Superconductivity and magnetism in $(R_{1.5-x}Pr_xCe_{0.5})Sr_2Cu_2NbO_{10-\delta}$ (R=Nd,Sm,Eu): Criteria for modeling the suppression of superconductivity by Pr in high-T_c cuprates

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We report on the electronic and magnetic phase diagram for $(R_{1.5-x}Pr_xCe_{0.5})Sr_2Cu_2NbO_{10-\delta}$ (R =Nd,Sm,Eu). The results indicate that Pr suppresses superconductivity in these materials in the same manner as in the $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ compounds and that this suppression is correlated with anomalous Pr magnetism, a reduced Pr effective moment, a metal-to-insulator transition, and an ion size effect. The significance of these results in terms of a generalization of this phenomenon, the criteria they establish for modeling these materials, and the role of f-electron hybridization is discussed.
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One of the most enigmatic and controversial problems in the field of high-temperature superconductivity (high T_c) is the suppression of superconductivity by the Pr ion in the $RBa_2Cu_3O_7$ (RBCO) structure.[1] This suppression is unconventional and is accompanied by other unusual properties such as a Pr Néel temperature T_N two orders of magnitude larger than expected, an insulating electronic state, strong interaction between the Pr $4f$ and CuO_2 planar electronic states, and a reduced Pr effective moment $\mu_{\rm eff}$ of $2.8\mu_B$ due to a nonsinglet $4f$ crystal field (CF) ground state (GS).[1] The underlying mechanisms responsible for the unusual properties of PrBCO are not well understood and are controversial.[1,2] Thus no specific model has gained full acceptance yet. However, in high-T_c compounds, where the presence of Pr does not affect superconductivity, Pr does not show anomalous magnetism, Pr has a singlet CF GS, and there is no evidence of f-electronic interactions.[1] Hence current attempts to understand PrBCO focus on the relationships among the Pr magnetism, f-electronic interactions, insulating electronic state, and suppression of superconductivity.[1,2]

Recent characterizations of the $(R_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$ [$(R_{1.5}Ce_{0.5})$SCNO] family of compounds indicate that $(Pr_{1.5}Ce_{0.5})$SCNO is not superconducting[3,4] and shows anomalous Pr magnetism,[3] a reduced Pr $\mu_{\rm eff}$ of $2.8\mu_B$, a $4f$ CF GS comparable to that of PrBCO,[3] and an insulating state, while all the other $(R_{1.5}Ce_{0.5})$SCNO compounds are superconducting.[3–7] This suggests that Pr suppresses superconductivity in $(Pr_{1.5}Ce_{0.5})$SCNO as in PrBCO and presents a unique opportunity to study this phenomenon in another high-T_c structure. In this paper we report on our investigation of the suppression of superconductivity in the $(R_{1.5-x}Pr_xCe_{0.5})$SCNO (R=Nd,Sm,Eu) series of compounds with resistivity $\rho(T)$, dc magnetization $M(T)$, and specific heat $C(T)$ measurements. The significance of these results lies in the generalization and characterization of this phenomenon and in the criteria they establish for modeling the suppression of superconductivity by Pr in these high-T_c cuprates.

Details of the sample synthesis, x-ray diffraction (XRD), and thermogravimetric analysis (TGA) are reported elsewhere.[8] XRD data showed that all samples possessed the reported $(R_{1.5}Ce_{0.5})$SCNO crystal structure and were typically 98% pure.[8] A TGA similar to that used by Cava *et al.* on $(Nd_{1.5}Ce_{0.5})$SCNO Ref. 6 indicated that all the samples are oxygen deficient with δ's of typically 0.045(5) that were not correlated with Pr content.[8]

$M(T)$ data were collected for $2\,K<T<300\,K$ with a Quantum Design MPMS superconducting quantum interference device magnetometer. Superconducting transition temperatures T_c were determined from shielding and Meissner data taken down to 2 K with $H=2$ Oe; the T_c's were taken from the 50% transition point of the shielding curves and error bars were taken from the 10% and 90% transition points. Zero-field-cooled (ZFC) and field-cooled (FC) $M(T)$ data were collected in a 500-Oe field over the range $5\,K \leq T \leq 200\,K$. The ZFC and FC $M(T)$ data for the $(Pr_{1.5}Ce_{0.5})$SCNO sample showed a cusp at 57 K that was previously identified by neutron scattering and magnetic measurements as the magnetic signature of a Cu spin reordering (the same measurements indicated a Cu T_N between 200 and 300 K).[3] A similar cusp was observed in the $M(T)$ data for the $(Eu_{1.5-x}Pr_xCe_{0.5})$SCNO samples for $x>0.6$, but the positions of the cusps $T_L(x)$ were shifted to lower temperatures with lower Pr doping (Fig. 1). Also, the ZFC and FC $M(T)$ data for the $(Pr_{1.5}Ce_{0.5})$SCNO sample showed large irreversibilities below 100 K, as previously reported.[3,7] These irreversibilities are indicative of the weak ferromagnetic behavior associated with a canted antiferro-

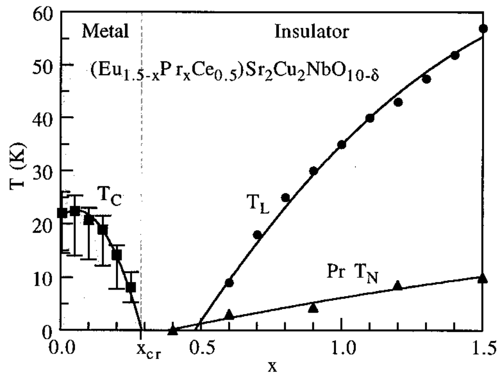

FIG. 1. Phase diagram of the $(Eu_{1.5-x}Pr_xCe_{0.5})$SCNO system. T_c (■) is the superconducting transition temperature, T_N (▲) is the Pr Néel temperature, and T_L (●) is a Cu spin structure reordering; the curves are only a guide to the eye.

magnetic Cu spin structure.[3,7] Similar irreversibilities were observed for the $(Eu_{1.5-x}Pr_xCe_{0.5})$SCNO samples for $x > 0.6$, but with the onsets shifted to lower temperatures with lower Pr doping.

$C(T)$ data for the $(Eu_{1.5-x}Pr_xCe_{0.5})$SCNO samples were collected from 0.6 to 60 K with a standard adiabatic heat-pulse calorimeter attached to a He^3 cryostat. The magnetic contribution $C_{mag}(T)$ to the $C(T)$ data was determined by subtracting a lattice specific heat $C_l(T)$ [determined from nonmagnetic $(Eu_{1.5}Ce_{0.5})$SCNO (Ref. 3)] and a nuclear Schottky anomaly (below 2 K) from $C(T)$, i.e., $C_{mag}(T) = C(T) - C_l(T) - C_n(T)$. The $C_{mag}(T)$ data for $(Pr_{1.5}Ce_{0.5})$SCNO showed a broad magnetic anomaly with a peak at 10 K that has been identified as an ordering of the Pr sublattice.[3] [An earlier paper by Felner *et al.*[7] questions Pr ordering in $(Pr_{1.5}Ce_{0.5})$SCNO since they saw no $C(T)$ anomaly; we find that an anomaly is clearly visible in our $C(T)$ data, which corresponds to a cusp near 10 K in the magnetic susceptibility of the Pr spins.[3]] The $C_{mag}(T)$ data for the $(Eu_{1.5-x}Pr_xCe_{0.5})$SCNO samples for $x \geqslant 0.4$ showed similar magnetic anomalies but with the peaks shifted to lower temperature with lower Pr content (Fig. 1). We interpret these peaks as the T_N for a diluted Pr sublattice and $x = 0.4$ as the percolation level for long-range order (LRO) for the Pr spins. The insulating state, high Pr T_N, and large Pr-Pr interatomic spacing[8] in $(Pr_{1.5}Ce_{0.5})$SCNO serve to exclude a Ruderman-Kittel-Kasuya-Yosida, dipolar, or direct exchange magnetic interactions. Hence a superexchange interaction, presumably through the nearest-neighbor planar oxygen atoms, is indicated as the underlying mechanism for the Pr magnetism.[3] This Pr magnetism is remarkably similar to that in PrBCO in terms of manifestation and mechanism, suggesting that they are of the same nature.[1,3]

Resistivity data were collected with a standard four-probe technique for resistances $R < 100\ k\Omega$ and a two-probe technique for $R > 10\ k\Omega$. A more comprehensive report of the magnetic, specific heat, and resistivity measurements is given elsewhere.[9]

Figure 1 shows the electronic and magnetic phase diagram for the $(Eu_{1.5-x}Pr_xCe_{0.5})$SCNO system based on our $\rho(T)$, $M(T)$, and $C(T)$ data.[9] As Pr is doped into $(Eu_{1.5}Ce_{0.5})$SCNO, $T_c(x)$ is suppressed and near $x = 0.3$ the system is no longer superconducting and undergoes a metal-

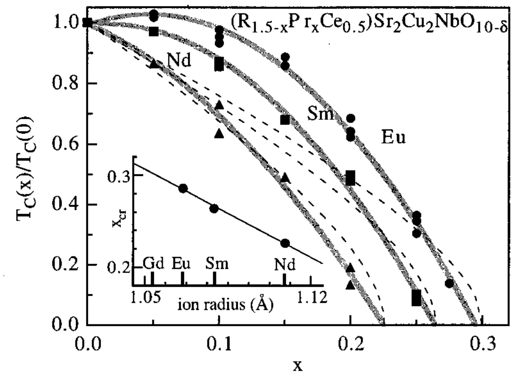

FIG. 2. Ion size effect for the suppression of T_c in the $(R_{1.5-x}Pr_xCe_{0.5})$SCNO, R = Nd (▲), Sm (■), and Eu (●), systems. The data represent multiple samples and demonstrate the repeatability of $T_c(x)$. The shaded curves are binomial fits of the data and the dashed lines are fits to the Abrikosov-Gor'kov formalism. The inset demonstrates that x_{cr} scales linearly with ion radii.

to-insulator (MI) transition. At $x \approx 0.4$, Pr LRO appears below 2 K and develops with increased Pr content into the 10-K T_N of $(Pr_{1.5}Ce_{0.5})$SCNO.[3] At $x \approx 0.6$, a Cu spin structure reordering T_L appears near 8 K and develops with further Pr doping into the 57-K reordering of $(Pr_{1.5}Ce_{0.5})$SCNO.[3] For the $(R_{1.5-x}Pr_xCe_{0.5})$SCNO (R = Nd,Sm) systems, T_c is suppressed more quickly with Pr doping; this ion size effect is illustrated in Fig. 2. The critical Pr doping level x_{cr} at which $T_c(x)$ reaches 0 K in these systems was determined from the intercept of binomial fits of the $T_c(x)$ data; the $T_c(x)$ data show a binomial profile as in the $(R_{1-x}Pr_x)$BCO systems.[1,10] The binomial fits describe the data well (Fig. 2) and yield x_{cr} values of 0.226, 0.264, and 0.286 for R = Nd, Sm, and Eu, respectively. These x_{cr}'s scale linearly with the ionic radii r_i of Nd, Sm, and Eu (Fig. 2) as in the $(R_{1-x}Pr_x)$BCO systems.[10]

Figure 3 summarizes the ρ data for the $(Eu_{1.5-x}Pr_xCe_{0.5})$SCNO system in terms of $\rho(x)$ at 100 K. The data demonstrate the two distinct regions for electronic transport (metallic for $x < 0.3$ and insulating for $x > 0.3$), the MI transition near $x = 0.3$, and that the resistivity of the system increases with Pr content. These results suggest that one effect of Pr on this system is to reduce the density of itinerant carriers n_e, thereby suppressing T_c. A possible interpre-

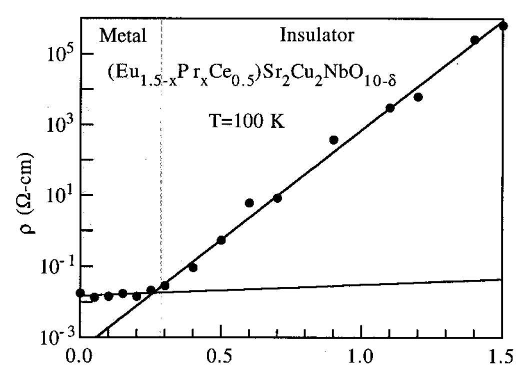

FIG. 3. Resistivity data for the $(Eu_{1.5-x}Pr_xCe_{0.5})$SCNO system at 100 K. The lines are linear fits of the data (on a logarithmic scale) for $x < 0.3$ and $x > 0.3$.

tation of this behavior is that all the $(R_{1.5}Ce_{0.5})$SCNO compounds have similar electronic structures and the insulating state of $(Pr_{1.5}Ce_{0.5})$SCNO is due to band filling from a mixed valent Pr and/or Ce ion. However, based upon the oxygen stoichiometry determined above and XRD, $C(T)$, $M(T)$, and electron energy loss spectroscopy measurements of the $(Eu_{1.5-x}Pr_xCe_{0.5})$SCNO system, which indicate trivalent Pr and tetravalent Ce in these compounds,[3,4,9,11] a straightforward valence count yields a carrier density of 0.20(1) holes per Cu ion for all these samples, which is near the optimal level for high-T_c cuprates. If all the $(Eu_{1.5-x}Pr_xCe_{0.5})$SCNO compounds have an electronic structure comparable to the $(R_{1.5}Ce_{0.5})$SCNO (R = Nd,Sm,Eu,Gd) compounds, we would expect them to be metallic and superconducting. Another possible source of the suppression of T_c is the unusual Pr magnetism. Accordingly, $T_c(x)$ for the $(R_{1.5-x}Pr_xCe_{0.5})$SCNO systems were fit to the Abrikosov-Gor'kov (AG) formalism for magnetic pair breaking:

$$\ln\left(\frac{T_c(x)}{T_c(0)}\right)=\Psi\left(\frac{1}{2}\right)-\Psi\left(\frac{1}{2}+\frac{1}{4}\,e^{-\gamma}\,\frac{x}{x_{\mathrm{cr}}}\,\frac{T_c(0)}{T_c(x)}\right), \qquad (1)$$

where Ψ is the digamma function, γ is Euler's constant, and values for x_{cr} were taken from the above binomial fits of the data. The results in Fig. 2 indicate that the $T_c(x)$ profiles are not characteristic of AG pair breaking and that the AG formalism generally fails to explain the suppression of $T_c(x)$ in these systems. Furthermore, pair breaking cannot account for the MI transition and its relationship to the suppression of T_c. Hence the role of pair breaking in these materials is unclear.

These results demonstrate that the suppression of superconductivity by Pr in the $(R_{1.5}Ce_{0.5})$SCNO structure is phenomenologically equivalent to that in the RBCO structure. In both structures the suppression of T_c is associated with a MI transition, anomalous Pr magnetism, a reduced Pr μ_{eff} of $\sim 2.8\mu_B$, a distinct Pr $4f$ CF GS, an ion size effect, evidence of a corresponding reduction of n_e, a linear relationship between x_{cr} and r_i, and a binomial profile for $T_c(x)$.[1,3,9] Furthermore, pair breaking and band filling fail to explain the unusual properties of these materials. These remarkable similarities are convincing evidence that the suppression of T_c by Pr in these structures is the same basic phenomenon and that the accompanying unusual properties are correlated with and are salient features of this suppression. Furthermore, they serve to generalize and characterize this phenomenon and allow us to accordingly define a *subclass of high-T_c cuprates*. Indeed, there is already some evidence of a subclass of high-T_c cuprates along these lines based upon the properties of CmBCO and (more recently) the $(Y_{1-x}Pr_x)Ba_2Cu_4O_8$ system and the anomalous Pr magnetism in the $PrBa_2Cu_2NbO_8$ and $MSr_2PrCu_2O_6$ [M = Hg,Tl,(Pb,Cu)] compounds.[1,12,13] These results also serve to establish criteria for modeling the suppression of superconductivity by the Pr ion in high-T_c cuprates and provide definitive physical attributes by which this class of materials is distinguished and modeled. Any viable and complete model must now address the salient features outlined above and be general enough to apply to all high-T_c cuprates that show this effect. Furthermore, these salient features indicate that the definitive physical attributes of this phenomenon are $T_c(x,r_i)$, $T_N(x)$, $x_{\mathrm{cr}}(r_i)$, $n_e(x,r_i)$, and the Pr $4f$ CF GS energy levels.

Studying this phenomenon in the $(R_{1.5}Ce_{0.5})$SCNO structure has the advantage that the properties of the $(R_{1.5}Ce_{0.5})$SCNO materials as high-T_c cuprates are distinct enough from those of the RBCO materials such that the generality of this phenomenon may be addressed effectively. This enables a stronger distinction between properties that are intrinsic to this phenomenon and those that are extrinsic (material or structure specific). For several examples, the $(R_{1.5}Ce_{0.5})$SCNO structure lacks the CuO chains of the RBCO structure and the difficulty they pose in characterizing and modeling transport in PrBCO.[1,3,16,17] Carriers are introduced into the CuO_2 planes of the RBCO structure through transfer of the excess charge on the CuO chains, whereas the $(R_{1.5}Ce_{0.5})$SCNO structure is doped by adjusting the stoichiometry of the R-Ce solid solution in a manner similar to the more familiar $(La_{2-x}M_x)CuO_4$ (M = Sr,Ba) materials.[8,9] The Pr magnetism of $(Pr_{1.5}Ce_{0.5})$SCNO is more complex than for PrBCO (Ref. 3) since the Pr sublattice is not square planar and suffers from inherent chemical and CF disorder due to the resident Ce^{4+} ions.[3] Figure 1 shows that unlike the $(Y_{1-x}Pr_x)$BCO system, the $(Eu_{1.5-x}Pr_xCe_{0.5})$SCNO system does not show a coexistence of Pr magnetism and superconductivity and instead shows a region where neither Pr magnetism nor superconductivity is present. Additional criteria may be inferred from these differences since they suggest that the doping mechanism, CuO chain structure, and Pr sublattice structure are not directly related to the suppression of T_c in these materials. However, the proximity of the Pr ions to the CuO_2 planes remains a general feature of these materials and is an issue given the relevance of f-electron interactions as related below. Finally, we mention that Pr-Ba disorder is also an issue for PrBCO (Refs. 16 and 17) and that $(Pr_{1.5}Ce_{0.5})$SCNO with Ce ions occupying 25% of the rare-earth site has more disorder than PrBCO ($\sim 6\%$) (Ref. 17) and is a much stronger insulator.[3,4]

A general correlation between these salient features and the suppression of superconductivity suggests that these features are each either a mechanism or a side effect of the mechanism for this suppression. The ion size effect and Pr $4f$ CF GS are in and of themselves effects and pair breaking fails to model these materials. However, a reduction of n_e is consistent with understanding the destruction of a superconducting state and MI transitions. How would Pr effect a reduction of n_e and the MI transition in these materials while other rare-earth elements do not? Electronic-structure calculations indicate that the primary difference between PrBCO and other RBCO compounds is that $4f$ density of states overlaps the Fermi energy E_F in PrBCO.[1,14] This indicates that the Pr $4f$ electrons interact with planar conduction states in PrBCO and suggests that they form a hybridized state.[1,14,16,17] Indeed, there is considerable evidence of f-electronic interactions in PrBCO and such interactions could account for the Pr $4f$ CF GS and a superexchange interaction.[1,3,16] The Pr $4f$-electronic states are therefore expected to have a significant impact upon the electronic properties of PrBCO and their interactions with the CuO_2 planar states may be responsible for a reduction of n_e and consequently the MI transition and suppression of T_c.[1] We mention that the electronic structure has been determined for $(Nd_{2-x}Ce_x)$SCNO,[15] but not for $(Pr_{1.5}Ce_{0.5})$SCNO. Nonetheless, the anomalous Pr magnetism and a generalization of this phenomenon imply the presence of hybridization in $(Pr_{1.5}Ce_{0.5})$SCNO. Based upon our results, we predict that electronic-structure calculations for $(Pr_{1.5}Ce_{0.5})$SCNO will find that the $4f$ density of states overlaps E_F and that f-electronic interactions are a primary issue in understanding the properties of $(Pr_{1.5}Ce_{0.5})$SCNO.

Recent theoretical activity on PrBCO has focused on how f-electron hybridization could reduce n_e and suppress T_c.[1,16,17] Notably, Fehrenbacher and Rice proposed a semiqualitative model in which a hybridized Pr $4f$ planar O $2p_\pi$ electronic state [Fehrenbacher-Rice (FR) state] is energetically competitive with the CuO_2 planar carrier states.[16] This FR state depletes carriers from the planar conducting states, reducing n_e and suppressing T_c. Liechtenstein and Mazin further developed the FR model by assuming that the FR states form a dispersive band and including f shell Coulomb correlations in their calculations.[17] Their results demonstrated how the position of the f band of the rare-earth element R can influence the rate of carrier depletion from the CuO_2 planes and lead to the observed ion size effect in the $(R_{1-x}Pr_x)$BCO materials. These models do not directly address superconducting parameters, the Pr $4f$ CF GS, or Pr magnetism in these materials. Furthermore, they are unable to account for the insulating state of PrBCO without relying on conjecture of chemical disorder and oxygen defects. However, they do provide a theoretical basis for understanding how hybridization can reduce n_e and lead to a suppression of T_c with an ion size effect; in principle, this hybridization can account for the observed CF effects and Pr magnetic interactions. While these models were developed specifically for the RBCO materials, they can be conceptually generalized and applied to $(Pr_{1.5}Ce_{0.5})$SCNO since the basic presuppositions of the models (hybridization, the FR state, and carrier depletion/localization) can be generally applied to Pr-based high-T_c cuprates in which the Pr ions are nearest neighbors of the CuO_2 planes. Modeling for this phenomenon would benefit from the application of generalized FR and Liechtenstein-Mazin models to the $(R_{1.5-x}Pr_xCe_{0.5})$SCNO systems. The lack of CuO chains in the $(R_{1.5}Ce_{0.5})$SCNO removes the difficulty posed by the predicted metallic transport in the CuO chains for PrBCO.[16,17] Also, the relationship between the CuO chains and CuO_2 planes makes it difficult to estimate $n_e(x)$ and the relationship between $n_e(x)$ and $T_c(x)$ in the $(R_{1-x}Pr_x)$BCO materials.[17] Determining these relationships in the $(R_{1.5}Ce_{0.5})$SCNO structure should be as straightforward as for the $(La_{2-x}M_x)CuO_4$ (M=Sr,Ba) materials.[8]

Our results indicate that Pr suppresses superconductivity in the $(R_{1.5}Ce_{0.5})$SCNO structure through the same mechanism as in the RBCO structure and that PrBCO and $(Pr_{1.5}Ce_{0.5})$SCNO form a subclass of high-T_c cuprates that show a suppression of T_c that is correlated with anomalous Pr magnetism, a reduced Pr μ_{eff} of $\sim 2.8\mu_B$, a characteristic Pr $4f$ CF GS, a MI transition, an ion size effect, a linear relation between x_{cr} and r_i, and a binomial-like profile for $T_c(x)$. These results establish definitive attributes and criteria by which models for these materials may be tested. Current models for PrBCO based upon hybridization should be generalized and developed to address these criteria and the general characteristics of this phenomenon. Finally, we mention that recently Pr has been reported to suppress T_c in the $(Y_{1-x}Pr_x)Ba_2Cu_4O_8$ system in conjunction with a MI transition and a reduced Pr μ_{eff} of $\sim 2.8\mu_B$.[13] We predict that a nonsinglet Pr $4f$ CF GS, anomalous Pr magnetism, f-electronic interactions, an ion size effect, a linear relation between x_{cr} and r_i, and a binomial profile for $T_c(x)$ will also accompany this suppression.

Note added. Recently, Zou *et al.*[18] reported superconductivity in $PrBa_2Cu_3O_4$ samples synthesized by their traveling-solvent floating-zone method. However, their results have yet to be reproduced in the literature.

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