The change of anisotropy by Zn or Ca substitution in YBCO single crystals

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Abstract. Zn and Ca substitution effects in YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals are presented, focusing on the anisotropy in overdoped regime. Overdoping by Ca substitution lowers the pseudogap temperature $T^*$, and $T^*$ vanishes for heavily overdoped samples. The effect of oxygen deficiency by Ca-substitution is negligible. Zn substitution effect on residual part of $c$-axis resistivity is hardly observed, which is in contrast to the steady increase for in-plane resistivities.

1. Introduction
Among various electronic properties of high-$T_c$ cuprate superconductors (HTSC), the anisotropy of resistivity typically indicates the anomalous electronic state. Low-temperature upturn of $c$-axis resistivity in underdoped regime reflects the opening of pseudogap around $(\pi,0)$ portion of Fermi surface[1]. On the other, above the pseudogap temperature $T^*$, Fermi surface fully retains its surface, and the electronic properties are expected rather normal. However it may be necessary to check how much the electronic state is 'normal' above $T^*$. For this purpose overdoped region is suitable, since $T^*$ decreases with increasing carrier concentration.

In this study we pick up the effect of Zn or Ca substitution in YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) on the anisotropy in normal state, focusing on the overdoped regime. In superconducting state, several reports indicate that anisotropy decreases by Zn substitution, mainly due to the modification along $c$-axis direction[2, 3, 4, 5]. It is interesting whether some corresponding changes is seen above $T_c$. In considering the effect of Zn substitution, we may have two different points of view. One is that Zn is strong scatterer for conduction carriers. Zn substitution normally enhances impurity scattering in in-plane conduction[6]. In a three dimensional system a similar effect should be observed in $c$-axis resistivity. The other is Zn substitution locally modulates the electronic state, and hence suppresses the pseudogap around the substitution site [7]. This may lead to a drastic modification of the electronic conduction along $c$-axis direction.

So far, Ca substitution effect has been studied in polycrystalline samples, assuming that the effect is mainly hole doping and the other effect is negligible. However it is known that there are accompanying effect: the increase of oxygen deficiency and decrease of maximum $T_c$. In order to check the effect of Ca-substitution on the electronic properties, it is preferable to observe the transport properties of Ca-substituted YBCO ((Y,Ca)BCO) single crystals. The $c$-axis resistivity of (Y,Ca)BCO also shows the degree of contribution of CuO chain electronic state to the $c$-axis conduction.
2. Experimental

YBCO single crystals were grown by a crystal pulling method. The Zn and Ca contents were estimated from inductively coupled plasma analysis. The samples were cut into pieces with rectangular shape and annealed in flowing oxygen. Several pieces of Ca substituted crystals were detwinned for in-plane measurement under uniaxial pressure. Zn-substituted samples were not detwinned. Resistivity was measured by standard four-probe method for both in-plane and c-axis resistivities. The samples we treated are thick enough to make contact for measuring resistivity in a standard way. It is worth noting that out-of-plane resistivities ($\rho_c$) for HTSC are usually hard to measure by four-probe method. The carrier concentration was estimated from the empirical relation $T_c/T_c(max) = 1 - 82.6(p - 0.16)^2$ [8]. The oxygen deficiency $\delta$ for Ca-substituted samples were estimated according to reference [9]. The Ca content in this study is 12 or 14 percent per Yttrium.

![Figure 1. In-plane resistivities along the a-axis $\rho_a$ of (Y,Ca)BCO single crystals.](image1)

![Figure 2. c-axis resistivities $\rho_c$ of (Y,Ca)BCO single crystals.](image2)

3. Results and discussion

Figure 1 shows $a$-axis resistivity of (Y,Ca)BCO single crystals. Systematic change is seen in the temperature dependence from convex curvature showing the appearance of pseudogap in slightly underdoped region to concave curvature in overdoped region. The pseudogap temperature $T^*$, below which the temperature dependence changes from $T$-linear to convex curvature, decreases with increasing carrier concentration, and above approximately $p > 0.18$ the signature of pseudogap dissapears. For further overdoped samples concave temperature dependence appears. The concave curvature of resistivity is one of the proofs that the electronic state of the present samples are well overdoped. Here we classifies the resistivities according to the hole concentration, irrespective of Ca content. The systematic change ensures that Ca substitution does not increases impurity scattering.

Corresponding to the change of in-plane resistivity, the out-of-plane resistivity also changes, as seen in figure 2. With increasing hole concentration, the low-temperature upturn, which is another signature of pseudogap, is weakened. In other words, the temperature where upturn of resistivity starts becomes lower. For $p$ higher than 0.18, the low temperature upturn vanishes above $T_c$. It is worth noting that the behavior is not so much affected by oxygen deficiency in CuO chains, which has been considered to contribute largely to the out-of-plane conduction in YBCO. For example, whereas the oxygen deficiency $\delta=0.207$ gives a slightly underdoped samples
for Ca-free YBCO, the sample with \((p, \delta) = (0.185, 0.207)\) is well overdoped. We have confirmed it in the Raman spectra for heavily overdoped Ca$_{0.12}$Y$_{0.88}$Ba$_2$Cu$_3$O$_y$ with \(T_c = 65\) K[10]. It is rather surprising that the \(\rho_c\) of (Y,Ca)BCO shows almost the same absolute value as \(\rho_c\) for the pure YBCO with the same carrier \(p\), as will be seen in figure 5. The metallic temperature dependence in figure 2 indicates that the \(c\)-axis conduction is dominated by the electronic state of the CuO$_2$-plane but less affected by oxygen deficiencies in the CuO chains in this doping regime.

![Figure 3](image.png) In-plane resistivities \(\rho_{ab}\) of Zn-substituted YBCO with \(p=0.182\).

![Figure 4](image.png) \(c\)-axis resistivities \(\rho_c\) of Zn-substituted YBCO with \(p=0.182\).

![Figure 5](image.png) The absolute values of \(\rho_{ab}\) (○) and \(\rho_c\) (◇) of Zn-substituted YBCO single crystals with \(p=0.182\) at 273 K. For comparison, the \(\rho_c\) value of Ca-substituted sample in figure 2 is also plotted (■). Lines are guides for the eyes.

In-plane and \(c\)-axis resistivities of Zn substituted samples with \(p=0.182\) are plotted in figure 3 and 4, respectively. Increase of residual scattering is obvious in \(\rho_{ab}\). On the other hand, the absolute values of \(\rho_c\) are almost the same as Zn-free sample. This is probably related to the difference of the conduction mechanism. In figure 5, the absolute values of resistivities at 273
K are summarized. Although a width is seen in the determination of absolute values, we may say that Zn substitution does not increase residual part of c-axis resistivity. Similar tendency for residual part of resistivity was observed in the other series of samples with different oxygen deficiencies. This can be considered as an evidence for incoherent charge transport along the c-axis.

It is of great interest to compare the anisotropy ratio above and below $T_c$. In the normal state, the anisotropy of (Y,Ca)BCO decreases with increasing $p$. In a well-overdoped sample with $p=0.185$, the anisotropy ratio $\gamma=(\rho_c/\rho_a)^{0.5}$ reaches to 5~6. On the other hand, if $\gamma$ is estimated from the anisotropy of upper critical field, the estimated $\gamma$ is about 3, which almost corresponds to a band calculation value [11]. The deviation of $\gamma$ above and below $T_c$ is probably related to the difference of conduction mechanism.

Next we compare Zn substitution effects on $\gamma$ above and below $T_c$. In superconducting state $\gamma$ decreases mainly due to the increase of interplane coupling along the c-axis [2, 3, 4, 5]. On the other hand, if $\gamma$ is estimated from $\rho_c$ due to incoherent transport along c-axis. Such a normal state picture reconcile with the picture below $T_c$ where josephson coupling plays an important role in the c-axis supercurrent. Here Zn substitution sites may largely enhance interplane coupling due to quasiparticles around them.

In summary, we have presented Ca and Zn substitution effects on the resistivities in overdoped YBCO, focusing on the c-axis resistivities and the modification of anisotropy ratio $\gamma$. Although the mechanisms are quite different, both substitution decrease anisotropy. To explain the deviation of the estimate $\gamma$ in normal state from that of superconducting state, incoherent transport along c-axis may be necessary.

3.1. Acknowledgments

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