The magnetic peaks may be indexed as the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ and $\{\frac{1}{2}\frac{1}{2}\frac{3}{2}\}$ Bragg reflections, which then show a 3D antiferromagnetic ordering of the Pr spins with a magnetic unit cell which is doubled along all three crystallographic directions. The solid line is a fit to the Gaussian instrumental resolution function.

peak clearly cancels out. The widths of the magnetic $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ and $\{\frac{1}{2}\frac{1}{2}\frac{3}{2}\}$ peaks are consistent with the instrumental resolution and shows that the Pr spins exhibit 3D long-range magnetic order. No search for possible 2D magnetic behavior has been made in present studies. For the 3D magnetic order we note that all three Miller's indices of the magnetic peaks are half-integer, which indicates that the magnetic unit cell is just double the nuclear one along all three crystallographic directions (since there is only one Pr atom per nuclear unit cell). Hence the underlying magnetic structure consists of nearest-neighbor spins along all three crystallographic directions being aligned antiparallel. The observed relative intensities of the magnetic peaks are consistent with the Pr moments being directed along the c axis. The saturated moment of the Pr ions, that we obtained by comparing the magnetic to the nuclear intensities, is $\langle\mu_z\rangle = 1.05 \pm 0.06\mu_B$. This value for the saturated moment is somewhat larger than the $0.74\mu_B$ found² for Pr 1:2:3:7, but is smaller than the $1.2\mu_B$ found⁷ for Pr 1:2:1:2:8. We believe that the difference in the saturated moment found for Pr in these three compounds is likely due to their different levels of hybridization as well as the difference in their crystalline electric-field environment.

The proposed spin structure of Pr in $\text{TlBa}_2\text{PrCu}_2\text{O}_7$ is shown in Fig. 3(b), where we have used the coordinate system with the Pr atoms located at the origin. The Pr spins alternate along all three crystallographic directions, with the moment directed along the c axis. This is the same type of spin structure for Pr as found in Pr 1:2:3:7 (Ref. 2) and Pr 1:2:1:2:8 (Ref. 7). The data in Fig. 4 reveal a typical order parameter with a Néel temperature of $T_N \approx 8$ K. This ordering temperature of the Pr spins is a factor of 2 smaller than that of Pr 1:2:3:7,² but is close to that of $\text{Pb}_2\text{Sr}_2\text{PrCu}_3\text{O}_8$.²¹ The hybridization between the Pr $4f$ state and the O $2p$ state in the CuO_2 -plane layers likely plays an important role in determining the nature of the cooperative behaviors of the Pr spins, but the mechanism that makes the Pr spins in layered cuprates have an ordering temperature which is more than two orders of magnitude higher than expected by a purely dipolar interaction is still not yet completely understood. The present study shows that the replacement of the CuO-chain layers by TlO layers does not alter the basic spins structure of Pr, but reduces the ordering temperature by a factor of 2, while the saturated moment increases by a factor of 1.5.

IV. DISCUSSION AND CONCLUSIONS

In summary, we have studied the antiferromagnetic ordering of both the Pr and the Cu spins in the semiconducting $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-y}$ compound by neutron diffraction. There are no CuO_2 -chain layers in the present compound to complicate the Pr and Cu magnetism, since they have been fully replaced by nonmagnetic

TlO layers. The Cu spins order with a Néel temperature around 370 K, and the ordering is similar to the "Cu-plane" ordering observed^{16,19} in Nd 1:2:3:6+ x and Pr 1:2:3:6+ x . The observed ordering of the Pr spins is 3D in nature, and we have not searched for possible 2D magnetic behavior in this study. The two dimensionality is believed to arise naturally from the crystallography since the c axis is more than three times as long as the a and b axes. More detailed studies with single crystal samples are needed to determine if there is a crossover from 2D to 3D character as has been observed for Pr,⁷ Nd,⁷ Er,^{23,24} and Dy,²⁵ in Pr 1:2:1:2:8, Nd 1:2:1:2:8, Er 1:2:3:7, and Dy 1:2:3:7, respectively.

The Pr spins order with $T_N \approx 8$ K, and this ordering temperature is a factor of 2 smaller than that of Pr 1:2:3:7 but is still much too high for purely dipolar interactions. Specific-heat²⁶ studies on $\text{Bi}_2\text{Sr}_2\text{PrCu}_2\text{O}_8$ showed no indication of Pr ordering at a temperature as low as 1.6 K. The magnetization measurement^{5,27} on the compounds where the Cu atoms in the CuO-chain layers were replaced, e.g., $\text{PrBa}_2(\text{Cu}_{1-x}\mathcal{M}_x)_3\text{O}_7$ with $\mathcal{M} = \text{Ga}, \text{Co},$ and Fe , T_N is effectively reduced by increasing the doping level. On the other hand, those compounds where the Cu atoms in the CuO_2 -plane layers were replaced, e.g., $\text{PrBa}_2(\text{Cu}_{1-x}\mathcal{M}_x)_3\text{O}_7$ with $\mathcal{M} = \text{Zn}$ and Ni , T_N is less effectively reduced by doping. Moreover, the T_N 's of the rare-earth ions in Pr 1:2:3:6+ x and Nd 1:2:3:6+ x have been observed to depend sensitively on the oxygen content in the CuO-chain layers.⁸⁻¹⁰ All of these results indicate that those atoms that are located in the CuO-chain layers have more influence on the Pr magnetism than those that are located in the CuO_2 -plane layers. This is quite unexpected, since the CuO-chain layers are the most distant layers from the rare-earth site.

It is clear that mechanisms other than dipolar interactions must play a dominant role in the magnetic properties of the Pr spins. It is likely that superexchange, enhanced by the Pr hybridization, is the most important exchange mechanism. Systematical investigations on the Pr ordering with compounds that have the Cu atoms in the CuO-chain layers only partially replaced may bring us a step closer to understanding the Pr magnetism in layered cuprates.

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