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RECENT STUDIES ON $PrBa_2Cu_3O_{7-y}$: EFFECT OF OXYGEN CONCENTRATION

P. M. Grant and A. Bezinge

IBM Research Division
Almaden Research Center
650 Harry Road
San Jose, California 95120-6099

M. E. López-Morales

Instituto de Investigaciones en Materiales
Universidad Nacional Autónoma de México
Apdo Postal 70-360
México, D.F., México

In the entire series of rare earth compounds isomorphic to $YBa_2Cu_3O_{7-y}$, only $PrBa_2Cu_3O_{7-y}$ is not a superconductor[1]. In fact, this material exhibits insulating behavior at all temperatures. Various explanations have been given for this unusual property, the most common being the speculation that in the 1-2-3 structure, Pr may indeed be tetravalent, rather than trivalent as is Y and the other lanthanide substitutions[2,3]. If this were true, then no excess positive charge would be present in stoichiometric $PrBa_2Cu_3O_{7-y}$ to produce metallic conduction and hence superconductivity.

In order to probe this speculation, we undertook to study the effect of oxygen concentration on the structural and physical properties of $PrBa_2Cu_3O_{7-y}$, paying particular attention to possible changes in Pr valency. Throughout most of this paper, unless otherwise indicated, the terms valency and ionicity will be used interchangeably. All of our samples were prepared using the standard solid state reaction techniques, but extended over many more regrinding cycles and longer reaction times (≃3 weeks) in order to insure a minimum amount of impurity phases such as $BaCu_2O_3$, $BaPrO_3$ and various Pr sub-oxides[4-6]. Portions of the resulting product were subsequently annealed in flowing argon and the final oxidation content determined by chemical titration[7]. The structural properties for values of 7-y ranging from 6.97 to 6.15 were measured by neutron powder diffraction[8] (only for the sample 7-y = 6.97) and x-ray powder diffraction[4-6]. As in the yttrium compound, we observe an orthorhombic to tetragonal transition when 7-y passes below roughly 6.4. The fact that this transition can occur in a totally insulating 1-2-3 single phase compound as well as in its superconducting isomorphs illustrates that the metal-insulator transition accompanying the structural transition in the latter is a fortuitous manifestation of long-range oxygen disorder at concentrations near that which the free hole concentration is drastically reduced, and is not associated with an electronic instability.

The temperature dependence of the resistivity and thermopower were determined for three oxygen concentrations in the sample set mentioned above: 7-y = 6.93, 6.60 and 6.46. The results are shown in Figs. 1 and 2, respectively. Figure 1 shows a qualitatively similiar insulating temperature dependence at all three concentrations; however, we were unable to uniquely ascribe the data to any of the common transport models for increased resistance with decreasing temperature. No single activation energy could be found, nor were we able to obtain fits to the usual formulas for variable range hopping in one, two or three dimensions[9]. On the other hand, we see from Fig. 1 that ρ increases by more than three orders of magnitude at all temperatures as the oxygen content is reduced. This suggests that near y = 0, a small number of holes do indeed exist that are capable of electrical conduction, and that this number decreases as oxygen is taken out. This interpretation is substantiated by the changes observed in thermopower as indicated in Fig. 2. The temperature dependence of the 7-y = 6.93 sample is in general agreement with that found by other workers[10] for nearly fully oxygenated $PrBa_2Cu_3O_{7-y}$. However, the magnitude of S at room temperature more than doubles as 7-y goes from 6.93 to 6.46, a standard indication that the number of carriers has been reduced. No sign change was observed as might be expected from simple single particle band structure arguments as the effective average copper valence was decreased below 2+, implying that the thermopower in high-Tc materials cannot be explained within such a simple framework. Due to the very high sample electrical resistances, we were not able to obtain thermopower data at very low temperatures, especially for the deoxygenated samples.

In contrast to ρ and S, the inverse magnetic susceptibility, χ^{-1}, shown in Fig. 3, does not exhibit a marked dependence on oxygen content. Typical values of the effective Bohr magneton, as determined from the Curie-Weiss fits denoted by the solid curves in Fig. 3, clustered in the narrow range 2.7 to 2.9. These values, interpolated between the measured moments for Pr^{3+} and Pr^{4+} oxides, suggest that the Pr charge in $PrBa_2Cu_3O_{7-y}$ is roughly +3.7 for all values of y. A Pr charge state significantly higher than 3+ which is invariant to oxygen content, as compared to the strong dependence of the transport properties, implies that whatever carriers are available for conduction must reside in the chains rather than the planes. Otherwise, one might expect metallic behavior and superconductivity near y = 0 (attempts to synthesize $PrBa_2Cu_3O_{7-y}$ with $y < 0$ by annealing under high oxygen pressure have not proved successful). Our observations are consistent with those models which propose that oxygen removal in 1-2-3 compounds first depletes carriers in the planes, and, when the hole population there reaches zero, further reduction in oxygen concentration takes holes out of the chains[11]. The principal difference between $PrBa_2Cu_3O_{7-y}$ and its superconducting homologues is that in the former, any charge on Pr in excess of 3+ has already trapped all plane holes that lead to the effects seen in the latter.

However, the above view, that of a nearly tetravalent Pr which localizes all itinerant plane holes, is most likely very oversimplified. Various core level spectroscopy observations strongly indicate that Pr is trivalent in $PrBa_2Cu_3O_{7-y}$[12,13]. Moreover, Raman[14] and structural measurements[8] yield Pr-O distances near those expected for Pr^{3+}. Finally, the relatively small effective moments obtained from the Curie-Weiss fits may result from strong crystalline electric fields which quench a nominally Pr^{3+} moment, thus mimicking Pr^{4+}.

A more appropriate electronic model, reconciling the above paradoxical situation as regards the Pr ionic state, is suggested by recent resonant photoemission data obtained by Kang, *et al.*[15] on $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ solid solutions. They observed, at all finite values of x, a large 4f electron density only 1 eV below the hole Fermi level pinned near the top of the oxygen 2p band. On the other hand, the constant initial state photoemission from these 4f levels has the same spectral dependence as the 4f state in Pr metal, where Pr is commonly assumed to be 3+. These data indicate that we must be careful not to strictly equate valency with ionicity when discussing the electronic state of Pr in $PrBa_2Cu_3O_{7-y}$. In fact, the spectroscopic results are typical of those found in mixed valent Pr, Ce and Tb oxides[16], and such a description should apply here as well. The idea that mixed, or fluctuating, valence models may supply an attractive framework for understanding $PrBa_2Cu_3O_{7-y}$ has been put forward by several groups[17,18]. We therefore propose the following lattice Anderson Hamiltonian[19-21] as the formalism most appropriate for characterizing the electronic properties of not only $PrBa_2Cu_3O_{7-y}$ but the entire rare earth 1-2-3 family in general:

$$\mathscr{H} = \mathscr{H}_{\{Ln\}} + \mathscr{H}_{\{CuO_2\}} + \mathscr{H}_{\{Ln\},\{CuO_2\}}. \tag{1}$$

Here we have partitioned the total Hamiltonian into a Ln sub-lattice term, a term treating only the CuO_2 planes and then an interaction term between these two systems. Explicitly, each of these terms are as follows:

$$\mathscr{H}_{\{Ln\}} = \sum_{i\alpha} \varepsilon^f_\alpha f^\dagger_{i\alpha} f_{i\alpha} + \sum_{i\alpha\beta\gamma\delta} U_{\alpha\beta\gamma\delta} f^\dagger_{i\alpha} f^\dagger_{i\beta} f_{i\gamma} f_{i\delta}, \tag{2}$$

where i indexes the Ln sites, $\alpha,\ldots,\delta$ index the degenerate states, including spin, of the Ln 4f shell, ε^f_α is the position of these states with respect to the Fermi energy of the planar CuO_2 holes, and $U_{\alpha\beta\gamma\delta}$ the Coulomb repulsion within and between these same states. $f^\dagger_{i\alpha}$ and $f_{i\alpha}$ are the appropriate fermion operators for the Ln 4f manifold. Essentially, the above expression is a zero-bandwith degenerate Hubbard Hamiltonian. Next, for the CuO_2 planes, we have:

$$\mathscr{H}_{\{CuO_2\}} = \sum_{j\neq j',\sigma} [t_{jj'}(1 - n_{j,-\sigma})d^{\dagger}_{j\sigma}d_{j'\sigma}(1 - n_{j',-\sigma})] + J\sum_{j} \mathbf{S}_j \bullet \mathbf{S}_{j+1}, \tag{3}$$

where j, j′ are the Cu site indices, σ the spin index of the CuO peroxide hole, $d^{\dagger}_j$, d_j and n_j its fermion and occupation operators, respectively, $t_{jj'}$ the effective hole hopping integral, J the nearest neighbor antiferromagnetic exchange integral between Cu^{2+} sites, and $\mathbf{S}_j$ the spin-1/2 operator on each of these sites. $\mathscr{H}_{\{CuO_2\}}$ is the effective one-band Hamiltonian derived by Rice and Zhang[22] from the two-band Hubbard model for planar CuO_2 in the small bandwidth limit. The third term in Eq. (1) represents the single particle interaction between the lanthanide and CuO_2 sub-lattices and is of the usual form for the Anderson impurity model:

$$\mathscr{H}_{\{Ln\},\{CuO_2\}} = \sum_{ij\alpha(\sigma)} [V^{\alpha}_{ij} f_{i\alpha(\sigma)} d_{j\sigma} + \text{h.c.}]. \tag{4}$$

in this term, V^{α}_{ij} is the spin-conserving interaction, or hybridization, parameter which takes an electron from the localized Ln 4f levels to annihilate the planar CuO_2 hole and vice versa. This term is characteristic of many mixed valence, fluctuating valence and heavy fermion models. We can see that, even in the presence of small V^{α}_{ij}, the tendency to trap holes in a lanthanide 4f state could be extremely strong. We are currently studying a simplified version of this model, but it is already clear that it is the relative magnitudes of ε^f and V_{ij} with respect to each other and to t_{ij} will dominate that part of the parameter phase diagram which separates superconducting from insulating behavior in the lanthanide 1-2-3 systems. In fact, this phase boundary must be crossed on moving from Pr 1-2-3 to Nd 1-2-3. It is interesting to note in this regard that many workers find Tc in Nd 1-2-3 to be considerably below 90 K, suggesting partial hybridization of the Nd 4f levels, although this depression may actually be due to partial substitution of Nd on the Ba site resulting in an overall lower hole concentration[23]. Finally, it is also interesting to speculate that the drastically reduced transition temperature obtained in $YBa_2Cu_3O_{7-y}$ doped with small amounts of Zn may be explained by the same model proposed here where instead of Pr 4f levels near E_F, we have the filled Zn 3d shell[24].

In conclusion, we have shown that removing oxygen from $PrBa_2Cu_3O_{7-y}$ induces a strong quantitative change of transport properties toward more insulating behavior, with little concomitant change in magnetic properties. These observations suggest that lowering oxygen concentration has virtually no effect on Pr ionicity, and that its principle impact is to remove holes from the chains. A simple interpretation of the inverse susceptibility would imply a $Pr^{+3.7}$ fractional charge state, but a more realistic approach should be taken by applying an appropriate Anderson impurity model to the lanthanide 1-2-3 series and showing that such a model predicts a superconductor-insulator transition at parameter values appropriate to $PrBa_2Cu_3O_{7-y}$. This work is in progress.

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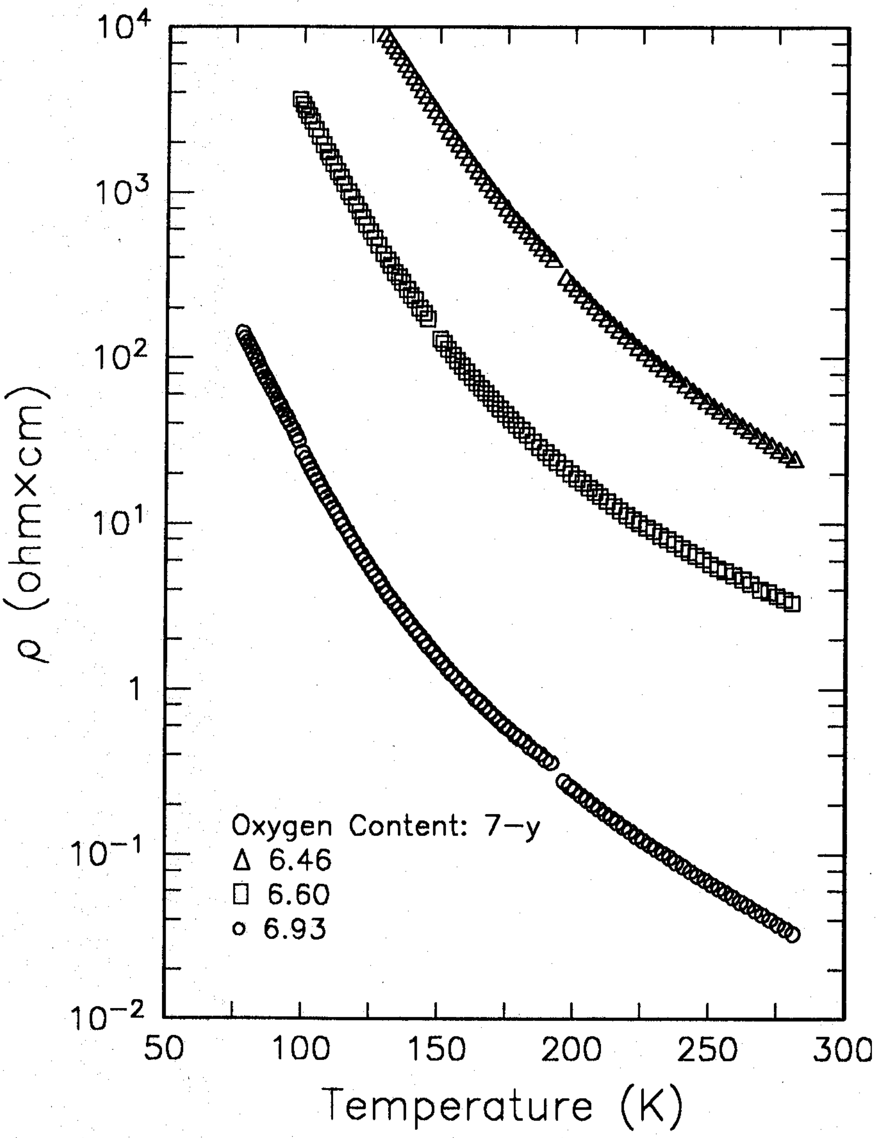

Fig. 1. Temperature dependence of the resistivity of $PrBa_2Cu_3O_{7-y}$ as a function of 7-y.

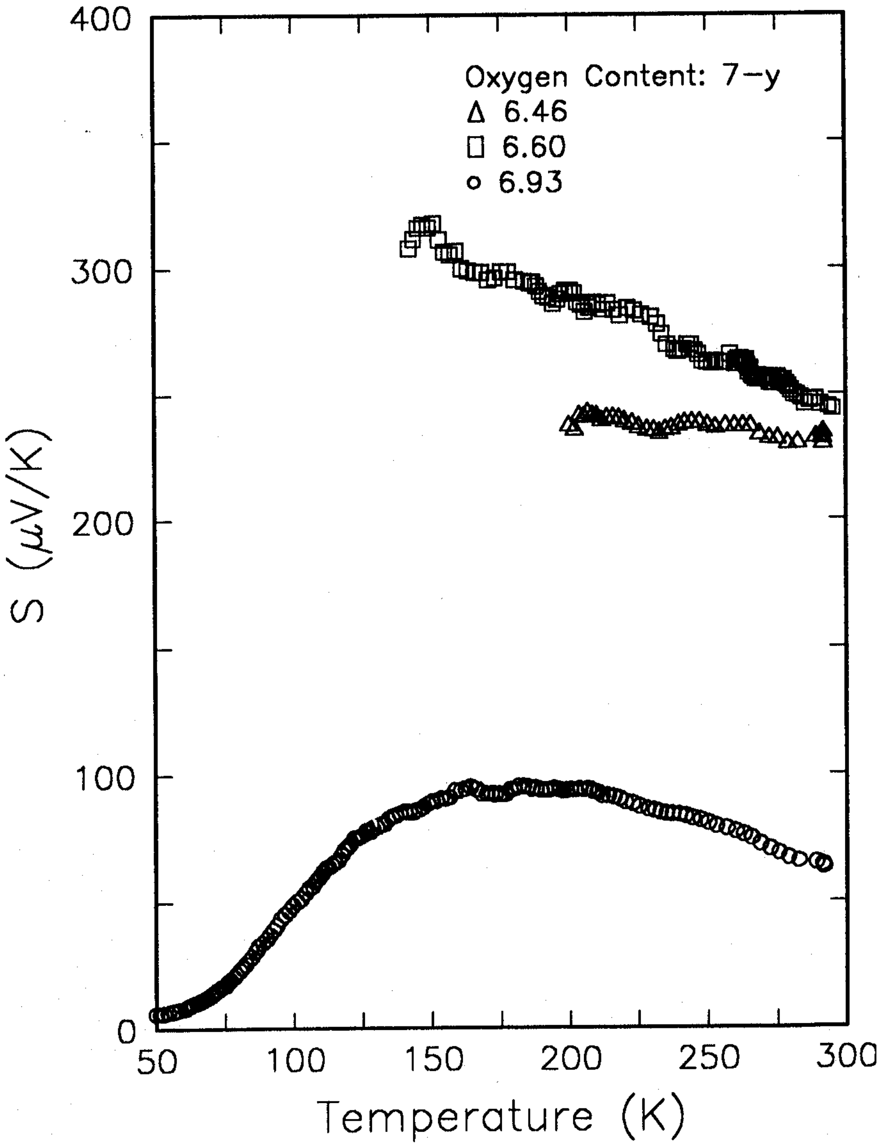

Fig. 2. Temperature dependence of the thermopower of $PrBa_2Cu_3O_{7-y}$ as a function of 7-y.

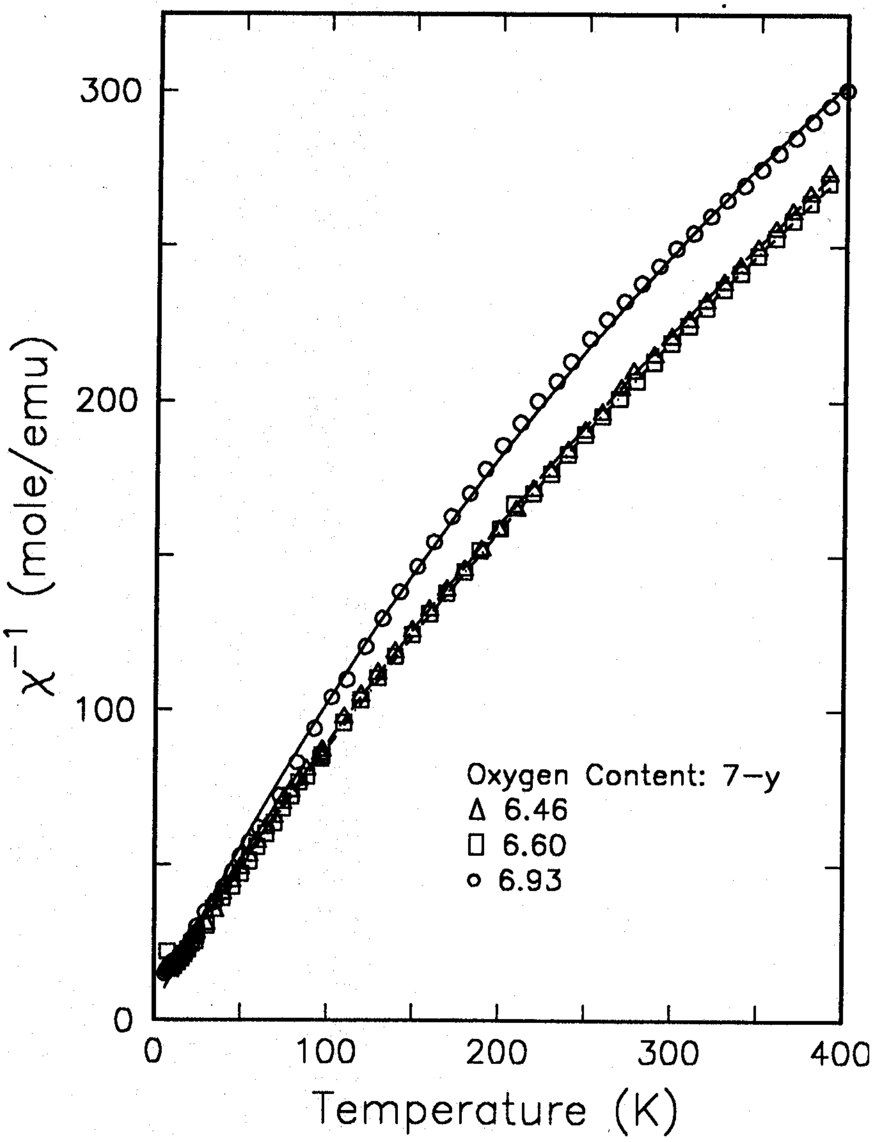

Fig. 3. Temperature dependence of the inverse susceptibility of $PrBa_2Cu_3O_{7-y}$ as a function of 7-y. The solid lines represent fits of the data to a Curie-Weiss law of the form $\chi = \chi_0 + C/(T + \theta)$, from which the effective Pr charge state was subsequently obtained.