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Charge Transfer and Superconductivity in Oxide Superconductor with YBCO-Structure

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A new method to control the mobile hole concentration in YBCO-system was proposed at the end of 1987 by the group of the author. By many works performed from then on including by other groups, the mechanism has been clarified as the charge transfer between CuO_2-sheet layer and the CuO-chain-like layer induced by the partial substitution of divalent Ba by trivarent element such as Nd. Using this method and the measurement of the Hall effect, a relation of T_c with mobile hole concentration in YBCO-system are elucidated. Further, based on these results the hole filling mechanism and pair breaking effects of Pr in YBCO-system has been investigated by the author's group. Some of the important results will be presented and discussed.

KEYWORDS: charge transfer, substitution effect, Hall coefficient, hole filling, pair breaking

§1. Introduction

From the beginning of the research on high-T_c oxide superconductors, it has been widely recognized that the hole concentration is an essential parameter for superconductivity of this kind of materials. For YBCO, it was shown in the early stage of the investigation that their superconducting properties depend critically on the oxygen content and the hole concentration is strongly affected by the oxygen content.[1,2] At the end of 1987, a new method to control the hole concentration in YBCO-like system was proposed by the group of the present author.[3] In the solid solution system $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+\delta}$, it was found by the Hall effect measurement that the hole concentration can be controlled by changing x as if the hole concentration of 1-2-3 phase is compensated by the partial substitution of divalent Ba by trivalent Nd. It was suggested that there exists an almost linear relationship between T_c and the hole concentration controlled by this method.[3-5] In March, 1988, Tokura *et al.* reported an extensive investigation of T_c and the hole concentration by using a chemical method to determine the hole concentration in $Y(La, Ba)_2Cu_3O_y$ and $(Y, Ca)_1Ba_2Cu_3O_y$ and so on.[6] It is shown by J. Kondo *et al.* that these experimental findings are interpreted qualitatively by the Madelung energy of the systems.[7]

According to our result in $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+\delta}$, it was revealed that the hole concentration p_H determined from the Hall coefficient R_H (by $p_H = 1/R_He$) almost coincided with the mobile hole concentration determined by Tokura method from chemical analysis at least in the region of $p_H \leqq 0.2$. This result in YBCO-like systems is in contrast to the case of $La_{2-x}Sr_xCuO_4$, where p_H shows large deviation from the chemically determined hole concentration.[8]

In this paper, at first we describe new results on x-dependence of hole concentration and hole concentration dependence of T_c investigated in the samples of $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+x}$ i.e. $\delta = x$ in $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+\delta}$.[9] This series of samples has been obtained for the first time by the annealing in oxygen at high pressure up to more than 600 atm. An essential importance of this series of samples is that the samples are characterized by only one parameter x and the average charge of [Cu–O] unit or the total hole concentration of the system is not changed for all samples in spite of the change of the substitution for Ba site. In this series of samples, it is clearly demonstrated that the mobile hole concentration is determined by a charge transfer between CuO_2 sheet-layer and CuO_{1+x} chain-layer.

Secondly, we describe experimental results of the suppression of the superconductivity induced by Pr in YBCO-system. Analysis based on a detailed measurement of the Hall effect will be presented, which indicates the existence of the pair breaking effect of Pr in YBCO.[10,11]

§2. Charge Transfer Mechanism Studied in $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+x}$

2.1 *Experimental results*

As first proposed by Tokura *et al.*[6] the superconducting properties of YBCO-like systems can be described by a kind of phase diagram as shown in Fig. 1. The abscissa represents 3 times of an average charge of [Cu–O] i.e. the total hole concentration per unit cell, and the ordinate represents oxygen content $(7+\delta)$, which is deduced from the chemical titration, in $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+\delta}$. The broken line A represents samples of $NdBa_2Cu_3O_{7-\delta'}$ just like YBCO, where $7-\delta'$ is controlled by reduction from about 7 toward 6. The plotted points along the broken line B, represents the samples of $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+\delta'}$ which are sintered and furnace-cooled in 1 atm. oxygen flow. By the annealing in oxygen at high pressure (600 ~ 1000 atm.) at around 350°C, we have been able to get a series of samples $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+\delta}$ which are plotted along a vertical line of C. This means that the average charge for [Cu–O]-unit in these samples i.e. the total hole concentration are not changed in spite of the change in x. In other words, the change of oxygen contents δ equals to the amounts of the substitution x in this system, i.e. $\delta = x$. This series of samples plotted in Fig. 1 are expressed as $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{6.96+x}$. This means

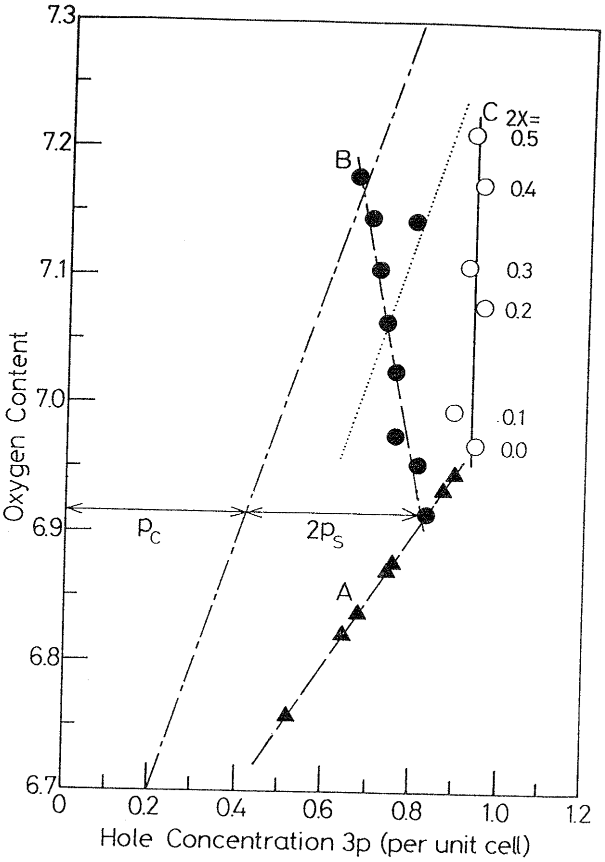

Fig. 1. Phase diagram of YBCO-like systems against the oxygen content ($7+\delta$) and the hole concentration. According to Tokura *et al.*,[6] hole concentration trapped on chain layer p_c and that of mobile hole on a CuO_2 sheet p_s (p_s is defined hole concentration per CuO_2 sheet-layer so mobile hole concentration per unit cell is $2p_s$) are given by the dot-dashed line as indicated. The broken line A represents the samples of oxygen-reduced $NdBa_2Cu_3O_{7-\delta'}$. The samples of $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+\delta'}$, sintered and furnace-cooled in 1 atm. oxygen flow, and annealed in oxygen at high pressure, are plotted around the broken line B and vertical line C, respectively. It should be noted that $\delta=x$ along the vertical line C as described in the text. The dotted line separates the superconducting and non-superconducting samples.

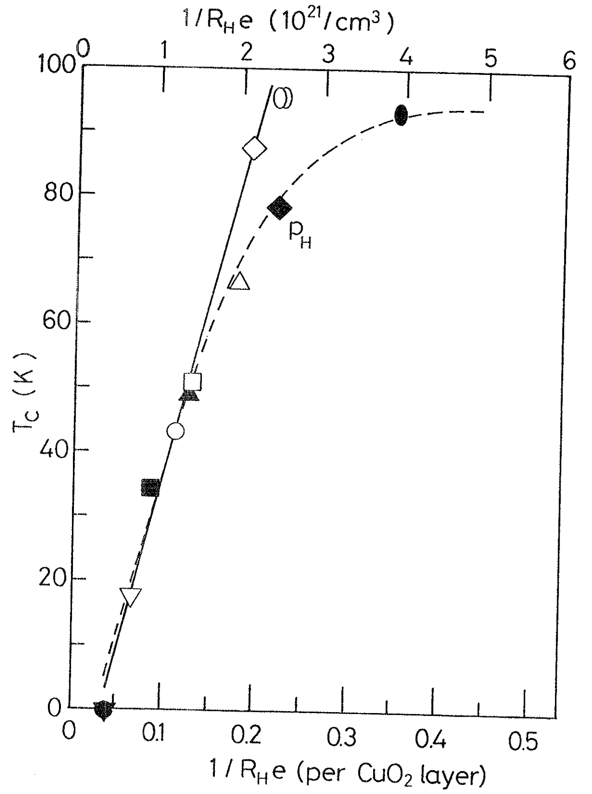

Fig. 2. T_c plotted against the effective hole concentration p_H ($=1/R_He$) at 100 K. Open symbols represent the result of $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+x}$ annealed in oxygen at high pressure. Closed symbols represent the result of $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+\delta}$ samples furnace-cooled in 1 atm. oxygen flow. $x=0.00$; (○): $x=0.05$; (◇): $x=0.10$; (△) $x=0.15$; (□): $x=0.20$; (○): $x=0.25$; (▽).

that we have obtained a series of samples which are expressed approximately as $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+x}$. In the former part of this section, the experimental results of the samples along the line C will be described in comparison with the samples along the line B.

In Fig. 2, T_c is plotted against the effective hole concentration p_H at 100 K. The dotted line in this figure shows our previous results for various systems sintered in 1 atm. pressure.[3-5] p_H at 100 K means substantially the hole concentration just above T_c. For the samples sintered under 1 atm., T_c shows almost linear dependence on p_H below 70 K but show a saturation above 80 K as shown by dotted curves. On the contrary, it has been found that the samples of $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+x}$ annealed under high pressure, T_c shows almost linear relationship with p_H up to 95 K as seen in Fig. 2.

In Fig. 3, the relation between T_c and the chemically determined hole concentration are shown by the plots for two kinds of samples: B series and C series in Fig. 1. According to an extrapolation of the assumption proposed by Tokura *et al.*,[6] hole concentration of a CuO_2 sheet-layer p_s is deduced from the average charge of [Cu-O]-unit p determined from a chemical titration. A relation of p_s and p is shown in the phase diagram of Fig. 1. As seen in Fig. 3. in spite of that T_c vs 3p relation is different for the samples which undergo different heat treatment, T_c vs p_s relation is almost the same. Furthermore, T_c vs p_s relation shows almost the same relation with T_c vs p_H in the case of the samples annealed under high pressure oxygen.

2.2 *Discussion on the charge transfer mechanism*

In the investigation in $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+\delta}$ systems, it is demonstrated that the effective hole concentration p_H deduced from Hall coefficient R_H gives almost same value to p_s which is a mobile hole concentration deduced from chemical analysis, suggesting that both method can give a real concentration of the mobile holes per CuO_2 sheet-layer in YBCO-system in the range of the present experiment. Furthermore, we have been able to make a series of samples where $\delta \simeq x$ by annealing in oxygen at high pressure. In this series of samples, it is clearly demonstrated that the mobile hole concentration changes with x, in spite of that the average charge of [Cu-O], i.e. the total hole concentration, is not changed.

Apart from a small deviation from the linear relation between hole concentration and x, which is mentioned in the previous section, the hole concentration of CuO_2 sheet decreases with increasing x in $Nd(Ba_{1-x}Nd_x)_2$

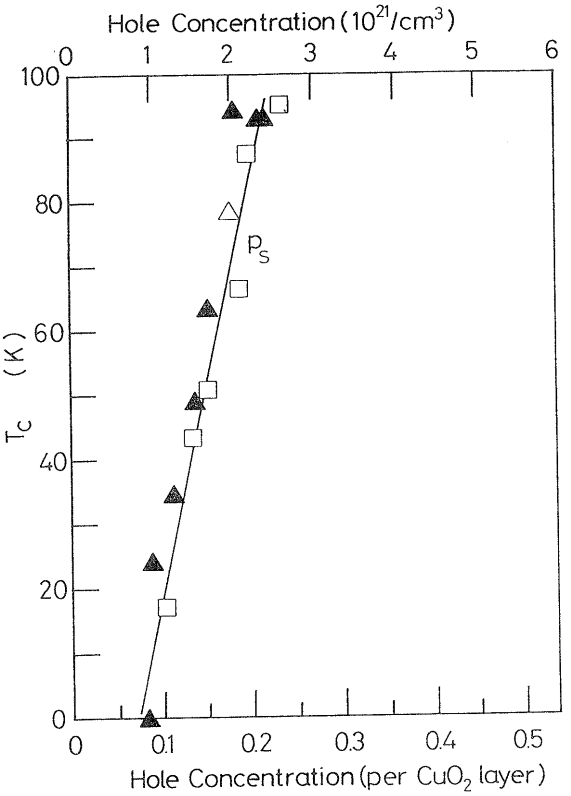

Fig. 3. T_c plotted against the chemically determined hole concentration of a CuO$_2$ sheet, p_s. Results are shown for two kinds of samples annealed under different condition. Open squares are for the samples annealed in oxygen at high pressure (line C in Fig. 1.). Closed triangles are for the samples furnace-cooled in 1 atm. oxygen flow (line B).

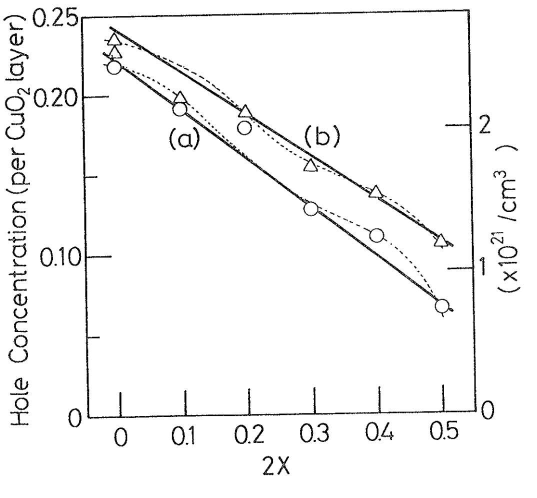

Fig. 4. x-dependence of hole concentration of CuO$_2$ sheet in Nd(Ba$_{1-x}$Nd$_x$)$_2$Cu$_3$O$_{7+x}$. Experimental results of p_s and p_H are plotted by △ and ○, respectively. Calculated results based on a simple charge transfer model are shown by dotted lines (a) is for $A_1=1.0B$, $A_2=2.1B$, $B_{11}=B_{12}=B_{22}=B$ and (b) is for $A_1=1.2B$, $A_2=1.8B$, $B_{11}=B_{12}=B_{22}=B$.

Cu$_3$O$_{7+x}$ as shown in Fig. 4. In the following, we will discuss about this relation based on a simple-minded model of charge transfer between CuO$_2$ sheet and CuO$_{1+x}$ chain-layer. As is well known, YBCO-structure consists of 6-layers as indicated in Fig. 5. We can assume that each layer has the average charge as indicated in Fig. 5, where ξ expresses the hole concentration of CuO$_2$ sheet. Taking into account the 2-dimensionality of the hole system, the hole of CuO$_2$ would have a band energy E_B

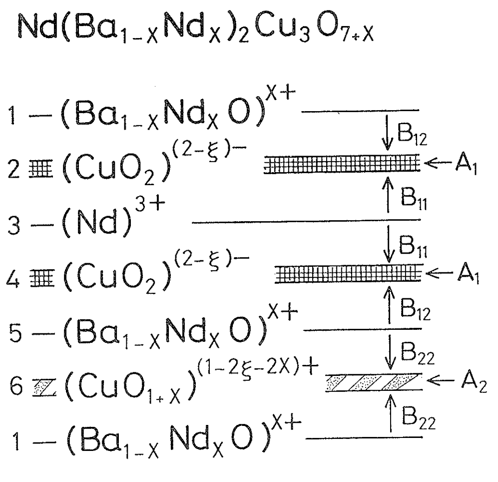

Fig. 5. Layer structure of Nd(Ba$_{1-x}$Nd$_x$)$_2$Cu$_3$O$_{7+x}$. Average charge of each layer is indicated. Meaning of the interaction coefficients, A_1, A_2 and B_{ij}, are shown schematically.

$$E_B=\frac{\pi\hbar^2}{2m^*}\xi^2, \tag{1}$$

where m^* is the effective mass of the hole. The band energy associated with other layers should be negligible. We consider the change of the electrostatic energy caused by the charge transfer between CuO$_2$ and CuO$_{1+x}$ layer, i.e. caused by the change of ξ. In Fig. 5, the constituents of each layer and the average charge of the layers are indicated. For example, the CuO$_2$ layer has the average charge of $-(2-\xi)$. The electrostatic energy in this layer would be expressed approximately in the form of $(A_1/2)(2-\xi)^2$ in the analogy with the case that the layer consists of the CuO$_2$-molecules. Similarly, the electrostatic energy associated with CuO$_{1+x}$ layer would be as $(A_2/2)(1-2\xi-2x)^2$. We take into account further the electrostatic interaction with the nearest neighbor layers of CuO$_2$ and CuO$_{1+x}$ layers. Using the coefficients B_{ij} of these interactions defined as indicated in Fig. 5, the electrostatic energy associated with holes of CuO$_2$, E_{el}, would be expressed as:

$$E_{el}=\frac{A_1}{2}(2-\xi)^2-3B_{11}(2-\xi)-B_{12}x(2-\xi), \tag{2}$$

where B_{11} and B_{12} are the interaction coefficient which express the effects of the charges of Nd and (Ba$_{1-x}$Nd$_x$)$_2$-layers on the hole of CuO$_2$. The electrostatic energy associated with the holes of CuO$_{1+x}$, E_{e2}, is expressed similarly as:

$$E_{e2}=\frac{A_2}{2}(1-2\xi-2x)^2+2B_{22}x(1-2\xi-2x), \tag{3}$$

where it is noted that $(1-2\xi)$ is the hole concentration of CuO$_{1+x}$. As there are two CuO$_2$ sheets and one CuO$_{1+x}$ chain-layer, the total energy per unit cell U_{tot} would be expressed as:

$$U_{\text{tot}}=2E_{\text{B}}+2E_{\text{el}}+E_{\text{e2}}. \tag{4}$$

Minimum energy condition, $\partial U_{\text{tot}}/\partial\xi=0$, gives a relation as follows:

$$\begin{aligned}\xi&=\left(\frac{\pi\hbar^2}{2m^*}+\frac{A_1}{2}+A_2\right)^{-1}\left\{\left(A_1+\frac{A_2}{2}-\frac{3}{2}B_{11}\right)\right.\\&\quad\left.-\left(A_2+\frac{B_{12}}{2}-B_{22}\right)x\right\}\\&\equiv\alpha-\beta x.\end{aligned} \tag{5}$$

This means that the x-dependence of the hole concentration ξ of CuO_2 sheet is expressed simply by eq. (5). If we assume further that the band energy is negligible compared to the electrostatic energy and $B_{11}=B_{12}=B_{22}\equiv B$, we obtain

$$A_1=\frac{5+2\alpha-6\beta}{4-2\alpha-3\beta}B, \tag{6}$$

and

$$A_2=\frac{2-\alpha+3\beta}{4-2\alpha-3\beta}B. \tag{7}$$

If we insert $\alpha=0.24$ and $\beta=0.54$ which are obtained experimentally from the chemical analysis, eq. (6) and (7) indicate that $A_1\simeq 1.2B$ and $A_2\simeq 1.8B$. If we insert $\alpha=0.22$ and $\beta=0.62$ which are from the Hall measurement, the equations give $A_1\simeq 1.0B$ and $A_2\simeq 2.1B$. In Fig. 4, examples of the calculated x-dependences based on this simple model are shown comparing with the experimental results. As is shown there, the experimental results of the x-dependences of the hole concentration of CuO_2 are reproduced well by the simple model using a set of reasonable values of the parameters. Thus it is clearly demonstrated by the present experiment that the mobile hole concentration in this system is determined by charge transfer between CuO_2 sheet-layer and CuO_{1+x} chain-layer. The charge transfer model in YBCO-like system has been proposed through experiments by Tokura *et al.*[6] and theoretical calculation by Kondo *et al.*[7] It is shown by the present experiment that this model is valid even in the region of large positive x ($x>0$ in CuO_{1+x}), where the transfer mechanism is rather simple because the ordering of the oxygen in CuO_{1+x}-chain layer is not expected.

In Fig. 6, we summarize schematically the data of the relation between T_c and the mobile hole concentration. The p_s-dependence of T_c in $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+x}$ was almost linear up to the highest T_c of about 95 K as is shown in Fig. 6(a). The relation obtained in the system including Ca deviates from the linear relation, showing a saturation value of $T_c\simeq 80$ K and decrease in higher p_s region. The difference of the maximum T_c in Ca-free system and the Ca-substituted system may suggest the difference of the amount of pair breaking effect between these systems. Similar relations investigated in Ca-substituted system are reported also by Tokura *et al.*[6] and Penney *et al.*[12]

In Fig. 6(b), p_H-dependences of T_c is schematically summarized for different kinds of samples, where p_H means the mobile hole concentration derived from the Hall coefficient R_H (at 100 K) using the relation $p_H=1/R_He$. In the case of the samples of $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+x}$ system, p_H at 100 K almost coincides with p_s. In the case of $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+\delta}$, p_H-dependence shows a deviation from p_s-dependence of T_c. The deviation is enlarged in the region of higher hole concentration as observed in $(Nd_{0.8}Ca_{0.2})(Ba_{0.99}Ca_{0.01})_2Cu_3O_{7-\delta}$.

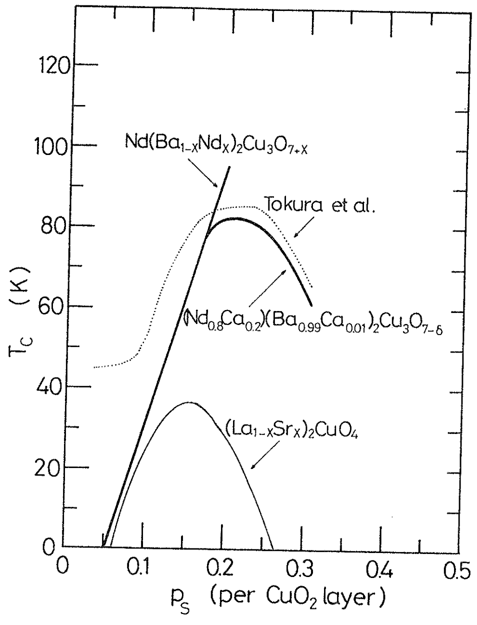

Fig. 6. (a) A relation between T_c and the mobile hole concentration p_s obtained in the present experiment is shown by thick solid lines and compared with $(La_{1-x}Sr_x)_2CuO_4$[8] and YBCO-system by Tokura *et al.*[6] An almost linear dependence up to T_c=95 K was observed for $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+x}$ and also for $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+\delta}$. For $(Nd_{0.8}Ca_{0.2})(Ba_{0.99}Ca_{0.01})_2Cu_3O_{7-\delta}$, however, the curve saturates and shows a decrease in higher p_s regions.

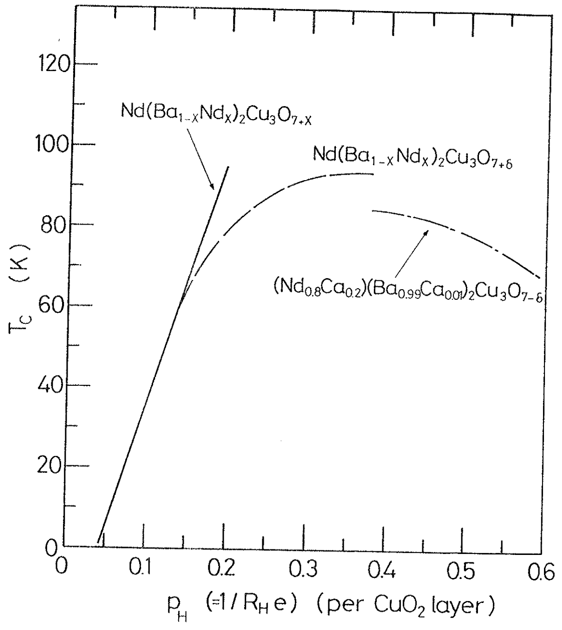

Fig. 6. (b) A relation between T_c and p_H obtained from Hall effect measurement is shown for different kinds of samples. $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+x}$ and $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7+\delta}$ are the samples annealed in high pressure oxygen and 1 atm. oxygen, respectively. The curve denoted by $(Nd_{0.8}Ca_{0.2})(Ba_{0.99}Ca_{0.01})_2Cu_3O_{7-\delta}$ was obtained using the samples with same metal composition and different oxygen content.

§3. Hole Filling and Pair Breaking Effects of Pr

It is currently of great interest to find out the mechanism of the suppression of superconductivity in the cuprate oxide with the YBCO-structure due to substitution of Pr for the Y-site, because it would help to understand the high-T_c superconductivity. Several reasons has been proposed so far for the suppression of superconductivity by a Pr ion in the YBCO-structure, i.e. hole filling effect,[13,14] pair breaking effect via exchange scatterings of the mobile holes by the Pr-magnetic moment,[14,15] a structural asymmetry of the CuO$_2$ planes increased by the substitution of Pr for the Y-site,[16] and hybridization between Pr-4f and O-2p orbitals which may transform the itinerant holes into small polarons,[17] and so on. In order to obtain a better understanding about the origin of the suppression of superconductivity by Pr, electrical properties are extensively investigated in the present work using several new systems including (Nd$_{1-x}$Pr$_x$)(Ba$_{1.9}$Nd$_{0.1}$)Cu$_3$O$_{7-\delta}$ and Pr$_x$Ca$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$.[11]

By the measurement of resistivity and the Hall coefficient R_H in these systems, we obtained experimentally a relation of T_c with two parameters of p_H $(=1/R_He)$ and Pr-contents. It should be emphasized that we have been able to prepare several pairs of samples whose R_H and temperature dependence are very similar each other in spite of the different Pr-contents.

The samples were prepared by solid state reaction. In (Nd$_{1-x}$Pr$_x$)(Ba$_{1.9}$Nd$_{0.1}$)Cu$_3$O$_{7-\delta}$ system, T_c decreased with increasing Pr-content and the superconductivity disappeared for x more than 0.35. Pr$_x$Ca$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$ system did not show superconductivity for $(1-x)$ less than 0.3.[11] The Hall coefficient R_H was measured in order to obtain the mobile hole concentration p_H $(=1/R_He)$ which relates with T_c. The value of p_H is decreased and its temperature dependence is also decreased systematically with increase in the Pr content.

Figure 7 shows a comparison of the temperature dependence of the mobile hole concentration p_H $(=1/R_He)$ between two systems of (Nd$_{1-x}$Pr$_x$)(Ba$_{1.9}$Nd$_{0.1}$)Cu$_3$O$_{7-\delta}$ and Pr$_x$Ca$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$. As seen here, we have prepared the samples whose p_H and its temperature dependence are very similar each other in spite of the difference of Pr-content. For example, Pr$_{0.7}$Ca$_{0.3}$Ba$_2$Cu$_3$O$_{7-\delta}$ shows similar temperature dependence of p_H to that for the Pr$_{0.1}$Nd$_{0.9}$(Ba$_{1.9}$Nd$_{0.1}$)Cu$_3$O$_{7-\delta}$ as seen Fig. 7. It should be emphasized here that the former sample with large Pr contents did not show superconductivity while the latter sample with small Pr-contents showed superconductivity at rather high temperature of 64 K in spite of the resemblance of the temperature dependence of p_H. Similar contrast is more clear for the pair of Pr$_{0.8}$Ca$_{0.2}$Ba$_2$Cu$_3$O$_{7-\delta}$ and Pr$_{0.3}$Nd$_{0.7}$(Ba$_{1.9}$Nd$_{0.1}$)Cu$_3$O$_{7-\delta}$. This fact strongly suggests that there are two distinct effects of Pr for the suppression of superconductivity: reduction of mobile hole concentration through hole filling or hole localization in CuO$_2$ plane, and pair breaking effect through strong magnetic or non-magnetic scattering.

Based on the R_H measurements for various systems, a kind of a phase diagram is shown for p_H $(=1/R_He)$ and Pr-contents in Fig. 8, using R_H at 100 K. Open symbols and closed symbols denote the superconducting and the non-superconducting samples, respectively. Half-open symbols denote the samples which do not show zero resistivity above 4 K in spite of a trace of superconducting transition. This diagram clearly shows that the boundary between superconducting and non-superconducting samples, denoted by line (b), is not independent of Pr-contents. This indicates the existence of the pair-breaking. If we assume that there is a magnetic pair-breaking effects by Pr and it is expressed by Abrikosov and Gor'kov expression,[18] we can estimate the value of the pair breaking parameter B as 50 K/Pr. This is less than

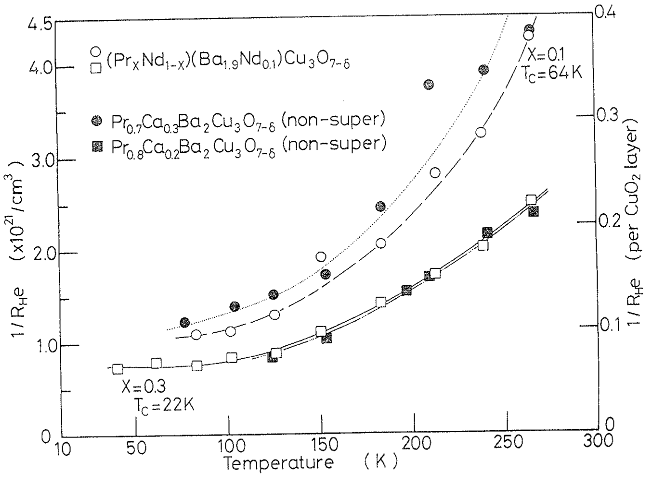

Fig. 7. Temperature dependence of the effective hole concentration p_H for pairs of samples with different Pr-contents.

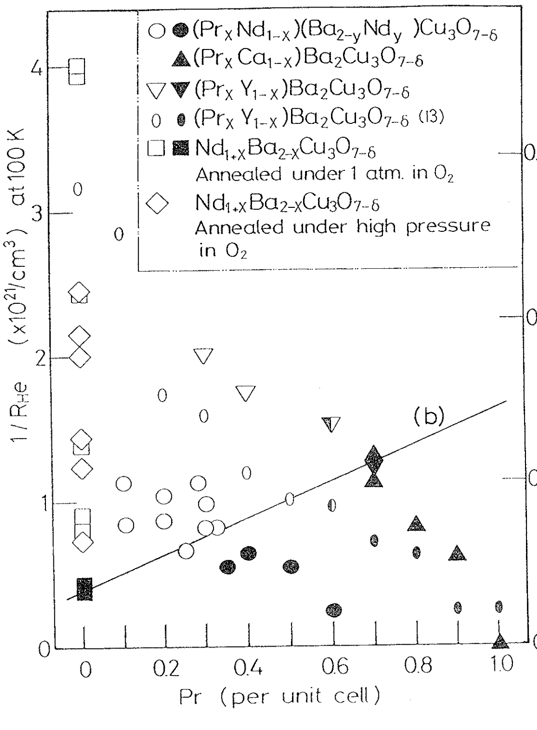

Fig. 8. Plots of the experimental points in Pr-p_H plane, where $p_H=1/R_He$ at 100 K. The straight line (b) separates the superconducting and non-superconducting samples.

half of the reported value14) but the pair breaking effect is clearly observable. It should be pointed out, however, that in the region of low Pr-content less than about 0.3, the plotted points suggest a smaller slope of the boundary (b). This may suggest some complex effect of Pr in these system and a more detailed experiment using single crystals is now in progress.

Acknowledgements

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References

1) Z. Z. Wang, J. Clayhold, N. P. Ong, J. M. Tarascon, L. H. Greene, W. R. McKinnon and G. W. Hull: Phys. Rev. **B36** (1987) 7222.
2) H. Takagi, S. Uchida, H. Iwabuchi, S. Tajima and S. Tanaka: in *Superconducting Materials*, ed. S. Nakajima and H. Fukuyama, (Jpn. J. Appl. Phys. series 1, 1988) p. 6.
3) K. Takita, H. Akinaga, H. Katoh, H. Asano and K. Masuda: Jpn. J. Appl. Phys. **27** (1988) L67.
4) H. Akinaga, H. Katoh, K. Takita, H. Asano and K. Masuda: Jpn. J. Appl. Phys. **27** (1988) L610.
5) K. Takita, H. Akinaga, H. Katoh and K. Masuda: Jpn. J. Appl. Phys. **27** (1988) L1676.
6) Y. Tokura, J. B. Torrance, T. C. Huang and A. I. Nazzal: Phys. Rev. **B38** (1988) 7156.
7) J. Kondo, Y. Asai and S. Nagai: J. Phys. Soc. Jpn. **57** (1988) 4334.
8) H. Takagi, T. Ido, S. Ishibashi, M. Uota, S. Uchida and Y. Tokura: Phys. Rev. **B40** (1989) 2254.
9) K. Takita, H. Akinaga, T. Ohshima, Y. Takeda and M. Takano: Physica C. (in press)
10) K. Takita and T. Ohshima: *Physica C in press* (Proceedings of M^2 S-HTSC III in Kanazawa JAPAN).
11) K. Takita and T. Ohshima: Physica **B165 & 166** (1990) 1547.
12) T. Penney, M. W. Shafer and B. L. Olson: Physica **C162–164** (1989) 63.
13) A. Matsuda, K. Kinoshita, T. Ishii, H. Shibata, T. Watanabe and T. Yamada: Phys. Rev. **B38** (1988) 2910.
14) J. J. Neumeier, T. Bjornholm, M. B. Maple and I. K. Schuller: Phys. Rev. Lett. **63** (1989) 2516.
15) J. L. Peng, P. Klavins, R. N. Shelton, H. B. Radousky, P. A. Hahn and L. Bernardez: Phys. Rev. **B40** (1989) 4517.
16) K. Kinoshita, A. Matsuda, H. Shibata, T. Watanabe and T. Yamada: Jpn. J. Appl. Phys. **27** (1988) L1642.
17) X. X. Tang, A. Manthiram and J. B. Goodenough: Physica **C161** (1989) 574.
18) A. A. Abrikosov and L. P. Gor'kov: Sov. Phys. JETP **12** (1961) 1243.