Magnetically inhomogeneous ground state below the first-order valence transition in (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_{3-δ}$

D. Phelan,* Kanwal Preet Bhatti,* M. Taylor, Shun Wang, and C. Leighton

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, USA

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Pr-based perovskite cobaltites, such as Pr$_{1.0}$Ca$_{0.7}$CoO$_{3-δ}$ and (Pr$_{1.0}$Y$_{0.7}$)$_{0.7}$Ca$_{0.3}$CoO$_{3-δ}$ have recently been discovered to undergo a first-order metal-insulator transition on cooling, thought to arise from an unusual shift in electron occupancy from Pr to hybridized Co-O orbitals. While this transition is known to generally suppress long-range ferromagnetic ordering, the true nature of the magnetic ground state remains unclear. In this work, we have performed structural, magnetic, transport, magnetotransport, and small-angle neutron scattering measurements on (Pr$_{1.0}$Y$_{0.2}$)$_{0.7}$Ca$_{0.3}$CoO$_{3-δ}$ (0.000 ≤ y ≤ 0.200) in order to develop a complete microscopic picture of the ground state and a full appreciation of the evolution of the first-order transition with Y doping. Our magnetization and zero-field resistivity measurements confirm the presence of an abrupt temperature-dependent metal-insulator transition on cooling, accompanied by a sharp drop in magnetization, setting in between y = 0.050 and 0.075. Small-angle neutron scattering measurements suggest the presence of critical ferromagnetic fluctuations above the metal-insulator transition for y = 0.075, indicating that the system is poised to order ferromagnetically. This magnetic scattering is suppressed at the metal-insulator transition but reemerges at lower temperatures (below 40–50 K) due to the formation of a ferromagnetic cluster state. The clusters have a mean correlation length of ~50 Å at 4 K, although magnetic inhomogeneity occurs across a broad spectrum of length scales, evidencing a highly inhomogeneous ground state, which we relate to the numerous sources of chemical and structural disorder. Interestingly, the magnetically inhomogeneous state manifests an intercluster magnetoresistance effect and a strong field-cooling effect on the low-temperature transport. We interpret these results, quite generally, in terms of the electronic shift from Pr to Co driving the system from the ferromagnetic side of the generic perovskite cobaltite magnetic phase diagram to the insulating side (where ferromagnetic clusters are well known to exist). These results thus shed significant light on the formation of the magnetically inhomogeneous ground state of Pr-based cobaltites undergoing a first-order metal-insulator transition and indeed provide clear and direct evidence of such.

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I. INTRODUCTION

The magnetic and electronic properties of perovskite cobaltites, ACoO$_3$ [where A can be a combination of lanthanides (with 3+ valence) and alkaline earth metals (with 2+ valence)], have been studied since the 1950’s [1] on account of a number of intriguing features, such as Co$^{3+}$ spin-state transitions [2–7], insulator-metal transitions [8], magnetoelectronic phase separation [9,10], and the existence of various magnetic states encompassing ferromagnetic, cluster glass [11–13], spin glass [11], and polaronic [14,15]. The “parent” cobaltite compounds such as LaCoO$_3$, PrCoO$_3$, and NdCoO$_3$, with Co in the 3+ valence state, have a ground state in which Co$^{3+}$ is nonmagnetic (low-spin: $t_{2g}^6e_g^0$, S = 0), but exhibit a gradual thermally induced Co$^{4+}$ spin-state transition to a paramagnetic state (intermediate-spin: S = 1 or high-spin: S = 2) [3,6,16,17]. While discussion of spin states within such an “atomic” framework can provide useful insight, hybridization, delocalization, and band formation significantly complicate the true picture. This is well illustrated in a recent letter through a combination of x-ray absorption spectroscopy (XAS), x-ray magnetic circular dichroism, and first-principles calculations that emphasize the mixing of $e_g$ and $t_{2g}$ states, as well as the importance of hybridization of Co 3d states with O 2p states [18]; moreover, recent results are suggestive of a strong sensitivity of magnetic properties to Co-O-Co angles [19]. In terms of electronic properties, these parent cobaltite compounds have insulating/semiconducting ground states. Hole doping through divalent ion substitution on the A-site results in stabilization of finite spin states, formation of ferromagnetic droplets (on the order of nanometers in size), and a magnetoelectronically phase separated state characterized by ferromagnetic clusters embedded in a non-ferromagnetic matrix over a doping range 0.04 < x < 0.22 in La$_{1−x}$Sr$_x$CoO$_{3−δ}$ (LSCO), for instance [9]. For x > 0.22 on the other hand, LSCO behaves as a uniform ferromagnetic metal [9]. The insulator-metal transition is percolative [20] and coincident with the onset of long-range ferromagnetic order. This behavior has been studied in particular detail in LSCO [9,21,22], but the general trend of long-range ordered ferromagnetic metallic states developing at sufficiently high doping has also been observed in numerous other hole-doped cobaltites, including La$_{1−x}$Ca$_x$CoO$_{3−δ}$ [23], La$_{1−x}$Ba$_x$CoO$_{3−δ}$ [24], Pr$_{1−x}$Sr$_x$CoO$_{3−δ}$ [25], Pr$_{1−x}$Ca$_x$CoO$_{3−δ}$ (PCCO) [26], Nd$_{1−x}$Sr$_x$CoO$_{3−δ}$ [27], and Nd$_{1−x}$Ca$_x$CoO$_{3−δ}$ (NCCO) [28].

More recently, the observation of a first-order magnetic/electronic transition in certain Pr-based compounds has established a new avenue of research in perovskite cobaltites. Namely, a simultaneous metal to insulator transition and sharp drop in magnetic moment have been observed upon cooling, e.g. at ~90 K in Pr$_{0.5}$Ca$_{0.5}$CoO$_3$ [29]. This is noteworthy as it has been argued that the impetus for this transition lies in a remarkable temperature-dependent change in the valence of
some fraction of the Pr ions (i.e. Pr$^{3+} \rightarrow$ Pr$^{4+}$), such that these sites absorb some of the holes originally associated with Co sites, or conversely, that electrons are transferred from the Pr 4$f$ levels into hybridized Co 3d–O 2$p$ orbitals [30]. That this manifests itself as a first-order phase transition at such low temperatures is quite unusual.

This valence transition (VT) has been observed in a number of Pr-based, hole-doped covalenties (where the average Co valence is above 3+). It was initially observed in PCCO with $x = 0.5$ [29], where a dramatic increase in the resistivity (ρ) concomitant with a metal-insulator transition, a precipitous drop in magnetization, a sharp peak in heat capacity, and an abrupt decrease in unit cell volume were observed upon cooling through the transition temperature ($T_{VT}$) of ~90 K. Subsequently, the VT was induced at lower hole concentrations (e.g. $x = 0.2$) in PCCO through the application of external hydrostatic pressure and also internal “chemical pressure” as in (Pr$_{1-x}$Y$_x$)$_{1-y}$Ca$_2$CoO$_{3-δ}$ (PYCCO), (Pr$_{1-x}$Tb$_x$)$_{1-y}$Ca$_2$CoO$_{3-δ}$, and (Pr$_{1-x}$Sm$_x$)$_{1-y}$Ca$_2$CoO$_{3-δ}$ [31,32]. Importantly, only materials with Pr are observed to undergo the VT [31,32], which led to the speculation that the VT was related to the trapping of holes in the Pr 4$f$–O 2$p$ hybridized orbitals in a somewhat analogous manner to the RE$^{3+}$ site in perovskites [33]. At temperatures below the VT, this band of states was shown to develop a gap, with some states shifted above the Fermi level. The Pr 4$f$ electron occupation is thus reduced, with electrons transferred to hybridized Co–O orbitals. In other words, the effective Co hole concentration is abruptly diminished on cooling, driving the system towards the nonferromagnetic, insulating side of the PCCO phase diagram. Subsequent confirmation of this picture has been provided by a number of x-ray absorption spectroscopy (XAS) measurements [34–38], as well as the observation of a Kramer’s doublet associated with the Pr$^{4+}$ state in heat capacity measurements [39]. Both DFT [30] and XAS experiments [36,38] strongly suggest the transfer of electrons into hybridized Co-O states.

Although both theoretical and experimental studies point to electron transfer from Pr 4$f$ states to Co 3d/O 2$p$ states as the origin of the VT, from XAS measurements and heat capacity measurements, it has also become quite clear that this transfer is only a partial one. Indeed, estimates of the average Pr valence below the VT lie between 3.15 and 3.5 for a variety of compounds that show the VT [34,35,37,38,40], meaning that the effective Co hole concentration is certainly reduced, but that the average valence remains higher than 3+.

That mixed-valent Pr and Co coexist and may form complex hybridized states with O 2$p$ states introduces the possibility of a highly complex magnetic state below $T_{VT}$. In a simplified ionic picture, although Pr$^{3+}$ has a singlet ground state and is not expected to order magnetically, there is a possibility of magnetic ordering involving Co$^{3+}$, Co$^{4+}$, and Pr$^{4+}$ (formally). Indeed, despite the decrease in magnetization upon cooling through $T_{VT}$, there is clearly some form of magnetic ordering or freezing that persists even to lower temperatures. For instance, in $x = 0.5$ PCCO, the magnetization ($M$) vs magnetic field ($μ_0H$) hysteresis loop is clearly open at 2 K [29,41], and coercivity is also apparent in measurements of the magnetic field dependence of the resistivity [29]. Knížek et al. [30] suggested that this results from ferromagnetic clusters in regions where the high-temperature (metallic) phase is retained, due to supercooling through the first-order VT. Moreover, dc and ac magnetization measurements revealed features at multiple (four) temperatures in a $x = 0.5$ PYCCO sample, which were interpreted as freezing of minor (low volume fraction) ferromagnetic regions or cluster-glass regions [41].

Aging effects and relaxation on long timescales, which indicate the presence of glassy magnetism, were also reported [41]. Large low field susceptibility was observed in PYCCO ($y = 0.15$) at 2 K and was attributed to relatively large paramagnetic clusters [42]. Furthermore, exchange bias was also reported at 2 K [42]. Considerable evidence is thus accumulating for the formation of ferromagnetic clusters in a highly magnetically inhomogeneous ground state below $T_{VT}$, but further work is necessary to understand this low-temperature magnetic state in full detail. In particular, more direct probes of this magnetic inhomogeneity would clearly be advantageous.

Further adding to the complexity of the low-temperature state is the issue of the Co$^{3+}$ and Co$^{4+}$ spin states, which could be categorized as low-spin ($S = 0$ for Co$^{3+}$, $S = 1/2$ for Co$^{4+}$), high-spin ($S = 2$ for Co$^{3+}$, $S = 5/2$ for Co$^{4+}$), or intermediate-spin ($S = 1$ for Co$^{3+}$ or $S = 3/2$ for Co$^{4+}$). Although the notion of localized spin states described in an atomic picture certainly cannot completely describe the physics of these systems, the degree of freedom in the spin state represented in this picture nevertheless reflects a genuine complication. X-ray absorption spectroscopy at the Co and O absorption edges has been interpreted as indicating that Co$^{3+}$ and Co$^{4+}$ have ground state low- and intermediate-spin configurations, respectively [38], or on the other hand, that both Co$^{3+}$ and Co$^{4+}$ have low-spin ground-state configurations [36]. Either interpretation suggests that the low-temperature magnetism is dominated by low- or intermediate-spin Co$^{4+}$, in addition to Pr$^{4+}$ (which is expected to have a $^2$F$_{5/2}$ ground state). As alluded to above, it has also been suggested that supercooled regions of the high-temperature phase could be retained at low temperatures [30,41], suggesting that some of the magnetism at low temperature would also involve Co$^{3+}$ in a high-spin or intermediate-spin state. These complex, in some cases conflicting, notions further highlight the need for additional characterization of the low-temperature magnetic state.

In this paper, we focus on the magnetic and transport properties of PYCCO ($x = 0.3$; $0.000 \leq y \leq 0.200$) in an effort to clarify the low-temperature ($T \ll T_{VT}$) behavior and fully elucidate the evolution of the VT with Y doping. This series, which was originally shown to undergo the first-order insulator-metal transition by Fujita et al. [32], is advantageous in the sense that it does not require high-pressure oxygen for sample synthesis [39]. Moreover, the “chemical pressure” is applied via the substitution of a nonmagnetic (Y$^{3+}$) ion rather than magnetic rare-earth ions, such as Sm$^{3+}$ and Tb$^{3+}$, rendering the interpretation of the magnetic properties somewhat simpler. First, we characterize the structural, magnetic,
and transport properties of such samples as a function of Y content ($y$), confirming the presence of the VT, and establishing its evolution with $y$, which we find to be consistent with the recent work of Hejtmánek et al. [40]. We then use small-angle neutron scattering (SANS) to directly establish that the ground state of a sample that undergoes the VT (at $y = 0.075$) involves the formation of ferromagnetic clusters with a mean short-range cluster size of \( \sim 50 \ \text{Å} \), coexisting with regions of longer-range ferromagnetic order. We then study magnetotransport properties, showing that the considerable magnetic inhomogeneity is also apparent from a hysteretic, isotropic negative magnetoresistance, which arises due to intercluster transport, as well as strong field-cooling effects on the resistivity. As discussed above, we argue that, because the VT reduces the effective hole concentration, the system is abruptly driven from the ferromagnetic/metallic side of the generic perovskite cobaltite phase diagram into the insulating, clustered regime. Our results thus serve to substantially clarify the nature of the inhomogeneous ground state of cobaltites undergoing such first-order VTs.

II. EXPERIMENTAL DETAILS

Bulk polycrystalline samples of PYCCO were synthesized by solid-state reaction using starting compounds of \( \text{Pr}_6\text{O}_{11} \), \( \text{Y}_2\text{O}_3 \), \( \text{Co}_3\text{O}_4 \), and \( \text{CaCO}_3 \). A thoroughly ground mixture of the powders was reacted at 1000 °C for 24 h in air. Following a second grinding, the samples were then cold-pressed into pellets, sintered at 1200 °C for 24 h in flowing \( \text{O}_2 \), and slowly cooled to ambient temperature at 0.5 °C/min in the flowing \( \text{O}_2 \). Thus, the synthesis conditions were quite similar to those reported in Ref. [39]. X-ray diffraction measurements were performed using a Cu-Kα source at 300 K. Transport measurements were performed in a liquid He cryostat in magnetic fields up to \( \mu_0H = 9 \ \text{T} \), using dc or ac techniques. Indium was soldered onto the sample as a contact material, and the measurements were performed in a van der Pauw geometry. Checks were made to verify Ohmic behavior. Magnetometry was performed using a superconducting quantum interference device (SQUID) magnetometer on small pellets of the samples over a temperature range of 5 to 300 K and a magnetic field range of \( \mu_0H = -9 \ \text{to} \ 9 \ \text{T} \). Small-angle neutron scattering measurements were performed on NG-3 at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) in Gaithersburg, Maryland, USA, with an incident neutron wavelength of \( \lambda = 6 \ \text{Å} \) on a pellet with \( y = 0.075 \) covering a range of wave-vector transfer (\( |Q| \)) from 0.005 to 0.315 \( \text{Å}^{-1} \). The sample was mounted in a closed-cycle refrigerator and measured over a temperature range of 4 to 300 K in \( \mu_0H = 0 \).

III. RESULTS AND ANALYSIS

A. Structural, magnetic, and transport properties of the PYCCO series

We have investigated the structural, magnetic, and electronic properties of the PYCCO series as a function of $y$, with fixed $x = 0.3$, in order to elucidate the effects of Y doping.

At $y = 0.000$, this system is known to have a ferromagnetic, metallic ground state [26], while with Y substitution, the VT is stabilized, certainly by $y = 0.0625$ [32,39]. The crystal structure of PYCCO has been described as an orthorhombic perovskite [with space group \( Pbnm \) (or equivalently \( Pnma \))] [39]. Our room temperature x-ray diffraction measurements, which are shown in Fig. 1 for $y = 0.000$, 0.075, and 0.100, are consistent with this symmetry, although some asymmetric peak broadening or peak shoulders were observed around strong Bragg reflections, potentially consistent with a very weak impurity phase. Rietveld refinement was performed (fits shown in Fig. 1) to determine the lattice parameters, but due to the weak scattering from oxygen by x rays, positional parameters obtained could not be refined to a high level of confidence. Given the small size of the Y$^{3+}$ ion, one would expect significant volume contraction upon substitution of Y$^{3+}$ for Pr$^{3+}$. Indeed, as shown in Fig. 2, the $b$ and $c$ lattice parameters, along with the unit cell volume, all decrease with $y$, evidencing successful incorporation of Y into the crystal structure. The $a$ lattice parameter actually displays a weak increase with $y$, although this increase is not sufficient to offset the decrease in $b$ and $c$ that lead to the decrease in unit cell volume. In the absence of detailed knowledge of the full atomic positions, it is not possible to understand the precise origin of the increase in $a$, although a strong possibility is that it is related to the $y$-dependent evolution of the rotation of the oxygen octahedra. Note that the temperature dependence of lattice parameters across the VT for $x = 0.5$ PCO similarly reveals a strong decrease in the $b$ and $c$ parameters, but very little change in the $a$ parameter [29].

The temperature dependence of $M$ in both zero-field-cooled (ZFC) and field-cooled (FC) conditions ($\mu_0H = 1 \ \text{mT}$) is
The large increase in vacancies to arise from magnetic exciton formation around oxygen length-scale of only 2–3 Co-O-Co bond distances, suspected to the onset of short-range ordered ferromagnetism, with a field-cooled magnetization reveals two main features, (relatively small) and [26], which revealed that the feature at 75 K (relatively large). These features are consistent with previous results at the same composition [26], which revealed that the feature at ~250 K corresponds to the onset of short-range ordered ferromagnetism, with a length-scale of only 2–3 Co-O-Co bond distances, suspected to arise from magnetic exciton formation around oxygen vacancies [43]. The larger increase in $M(T)$ at $T_c \sim 75$ K, on the other hand, marks development of long-range ordered ferromagnetism. We refer the reader to a more expanded discussion of the complex interplay between these two states in Ref. [26]. Upon Y substitution, the magnetic properties are rapidly altered as the VT sets in. The VT is detectable from a reduction in the $ZFC M$ at $T_{VT}$ that appears upon cooling and is evident at increasing temperatures as $y$ is increased, as shown in Fig. 3(c), similar to the work of Hejtmánek et al. [40]. Importantly, the onset of the VT is manifest by significant changes in $M(T)$ at even lower temperatures. The most dramatic change is apparent in Fig. 3(a), which shows that the rise in the FC $M$ that occurs at $T_c$ for $y = 0.000$ is suppressed to lower $T$ upon increasing $y$, even for $y = 0.025$. The functional form of the rise of $M(T)$ gradually changes from a second-order phase transition at $y = 0.000$ to a less well-defined shape at higher $y$. This rise is clearly inconsistent with the $1/(T - \theta)$ dependence of a simple interacting paramagnet, and furthermore, the ZFC and FC $M(T)$ traces do not overlap. Thus, the rise is indicative of some type of ordering or freezing into a state that is unlikely to be a simple, homogeneous long-range ordered ferromagnet. This suppression of the ordering into a long-range ferromagnetic state obviously results from the stabilization of the VT as $y$ is increased and is further exemplified by the closing of $M$ vs $H$ loops at low $T$ as shown by Hejtmánek et al. [39] and demonstrated in Fig. 4(a) at 5 K. Indeed, though some finite coercivity and remanence are still present at 5 K in samples that undergo the VT, indicating that they are not simple paramagnets, these values significantly drop with increasing $y$ as illustrated in Figs. 4(b) and 4(c). Despite this suppression of simple long-range ferromagnetic ordering with increasing $y$, the signatures of freezing or ordering in the magnetization clearly merit further investigation, which we provide below using SANS and magnetotransport measurements.

The related progression of the temperature dependence of the zero-field resistivity with $y$ is summarized in Fig. 5. For $y = 0.000$ and 0.025, $\rho$ is of the order of 1 m$\Omega$cm at 5 K, with a very weak temperature dependence. The relatively low magnitude of $\rho$, combined with the weakly negative $d\rho/dT$, suggests that the ground state is probably metallic, although the true form of $\rho(T)$ is very likely obscured by grain-boundary effects. Further increase in $y$ leads to dramatic increases in $\rho$ at low $T$ below $T_{VT}$, which is well illustrated by the $y$ dependence of
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FIG. 4. (Color online) (a) Magnetization (M) vs magnetic field (\(\mu_o H\)) loops at \(T = 5\) K for \(y = 0.000\) and 0.200. Also, \(y\) dependence of (b) magnetic coercivity (\(\mu_o H_c\)) at 5 K, (c) remanence (\(M_r\)) at 5 K, (d) resistivity (\(\rho\)) at 40 K, and (e) valence transition temperature (\(T_{VT}\)). Here, \(T_{VT}\) was determined from the resistivity measurement.

\(\rho(40\text{ K})\) as shown in Fig. 4(d). Here, \(T_{VT}\) agrees well with that observed in the magnetization (see Fig. 3) and increases with \(y\) as shown in Fig. 4(e). The relationship between \(T_{VT}\) and \(y\) is nearly linear, and the onset of finite \(T_{VT}\) is remarkably close to \(y = 0\). It is important to mention here that, although the VT is apparently truly first-order in nature (see e.g. Ref. [44]), the upturn in \(\rho(T)\) in our measurements, upon close inspection, is not as sharp as has been reported for certain samples [39,40].

We speculate that this is due to an inhomogenous distribution of Y ions and/or O vacancies at some nonnegligible level. Correspondingly, the increase in \(\rho\) in the “insulating” state below \(T_{VT}\), although clearly apparent in Fig. 5, is not quite as large as has been observed in some prior work [39,40].

B. Small-angle neutron scattering

Generally, the SANS cross-section results from the contrast that arises from inhomogeneties in neutron scattering length density. Since a net magnetic moment typically results in appreciable scattering length density, a coherent, elastic magnetic SANS cross-section can arise when the entire volume of a sample is not uniformly magnetically ordered, i.e. not single domain. Thus, SANS provides an effective means to detect ferromagnetic clusters and determine their length scales (i.e. correlation lengths) [45] and has been used to study various cobaltites including LSCO [22], PCCO [26], Pr_{1-x}Sr_{x}CoO_{3-\delta} [25], and NCCO [28]. Here, we have performed SANS measurements on a sample of PYCCO with \(y = 0.075\) in order to elucidate the nature of the magnetic ground state which, on the basis of the above discussions, we anticipate could be distinctly nonuniform.

Figure 6(a) shows the SANS differential cross-section (\(d\Sigma/d\Omega\)) at 300 K. The apparently linear dependence of the logarithm of \(d\Sigma/d\Omega\) on the logarithm of \(|Q|\) at 300 K suggests that \(d\Sigma/d\Omega\) is dominated by a contribution that follows a power law, i.e. \(I = I_0|Q|^{-n}\) over some range at low \(|Q|\). While deviations from this law are apparent at the very lowest \(|Q|\) values, \(d\Sigma/d\Omega\) can reasonably be fit to such a power law over the range \(0.009 < |Q| < 0.03\text{ Å}^{-1}\) with \(n = 4\), as indicated by the dashed line in the figure. The case \(n = 4\) is a special case of the Porod law, implying that the scattering objects are smooth surfaced and three dimensional, with diameter \(\gg 2\pi/|Q|\) (\(\sim 700\text{ Å}\) for the fitting range used here). At 300 K, the system is paramagnetic, so the scattering is anticipated to be dominantly nuclear. The strong Porod term at this temperature therefore most likely arises due from scattering off the grain structure of the sample.
at higher $|Q|$ and is appropriate for describing ferromagnetic correlations following an Ornstein-Zernike function [46]. The correlation length $\xi$ is given by the inverse of the half width at half maximum of the Lorentzian. From these fits, we find that $\xi$ is small, $17 \pm 12$ and $11 \pm 6$ Å at 100 and 80 K, respectively, but dramatically larger, $\sim 59 \pm 25$ Å at 4 K. This is a direct indication of the presence of short-range ferromagnetic clusters in the ground state of this system. The Porod term in $\Delta(d\Sigma/d\Omega)$, however, is more complex and cannot necessarily be interpreted as having a single origin. Rather, we believe it to be a superposition of a magnetic contribution and a nuclear contribution. The magnetic contribution to this intensity results from small volume fractions of longer-range ferromagnetic order that form at low temperature. The temperature dependence of this term, discussed below, supports this argument, thereby suggesting a coexistence of short-range and long-range ferromagnetically ordered clusters. Nevertheless, there is also clearly a possibility of a nuclear contribution related to the isomorphic structural phase transition that occurs at $T_{\text{VT}}$ [29], which likely alters the microstructure and thus may very well affect the nuclear contribution to $d\Sigma/d\Omega$. In fact, there are few crystals that are known to undergo isomorphic transitions with no change in space group [47], so there is no well-established paradigm that describes how the microstructure should be altered. We note, however, that there has been some discussion of isomorphic transitions leading to domain rearrangement in ferroelectrics [48], and it is possible that a rearrangement of orthorhombic domains takes place at or below $T_{\text{VT}}$, thereby leading to a change in the nuclear Porod scattering. Since the nuclear Porod scattering is the strongest contribution to the raw $d\Sigma/d\Omega$, small changes may appear substantial in a difference plot of the type shown in Figs. 6(b)–6(e).

To further understand the Lorentzian and Porod contributions to $d\Sigma/d\Omega$, it is useful to consider their temperature dependence. The sum of $d\Sigma/d\Omega$ collected over the higher-$|Q|$ range of $0.04 < |Q| < 0.1$ Å$^{-1}$ is plotted in Fig. 7(a) in order to capture the temperature dependence of the Lorentzian-like contribution from ferromagnetic correlations. This contribution is relatively flat between 300 and $\sim 125$ K, below which it increases and then peaks at $\sim 80$ K. It then decreases to a minimum at 50 K with approximately the same intensity as was present at 300 K. This disappearance of the Lorentzian component is confirmed by comparing $\Delta(d\Sigma/d\Omega)$ at 80 K [Fig. 6(c)] to that at 50 K [Fig. 6(d)]. In fact, the absence of visible data points in $\Delta(d\Sigma/d\Omega)$ at 50 K [Fig. 6(d)] on the logarithmic scale is an indication that $d\Sigma/d\Omega$ (125 K) is actually slightly larger than $d\Sigma/d\Omega$ (50 K) so that there is a weak oversubtraction. The increase in scattering from 125 to 80 K can be interpreted as a manifestation of critical scattering that appears above $T_c$ in ferromagnets that undergo a second-order phase transition (see, e.g. Refs. [22,26,28] for examples of critical scattering from ferromagnetic cobalites measured by SANS). This is because, above $T_{\text{VT}}$, the system behaves as if it is about to order ferromagnetically with a putative Curie temperature $T_{\text{Curie}}^\text{putative} \sim 63$ K, at which this sample would ferromagnetically order in the absence of a VT. This $T_{\text{Curie}}^\text{putative}$ was estimated by assuming that $T_c$ (determined by the temperature at which the second temperature derivative of the magnetization peaks) scales linearly with A-site ionic radius between PCCO ($x = 0.3$, 0.7), 0.523 cm$^{-1}$ for 100 K. The dominant contribution to the scattering is clearly still the Porod term that was identified at 300 K, again illustrated by a dashed line, but in comparison to 300 K, there is a clear increase in $d\Sigma/d\Omega$ at $|Q| \gtrsim 0.2$ Å$^{-1}$. To more clearly illustrate the differences in $d\Sigma/d\Omega$ that occur with temperature, $\Delta(d\Sigma/d\Omega)$ has been plotted at 100, 80, 50, and 4 K in Figs. 6(b)–6(e) with $d\Sigma/d\Omega$ (125 K) subtracted as a background. As shown more clearly below, we chose $d\Sigma/d\Omega$ (125 K) to serve as a background because the magnetic effects are strongly diminished at 125 K and above. Here, $\Delta(d\Sigma/d\Omega)$ at 100, 80, and 4 K does not simply follow a Porod law, but clearly has an additional contribution at higher $|Q|$ [$d\Sigma/d\Omega$ (50 K) will be discussed below]. In fact, at these three temperatures $\Delta(d\Sigma/d\Omega)$ is well fit (solid line in figures) by a combination of a Porod term ($n = 4$) and a Lorentzian term, which describes the scattering
shown in Fig. 7(b). This $I_0$ is relatively flat between 300 and 150 K, below which it increases to $T_{\text{VT}} \sim 80$ K. At $T_{\text{VT}}$, $I_0$ anomalously flattens, which may be influenced somewhat by the Lorentzian component that clearly decreases over the same temperature range. Below 40 K, $I_0$ steadily rises, likely due to a low-volume fraction contribution of long-range ordered ferromagnetic clusters. Note that this occurs $\sim 20$ K below $T_{\text{c}}^{\text{putative}}$, which suggests that these clusters are not simply regions of the sample where the VT has not occurred, but rather have a lower $T_c$ due to a reduction in the effective hole concentration.

In summary, the SANS data point to a highly inhomogeneous ground state that is characterized by ferromagnetic clusters forming across a broad distribution of length scales, with the ground-state SANS well described as a combination from a Lorentzian contribution with mean $\xi \sim 50$ Å and a small but distinct Porod contribution with $\xi \gg 700$ Å.

**C. Magnetoresistance**

Magnetoresistance (MR) is a powerful probe of local magnetic correlations and has thus been used to investigate many covalent systems, such as LSCO [22,49,50], Pr$_{1−x}$Sr$_x$CoO$_{3−δ}$ [25], Nd$_{1−x}$Ca$_x$CoO$_{3−δ}$ [28], and La$_{1−x}$Ba$_x$CoO$_{3−δ}$ [51]. For instance, on the insulating side of the phase diagram of LSCO, where nanoscopic ferromagnetic clusters are embedded in a nonferromagnetic matrix, but long-range ferromagnetic ordering is absent, large negative MR $\{\text{MR} = (\rho(\mu_0 H) - \rho(0))/(\rho(0))\}$ of up to $\sim$90% (under $\mu_0 H = 9$ T) has been observed and attributed to an intercluster MR effect [22]. Essentially, this effect is the result of enhanced intercluster tunneling/hopping when the clusters’ moments are aligned parallel to one another by a magnetic field. In the ferromagnetic metallic regime, where clusters percolate into a long-range ordered network, the intercluster MR disappears, but a peak in the negative MR is observed at $T_c$ [50], which can be understood in terms of maximization of spin-disorder scattering when the magnetic susceptibility diverges at $T_c$.

We have performed MR measurements on samples of PYCCO that undergo the VT ($y = 0.075$ and $y = 0.100$). Figure 8 shows the temperature dependence of the resistivity under different magnetic field conditions. Because we have found that both the magnetic history and cooling protocol affect the MR, we have plotted $\rho$ as measured under specific cooling and measuring conditions with respect to the applied magnetic field. We use the notation, $\rho(\mu_0 H_{\text{mean}}, \mu_0 H_{\text{FC}})$, where $H_{\text{mean}}$ denotes the measuring field and $H_{\text{FC}}$ denotes the cooling field. Specifically, we measured $\rho(0, 0)$ upon cooling and warming, respectively. We then cooled the sample in zero field down to 5 K, applied $\mu_0 H = 9$ T at 5 K, and measured $\rho(9$ T, 0) upon warming. The sample was then cooled in $\mu_0 H = 9$ T, and a measurement of $\rho(9$ T, 9 T) was performed during cooling. Finally, after cooling in $\mu_0 H = 9$ T, the field was removed at 5 K, and $\rho(0, 9$ T) was measured upon heating. The effects of the magnetic field and cooling protocol are apparent in the raw data for the $y = 0.075$ [Fig. 8(a)], but are subtle (even more so for $y = 0.100$ [Fig. 8(b)]), so they are more clearly demonstrated by plotting a normalized change, e.g. the MR.
For samples that have a very sharp first-order insulator-metal transition, the magnitude of this peak would be expected to be very large; in this context, it is important to recall that our samples exhibit slightly more rounded transitions at $T_{VT}$ which we have argued is likely related to inhomogeneities in the distributions of Y ions and/or O vacancies. Our samples do show significant peaks of $\sim -43\%$ ($y = 0.075$) and $-13\%$ ($y = 0.075$) in their ZFC MR, however. The magnitude of the peak in the MR is larger for $y = 0.075$ since its VT is sharper in $\rho(T)$. As the temperature is lowered below the $T_{VT}$, the MR remains negative and nonzero for both $y = 0.075$ and 0.100, for all temperatures, though the magnitude is diminished as $T \to 0$. The presence of negative MR as $T \to 0$ would be unexpected if the MR were simply a result of the VT. However, from the SANS data presented above, it is clear that there exist ferromagnetic clusters at low temperature with a mean correlation length of $\sim 50$ Å, and we thus argue that the MR does not simply result from the VT, but that there also exists a low-temperature contribution from negative intercluster MR. In fact, this is exemplified by a large field-cooling effect on the magnitude of the resistivity. To illustrate the effect of the field cooling, we have plotted the field-cooled magnetoresistance (FCMR), where $\text{FCMR} = [\rho(0, 9 \text{ T}) - \rho(0, 0)]/\rho(0, 0)$, in Figs. 9(b) and 9(d) for $y = 0.075$ and 0.100, respectively. The FCMR describes the relative change in the resistivity between field cooling and zero-field cooling, with no measuring field applied in either case. For both Y dopings shown, a large negative FCMR is observed at low temperatures, meaning that field cooling has the effect of reducing $\rho$, and clearly strongly influences the low-temperature magnetic state. Note that, for $y = 0.075$, the FCMR sets in at a temperature close to that at which the high-$q$ SANS intensity, which originates from the magnetic clusters, turns on [see Fig. 7(a)], implying that the low-temperature FCMR is a direct consequence of the cluster formation. In simple terms, field cooling partially aligns cluster magnetizations along the field direction, which increases the probability of intercluster hopping. It is important to note that, even after the magnetic field is removed at low temperature, the field-cooling effect persists and, for $y = 0.075$, actually has a stronger effect on the resistivity than an applied 9 T field after zero-field cooling. These observations imply that the relaxation of the cluster alignments occurs on long timescales and that the local orientation of the magnetization of a cluster is quite robust against an applied field once it has been set in place. This attribution of the FCMR to field-induced cluster alignment is strengthened by a similar observation of FCMR within the ferromagnetic cluster regime of LSCO [49], although it should be pointed out that some additional contribution from spin-glass regions is also possible.

We have further investigated the negative intercluster MR by performing isothermal field sweeps after zero-field cooling. As shown in Figs. 10(b) and 10(e) for $y = 0.075$ and 0.100, respectively, negative MR is apparent upon application of a magnetic field. The ZFC resistivity at 0 T is larger than the largest resistivity achieved when sweeping through the magnetoresistive coercivity $H_{\text{MR}}$, which is the field at which there is the greatest dispersion in cluster magnetization and hence largest resistance after field poling. Such effects have been interpreted in terms of local magnetic interactions between clusters (or nanoparticles) as in the case of Co-SiO$_2$.
granular films [52]. However, in our case, the presence of magnetocrystalline anisotropy in a polycrystalline sample sufficiently complicates the situation to the point that this simple picture does not strictly hold, and a complete understanding of this effect would require an analysis of the magnetic anisotropy using single crystals, which is beyond the scope of the present work.

The 5 K field sweeps also reveal a substantial $H_{\text{cMR}}$ for both samples, which as illustrated by comparing Figs. 10(a) with 10(b), and 10(d) with 10(e), is remarkable in that field sweeps of the magnetization reveal a different, significantly smaller, coercivity ($H_c$). In fact, a similar effect is actually apparent in the original work of Tsubouchi [53] for PCCO $x = 0.5$. Simple calculations based on the Sharrock formula [53] indicate that differences between $H_{\text{cMR}}$ and $H_c$ cannot be accounted for by the differences in field sweep rates. Rather, we suggest that the discrepancy stems from the sensitivities of these measurements to different components of the sample magnetization, which is important as we have argued above that there exist ferromagnetic clusters that span a large spectrum of length scales at low temperatures. Magnetization measurements are sensitive to the net magnetization integrated over the entire sample volume, whereas $MR$ measurements are only sensitive to the magnetizations of the clusters that dominate the intercluster $MR$, which exist at the low-diameter end of the distribution, as it is known that this form of $MR$ disappears as the clusters increase in size and percolate into a long-range network [22]. Given that the coercivity is expected to increase on decreasing cluster size [54], the $MR$ is thus sensitive to only the magnetically hardest components present, naturally leading to the discrepancy between $H_{\text{cMR}}$ and $H_c$. Thus, the discrepancy between $H_{\text{cMR}}$ and $H_c$ is in fact a further confirmation of the highly magnetically inhomogeneous nature of the ground state. As a final comment on these data, we note that the source of this low-temperature $MR$ cannot be conventional intergranular magnetoresistance (TMR) as: (i) this would be expected to be very weak in the limit of the grain sizes studied in this work (micrometers); (ii) intergranular TMR is sensitively dependent on spin polarization, which is expected to be very low in the present short-range ordered samples; and (iii) for conventional TMR, one would nominally expect to observe the same coercivity in both $MR$ and magnetization measurements.

We have also performed isothermal field sweeps very close to $T_{\text{VT}}$ as shown in Figs. 10(c) and 10(f). Consistent with the temperature sweeps, we observe modest values of negative $MR$ which we attribute to the broadening of the first-order VT due to chemical inhomogeneity. Weak hysteresis is apparent in the field sweeps of $y = 0.075$, however, likely because it has the sharper VT between these two compositions.

IV. DISCUSSION AND CONCLUSIONS

The key result of this paper comes from SANS and magnetotransport measurements providing strong signatures of a magnetic ground state in PYCCO characterized by ferromagnetic clusters that span a broad range of length scales. This leads to important questions regarding why and how these clusters form and which magnetic ions form them. A reasonable explanation is that, since the VT does not involve a complete transformation of all formally Co$^{3+}$ ions to Co$^{4+}$ (a general consensus from the XAS measurements discussed in the Introduction), the low-temperature state has a significantly reduced average hole concentration ($x$) that is in fact below the percolation threshold for the insulator-metal transition. From numerous studies of the magnetic properties of cobalt-based perovskites, it has been established that magnetoelectronic phase separation occurs below this percolation threshold with ferromagnetic clusters embedded in a nonferromagnetic matrix. Thus, to a first approximation, one can interpret the clusters as forming as a result of PYCCO being driven into this regime by the VT. However, there are important differences between low-temperature PYCCO and phase-separated LSCO. For example, our estimate of the mean cluster size that gives rise to the Lorentzian scattering in SANS measurements on PYCCO ($\sim 50$ Å) is significantly larger than the largest cluster size ($\sim 25$ Å) observed on the insulating side of the percolative transition in LSCO [4,9]. Indeed for LSCO, once the $\sim 25$ Å range is exceeded, percolation sets in and leads to long-range magnetic order. This percolation occurs at an average Co valence of $\sim 3.17$ in LSCO [9]; yet, the average Co valence below $T_{\text{VT}}$ in PYCCO ($y = 0.075$)
is ∼3.20 [40]. The lack of a percolated network in PYCCO implies that the density of nanoscopic ferromagnetic clusters in PYCCO is significantly smaller than in LSCO and is indicative of greater inhomogeneity in PYCCO. Similarly, the porod component of the SANS is also suggestive of the presence of weak longer-range ferromagnetic order, coexisting with these nanoscopic clusters, again reinforcing the conclusion that PYCCO has a more inhomogeneous ground state than LSCO, with magnetic phase separation over a wider range of length scales. We suggest that these differences are related to the inherent chemical complexity of PYCCO in comparison to LSCO. Our prior work [9] demonstrated that the magnetic and electronic inhomogeneities that occur in LSCO on nanoscopic length scales are entirely consistent with the unavoidable local compositional fluctuations that must occur in any randomly doped system. Thus, the physics results from the compositional inhomogeneity that is intrinsic to a doped solid on short length scales. Here, LSCO is a simpler system in that the sources of quenched disorder arise from a single A-site substitution, with little oxygen deficiency (at least for x around or below the percolative transition). On the other hand, PYCCO has three A-site ions with quite disparate ionic radii and a much higher O vacancy concentration. These sources of disorder likely increase the structural and chemical inhomogeneity in PYCCO, which is then reflected in its magnetic properties. In this context, it is important to note that all of our samples have a final synthesis step carried out at ∼1200 °C, followed by slow cooling. These conditions are known to yield grain sizes in the 1–10 μm range, which are much larger than the key length scales in this problem. We do not therefore expect that dopant segregation at grain boundaries is the impetus for the observed magnetic inhomogeneity. Although we have not excluded the possibility of some nonrandom dopant segregation seeding some of the magnetic inhomogeneity in the studied samples, we note that several prior works on related materials [55–57] have shown that gross dopant segregation is effectively removed at such high processing temperatures. However, the natural compositional fluctuations at the nanoscale remain, seeding the magnetoelectronic inhomogeneity we observe.

It is also worthwhile to consider some related interpretations of the cluster formation in the ground state of PYCCO. One possibility advanced by Knizek et al. is that some regions of the high-temperature state persist into the ground state as nanoscopic ferromagnetic clusters (on a spectrum of length scales) embedded in a nonferromagnetic matrix. We characterize by ferromagnetic clusters (on a spectrum of length scales) embedded in a nonferromagnetic matrix. We interpret these clusters as resulting from the fact that the VT is incomplete and drives the system into the insulating side of the global perovskite cobaltite phase diagram. Future efforts to fully understand the magnetic and electrical properties below the VT could involve measuring high-quality single crystals (if such can be synthesized), which would potentially provide a more complete understanding of the importance of the various sources of structural and chemical disorder, as well as the intercluster interaction effects suggested by magnetotransport data.

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