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Electronic properties of $Ba_2Y_{1-x}Pr_xCu_3O_{7-\delta}$

Azusa Matsuda, Kyoichi Kinoshita, Takao Ishii, Hiroyuki Shibata
Takao Watanabe, and Tomoaki Yamada
NTT Basic Research Laboratories, 3-9-11 Midori-cho, Musashino-shi Tokyo 180, Japan
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Measurement of the Hall coefficient in the $Ba_2Y_{1-x}Pr_xCu_3O_{7-\delta}$ system has revealed that an increase in Pr concentration reduces the Hall carrier number ($1/eR_H$) and its strong temperature dependence. The Cu formal valence calculated from the Pr valence, which has been determined to be $\sim+3.5$, shows a weakly decreasing dependence on Pr concentration. T_c shows a stronger dependence on the Hall carrier number and the Cu-O formal valence than in the oxygen-depleted $Ba_2YCu_3O_{7-\delta}$ system. The persistence of the chain band explains this observed difference, suggesting that the actual Cu-O valence dependence of the 90-K superconductor is stronger than that of the 40-K superconductor.

Of known Ba_2[lanthanide]$Cu_3O_{7-\delta}$ compounds, only the Pr compound shows neither superconductivity nor metallic conduction, although it has an orthorhombic structure isomorphic to that of $Ba_2YCu_3O_7$ (Refs. 1 and 2). Thus, the difference in the electronic and/or the crystal structure between these compounds might be a key parameter controlling superconductivity as well as normal-state properties of the high-T_c copper oxides. It is known that a series of single-phase $Ba_2Y_{1-x}Pr_xCu_3O_{7-\delta}$ can be synthesized.[3,4] They continuously range from superconductors to insulators. It is generally accepted that in high-T_c copper oxides, the total carrier density is a crucial parameter by which the conduction properties are determined. There are several systems, for example, $[La,Sr]_2CuO_4$ (Ref. 5), $Ba_2YCu_3O_{7-\delta}$ (Ref. 6), and $Ba_{2-x}La_{1+x}Cu_3O_{7-\delta}$ (Ref. 7), which show a strong correlation between T_c and formal valence of Cu-O. These relations have also been confirmed by Hall effect measurements.[5,8] However, it is pointed out that the present $Ba_2Y_{1-x}Pr_xCu_3O_{7-\delta}$ solid solution system cannot be understood on the same basis as a valence-changing system.[4] In this report, the Cu-O valence is estimated by the precise measurement of the Pr moment and the results are compared with the Hall effect measurement. Hall effect provides a more direct and physical way of showing such a correlation and a deeper insight into electronic properties of the system.

The $Ba_2Y_{1-x}Pr_xCu_3O_{7-\delta}$ system has an advantage as a valence tunable system over systems such as oxygen-depleted $Ba_2YCu_3O_{7-\delta}$ or $Ba_{2-x}La_{1+x}Cu_3O_{7-\delta}$, because there is no essential change in the crystal structure within the whole range of Pr concentration. Another interesting point in the 90-K superconductor is the existence of two different carriers: namely, a Cu-O_2 plane and a Cu-O_3 chain. The present system is very suitable for identifying the roles because the chain-site structure remains unchanged. Experimental results will be discussed from this point of view.

A series of $Ba_2Y_{1-x}Pr_xCu_3O_{7-\delta}$ samples was synthesized from 99.99% pure $BaCO_3$, 99.99% pure Y_2O_3, 99.99% pure Pr_6O_{11}, and 99.99% pure CuO powders. The powders were mixed, ground, calcined, reground, pressed into pellets, and sintered at 920 °C for 50 h in an oxygen atmosphere. Their crystal structure was checked by the powder x-ray-diffraction pattern. All the samples showed a single-phase oxygen-deficient perovskite structure, except for a small trace of $BaCuO_2$ observed in the samples for which $x\neq0$. The existence of $BaCuO_2$ may indicate that a small amount of Pr is substituted into the Ba site as pointed out by Okai *et al.*[4] The molar fraction of $BaCuO_2$ estimated from the diffraction peak ratio is less than 4% for $x<0.5$, and less than 6% for $0.5<x<1$. Therefore, in the following discussion, the effect of $BaCuO_2$ will be neglected. The results of the detailed structure analysis using the Rietveld method will be published elsewhere.

All the samples showed an orthorhombic structure with an almost constant orthorhombic distortion throughout the series. Total oxygen content was measured by thermogravimetry (TG) and chemical analysis. The resulting oxygen content was almost constant ($0.03<\delta<0.12$). These results indicate that the Cu-O chain site is ordered as in the Y compound for all Pr concentrations.

Temperature dependences of electric resistivity were measured by standard four-probe configuration with additional 3 electrodes for Hall voltage measurement. Rectangular bars of size $8\times2.5\times0.3$ mm were sliced from the as-grown sintered pellets. Electrodes were shaped from gold paste and annealed at 850 °C for low contact resistance. The system is metallic down to $x<0.6$ and shows characteristic T linear temperature dependence for $x<0.4$. For $x>0.7$, the system becomes insulating. In Fig. 1, experimental data with three-dimensional variable range-hopping (VRH) parametrization are shown. Resistivity does not show simple behavior and neither VRH nor activation type T dependence fits the data in the insulating region. In Fig. 2(a), T_c is plotted as a function of x, where error bars indicate the transition width. Figure 2(b) shows superconducting volume fraction, which is obtained as a strength of a diamagnetic signal normalized at $x=0$ at 5 K in a 100-G magnetic field. T_c and the volume fraction decreases with increasing x, while transition widths remain rather narrow.

Magnetic susceptibility (χ) was measured by a superconducting quantum interference device (SQUID) mag-

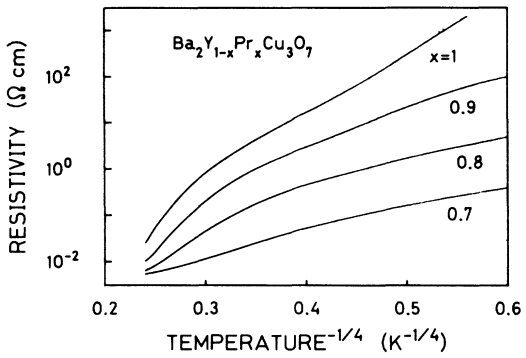

FIG. 1. Temperature dependence of resistivity for samples with $x > 0.7$. The temperature scale is plotted as $T^{-1/4}$.

netometer in a magnetic field of 1 kG in a temperature range of 5 to 300 K. Since Pr is a major magnetic atom in the system and the moment is a function of the valence, the Pr valence can be estimated from the susceptibility data. Pr^{+3} and Pr^{+4} have moments of $3.6\mu_B$ and $2.5\mu_B$, respectively.

The temperature dependence of the χ obtained was expressed as $\chi_0+C/(T-\theta)$, where χ_0 is a temperature-independent component of the susceptibility and $C/(T-\theta)$ is the Curie-Weiss contribution. This temperature-dependence well reproduces experimental data for $T > 50$ K, with $\theta \simeq 0$. For $T < 50$ K and $x > 0.5$, deviation from this form becomes evident, indicating the domination of the singlet ground state. The hatched area in Fig. 2(c) represents the estimated effective Pr moments. Ambiguity comes from the Cu moment (μ_{Cu}) estimation. The solid line and the dashed line represent the eye guides for $\mu_{Cu}=0\mu_B$ and $0.3\mu_B$, respectively. In either way, the obtained Pr moment is about $3\mu_B$. This means that Pr valence is about +3.5, which is consistent with the domination of the singlet ground state. The valence obtained was different from the +3.9 obtained by Okai *et al.*[4] The difference may be due to their neglect of the χ_0 term. The Cu valence calculated from the Pr valence and the oxygen content is displayed in Fig. 2(d).

The temperature-independent part of susceptibility χ_0 increases rapidly with x, as shown in Fig. 2(c). Since it is not proportional to x, the major contribution to χ_0 might come from Cu electrons. This is in contrast with the oxygen-depleted $Ba_2YCu_3O_{7-\delta}$ system where χ_0 decreases rapidly with increasing oxygen deficiency.[9]

The Hall effect was measured in a magnetic field of 5 T with a current of 10 to 50 mA. Figure 3 shows V/eR_H as a function of temperature. Here V and R_H are a unit-cell volume and a Hall coefficient. Thus V/eR_H means carrier number within a unit cell, if the system has a single flat band. As reported by many authors,[5,6,8] at $x=0$, V/eR_H is positive and shows remarkably linear temperature dependence. With increasing x, linear dependence of T reduces rapidly and overall magnitudes decrease montonically. Recent single-crystal measurements reveal that T linear dependence is one of the characteristic features of the transport properties of the Y compound.[10]

Since V/eR_H has strong temperature dependence, the

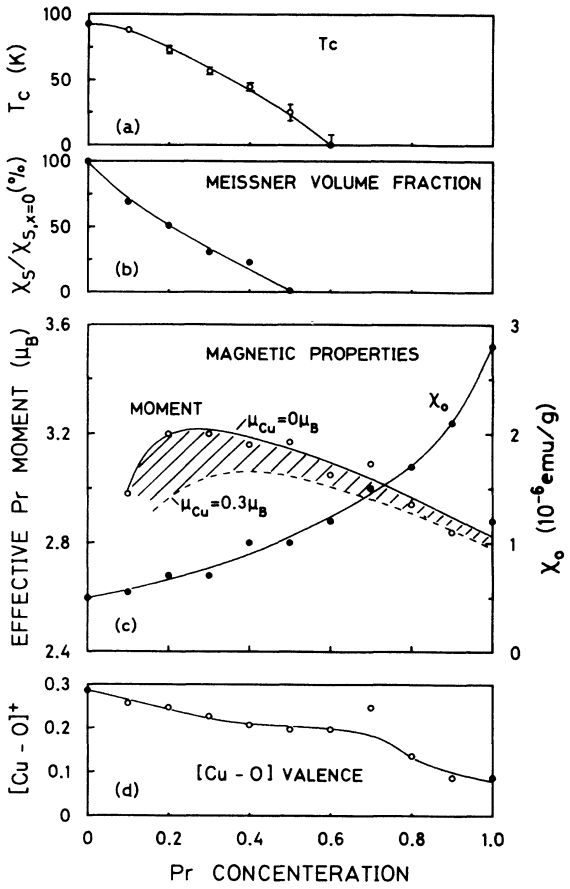

FIG. 2. (a) Superconducting transition temperature as a function of Pr concentration (x). Error bars show the transition width. (b) The Meissner volume fraction normalized at $x=0$. (c) Magnetic properties of $Ba_2Y_{1-x}Pr_xCu_3O_{7-\delta}$. Open circles show the Pr effective moment obtained by assuming $\mu_{Cu}=0\mu_B$. The dashed line shows the Pr moment obtained by assuming $\mu_{Cu}=0.3\mu_B$. Solid circles represent temperature-independent component of susceptibility. (d) Cu valence calculated from the Pr moment and the oxygen content δ.

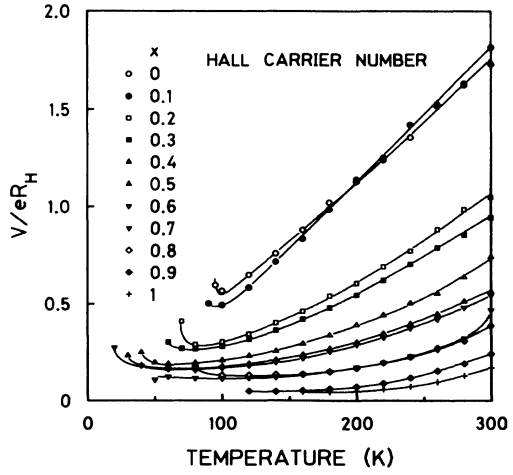

FIG. 3. Temperature dependence of Hall carrier number V/eR_H. V indicates the unit-cell volume.

simple interpretation of this quantity, like a carrier number, is impossible. Wang *et al.*[8] have proposed a two-carrier model. It consists of a two-dimensional (2D) $Cu-O_2$ plane band together with a one-dimensional (1D) $Cu-O_3$ chain band, with carrier densities and mobilities of n_{2D}, μ_{2D} and n_{1D}, μ_{1D}, respectively. However, this model is inconsistent, if the simple Drude two-carrier expression and the $1/T$ dependence of μ_{2D}, which is realized in the doped La_2CuO_4 system, are adopted. The simple calculation shows the Hall coefficient has $1/T$ temperature dependence only if $\mu_{1D} \gg \mu_{2D}$ holds. This condition is hard to realize in the actual system. The recent experiments show that the system should be understood as a highly correlated Fermion system having large on-site Coulomb repulsion.[11] In such a system, Hall coefficient may be temperature dependent because of a strong renormalization effect in a nearly half-filled Hubbard band.

Since overall magnitudes of V/eR_H change monotonically and temperature dependence weakens due to Pr substitution, the value at a fixed temperature can be used as a measure of carrier density. Figure 4(a) shows the Hall carrier at 100 K as a function of the formal Cu-O valence, which is defined as the Cu valence minus two. There is a linear relation between these two quantities, as expected. In Fig. 4(b), T_c is plotted as a function of the Cu-O valence. The hatched area surrounded by solid lines indicates ambiguity stemming from the estimation of the Cu moment. The dotted line and dash-dotted line indicates the relations for oxygen-depleted $Ba_2YCu_3O_{7-\delta}$ (Ref. 8) and doped La_2CuO_4,[5] respectively. Figure 5(a) shows T_c as a function of Hall carrier at 100 K. The dashed line indicates the result obtained by Wang *et al.*[8] for the oxygen-depleted Y compound. The clear difference between present results and other systems can be seen both in Figs. 4(b) and 5(a).

In the present system, the oxygen vacancy concentration and the degree of the oxygen ordering remains unchanged. This means that a 1D $Cu-O_3$ band exists throughout the series. The $Pr^{3.5+}$ substitution into Y^{3+} site simply compensates the Cu valence and, thus, the hole concentration.

Figure 5(b) shows the simplified band picture of the present system and that of the oxygen-depleted Y compound. There exist 1D and 2D bands both of which have a Mott-Hubbard gap above the Fermi level (E_F). Considering that the Cu in the chain site tends to be trivalent, the gap edge of the 1D band might be higher than that of the 2D band. In the present system, E_F increases monotonically with x. At about $x=0.5$, E_F reaches the gap edge of the 2D band, making T_c zero. There, 1D carrier still exists. However, as is well known, the 1D carrier is easily localized by a small imperfection, resulting in VRH-type conduction. The complex temperature dependence of the resistivity for $x > 0.6$, as shown in Fig. 1, can be understood as the behavior of the almost localized 1D electron system. On the other hand, in the oxygen-depleted system, the removal of oxygen from a chain site strongly affects the 1D band. At $\delta \sim 1$, chain site Cu is thought to adopt a monovalent state. Therefore, the oxygen removal not only elevates E_F but also lowers the 1D band position which will be reduced to a localized atomic

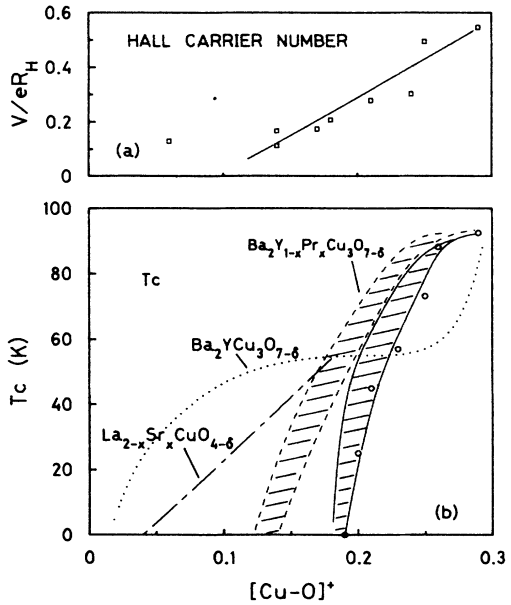

FIG. 4. (a) Hall carrier number at 100 K as a function of Cu-O valence. (b) T_c as a function of Cu-O valence. The hatched area surrounded by the solid lines shows ambiguity caused by the Cu moment estimation. The dotted line indicates the relation in oxygen-depleted $Ba_2YCu_3O_{7-\delta}$ after Ref. 8. The dot-dashed line represents the relation held in $La_{2-x}Sr_xCuO_{4-\delta}$ after Ref. 5. Dashed lines indicate the relation obtained by assuming that the 1D carrier remains constant in the $Ba_2Y_{1-x}Pr_xCu_3O_{7-\delta}$ system.

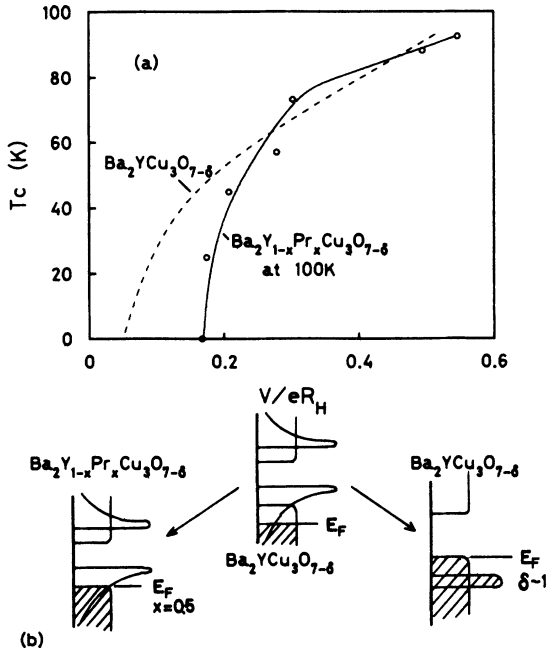

FIG. 5. (a) T_c as a function of Hall carrier number at 100 K. The dashed line represents the result of the oxygen-depleted $Ba_2YCu_3O_{7-\delta}$ after Ref. 8. (b) Proposed band picture of $Ba_2Y_{1-x}Pr_xCu_3O_{7-\delta}$.

level. These movements explain complex Hall carrier behavior obtained by Wang *et al.*[8]

Now, the differences appearing in Figs. 4(b) and 5(a) can be easily understood on the basis of the band picture. The apparent difference in the Hall carrier concentration at which $T_c=0$ shows a existence of 1D chain electrons in the present system. This indicates, as a rough estimate, $n_{1D}\sim 0.12$ at $T_c=0$. Since n_{2D} is estimated to be about 0.18 at $T_c=60$ K, it can be said that the chain band carriers a substantial amount of carriers. This leads to one conclusion that the existence of the chain has essentially no effect on superconductivity. The stronger carrier number dependence on T_c simply reflects the fact that fewer electrons are needed to fill the fixed 1D band. It is difficult to know the actual carrier concentration n_{2D} from the Hall coefficient and even from the Cu formal valence. In this sense, the empirical formula which connects the formal Cu valence and T_c does not have any theoretical base. However, the Cu-O valence can be estimated in the extremum case where n_{1D} stays constant. This simply means all the substituted Pr ions compensate holes in Cu-O_2 plane. Even in such an extreme case, which is displayed as the hatched area surrounded by dashed lines in Fig. 4(b), the result shows stronger dependence than that of the La system. The present discussion provides a view that true n_{2D} really has a stronger dependence on T_c. Finally, the observed increase in temperature-independent susceptibility χ_0 should be explained on the same basis. It can be understood as a result of the 1D band filling, which provides a divergent state density. However, more experimental and theoretical work should be done to exclude other possibilities, for example, the effect of disorder in the Y-Pr plane.

In conclusion, the magnetic susceptibility measurement of the $Ba_2Y_{1-x}Pr_xCu_3O_{7-\delta}$ system has revealed that Pr valence is about +3.5. The Cu formal valence has showed a slowly decreasing dependence on Pr concentration. The measurement of Hall coefficient of the system showed that increase in Pr concentration reduces Hall carrier density and strong temperature dependence ($R_H\propto 1/T$). T_c showed stronger dependence on Hall carrier density as well as Cu-O formal valence than in the other valence tunable system. The simple band picture was proposed based on the fact that the chain structure persists for the whole x range. The existence of the chain band explains the major difference between the present results and those of the oxygen-depleted $Ba_2YCu_3O_{7-\delta}$ system. The experiment suggests that the actual Cu-O valence dependence of Y compound is stronger than that of the doped La_2CuO_4 system.

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