Unusual Electronic Structure of $PrBa_2Cu_3O_7$

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A model for the electronic structure of $PrBa_2Cu_3O_7$ is proposed with three independent components: insulating CuO_2 planes with oxidation state Cu^{II}, mixed valent Pr ions with almost equal numbers of Pr^{III} and Pr^{IV}, and CuO_3 chains described by a t-J model with filling $\approx \frac{1}{2}$. The difference from the high-T_c superconductors comes from an enhanced stability of the Pr^{IV} state due to the hybridization with O neighbors, and involves a transfer of holes from primarily planar O $2p_\sigma$ to $2p_\pi$ states. The insulating nature of $PrBa_2Cu_3O_7$ is ascribed to the extreme sensitivity of the dc conductivity of the mixed valent Pr ions and the CuO_3 chains to vacancies and impurities.

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In spite of many experiments, and several theoretical proposals, the dramatic suppression of superconductivity (SC) upon substituting Y by Pr in $YBa_2Cu_3O_7$ (Y-O_7) [1] is still not well understood. The first proposal to explain the insulating character of $PrBa_2Cu_3O_7$ (Pr-O_7) was based on high-temperature susceptibility data showing an effective Pr moment $\sim 2.7\mu_B$, comparable to that of a free Pr^{4+} ion ($2.54\mu_B$) [2], and proposed that one hole per formula unit was transferred off the Cu ions, making fully ionized Pr^{4+} ions in contrast to Y-O_7. This proposal was criticized in view of results obtained from several high energy spectroscopies (XAS [3], RESPES [4], EELS [5]) which were interpreted in terms of a simple Pr^{3+} ion. This valence was also found in band structure calculations [6], and the T_c suppression was attributed to a magnetic pair-breaking effect. On the other hand, recent results on Cu NMR [7], Ca substitution to form $Pr_{0.5}Ca_{0.5}$-O_7 [8], and optical reflectivity [9] support the original hole depletion proposal. A third possibility, that each Cu in the Cu-O_3 chains is oxidized to Cu^{III} [10], was suggested lately [11]. However, no model allows for a consistent interpretation of all experimental data.

New information on the charge distribution was obtained from optical reflectivity spectra of single-domain Pr-O_7 [9]. Most striking was a difference spectrum between light polarized along the a and b axes, determining the optical response of the CuO_3 chains. The effective carrier density calculated from the integrated spectral weight was *almost identical* (≈ 0.5/Cu) to that in Y-O_7, i.e., the hole concentration in the chains is unaffected by the Pr substitution. On the other hand, the planar response did not show substantial variation compared to Y-O_6, confirming the insulating nature of the antiferromagnetic (AF) CuO_2 planes in both materials.

In view of this result, we reexamined our earlier proposal [12] that all Pr ions are in a Pr^{IV} oxidation state stabilized by hybridization with O neighbors. This required all Cu sites to be in Cu^{II} oxidation states, and all three components (Pr, CuO_2 planes, and CuO_3 chains), having integer oxidation states, would be Mott insulators. The optical data force us to a different proposal, in which the electronic charge rearrangement from the Y-O_7 configuration takes place only between the Pr sites and CuO_2 planes. Consequently, the only component with an integer oxidation state is the CuO_2 planes while the Pr and the CuO_3 chains have nonintegral ones. This novel electronic structure for Pr-O_7 contains chains as realizations of a one-dimensional (1D) t-J model, and *mixed valent* Pr ions. The insulating character of Pr-O_7 must then be *extrinsic* in origin. Below, we show that this rearrangement involves primarily planar O $2p$ orbitals, so that it is plausible that the CuO_3 chains are unaffected.

Let us now explain in more detail the electronic structure of Pr^{IV}. The standard Pr^{4+} ($4f^1$) configuration is clearly too simple. In this Letter, we will show that the crystal structure explicitly favors a strong hybridization of $4f^2\underline{L}$ and $4f^1$ configurations, where $\underline{L}$ denotes a ligand hole on the O neighbors. The eightfold, almost cubic Pr-O coordination allows the formation of a low-energy hole state which is a superposition of $2p_\pi$ O orbitals with f *symmetry* with respect to the central Pr ion [13].

Our thesis is that this Pr^{IV} hole state is competitive in energy to the planar singlet [14] formed from hybridized $3d_{x^2-y^2}$ Cu and $2p_\sigma$ O orbitals. Constraining the hole density in the chains to $n_{\mathrm{ch}} \approx 0.5$, a simplified Hartree calculation shows that for the material parameters of all members of the rare-earth (RE) RE-O_7 series, the only stable solutions for the hole distribution are the two extrema $n_F = 0$, $n_P = (1 - n_{\mathrm{ch}})/2$ or $n_F = 1 - n_{\mathrm{ch}}$, $n_P = 0$ (n_F is the density of RE^{IV} ions and n_p is the hole density in the CuO_2 planes). We will derive a critical value Δ_c of the energy difference between the planar Cu^{III} and the RE^{IV} state, above which the solution with $n_P = 0$ becomes stable. Thus, we are left with little option but to conclude that the essential difference between Pr and the other RE is the crossing of these two solutions.

We describe the low energy electronic properties of Pr-O_7 by the model Hamiltonian

$$H = \sum_{ijs} \epsilon_{ij} c_{is}^\dagger c_{js} + \sum_{iss'} U_i c_{is}^\dagger c_{is} c_{is'}^\dagger c_{is'} + \epsilon_f \sum_{m,s,\nu} {}^{\nu}f_{ms}^\dagger\, {}^{\nu}f_{ms} + \sum_{\langle m,i\rangle \nu s} t_{mi}^{\nu} ({}^{\nu}f_{ms}^\dagger c_{i-s}^\dagger + \mathrm{H.c.}) + U_f \sum_{m,\nu,\nu',s,s'} {}^{\nu}f_{ms}^\dagger\, {}^{\nu}f_{ms}\, {}^{\nu'}f_{ms'}^\dagger\, {}^{\nu'}f_{ms'} + \sum_m H_m^{\mathrm{at}}, \tag{1}$$

where i,j label planar Cu and O sites, m Pr sites, $c_{is}^{\dagger}$ create $3d_{x^2-y^2}$ Cu and $2p_{\sigma,\pi}$ O *holes*, ${}^{v}f_{ms}^{\dagger}$ create Pr $(4f, l_z=v)$ *electrons*, and s is the spin index. We use $2p_{\pi}$ orbitals which make an angle of 45° with the CuO_2 (ab) plane, and point towards a Pr site. The ϵ_{ij} include the usual on-site energies (in eV) $\epsilon_d=0$ (by convention), $\epsilon_{p\sigma}=3.6$, $\epsilon_{p\pi}$, and the nearest neighbor (nn) hopping integrals $t_{pd}=1.2$, $t_{p\sigma}=0.62$, $t_{p\pi}=0.46$, $t_{p\pi}^{\perp}=0.5$, where $t_{p\pi}^{\perp}$ describes hopping in the c direction ($\epsilon_{p\pi}$ will be discussed later). These latter values were obtained using the Slater-Koster tables [15] with parameters $V_{pp\sigma}, V_{pp\pi}, V_{pd\sigma}, V_{pd\pi}$ from Ref. [16] (rescaled to the bond lengths of PrO_7, according to [15]). The on-site Coulomb repulsions are $U_d=10.5$, $U_p=4$, with values from Ref. [17] (also $\epsilon_{p\sigma}$). The f parameters taken from Ref. [18] include the on-site energy $\epsilon_f-\epsilon_{p\pi}=-10$, the t_{pf}^{v} between $2p_{\pi}$ and $4f_v$ orbitals (all other t_{mi}^{v} are negligible), and the on-site Coulomb repulsion $U_f=10.5$ (t_{pf}^{v} will be discussed below). Finally, H_m^{at} describes the *atomic* Coulomb, exchange, and spin-orbit interactions on the Pr sites. The vacuum $|\,\rangle$ is defined as *filled* Cu $3d^{10}$, O $2p^6$, and *empty* Pr $4f^0$ shells. H_m^{at} is taken into account, by restricting the Hilbert space to include only the $4f$ Hund's rule multiplet ground states (the first excited states involve an excitation energy ~0.25 eV [19]).

Consider the possible hole states on the eight O atoms surrounding a Pr site (see Fig. 1). There exists a *unique* linear combination ${}_{f}^{2}\pi_{ms}$ of $2p_{\pi}$ O orbitals, for which the kinetic energy from O-O overlap (characterized by $t_{p\pi}, t_{p\pi}^{\perp}>0$) *and* the kinetic energy due to $4f$-$2p_{\pi}$ hybridization (given by t_{pf}^{v}) are minimized at the same time. Since ${}_{f}^{2}\pi_{ms}$ has $f_{z(x^2-y^2)}$ symmetry around Pr site m, it is orthogonal to all other f orbitals, and hybridizes only with ${}^{\pm 2}f_{ms}$ with a matrix element $V=\sqrt{8}t_{pf}$ ($t_{pf} := t_{pf}^{v}, v=2$). The O-O hopping energy of ${}_{f}^{2}\pi_{ms}$ is minimized at $-2t_{p\pi}-t_{p\pi}^{\perp}$ due to the optimal phase coherence in this state.

The proposed local hole state, Pr^{IV}, can be written as a linear combination

$$|G_m\rangle=\sum_{v,s}\lambda_v^s\,{}^{v}f_{ms}^{\dagger}|\,\rangle+\sum_{v,v',s,s',s''}\kappa_{vv'}^{ss's''}\,{}^{v}f_{ms}^{\dagger}\,{}^{v'}f_{ms'}^{\dagger}\,{}_{f}^{2}\pi_{ms''}^{\dagger}|\,\rangle\,, \tag{2}$$

i.e., a mixture of Pr^{4+} and Pr^{3+} + *ligand hole.* The coefficients $\lambda_v^s, \kappa_{vv'}^{ss's''}$ have to be calculated by diagonalizing (1) in the subspace $\mathfrak{H}_m$ which contains the six J_z states of the $J=\frac{5}{2}$ multiplet ($Pr^{4+}O_8^{16-}$), and the 9×2 product states combining the $J=4$ multiplet with the two hole states ${}_{f}^{2}\pi_{ms}$ ($Pr^{3+}O_8^{15-}$). The relevant part of (1) then becomes

$$H_m=\tilde{\epsilon}_{\pi}\sum_{s}{}_{f}^{2}\pi_{ms}^{\dagger}\,{}_{f}^{2}\pi_{ms}+\epsilon_f\sum_{v,s}{}^{v}f_{ms}^{\dagger}\,{}^{v}f_{ms}+V\sum_{V\in\{2,-2\}s}({}^{v}f_{ms}^{\dagger}\,{}_{f}^{2}\pi_{m-s}^{\dagger}+\mathrm{H.c.})+U_f\sum_{m,v,v',s,s'}{}^{v}f_{ms}^{\dagger}\,{}^{v}f_{ms}\,{}^{v'}f_{ms'}^{\dagger}\,{}^{v'}f_{ms'}\,, \tag{3}$$

where $\tilde{\epsilon}_{\pi}=\epsilon_{p\pi}-2t_{p\pi}-t_{p\pi}^{\perp}$. H_m splits $\mathfrak{H}_m$ into four decoupled subspaces, $\mathfrak{H}_m^{\pm 5/2}$ (each seven dimensional) containing the states coupled to $|4f^1;J_z=\pm\frac{5}{2}\rangle$, $|4f^1;J_z=\mp\frac{3}{2}\rangle$, and $\mathfrak{H}_m^{\pm 1/2}$ (each five dimensional) containing the states coupled to $|4f^1;J_z=\pm\frac{1}{2}\rangle$. Since all eight O atoms are equivalent, the states can be classified according to the irreducible representations of the double cubic group O^{+} [19]. The diagonalization of (3) yields a fourfold degenerate ground state belonging to Γ_8, and the first excited states belonging to the doublet Γ_7, as expected for a $J=\frac{5}{2}$ multiplet in cubic symmetry.

An alternative state for the hole is a planar singlet formed from $3d_{x^2-y^2}$ Cu, and $2p_{\sigma}$ O orbitals, i.e., a Cu^{III} oxidation state [14]. In both alternative, Cu^{III} and Pr^{IV}, the hole is primarily in planar O $2p$ states, so that we can rationalize the experimental fact that the hole concentration on the chains $n_{\mathrm{ch}}\approx 0.5$ is unaffected. The distribution of the remaining holes ($1-n_{\mathrm{ch}}$ per unit cell) among these two states can be calculated within a simplified Hartree approach. The Hartree energy of a double layer is composed of (i) the two 2D t-J bands originating from the planar Cu^{III} (hole density n_P) and (ii) the Pr^{IV} states (concentration n_F) subject to the *constraint*

$$2n_P+n_F=1-n_{\mathrm{ch}}\,. \tag{4}$$

Cu^{III} and Pr^{IV} states interact via the Coulomb repulsion $U_p\approx 4$ eV resulting from simultaneous $2p_{\sigma,\pi}$ occupation on O sites, so the Hartree energy with an *averaged* repulsion has the form

$$E_{\mathrm{Hartree}}(n_P,n_F)=2(\epsilon_P+\gamma)n_P+\alpha n_P^2+\epsilon_F n_F+\tfrac{1}{2}\beta n_F^2+2U_{\mathrm{av}}n_P n_F\,, \tag{5}$$

where ϵ_P, ϵ_F represent the energy of a *localized* planar singlet and Pr^{IV} state, respectively. U_{av} is determined by the product of the probability for a hole in the t-J band to sit on an O site nn of an occupied Pr^{IV} state, and the probability of the hole in that state to be on the same O site (see Fig. 1), giving $U_{\mathrm{av}}\approx U_p/4\approx 1$ eV. The term $2\gamma n_P+\alpha n_P^2$ approximates the total energy of the t-J model at hole filling n_P on both planes. The coefficients $\gamma\approx -1$ eV, $\alpha\approx 2$ eV can reliably be estimated from high-temperature expansion data for realistic values of $J=0.1$ eV, $t=0.4$ eV (a quadratic polynomial gives a remarkably good fit to the data points) [20]. Finally, $\beta n_F^2/2$ results from the linear term in an expansion of the chemical potential $\mu_F(n_F)$ for the band of states arising from Pr^{IV}. Strong suppression of coherent hole hopping between adjacent Pr^{IV} and Pr^{III} configurations by (i) a small total overlap matrix element and (ii) a strong coupling to the spin degrees of freedom [as expressed in (2)], in conjunction with a small *effective* interaction between different Pr^{IV} states due to the low denisty $n_F\lesssim 0.5$, suggests $|\beta|\ll|\gamma|,|\alpha|$, i.e., a very narrow band.

Using the constraint (4), we find an extremum of

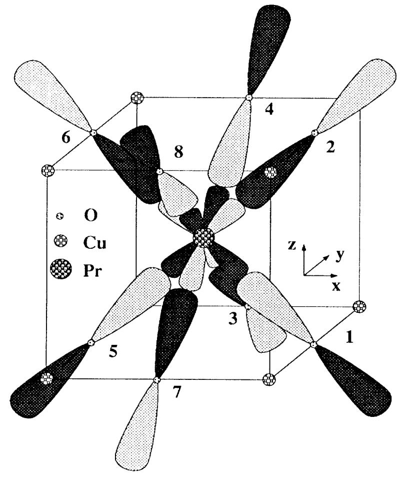

FIG. 1. Schematic diagram of the eight $2p_\pi$ O orbitals pointing towards Pr site m, and the $4f_{z(x^2-y^2)}$ Pr orbital. The superposition ${}^{2}_{f}\pi_{ms} = (1/\sqrt{8})\sum \zeta_{mi}(-1)^{M_{mi}}\pi_{mis}$, where ζ_{mi} is the vector connecting Pr site m with the neighboring O site i, $M_{mi}=1$ for $i \in \{2,3,6,7\}$, and $M_{mi}=2$ for $i \in \{1,4,5,8\}$, has $f_{z(x^2-y^2)}$ symmetry, and hence its overlap with all f states apart from $4f_{z(x^2-y^2)}$ vanishes. Its phase coherence is indicated by dark (+) and light shading (−), as for the $4f_{z(x^2-y^2)}$ Pr orbital.

E_{Hartree} which, however, is a *maximum* when

$$\tfrac{1}{2}\alpha + \beta - 2U_{\text{av}} < 0\,, \tag{6}$$

which is the case for the parameters stated. Therefore, the minimum occurs at either $n_F = 0$, or $n_F = 1 - n_{\text{ch}}$. This leads to a criterion for the stability of the nonsuperconducting solution $n_P = 0$, $n_F = 1 - n_{\text{ch}}$ (setting $n_{\text{ch}} = \frac{1}{2}$),

$$\Delta_{PF} := \epsilon_P - \epsilon_F > \Delta_c := -\gamma - \tfrac{1}{8}\alpha + \tfrac{1}{4}\beta \approx 0.75\ \text{eV}\,. \tag{7}$$

Since the dependence of (6) on the particular RE atom is only via β (estimated to be negligibly small compared to $\alpha/2 - 2U_{\text{av}}$), the inequality is satisfied for *all* members of the RE series. This naturally explains the absence of a T_c intermediate between 0 and 90 K in this series, since the only stable solutions are $n_F = 0$ or $n_P = 0$.

The stability of the solutions from (7) is determined by the energy difference Δ_{PF} between the Cu^{III} and the Pr^{IV} state. We calculate Δ_{PF} from (1), and in Table I, quote the average $4f$ occupation n_f of Pr^{IV} and the energy difference $\Delta_{PF} - \Delta_c$ as a function of the hybridization matrix element t_{pf}, and the O-site energy difference $\Delta_{\sigma\pi} = \epsilon_{p\sigma} - \epsilon_{p\pi}$. The criterion (7) is satisfied for values $\Delta_{\sigma\pi} \geq 1.5$ eV, and $t_{pf} > 0.3$ eV. A positive $\Delta_{\sigma\pi}$ results from the Coulomb repulsion $U_{pd} \approx 1.2$ eV [17] between a hole in the $3d_{x^2-y^2}$ Cu and O $2p$ orbitals. Note that this repulsion affects mostly the $2p_\sigma$ orbitals (which form the Cu^{III} singlet), since the $2p_\pi$ orbitals of the Pr^{IV} state are perpendicular to the Cu orbital. We also considered the possibility of additional stabilization of Pr^{IV} by hybridization onto the CuO_3 chains via O(2,3)-O(1) overlap. However, the effective nn hopping matrix element vanishes by symmetry. The delicate energy balance from Table I indicates that a reduced t_{pf} due to the lanthanide contraction combined with unfavorable values of ϵ_f, U_f is responsible for the stability of the superconducting solution ($n_F = 0$) for the RE with atomic number $Z > 59$.

TABLE I. The critical energy difference $\Delta_{PF} - \Delta_c$ in eV, together with the corresponding $4f$ occupation n_f of Pr^{IV} as a function of t_{pf}, for $\Delta_{\sigma\pi} = 1.5$ eV. Δ_{PF} is given by the energy shift between the planar singlet ($\epsilon_P = -0.43$ eV, $\epsilon_d = 0$), and the Pr^{IV} state. $\Delta_c \approx 0.75$ eV from Eq. (7). Stability of the nonsuperconducting solution is indicated by a positive $\Delta_{PF} - \Delta_c$. Note that $\Delta_{PF}(\Delta_{\sigma\pi}) = \Delta_{PF}(\Delta_{\sigma\pi} = 0) + \Delta_{\sigma\pi}$.

	$t_{pf}=0.2$	$t_{pf}=0.3$	$t_{pf}=0.4$	$t_{pf}=0.5$
$\Delta_{PF} - \Delta_c$	−0.38	−0.13	0.13	0.40
n_f	1.73	1.66	1.63	1.60

Some comments on experimental results in view of our model: (a) The total probability of the $4f^1$ Pr configuration is roughly $n_F(2 - n_f) \approx 0.15$–$0.2$. This explains the spectroscopic results revealing a valence $\approx \text{Pr}^{3+}$ quoted above. (b) The RE-O bond lengths in RE-O_7 show a linear scaling with the corresponding RE^{3+} ionic radii, the only exception being Pr, for which an anomalous shrinking of the Pr-O(2) distance was observed [21]. This distortion to an almost cubic O cage about the Pr favors a Pr^{IV} configuration. (c) The anomalous pressure dependence of $T_c(x)$ in $\text{Y}_{1-x}\text{Pr}_x$-$\text{O}_7$ was earlier interpreted as a sign of hybridization effects [22]. (d) Spectra from inelastic neutron scattering [23] show three rather broad low-energy crystal-field (CF) transitions. This is a clear manifestation of mixed valent Pr, since for pure Pr^{III} ($J=4$) only two transitions (the ground state being a triplet, weakly split into three singlets by the orthorhombicity) and for pure Pr^{IV} just one transition (between the two weakly split doublets of Γ_8) are expected. The strong broadening can be explained by the possible decay of a magnetic excitation on the Pr into AF spin waves on the CuO_2 planes, which strongly reduces the lifetime of these excitations. (e) In the alloy $\text{Y}_{1-x}\text{Pr}_x$-$\text{O}_7$, the Pr^{IV} state not only absorbs holes [7,8], it can also act as a pair breaker, since there exists a small exchange coupling to the $2p_\sigma$ O orbitals. (f) Concerning the $(\text{Y-O}_7)_M(\text{Pr-O}_7)_N$ superlattices [24], we can now rule out the possibility of significant charge transfer between Y and Pr blocks which we suggested to explain $T_c(M,N)$ [12]. The similar hole densities on the chains in Y-O_7 and Pr-O_7, and the fact that a hole occupying a Pr^{IV} state spends most of its time on O sites belonging to the CuO_2 planes (just like holes doped into the SC t-J band of Y-O_7), suggest that the charge distributions in Y-O_7 and Pr-O_7 are very similar.

Even though a consistent picture of the electronic structure of Pr-O_7 has now emerged, there still remain some open questions.

(a) The reason for the semiconducting resistivity is not obvious. A hopping of a hole between nn $\mathrm{Pr}^{\mathrm{III}}$ and $\mathrm{Pr}^{\mathrm{IV}}$ is in principle possible via O $2p$ orbitals, even though the effective matrix element is small. This is due to the orthogonality of the involved orbitals on shared O sites of neighboring Pr cubes, and a cancellation effect due to the symmetry of the ${}^{2}_{f}\pi_{ms}$ state. We can only make plausible that the combination of a small bandwidth, a relatively large $\mathrm{Pr}^{\mathrm{IV}}$-$\mathrm{Pr}^{\mathrm{IV}}$ nn repulsion, strong coupling to spin degrees of freedom, and potential disorder renders the carriers localized. The absence of dc conductivity of the chains [9] can be due to O vacancies. In contrast to Y-O_7, the possibility to circumvent an O vacancy via the CuO_2 planes is excluded by the insulating gap. This interpretation is consistent with the strong increase of the resistivity ρ upon reducing oxygen in $\mathrm{PrBa_2Cu_3O_{7-y}}$. The absolute value of ρ is therefore a criterion for the amount of oxidation of a sample. Another remarkable feature is the optical conductivity $\sigma(\omega)$ of the CuO_3 chains, which is dominated by a broad midinfrared peak in both Pr-O_7 and Y-O_7 [9]. Even though we claim that the chains are realizations of a 1D t-J model, this model alone is not sufficient to explain the observed $\sigma(\omega)$. Work on this point is in progress.

(b) The nature of the Pr AF below $T_N = 17$ K [25] is sophisticated, especially considering the mixed valency. This, and the only slightly reduced $T_N = 10$ K in Pr-O_6 (with only $\mathrm{Pr}^{\mathrm{III}}$), requires the existence of a substantial exchange interaction between $\mathrm{Pr}^{\mathrm{III}}$ configurations in addition to $\mathrm{Pr}^{\mathrm{IV}}$-$\mathrm{Pr}^{\mathrm{IV}}$ coupling. The anomalously large T_N suggests a superexchange mechanism which for the $\mathrm{Pr}^{\mathrm{IV}}$-$\mathrm{Pr}^{\mathrm{IV}}$ case can occur via doubly occupied O $2p_\pi$ orbitals. The most likely superexchange path for $\mathrm{Pr}^{\mathrm{III}}$-$\mathrm{Pr}^{\mathrm{III}}$ (also $\mathrm{Pr}^{\mathrm{III}}$-$\mathrm{Pr}^{\mathrm{IV}}$) coupling involves hopping from Pr $4f$ via O $2p_\pi$ to O $2p_\sigma$ orbitals on different O sites, i.e., low-energy virtual Pr^{4+} excitations. This is an allowed process because the ground state of the AF-ordered CuO_2 planes contains an appreciable admixture of doubly (hole) occupied O $2p_\sigma$ orbitals. The resulting coupling can be estimated to be of the order of 1 meV. A more detailed discussion will be published elsewhere.

In conclusion, we presented a consistent description of the electronic structure of Pr-O_7. The absence of SC was explained by the existence of a local $4f$-Pr-$2p_\pi$-O ($\mathrm{Pr}^{\mathrm{IV}}$) hybridized state which binds doped holes to Pr sites. Given a constant hole density in the chains ≈ 0.5, we determined the distribution of the remaining holes between $\mathrm{Pr}^{\mathrm{IV}}$ and the planar singlet state ($\mathrm{Cu}^{\mathrm{III}}$) from a Hartree calculation. The only stable solutions for *all* members of the RE-O_7 series were shown to correspond to a maximum occupation of either $\mathrm{RE}^{\mathrm{IV}}$ ($T_c = 0$) or $\mathrm{Cu}^{\mathrm{III}}$ ($T_c \neq 0$). The electronic structure of Pr-O_7 is very unusual, with three *independent* components, CuO_3 chains described by a 1D t-J model, mixed valent $\mathrm{Pr}^{\mathrm{III}}$-$\mathrm{Pr}^{\mathrm{IV}}$ configurations, and insulating CuO_2 planes. Pr-O_7 is *not* a usual Mott insulator with integer valence configurations, but the insulating character arises because of the extreme sensitivity of the 1D chains and the $\mathrm{Pr}^{\mathrm{III}}$-$\mathrm{Pr}^{\mathrm{IV}}$ mixed valent state to O vacancies and other defects.

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[1] L. Soderholm *et al.*, Nature (London) **328**, 604 (1987); for a recent review see, e.g., H. B. Radousky, J. Mater. Res. **7**, 1917 (1992).
[2] Y. Dalichaouch *et al.*, Solid State Commun. **65**, 1001 (1988).
[3] U. Neukirch *et al.*, Europhys. Lett. **5**, 567 (1988).
[4] J.-S. Kang *et al.*, J. Less-Common Met. **148**, 121 (1989).
[5] J. Fink *et al.*, Phys. Rev. B **42**, 4823 (1990).
[6] G. Y. Guo and W. M. Temmermann, Phys. Rev. B **41**, 6372 (1990).
[7] A. P. Reyes *et al.*, Phys. Rev. B **43**, 2989 (1991).
[8] D. P. Norton *et al.*, Phys. Rev. Lett. **66**, 1537 (1991); J. J. Neumeier *et al.*, Phys. Rev. Lett. **63**, 2516 (1989).
[9] K. Takenaka *et al.*, Phys. Rev. B **46**, 5833 (1992).
[10] A. W. Sleight, in *Proceedings of the 39. Scottish Universities Summer School in Physics, St. Andrews, United Kingdom* (Adam Hilger, Bristol, 1991), p. 97, discusses the term "oxidation state."
[11] D. Khomskii, J. Supercond. **6**, 69 (1993).
[12] R. Fehrenbacher and T. M. Rice, in *Electronic Properties of High-T_c Superconductors*, edited by H. Kuzmany *et al.* (Springer, Berlin, 1993), p. 391.
[13] Note that the direct hybridization of the Pr $4f$ states with the O $2p_\sigma$ orbitals vanishes by symmetry, and the one with the Cu $3d_{x^2-y^2}$ is very small. Therefore, the direct effect of the Pr states on the conduction band is negligible, in contrast to a suggestion in Ref. [5].
[14] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).
[15] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Dover, New York, 1989).
[16] A. K. McMahan, R. M. Martin, and S. Satpathy, Phys. Rev. B **37**, 3759 (1988).
[17] M. S. Hybertsen *et al.*, Phys. Rev. B **41**, 11068 (1990).
[18] H. Ogasawara *et al.*, Phys. Rev. B **43**, 854 (1991).
[19] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Dover, New York, 1987).
[20] W. O. Putikka (unpublished).
[21] M. Guillaume *et al.*, Z. Phys. B **90**, 13 (1993).
[22] J. J. Neumeier *et al.*, Physica (Amsterdam) **156C**, 574 (1988).
[23] H.-D. Jostarndt *et al.*, Phys. Rev. B **46**, 14872 (1992).
[24] J. M. Triscone *et al.*, Phys. Rev. Lett. **64**, 804 (1990).
[25] A. Kebede *et al.*, Phys. Rev. B **40**, 4453 (1989).