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LETTER TO THE EDITOR

Magnetic ordering in single crystals of $PrBa_2Cu_3O_{7-\delta}$

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Abstract. Heat capacity measurements on pure but twinned single crystals of $PrBa_2Cu_3O_{7-\delta}$ reveal a sharp peak at $T_N^{Pr} = 16.6$ K, which according to thermal expansion, neutron diffraction, and magnetic susceptibility measurements originates from an antiferromagnetic ordering of the Pr-ion moments. A modest coupling to the Cu(2) spin system is observed. Below T_N^{Pr} a first-order transition in the magnetic structure of the Pr spin system (at 13.4 K in warming; ≈11 K in cooling) is found. Field-dependent heat capacity data show anisotropic temperature dependences of the c_p-peaks and recover a Schottky-like anomaly due to the crystal-field-split ground state of the Pr^{3+}.

The electronic and magnetic properties of cuprates containing Pr have been a topic of intense interest since it was discovered that superconductivity is suppressed in most of these materials. This contrasts with the typical behaviour where the rare-earth moments order at very low temperature (∼1 K) and this order readily coexists with superconductivity. In particular, all the rare earths (R) that form the stable $RBa_2Cu_3O_7$ (RBCO) structure are superconductors with $T_c > 90$ K, except Pr which is an insulator [1]. The antiferromagnetic (AF) ordering of the Pr with ordered moments of $0.74\mu_B$ is also anomalous in that the Néel temperature is an order of magnitude higher ($T_N^{Pr} \simeq 17$ K) than for other RBCO systems despite the small ordered Pr moment [2].

A general understanding of the behaviour of Pr in the cuprates has emerged in terms of strong hybridization of the 4f electrons near the Fermi level, which results in a larger exchange interaction as well as the loss of superconductivity [1]. However, a recent NMR study [3] has challenged this picture, and concluded that the Pr in the RBCO, and by extension in the other cuprates as well, has only a very small ordered magnetic moment. The anomalies in the specific heat and susceptibility, along with the new magnetic diffraction peaks that develop at low temperatures, were then explained as due to a change in the Cu spin structure rather than from Pr order. Such a possibility could not be excluded on the basis of previous data because the Pr and Cu moments are comparable in size, and because the Pr system is especially sensitive to dopants which strongly affect the magnetism. In single crystals, the magnetic properties were found to be drastically affected by inadvertent contamination from the crucible.

Here we report data on the specific heat of twinned contamination-free single crystals of $PrBa_2Cu_3O_{7-\delta}$ (PBCO), in magnetic fields of up to 16 T along or perpendicular to the c-axis.

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Detailed neutron diffraction, thermal expansion, and magnetic susceptibility measurements were also performed on the same crystals. Our results show that simple long-range AF order of Pr^{3+}-ion moments develops in PBCO at $T_N^{Pr} = 16.6$ K, accompanied by a change in the Cu(2) spin structure, while a first-order transition with a pronounced hysteresis occurs a few K below T_N^{Pr} in the Pr spin structure. The behaviour of $c_p(T)$ in magnetic fields reflects the anisotropy of the Pr spin system, and demonstrates that the valence state of the Pr ions is predominantly 3+.

The magnetism of RBCO has a complicated behaviour, as both Cu and R ions can order magnetically. In PBCO the Cu moments in the plane sites (Cu(2)) order antiferromagnetically near or above room temperature [4, 5], and thus the Cu moments are fully ordered at low temperatures where the Pr ions become ordered. The Cu ions at the chain positions (Cu(1)) are not expected to carry a moment. However, one of the complications of the Pr system is that even small concentrations of dopants at the chain sites can induce moments on the Cu(1), which then order. Moreover, the symmetry of the magnetic structure when both Cu sites order is the same as reported for the Pr in the initial powder diffraction work [2].

A ^{141}Pr NMR study [3] of a single crystal of PBCO gave a value of only $0.017\mu_B$ for the Pr moment, which was found to be in the *ab*-plane. This contrasts with the earlier neutron diffraction study [2], which indicated an ordered magnetic moment of $\approx 0.74\mu_B$ that was tentatively assigned as being directed along the *c*-axis. Mössbauer [6] and later neutron studies [7] suggested that the Pr moment was directed at an angle of $\approx 30^\circ$ to the *ab*-plane. The neutron investigation by Boothroyd *et al* [8] of a single crystal of PBCO that was free of Al, but contained Sr (0.7 at.%) and Mg, found a different *c*-axis magnetic structure for the Pr ions, but with a large ($\approx 0.5\mu_B$) ordered Pr moment that makes an angle of $55^\circ \pm 20^\circ$ with the *ab*-plane. They also found a substantial coupling between the Cu and Pr moments, which can in part be attributed to the fact that the Pr magnetic structure that they observed had the same symmetry as the Cu spin structure. This contrasts with the present single-crystal results, which exhibit a more modest coupling as observed in recent powder diffraction measurements [9], along with the basic AF structure of the Pr moments originally observed.

The use of unreactive $BaZrO_3$ crucibles has made it possible to grow high-quality single crystals that are free from all detrimental impurities and especially Al down to the ppm level [10]. The single crystals were annealed in flowing oxygen (1 bar) at 500 °C for 200 h, resulting in an oxygen content of 6.92 according to the calibration in reference [11]. Heat capacity measurements were performed from 2.1–40 K and with magnetic fields of up to 16 T acting parallel and perpendicular to the *c*-axis, using a heat pulse method on a batch of four single crystals (mass 11.8 mg). Precise calibration of the addenda enabled a reduction of the relative error to ≈3% at 4 K to be achieved. The thermal expansion was measured using one of these crystals and a high-resolution capacitive dilatometer [12]. Neutron diffraction measurements were performed on a single crystal of mass 3.8 mg using a triple-axis spectrometer in the double-axis mode at the NIST research reactor. A pyrolytic graphite PG(002) monochromator and a PG filter were used, with typically a wavelength of 2.351 Å and angular collimations in front of and behind the monochromator of 60′–40′ (FWHM), and an open detector. Directional magnetic susceptibilities, χ_{ab}, χ_c, were measured using a SQUID magnetometer in a field of 1 T.

In order to arrive at the magnetic (4f-electron-related) contribution to the specific heat $c_{mag}(T)$, the lattice contribution was estimated by applying mass scaling to the equivalent Debye temperature $\Theta_D(T)$ for PBCO on the basis of the corresponding values for $YBa_2Cu_3O_{7-\delta}$ [13]. $c_{mag}(T, H)$ was obtained after subtracting this lattice contribution

(independent of H) from the measured $c_p(T, H)$.

Figure 1(a) displays the thermal expansion in the twinned ab-plane. We observe at $T_1 = 16.8$ K a sharp peak with $\Delta\alpha_{ab} = 2.57 \times 10^{-6}$ K^{-1} and a roughly ten-times-smaller peak at $T_2 = 13.5$ K. Figures 1(b) and 1(c) show $c_{\rm mag}(T, H)/T$ in zero field and in selected applied magnetic fields, for $\boldsymbol{H}$ parallel and $\boldsymbol{H}$ perpendicular to the c-axis. In zero field, a sharp peak appears at $T_1 = 16.6$ K whose height is 7.0 J mol^{-1} K^{-1} (using an extrapolation from above T_1). Another smaller peak occurs at $T_2 = 13.4$ K. The height of this peak is $\approx$0.4 J mol^{-1} K^{-1}. The integrated magnetic entropy $S_{\rm mag}(T)$ is 4.4 J mol^{-1} K^{-1} near T_1 which is about 76% of $R \ln 2$ and is sufficient for 2D Ising AF ordering of the Pr sublattice. The entropy associated with the peak at T_1 is 0.52 J mol^{-1} K^{-1} which is 12% of the total entropy. At 40 K, $S_{\rm mag}(T)$ tends to saturate at $\approx R \ln 3$. By using the Clausius–Clapeyron equation, we calculate a uniaxial pressure dependence of $+0.6$ K GPa^{-1} for the phase transition at T_1.

Measurements were performed at ten different fields up to 16 T. Not all of the data have been plotted, for the sake of clarity. Our data show (figure 1(b)) that the peak at T_1 is strongly depressed both in temperature and size for fields $\parallel$ c-axis where $T_1(0) - T_1(H)$ follows quite well an H^2-dependence (see figure 1, inset). The small peak at T_2 broadens and vanishes above 7.5 T at temperatures around 9 K for $\boldsymbol{H} \parallel c$-axis. In a field of 16 T, the magnetic ordering peaks have vanished almost completely (traces are visible below 8 K), leaving only a broad rounded peak characteristic of a Schottky anomaly, which will be discussed below.

The dependence of $c_{\rm mag}(T)/T$ on field in the ab-plane is given in figure 1(c). In this case we observe a splitting of the larger peak at T_1. One component shifts towards lower temperatures as in the case of the field $\parallel$ c-axis, but at 16 T it is depressed to only $\approx$10.8 K where it is still a relatively sharp hump. The second component remains more or less at the same temperature T_1 at all fields, and its peak height is reduced with increasing field. While the former behaviour is characteristic of an AF ordering, the latter may indicate a weak ferromagnetic component in the ab-plane. The field-dependent depression of the T_2-peak with $\boldsymbol{H} \perp \boldsymbol{c}$ is weaker than for $\boldsymbol{H} \parallel c$-axis.

Cooling curves $T(t)$ of the 3.8 mg sample on the sample holder of the calorimeter down to the bath temperature were also measured. The cooling rate $\mathrm{d}T/\mathrm{d}t$ varies slightly at the phase transitions. Figure 1(d) shows $\Delta(\mathrm{d}T/\mathrm{d}t)$ obtained by subtraction of a smooth background curve from $\mathrm{d}T/\mathrm{d}t$. While we find a peak exactly at T_1, the lower temperature transition T_2 is shifted to 11.5 K, i.e. it shows hysteresis. The peak at T_2 is also much more pronounced in cooling than while warming up.

The magnetic susceptibility was measured with a field of 1 T in the ab-plane and along the c-axis. The easy axis of magnetization at low T is the c-axis. The transition at 16.7 K $= T_1$ is found to occur in both cases as a weak cusp. There are also barely visible cusps at $\approx T_2$ in both measurements. The magnetic anisotropy ratio χ_c/χ_{ab} increases with decreasing temperature and is $\approx$1.8 at T_2. We also find that, at $\approx$270 K, χ_{ab} and χ_c cross, and $\chi_c/\chi_{ab} \approx 0.7$ above 290 K, marking the AF ordering of the Cu(2) sublattice, as previously observed [14].

Neutron diffraction measurements were used to monitor the variation in the spin structures and ordered moments as a function of temperature. Magnetic Bragg peaks of the $(h/2, k/2, l)$ type (denoted whole-integer type, since l is an integer), originating from the magnetic ordering of the plane Cu(2) moments, become evident below the Néel temperature ($T_{\rm N}^{\rm Cu}$) of 281(1) K. The intensities of these peaks increase smoothly with decreasing temperature in the usual way, and, at 25 K, a series of integrated intensities was obtained. A refinement based on the usual model for Cu plane ordering [5] provided

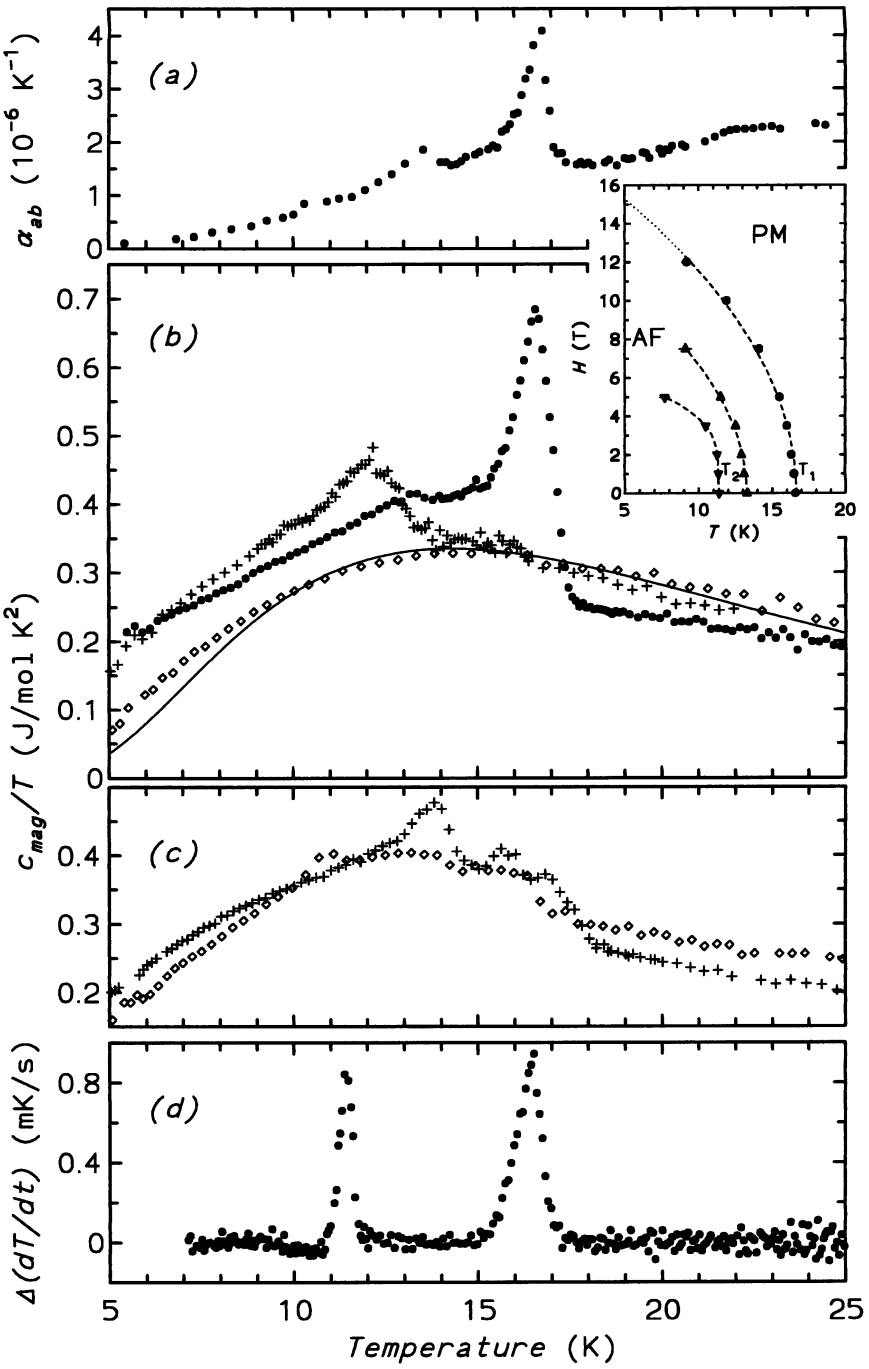

Figure 1. The thermal expansion coefficient α_{ab} perpendicular to the c-axis (a), and the magnetic specific heat $c_{\rm mag}/T$ of $PrBa_2Cu_3O_{7-\delta}$ with $H = 0$ T (•), 10 T (+), and 16 T (◇) parallel (b), and H perpendicular (c) to the c-axis. The solid line shows the calculated Schottky specific heat (see the text). (d) The variation of the cooling rate $\Delta(\mathrm{d}T/\mathrm{d}t)$ versus T (see the text). Inset: the magnetic phase diagram ($\boldsymbol{H} \parallel \boldsymbol{c}$) showing transitions T_1 (•) and T_2 (cooling, ▽; warming, △).

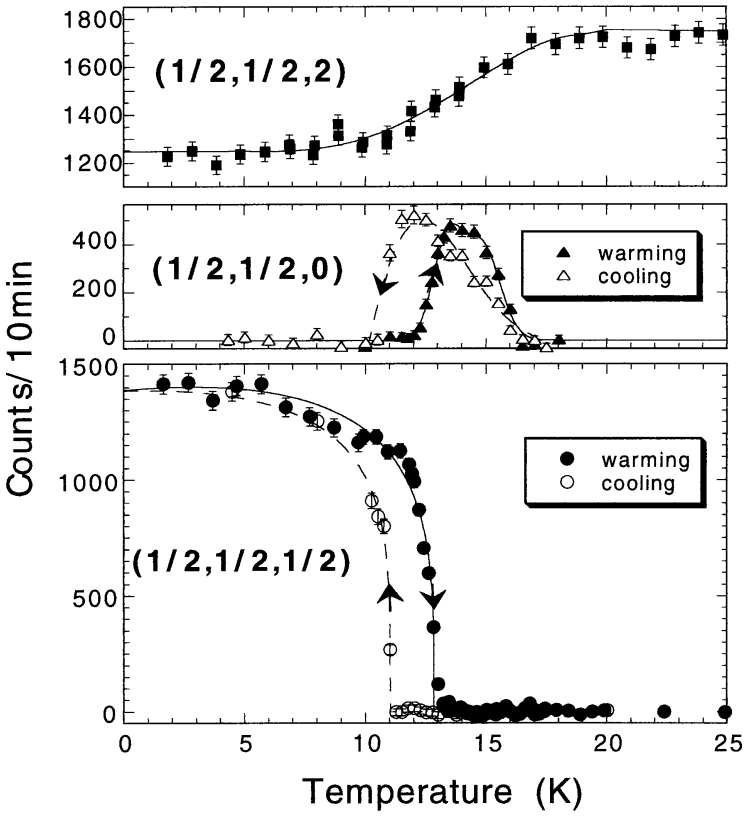

Figure 2. The temperature dependence of the $(\frac{1}{2}, \frac{1}{2}, 2)$ (top), $(\frac{1}{2}, \frac{1}{2}, 0)$ (centre), and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (bottom) magnetic Bragg peaks in $PrBa_2Cu_3O_{7-\delta}$ in warming and cooling.

a good fit to the data, with a saturated ordered moment of $0.62(2)\mu_B$. A refinement of the nuclear intensities gave an oxygen content of 6.97(5), in agreement with value of 6.92 already noted. Below $T_1 \approx 17$ K, the data in figure 2 (top) show that the intensities of these peaks exhibit a modest decrease over a fairly broad temperature range, corresponding to a reduction in the moment of $0.09\mu_B$. Accompanied by this decrease is the development of a magnetic Bragg peak at the $(\frac{1}{2}, \frac{1}{2}, 0)$ position, signalling that a phase transition has occurred (middle part of figure 2). No additional magnetic Bragg peaks were observed until $T = 11$ K, where the $(\frac{1}{2}, \frac{1}{2}, 0)$ peak abruptly drops in intensity while new magnetic Bragg peaks of the $(h/2, k/2, l/2)$ type (denoted half-integer type) develop (figure 2), i.e. a well-defined transition takes place at 11 K. We also find that there is hysteresis of $\approx$2 K in both the $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ peaks (figure 2). In warming we find the transition at 13.5 K marked by the specific heat, thermal expansion and susceptibility anomalies. All of the magnetic Bragg peaks are resolution limited, indicating magnetic long-range order. This contrasts with the results of Boothroyd *et al* [8], in that they found only whole-integer reflections at all temperatures, with broad widths at low temperatures. We collected a set of integrated intensities for both the half-integer and whole-integer peaks at 5.0 K and 1.7 K, and refinements based on models involving Cu chain spins were found to be qualitatively inconsistent with the measurements. In particular, the half-integer peaks cannot originate from a spin reorientation in the Cu(2) sublattice (or Cu(1) chain spin ordering) since this

would have to be reflected by a dramatic decrease in the $(\frac{1}{2}, \frac{1}{2}, 2)$-type intensities (to ≈ 0 intensity in order to preserve the overall moment). Rather, the smooth variation of the half-integer magnetic intensities with l, as observed for the heavy rare earths with this type of structure, strongly suggests that it is the Pr moments that are ordering, and a refinement based on this model yields an ordered moment of $\approx 0.8\mu_B$ at an angle of $\approx 60^\circ$ from the c-axis (depending on the specific non-collinear magnetic structure assumed). However, the small size of the crystal currently precludes a determination, via the magnetic form factor, of the contributions from the Cu and Pr ions separately in each of these magnetic phases. This is a particular problem because of the close similarity of the measured Cu form factor [15] to the (free-ion) form factor expected for Pr. A similar difficulty was encountered by Boothroyd *et al* in their analysis [8].

The data of figure 2, together with the specific heat, thermal expansion, and susceptibility data, indicate that at $T_1 = 16.8\ \mathrm{K} = T_N^{Pr}$ the Pr spins order magnetically as indicated by the $(\frac{1}{2}, \frac{1}{2}, 0)$ Bragg peak. The coupling of nearest-neighbour Pr spins is *antiparallel* in the a- and b-directions, but is *parallel* along the c-axis; the decrease in the $(\frac{1}{2}, \frac{1}{2}, 2)$ peak is then a result of the magnetic structure factor as the Pr moment develops, along with a possible distortion of the Cu spin structure. At 11 K (on cooling; at $T_2 \approx 13.5$ K in warming) a first-order transition occurs, where the Pr spins become *antiparallel* along the c-axis. Note that this first-order transition is not reflected in the intensity of the $(\frac{1}{2}, \frac{1}{2}, 2)$ peak, indicating that the Cu spin system is only weakly perturbed by the Pr spin system. We conclude that these are two separate phenomena, with the half-integer peaks at low T being associated primarily with the 3D AF ordering of Pr moments, consistent with the specific heat and susceptibility measurements.

Hilscher *et al* [16] investigated $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ using inelastic neutron scattering (INS), specific heat and magnetic susceptibility measurements on polycrystalline samples, and concluded that Pr is predominantly trivalent and confirmed the crystal-field splitting of the $J = 4$ ground multiplet of Pr^{3+}. They suggested the low-lying energy level scheme to be 0, 1.9, 3.2 meV with the sequence of the 'ground-state' singlets as $\Gamma_4, \Gamma_2, \Gamma_1$ (Koster notation) using INS data and additional assumptions about the magnetic anisotropy. In the fit to their INS, they considered J-mixing of the lowest three multiplets with intermediate-coupled wave functions. Boothroyd *et al* [17] proposed levels of 0, 3.4, and 4.8 meV with the sequence as $\Gamma_2, \Gamma_4, \Gamma_1$, allowing for J-mixing of all 91 levels and a molecular-field interaction term. Uma *et al* [14] fitted their anisotropic susceptibility data on single crystals of Al-contaminated $PrBa_2Cu_3O_{7-\delta}$ and the reported INS energy levels by considering J-mixing of all thirteen multiplets and proposed a scheme of $0(\Gamma_4)$, $3.9(\Gamma_1)$, and $4.7(\Gamma_2)$ meV. Despite the difference in the sequence of levels, the spacing is less than 60 K in all three cases and the interaction term for Γ_2 and Γ_4 contributes to the ordering.

Our experimental $c_{mag}(T)$ at $H = 16$ T can be fitted by a Schottky anomaly (c_{Sch}) with singlet energy levels at 0 K, 40 K, and 70 K. The fit is shown by a continuous line in figure 1(b). The crystal-field energy levels in PBCO are, however, modified by exchange fields, and (in external H-fields) also by the Zeeman effect. Nevertheless, our fit as well as the above-mentioned results clearly indicate a low-lying quasitriplet with spacing less than 70 K. Also, the entropy $S_{mag}(T)$ tends to saturate to $\approx R \ln 3$ at 40 K. This is additional evidence for a low-lying quasitriplet and thereby a 3+ valence state of Pr in PBCO.

We conclude that two magnetic transitions occur in the Pr sublattice of $PrBa_2Cu_3O_{7-\delta}$ at 16.6 K and 13.4 K, of which the sharp heat capacity peak at 16.6 K is associated with the magnetic ordering of the Pr sublattice and the beginning of a spin-reorientation transition in the Cu sublattice. The smaller $c_p(T)$-peak at 13.4 K is related to the spin reordering of the Pr^{3+} ions. This ordering is almost completely destroyed by a field of about 16 T at which

field we observe a Schottky-like anomaly arising from the 'quasitriplet' ground state of the Pr^{3+} ion. This scenario is supported by neutron diffraction, thermal expansion and magnetic susceptibility measurements. We find a pronounced anisotropy in the (twinned) *ab*-plane including a weak ferromagnetic component. The Cu(2)-site spin-reorientation process is found to be coupled with the AF ordering of the Pr ions. This may arise from the large spatial extension of the Pr^{3+} orbitals and the presence of a Pr(4f)–O(2p) hybridized state which can be expected to couple the Pr sublattice to the Cu(2) sublattice.

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