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# OXYGEN DEFICIENCY $\delta$ AND ITS EFFECT ON $T_c$ IN SUPERCONDUCTING $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$

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**Abstract.** —  $Y^{3+}$  ion is substituted with  $Ca^{2+}$  ion in  $Y_{1-x}Ba_xCu_3O_{7-\delta}$ , where the ionic radii of both ions are almost the same. The substitution does not change the average valence of Cu ion, but the amount of oxygen deficiency  $\delta$  increases linearly with  $x$  up to  $x = 0.15$ . Crystal structure, critical temperature  $T_c$ , magnetization,  $\delta$ , electrical resistivity, and Hall effect were measured for the Ca system, and an abrupt increase in Hall mobility  $\mu$  was observed at  $\delta = 0.56$  corresponding to the sharp change of  $\delta$  there.

## Introduction

In an attempt to explain the physical mechanism of the high  $T_c$  in  $YBa_2Cu_3O_{7-\delta}$  (YBCO), an  $Y^{3+}$  ion is substituted with a  $Ca^{2+}$  ion, where the ionic radius of  $Y^{3+}$  is almost the same as that of  $Ca^{2+}$  ( $Y^{3+} = 1.019 \text{ \AA}$ ,  $Ca^{2+} = 1.120 \text{ \AA}$ ) [1]. The changes of the valence of Cu ion and the amount of oxygen deficiency  $\delta$  were examined. There have been many investigations on the possible electrical conduction paths in  $Y_{1-x}Ba_xCu_3O_{7-\delta}$  by changing the constituent ions, and an understanding that the layer of  $CuO_2$  (O4 or O5 site) in this structure may be responsible for the electrical conduction is becoming acceptable, but it has not been still recognized as concluding. There was proposed another possibility of the BaO layer (O3 site) that has positive holes for the conduction, or that of maximum  $T_c$  at the maximum carrier number [2, 3].

In this paper, the effect of  $Ca^{2+}$  substitution into  $Y^{3+}$  site will be described to examine the change of the valence of Cu or that of the amount of deficiency  $\delta$ .

## Experimental results and discussion

All the specimens were made by mixing the starting materials of  $Y_2O_3$ ,  $BaCO_3$ ,  $CuO$ , and  $CaCO_3$ , firing at  $800^\circ\text{C}$  for 3 hours in air, and furnace-cooling. After that, they were heated at  $900^\circ\text{C}$  for 5 hours in air, and furnace-cooled. The content  $x$  of Ca was chosen as 0, 0.05, 0.10, 0.15 and 0.20. It is confirmed by X-ray diffraction that the crystal structure is of the oxygen-deficient three-layered orthorhombic perovskite the same as the starting composition of YBCO, and that only  $a$ -axis increases with  $x$  above 0.15. The amount of oxygen of the system is measured by an iodometry, and the deficiency  $\delta$  was determined for the system. In figure 1,  $T_c$  (midpoint) is shown as the function of  $\delta$ . The solid curve is the present result for the Ca-substitution system, and the dotted one is for the YBCO system [4]. In the former curve, its  $T_c$  is higher than the latter for the same value of  $\delta$ . It means that the substituted  $Ca^{2+}$  releases the  $O^{2-}$  on the O3 layer. In figure 2, the oxygen content ( $7 - \delta$ ) of the system as determined by the iodometry is plotted against  $x$ , and the average valence of Cu ions as de-

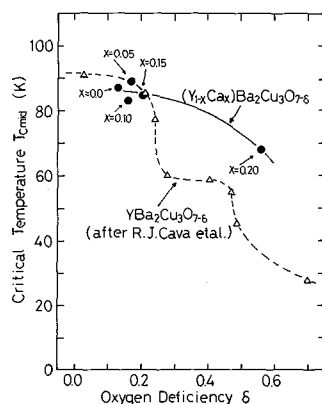


Fig. 1. — Critical temperature of  $T_{mid}$  against oxygen deficiency  $\delta$  for the systems  $(Y_{1-x}Ca_x)Ba_2Cu_3O_{7-\delta}$  and  $YBa_2Cu_3O_{7-\delta}$  (Ref. [3]).

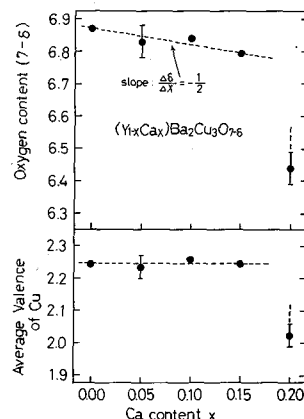


Fig. 2. — Oxygen content ( $7 - \delta$ ) and average valence of Cu ions against  $x$ .

terminated from the measured amount of  $(7 - \delta)$ . The slope of the former against  $x$ ,  $\Delta\delta/\Delta x$  is equal to  $-1/2$ : it means that the substitution of a  $Y^{3+}$  ion with  $Ca^{2+}$  ion is compensated electrically with one half of  $O^{2-}$  ion, and this straight line lasts up to about 0.15 of  $x$ . Above this amount of  $x$ ,  $(7 - \delta)$  and the average valence of Cu ion decrease very sharply against  $x$ , and it shows that there is a critical value of  $x$  to hold the system superconducting in a rather high temperature region. It tells us that the vacancy of oxygen is made on O4 or O5 site continuously between 0 and 0.15 and  $x$ , and above that values of  $x$ , the oxygen vacancy is made on another site (O3 or O1 site). This fact may be related to clarifying the superconducting path in YBCO system. In figure 3 are shown both Hall coefficient  $R_H$

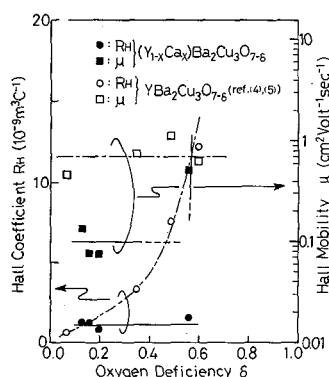


Fig. 3. - Hall coefficient  $R_H$  and Hall mobility  $\mu$  against  $\delta$ .

and Hall mobility  $\mu$  against  $\delta$ .  $R_H$  is always positive in these system. For the YBCO system after Uchida *et al.*, Ong *et al.*, and Takagi *et al.* [4, 5],  $R_H$  increases against  $\delta$ , and  $\mu$  is almost constant. For the present Ca system,  $R_H$  seems almost constant, too, but as for the  $\mu$ , it increases abruptly at 0.56 of  $\delta$ , and it suggests us that  $\mu$  changes according to its change on different sites.

## Conclusion

By the substitution of  $Y^{3+}$  with  $Ca^{2+}$ , there is produced the vacancy of  $O^{2-}$  in the layer of  $CuO_2$ , and it compensates the unbalance of electrical charge. The substitution does not change the average valence of copper ion. Such tendency lasts up to less than 0.15 of  $x$  of Ca content. At about 0.2 of  $x$ , the oxygen content  $(7 - \delta)$  and the average valence of copper decrease abruptly with  $x$ . This shows that the oxygen vacancy does not increase in  $CuO_2$  layer more than 0.2 (including the first stage vacancy in the layer of  $CuO_{1-\delta}$ ), but it seems to be made discontinuously in the further layer ( $BaO$  or  $CuO_{1-\delta}$ ). It corresponds to the sharp increase in the Hall mobility  $\mu$  with  $\delta$  of the present system (Fig. 3), contrary to the constant values of  $\mu$  in the YBCO system in spite of the increase in  $R_H$  in the same system. The substitution of  $Ca^{2+}$  does not seem to change the initial number of positive holes in  $CuO_{1-\delta}$  layer in the pure YBCO system as revealed in the Hall effect experiment (Fig. 3).

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- [1] Shannon, R. D., *Acta Crystallogr. A* **32** (1976) 751.
- [2] Takayama-Muromachi, E., Uchida, Y., Fujimori, A. and Kato, K., *Jpn J. Appl. Phys.* **26** (1987) L1546.
- [3] Uwe, H., Sakudo, T., Hajime, A., Han, T., Yagi, K., Harada, R., Iha, M. and Yokoyama, Y., *Jpn J. Appl. Phys.* **27** (1987) L577.
- [4] Eds. K. Fueki and K. Kitazawa, *Chemistry of Oxide Superconductors* (in Japanese), Kodansha, Tokyo (1988) p. 78.
- [5] *Ibid.*, p. 14.