Structural and Magnetic Studies on
Electrochemically Lithiated PrBa$_2$Cu$_3$O$_y$

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A lithiated compound Li$_{0.1}$Pr^{3+}Ba$_2$Cu$_3$O$_y$ has been successfully prepared by electrochemical method, which is achieved with a two electrode cell of the type: Metal(Li)/(Li$^+$, ClO$_4^-$) + propylene carbonate/PrBa$_2$Cu$_3$O$_y$. All Pr ions in the lithiated compound are stabilized with a trivalent state as the other rare earths (III) substituted in the 90K superconductor lattice (Y$_{1-x}$Ln$_x$-Ba$_2$Cu$_3$O$_{7-\sigma}$). Powder X-ray diffraction analysis shows that both compounds, PrBa$_2$Cu$_3$O$_y$ and Li$_{0.1}$PrBa$_2$Cu$_3$O$_y$, are isostructural with the 90 K superconductor, (YBa$_2$Cu$_3$O$_{7-\sigma}$), nevertheless both of them are non-metallic and also non-superconducting down to 10K. Magnetic susceptibility χ vs. temperature data indicate that Curie contribution from the magnetic ions (Pr and Cu) is weakened on the one hand, but on the other hand temperature-independent part of susceptibility χ_o increases depending upon the rate of lithium intercalation in PrBa$_2$Cu$_3$O$_y$ lattice.

Introduction

After the discovery of superconductivity above 90 K in YBa$_2$Cu$_3$O$_{7-\sigma}$,[1] considerable excitement has been generated in this field. And it has been confirmed that the complete substitution of Y by the trivalent rare-earths from La to Lu in YBa$_2$Cu$_3$O$_{7-\sigma}$, with the exception of Ce, Pr, and Tb, does not affect the superconductivity[2-5]. The three exceptional rare earth ions, Ce, Pr and Tb, have a stable trivalent and tetravalent states in common. Among the three R′Ba$_2$Cu$_3$O$_y$ compounds (R[III, IV] = Ce, Pr and Tb), only PrBa$_2$Cu$_3$O$_y$ could be prepared as a single phase, and Pr ion in the PrBa$_2$Cu$_3$O$_y$ compound exists as a mixed valency state of III and IV[6]. It has been assumed that the mixed valent state of Pr affects not only the electronic states of the system, but also the superconducting properties of the Cu-O planes.

In this work, an attempt was made to stabilize the Pr with an oxidation state of 3$^+$ only in the 123 lattice as the other lanthanide (III) superconductor, RBa$_2$Cu$_3$O$_{7-\sigma}$ (R[III] = La∼Lu). In order to solve such a problem, we have prepared, at first, PrBa$_2$Cu$_3$O$_y$ compound with crystallographically single phase and reduced it electrochemically by lithium insertion in order to stabilize the Pr^{3+} only in the lattice as follows:

$$Pr_{1-x}^{3+}Pr_x^{4+}Ba_2Cu_3O_y + xLi \rightarrow Li_xPr^{3+}Ba_2Cu_3O_y$$
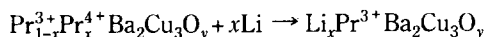
Experimental

Samples of PrBa$_2$Cu$_3$O$_y$ have been prepared from thermal decomposition of the corresponding metal nitrates. The nitrate samples were obtained by dissolution of stoichiometric quantities of PrO$_2$, Ba(NO$_3$)$_2$, and Cu metal in a concentrated nitric acid. The product obtained from heat treatment at 700 °C was ground, pressed into pellets and heated at 860 °C for 17 hours in oxygen atmosphere and furnace cooled. Then it was reground, repressed into pellets, and sintered at 930 °C for 20 hours and cooled at 15 °C/10 min. and then annealed at 480 °C for 17 hours in oxygen atmosphere.

X-ray diffraction pattern was recorded with Cu-K$_\alpha$ radiation (λ = 1.5418 Å) using a Ni filter on a Jeol diffractometer. NaCl powder was used as an internal standard.

Electrochemical lithium intercalation in PrBa$_2$Cu$_3$O$_y$ was carried out with a two electrode cell:
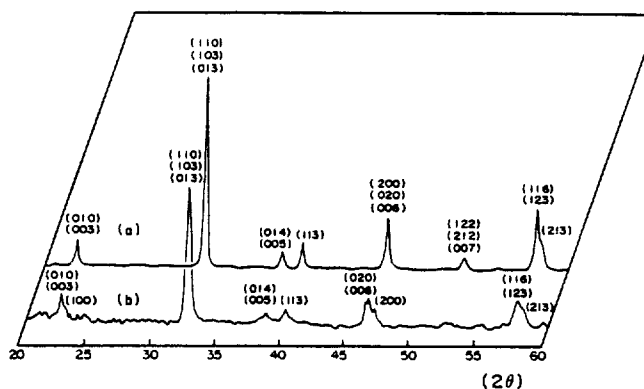

Figure 1. XRD patterns of PrBa$_2$Cu$_3$O$_y$ (a) and Li$_{0.1}$PrBa$_2$Cu$_3$O$_y$ (b).

Li-metal/(Li$^+$, ClO$_4^-$) + propylene carbonate/PrBa$_2$Cu$_3$O$_y$
(Anode)   (Cathode)

A propylene carbonate solution of LiClO$_4$ was used as an electrolyte. The solution was soaked in a separator made of porous glass paper. Cell was kept in an argon filled glove box during the electrochemical treatment. The sample was reduced by discharging the cell at constant current density (30 μA/cm^2). Open-circuit voltage (OCV) was recorded in the discharging process after the cell has been equilibrated for 100 hours.

Electrical resistance measurement was performed by the four probe method with silver paint contacts, and the temperature was measured using a Lake Shore diode from 10 to 300 K. Two copper- constantan thermocouples were attached to the sample to insure thermal equilibrium between thermometer and sample during the measurement.

Magnetic susceptibility measurement was carried out with a Faraday type magnetobalance from 77 to 300 K, and correction for core diamagnetic contribution[7] was performed.

Results and Discussion

According to the power X-ray diffraction analysis, a single phase of PrBa$_2$Cu$_3$O$_y$ was identified as an orthorhombic crystal structure (Figure 1), but the degree of orthorhombic distortion relative to the corresponding tetragonal struc-
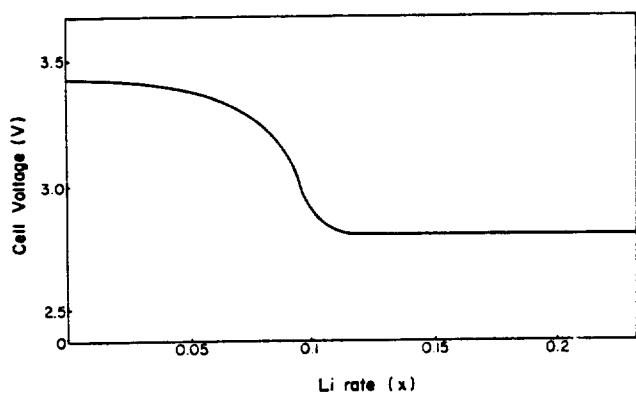
Figure 2. Variation of thermodynamic emf vs. Li rate in Li // PrBa$_2$Cu$_3$O$_y$ cell ($I = 30$ fA/cm^2).

Table 1. Calculated d - values (Å) of Li$_{0.1}$PrBa$_2$Cu$_3$O$_y$ with Orthorhombic Structure and Comparison with the Observed d - values (Å) and Intensities.

$(h\ k\ l)$	d - cal.	d - obs.	I/I_o
(0 0 3)	3.921	3.920	13
(0 1 0)	3.923	3.920	
(1 0 0)	3.884	3.884	3
(0 1 3)	2.774	2.766	
(1 0 3)	2.760	2.766	100
(1 1 0)	2.760	2.766	
(0 1 4)	2.353	2.350	7
(1 1 3)	2.257	2.260	13
(0 2 0)	1.962	1.963	36
(0 0 6)	1.961	1.963	
(2 0 0)	1.942	1.941	15
(1 2 3)	1.599	1.599	47
(1 1 6)	1.599	1.599	
(2 1 3)	1.591	1.590	10

Figure 3. Idealized model of lithium intercalation reaction in PrBa$_2$Cu$_3$O$_y$.

Figure 4. Temperature dependence of the normalized electrical resistivity $\rho/\rho_{300\ K}$ for Li$_{0.1}$PrBa$_2$Cu$_3$O$_y$. The inset is that for PrBa$_2$Cu$_3$O$_y$.

ture is very weak. The lattice parameter could be estimated as a = 3.907 Å, b = 3.902 Å, and c = 11.700 Å, which coincides with the previous work[4]. Li$_{0.1}$PrBa$_2$Cu$_3$O$_y$ was prepared successfully by electrochemical intercalation of lithium in PrBa$_2$Cu$_3$O$_y$ as shwon in the following scheme.

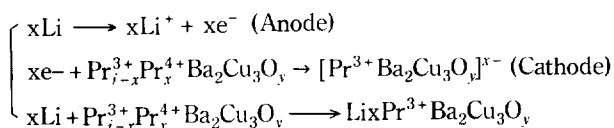$$\begin{cases} x\text{Li} \longrightarrow x\text{Li}^+ + x\text{e}^- \ (\text{Anode}) \\ x\text{e}- + \text{Pr}^{3+}_{1-x}\text{Pr}^{4+}_{x}\text{Ba}_2\text{Cu}_3\text{O}_y \rightarrow [\text{Pr}^{3+}\text{Ba}_2\text{Cu}_3\text{O}_y]^{x-} \ (\text{Cathode}) \\ x\text{Li} + \text{Pr}^{3+}_{1-x}\text{Pr}^{4+}_{x}\text{Ba}_2\text{Cu}_3\text{O}_y \longrightarrow \text{Li}x\text{Pr}^{3+}\text{Ba}_2\text{Cu}_3\text{O}_y \end{cases}$$

Figure 2 shows the variation of Open Circuit Voltage (OCV) of the Li//PrBa$_2$Cu$_3$O$_y$ cell in the discharging process. The OCV was 3.42 V at the beginning ($x = 0$) and was decreased upon the increase of lithium content. A plateau of cell voltage (2.8 V) was maintained (biphase) after a sharp drop around $x = 0.1$, which indicates that the solubility of Li in PrBa$_2$Cu$_3$O$_y$ oxide lattice is strongly limited under this value ($x = 0.1$). Because the reduction potential of Pr^{4+}/Pr^{3+} (2.9 ± 0.2 V)[8] is higher than that of Cu^{3+}/Cu^{2+} (0.45 $\sim$ 1.02 V)[9], it is expected that Pr^{4+} might be preferentially reduced rather than Cu^{3+}. The potential around $x = 0.1$ in Figure 2 shows that Pr^{4+} is reduced to Pr^{3+} as lithium is intercalated, and the ratio of
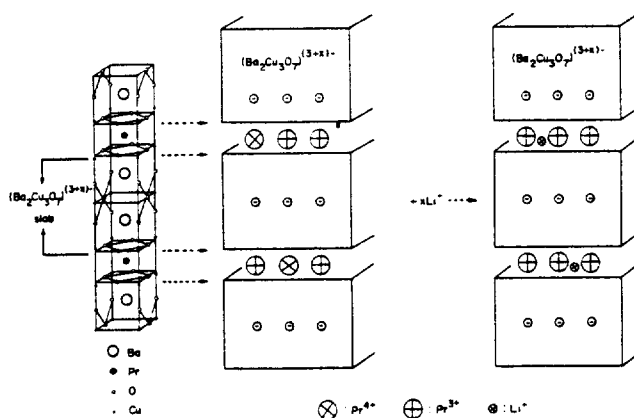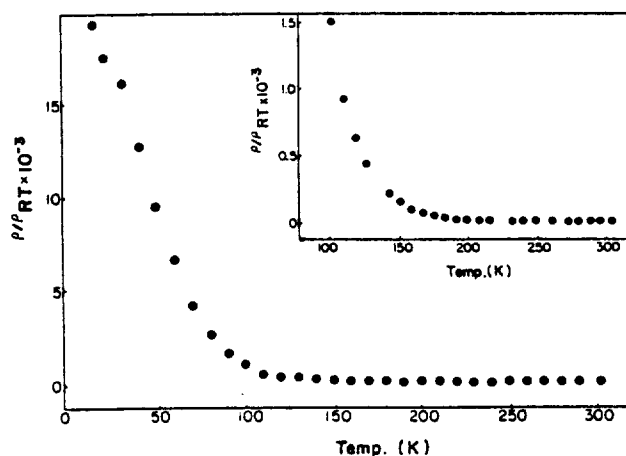
Pr^{4+} to Pr^{3+} in PrBa$_2$Cu$_3$O$_y$ could be estimated approximately 0.1:0.9, which is well consistent with the spectroscopic measurements.[10,11]

From the X-ray diffraction analysis, Li$_{0.1}$PrBa$_2$Cu$_3$O$_y$ can be indexed to the orthorhombic structure with lattice parameter a = 3.884 Å, b = 3.923 Å, and c = 11.764 Å (Table 1). The increased orthorhombic distortion results not from the change of oxygen content but from the reduction of Pr^{4+} to Pr^{3+} and the oxidation of intercalated lithium. Therefore, occupancy of each oxygen position as well as total oxygen content is remained the same though all Pr ions are stabilized with a trivalent state in the Li$_{0.1}$PrBa$_2$Cu$_3$O$_y$ lattice. It is worthy to note that the lattice parameter c of 11.764 Å is increased relatively (Δ = 0.064 Å) due to the reduction of Pr^{4+} to Pr^{3+} (The ionic radii for Pr^{4+}, Pr^{3+}, and Li$^+$ are 0.99 Å, 1.14 Å and 0.59 Å, respectively.[12]).

Although precise knowledge of the lithium distribution in the lattice requires neutron diffraction investigation, a model for lithium intercalation reaction in PrBa$_2$Cu$_3$O$_y$ lattice could be proposed as presented in Figure 3. The entire lattice can be thought to consist of Pr cation and negatively charged [Ba$_2$Cu$_3$O$_7$]$^{(3+x)-}$ slab in turn like the typical 2D sheets of cation exchangeable layered aluminosilicate, and as the oxygen
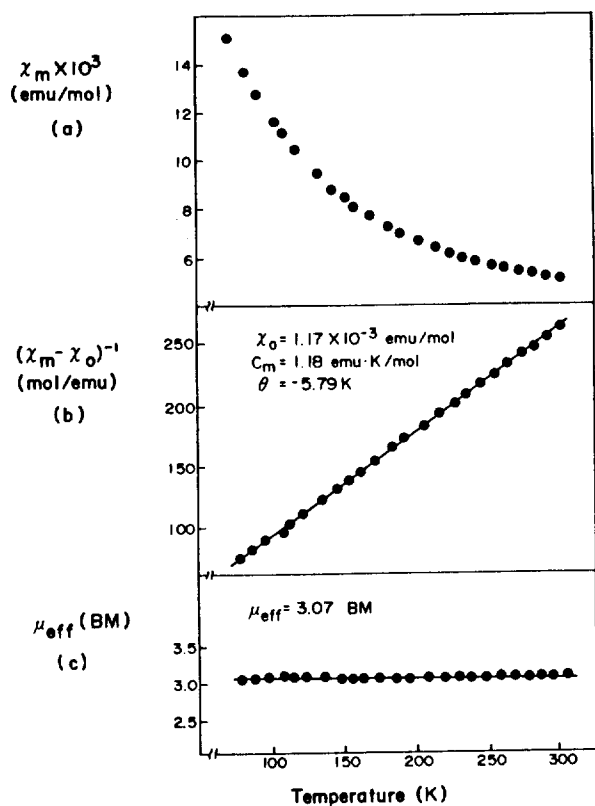
Figure 5. Temperature dependence of molar magnetic susceptibility χ_m (a), inverse ($\chi_m - \chi_o$) (b), and effective magnetic moment μ_{eff} (c) of $PrBa_2Cu_3O_y$.

vacancies around Pr ion may provide enough space for Li ion, which could be stabilized in-between the negatively charged slabs according to the charge neutrality principle.

Electrical resistance data for the $PrBa_2Cu_3O_y$ and $Li_{0.1}PrBa_2Cu_3O_y$ are shown in Figure 4. In general, the complete replacement of Y by the trivalent rare earths leads to a formation of superconducting phase with a transition temperature almost identical with that reported for the yttrium compound (*ca.* 90 K). Hence we hopefully expected a superconductivity for the Li-complex in which all Pr ions are in the trivalent state. But as shown in Figure 4, no superconductivity could be observed on the lithium derivative down to 10 K. In the $YBa_2Cu_3O_{7-\sigma}$ system, the dramatic depression of T_c has been explained by the transition from orthorhombic to tetragonal symmetry, which is surely due to the disordering of oxygen vacancies[13]. Similar disordering of the oxygen vacancies expected in the pseudo-tetragonal $PrBa_2Cu_3O_y$ was suspected to result in the non-superconductivity of the $PrBa_2Cu_3O_y$[14-17]. But in recent literature, the absence of superconductivity in $PrBa_2Cu_3O_y$ is thought not merely due to the orthorhombicity but due to the hybridization of the Pr 4f electrons with the hole carriers of the Cu-O planes. The semiconducting behavior observed in the orthorhombic $Li_{0.1}Pr^{3+}Ba_2Cu_3O_y$ compound suggests that the hybridization rather than the reduced orthorhombicity results in the non-superconductivity.

The magnetic susceptibility data for the $PrBa_2Cu_3O_y$ and $Li_{0.1}PrBa_2Cu_3O_y$ are presented in Figure 5 and 6 respectively. The $\chi(T)$ data for both compounds can be described quite well by the sum of a temperature independent contribution to
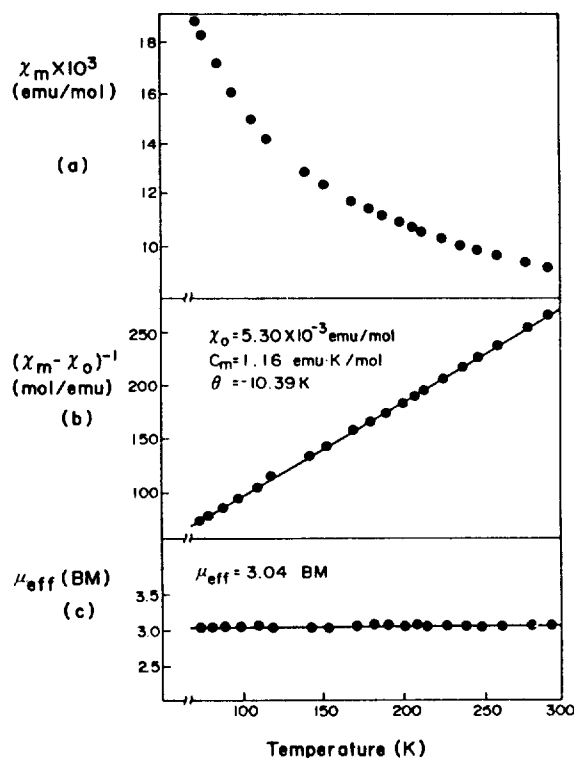

Figure 6. Temperature dependence of molar magnetic susceptibility χ_m (a), inverse ($\chi_m - \chi_o$) (b), and effective magnetic moment μ_{eff} (c) of $Li_{0.1}PrBa_2Cu_3O_y$.

Table 2. Temperature Independent Susceptibility χ_o, Effective Magnetic Moment μ_{eff}, and Weiss Constant θ of $PrBa_2Cu_3O_y$ and $Li_{0.1}PrBa_2Cu_3O_y$

Compound	χ_o (emu/mole)	μ_{eff} (B.M.)	θ (K)
$PrBa_2Cu_3O_y$	1.17E–3	3.07	–5.79
$Li_{0.1}PrBa_2Cu_3O_y$	5.30E–3	3.04	–10.39

susceptibility χ_o and a Curie–Weiss contribution; *i.e.*,

$$\chi = \chi_o + C/(T - \theta) \tag{1}$$

where C and θ are Curie constant and Weiss one. The equation (1) can be rewritten as follows;

$$\chi T = \chi_o T + \theta \chi + (C - \chi_o \theta) \tag{2}$$

Therefore χ_o, θ, and C can be obtained by the least squares fit of χT *vs.* T and χ with equation (2), and values of the constants χ_o, θ, and μ_{eff} are given in Table 2. The average oxidation state of Pr ion obtained from the result of OCV-curve was estimated approximately +3.1, so $\mu_{cal} = 3.49$ BM can be expected for $PrBa_2Cu_3O_y$ considering the free ion magnetic moment of Pr^{3+} ($^3H_4$) with 3.58 BM and Pr^{4+} ($^2F_{5/2}$) with 2.54 BM. But the observed effective magnetic moment, $\mu_{obs} = 3.1$ BM with $\chi_o = 1.17$ E–3 emu/mole, is relatively smaller than the expected value. In $Li_{0.1}PrBa_2Cu_3O_y$ case, the temperature independent paramagnetism (TIP) is almost five times greater than in $PrBa_2Cu_3O_y$ with little change in effective magnetic moment. In the recent reports for $PrBa_2Cu_3O_y$[12-15], the magnetic contribution from Cu ion is neglected because

Cu is considered as a minor magnetic ion compared with Pr in this system. Since Pr is a major magnetic ion in this system and the moment is a function of the valence, it is thought that Pr valence can be estimated from the susceptibility data. But the hybridization of Pr 4f electrons with the hole carriers of the Cu-O planes can change the effective number of Pr 4f electrons, which leads to the reduced magnetic moment of the $PrBa_2Cu_3O_y$ as well as $Li_{0.1}PrBa_2Cu_3O_y$. Therefore we believe that the reduced magnetic moment (3.1 BM) indicates that there is a significant hybridization of the 4f electrons with the valence band states. The increased TIP contribution found in Li-compound seems to arise from the perturbation effect of Li ion on the symmetry around Pr site.

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