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Composition dependence of the pressure effect on T_c in $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$

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The effect of pressure on the superconducting transition temperature T_c of $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ is investigated for oxygen contents z from $z=6.43$ to $z=6.78$. The pressure derivative dT_c/dP shows decreasing positive values for the hole-concentration region where T_c increases with the hole concentration in the CuO_2 plane, p_{pl}, and negative constant values for the region where T_c decreases with p_{pl}. The sign and magnitude of dT_c/dP may be determined by not only the carrier type but also pressure-induced enhancements of both the hole concentration and intraplane coupling in the CuO_2 plane.

I. INTRODUCTION

$YBa_2Cu_3O_{7-\delta}$ (1:2:3), a hole-doped superconductor, with a superconducting transition temperature T_c above 90 K, has a perovskite-based structure with oxygen deficiencies. There include two Cu sites: Cu(1) forming one-dimensional CuO chains, and Cu(2) forming two-dimensional CuO_2 planes. The oxygen stoichiometry dramatically affects the physical properties including T_c: When the oxygen deficiency δ increases from 0 to 1, T_c decreases from 90 to 0 K. In the diagram of T_c versus the oxygen deficiency δ, two plateaus on T_c are observed near 90 K for $0 \leq \delta \leq 0.2$ and 60 K for $0.3 \leq \delta \leq 0.5$. Tokura and co-workers[1] have demonstrated that the hole concentration in the CuO_2 plane p_{pl} is a predominant factor in determining T_c and the CuO chains merely work as insulating hole reservoirs in the 1:2:3 system. However, unlike the case of $(La_{1-x}Sr_x)_2CuO_4$ (2:1:4),[2] it was difficult to obtain 1:2:3 samples with higher hole concentrations which result in a T_c decreasing region beyond the maximum T_c, because, for example, a simple Ca^{2+} doping for Y^{3+} easily removes the oxygens in the chain site due to charge compensation.[1,3,4] Recently, we prepared sintered samples of $(YB_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ with various hole concentrations, and confirmed that T_c of the 1:2:3 system decreased in the higher hole-concentration region beyond the optimum,[5] similar to the 2:1:4 system.[2]

A number of experiments[6-20] on the pressure dependence of T_c have been performed for both the hole-doped and the electron-doped superconductors. Below a hydrostatic pressure of 2 GPa, the electron-doped superconductors indicate negative or zero-pressure coefficients,[6,7] while, in the hole-doped superconductors, T_c generally increases as the pressure is increased,[6,8-16] except for $Tl_2Ba_2CuO_z$.[19,20] The pressure effect, dT_c/dP, in the 1:2:3 compounds is strongly dependent on the oxygen deficiency:[10,15,16] A large pressure coeffficient of 4–9 K/GPa has been reported for the 1:2:3 sample with $T_c \leq 60$ K and a small coefficient of 0–1 K/GPa for that with T_c around 90 K. However, the pressure dependence of T_c for the 1:2:3 samples with higher hole concentrations in the region where T_c decreases with p_{pl} has not been reported so far. This type of measurement has been made only in the $(La_{1-x}Sr_x)_2CuO_4$ system by a few groups.[8,9] Tanahashi *et al.*[8] have demonstrated that, at a very low Sr doping level, the dT_c/dP decreases with Sr doping and beyond a minimum, dT_c/dP increases with Sr content. Schirber *et al.*,[9] on the other hand, reported that the dT_c/dP for $x<0.15$ increases with Sr but that for $x>0.15$ decreases with Sr. These two results clearly conflict with each other.

In this paper, we report on the study of the pressure dependence up to 2 GPa of the superconducting transition temperature for a series of $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_x$ samples with different oxygen contents z. We clearly show that the pressure coefficient is positive in the hole-concentration region where T_c increases with hole concentration, while it is negative in the region where T_c decreases with hole content. Unlike the general trend previously reported for hole-doped[6,9] and electron-doped[6,7] superconductors, the results provide a clear view, i.e., the sign of dT_c/dP depends not only on the carrier type but on the carrier concentration in the CuO_2 plane. We also discuss the hole-concentration dependence of dT_c/dP, taking into account pressure-induced structural changes.

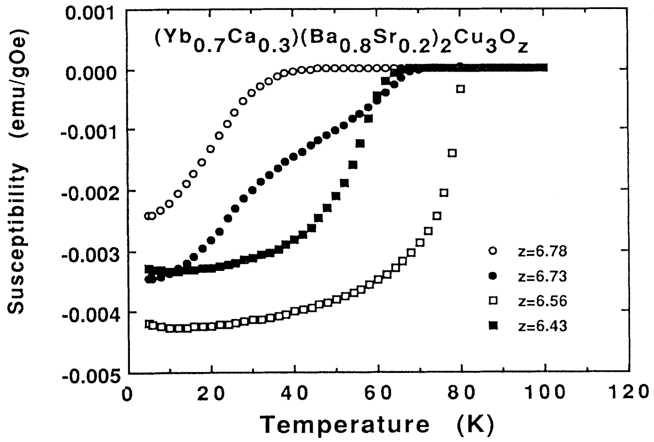

FIG. 1. Temperature dependence of the field-cooled magnetization for the samples of $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$. The measurement was performed in a field of 10 Oe.

II. EXPERIMENT

A. Sample preparation and characterization

Single-phase polycrystalline samples of $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ were prepared by a solid-state reaction method using high-purity powders of Yb_2O_3, $CaCO_3$, $BaCO_3$, $SrCo_3$, and CuO. Details of the sample preparation have been presented elsewhere.[5] After mixing appropriate amounts of the powders, the samples were calcined and compacted into bar shapes. The bars were sintered at 850 °C for 20 h in a mixed gas flow of nitrogen with 1% oxygen. The fully oxygeneated sample with $z \sim 6.8$ was obtained by post-annealing at an oxygen partial pressure of 40 MPa and 600 °C for 3 *h*, and, subsequently, at 400 °C for 3 *h*, employing an oxygen Hot Isostatic Pressing (O_2-HIP) apparatus made by Kobe Steel. Samples with lower oxygen contents were prepared by a quenching and annealing technique. Samples were re-heat-treated at 300 °C, or 500 °C for 3 *h* in air and then quenched into liquid nitrogen. Furthermore, to improve the homogeneity of oxygen distribution throughout the samples, they were post-annealed at about 450 °C in evacuated silica tubes.

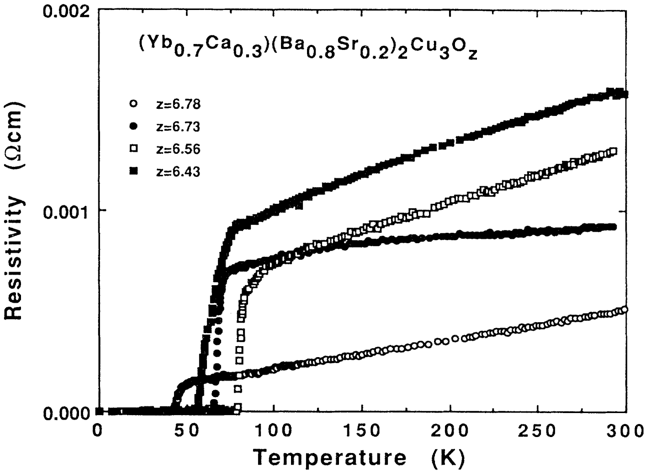

FIG. 2. Temperature dependence of the resistivity for the samples of $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$.

Figure 1 shows the temperature dependence of the field-cooled magnetization for the samples. This measurement was performed in a field of 10 Oe by SQUID magnetometer (Quantum Design). The data show that the samples exhibit bulk superconductivity. The volume fractions of superconductivity for the samples were estimated to be more than 15%. The temperature dependence of the resistivity for the samples is shown in Fig. 2. All the samples studied here showed metallic behavior in the normal state. The resistivity at 294 K decreased with oxygen content, which may imply the increase of carrier number by oxygenation. The midpoints of the resistive transition are in good agreement with the onset temperature of the Meissner signal. Table I summarizes several parameters of the samples, i.e., the oxygen content, the crystallographic parameters, T_c obtained from resistivity measurements, and the resistivity at 294 K. The samples with the two lowest oxygen contents have the tetragonal structure, and the other two samples are orthorhombic. In general, the length of the *c* axis in the $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ system tends to decrease with increasing oxygen content.[5] The maximum T_c of 80 K is observed at $z = 6.56$ in the tetragonal structure.

TABLE I. Oxygen content, crystallographic unit-cell parameters, superconducting transition temperature, and normal-state resistivity for samples of $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$.

Oxygen content z[a]	Structure	Crystallographic unit-cell parameters a (nm)	 b (nm)	 c(nm)	T_c (K)[b]	Resistivity[c] (mΩ cm)
6.78	ortho.	0.3794(1)	0.3851(1)	1.1622(1)	44.6	0.516
6.73	ortho.	0.3797(1)	0.3856(1)	1.1593(1)	67.6	0.926
6.56	tetra.	0.3830(1)		1.1677(1)	80.3	1.30
6.43	tetra.	0.3822(1)		1.1708(1)	66.3	1.59

[a] The oxygen content was analyzed by Coulometric titration.

[b] T_c was determined by resistivity measurements as the temperature at which the resistivity is equal to 50% of its extrapolated normal-state value.

[c] The resistivity was measured at 294 K and 0.1 MPa.

B. Experimental procedure

The electrical resistivity of the samples was measured at pressures up to 2 GPa employing a standard four-probe technique. Nearly hydrostatic pressure was generated by means of a piston-cylinder apparatus set in a cryostat, using a Teflon cell with a mixture of Fluorinert No. 70 and No. 77 as the pressure-transmitting medium. The load applied to the piston was changed only at room temperature, and was maintained constant during the resistivity measurements. Temperature was measured by a calibrated platinum resistance thermometer.

III. RESULTS

The normal-state resistivity at 294 K decreased with pressure at a rate of $(1/\rho)(d\rho/dP) \sim -0.066$, -0.087, -0.046, and -0.069 GPa^{-1} for samples of $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ with $z=6.43$, 6.56, 6.73, and 6.78, respectively. This suggests two possible explanations: an increase in the carrier concentration or an improvement in the intergrain contact. In a resistive measurement of sintered samples, the latter case may be more likely. Temperature dependence of the relative resistance for $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6.73}$ at various pressures are shown in Fig. 3. A clear decrease in T_c is observed with increasing pressure without any broadening of the transition width. The pressure derivative of T_c, dT_c/dP, can be estimated to be about -1.25 K/GPa.

Figure 4 shows the pressure dependences of the shift in the reduced T_c, normalized by the T_c at 0.1 MPa, for pressures up to 2 GPa for the samples. The samples with the lowest oxygen content of $z=6.43$ shows a large nonlinear pressure dependence of T_c unlike the other samples, which may come from inhomogeneous oxygen distribution. Average values of dT_c/dP up to 2 GPa were estimated to be 6.16, 0.95, -1.25, and -1.25 K/GPa for the samples with $z=6.43$, 6.56, 6.73, and 6.78, respectively. These values include little statistical error, except for the sample with $z=6.43$ showing the nonlinear behavior. The dT_c/dP for samples having $z=6.43$ and 6.56 are in agreement with previously reported values[10,16] for 60-K and 90-K samples in $LBa_2Cu_3O_{7-\delta}$ ($L=$Y,Eu), respectively. We note that the values of the pressure derivative for samples with oxygen contents greater than ~ 6.7 of the 1:2:3 system are negative. This result clearly shows that the sign and magnitude of the pressure coefficient of T_c depend on the oxygen content, i.e., hole concentration in the CuO_2 plane.

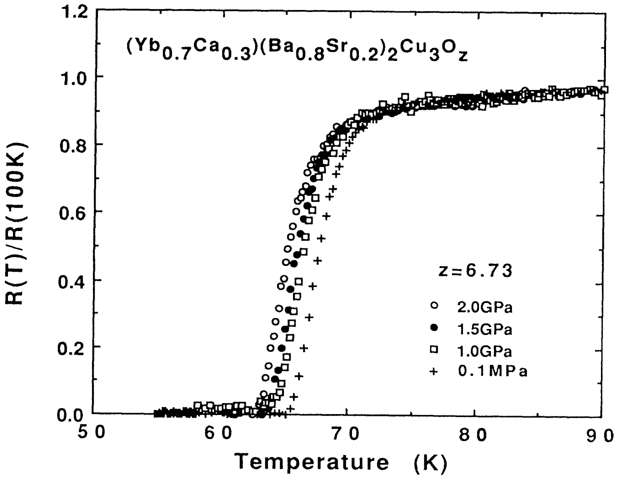

FIG. 3. Temperature dependence of the relative resistance for $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6.73}$ at various pressures. The relative resistance is normalized to that at 100 K.

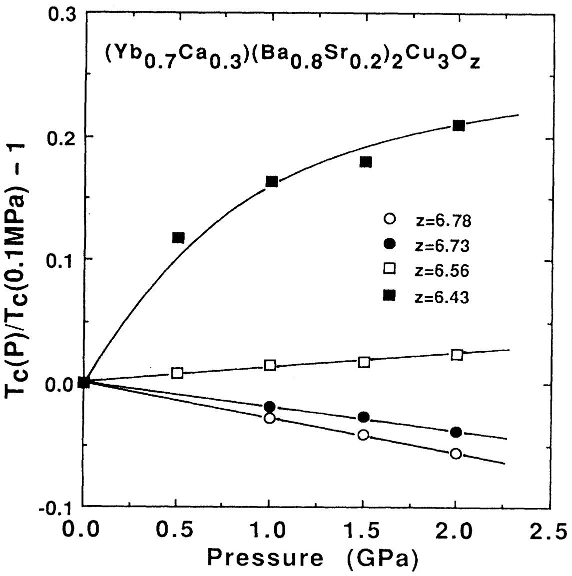

FIG. 4. The pressure dependence of the shift in reduced superconducting transition temperature T_c normalized to that at 0.1 MPa measured up to 2 GPa for the four $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ samples. The lines drawn through the data are guides to the eye.

Similar results were reported by several groups. Klotz *et al.*[17] and Koch *et al.*[18] observed that, from measurements of T_c of $YBa_2Cu_3O_{7-\delta}$ single crystals under pressure up to more than 10 GPa, T_c increases with pressure and then passes through a maximum. Although Koch *et al.*[18] also reported negative dT_c/dP values for two 1:2:3 crystals, it is not clear what is responsible for the large difference in pressure dependence of T_c. Mutata *et al.*[15] reported that dT_c/dP in $YBa_2Cu_3O_z$ decreases with increasing oxygen content and finally becomes small and negative value for samples with $T_c \sim 90$ K ($z \sim 0.18$). Most of the 1:2:3 compounds with $T_c \sim 90$ K, however, are reported to have small positive dT_c/dP values below 2 GPa.[10,12,16]

IV. DISCUSSION

In order to compare the results with theoretical models, it is useful to evaluate $d \ln T_c / d \ln V$. Using the value of the bulk modulus $B=112$ GPa for $YBa_2Cu_3O_{6.60}$,[21] the values of $d \ln T_c / d \ln V$ are calculated to be -10.4, -1.32, 2.07, and 3.13 for samples with $z=6.43$, 6.56, 6.73, and 6.78, respectively. The largest value of 10.4 in $|d \ln T_c / d \ln V|$ appears for the sample with $z=6.43$, which is greater than the typical value of ~2 allowed by BCS theory with electron-phonon interactions.[10] Although the mechanism for high-T_c superconductivity is still quite puzzling at the present time, several reasons for the change in the sign and magnitude of the pressure dependence of T_c can be considered, such as (1) electronic phase transition, (2) oxygen ordering effect, and (3) increase in carrier concentration in the CuO_2 plane. We will discuss these candidates for the source of the pressure dependence of T_c in this system.

The change in the sign of dT_c/dP from positive to negative was reported in the $(Y_{1-x}Pr_x)Ba_2Cu_3O_z$ system.[11] This seems to come from the pressure-induced electronic phase transition due to the hybridization between Pr $4f$ and valence-band states. However, in the present case, such an electronic phase transition is unlikely because of absence of any elements, such as Pr, Ce, and Tb, which are known to depress superconductivity in the 1:2:3 system.

Sieburger *et al.*[20] suggested that pressure-induced oxygen ordering effects may have a significant influence on the magnitude of dT_c/dP through observations of the broadening of the transition width ΔT_c in the $Tl_2Ba_2CuO_z$ system. We observed no broadening of ΔT_c under pressure for any of the samples. Thus, this suggests that oxygen ordering under pressure as suggested by Sieburger *et al.*[20] cannot explain the change in the sign of dT_c/dP.

It is well known that T_c of the 1:2:3 system strongly depends on the hole concentration in the CuO_2 plane p_{pl}.[1] We evaluated p_{pl} using the model of Tokura *et al.*[1] Tokura and co-workers[1] proposed a model for the 1:2:3 system that the hole concentration in the CuO_2 plane mainly determines T_c and the CuO chain merely provides an insulating reservoir of holes. The hole concentrations in the CuO_2 plane, p_{pl}, and the CuO chain, p_{ch}, are calculated as follows. The average hole concentration per Cu, p, is obtained from the average Cu valence, v, using a relation of $p=v-2$ and the critical hole concentration per Cu, p_c, is estimated from the empirical relation

$$p_c=-2.21+0.34z \ ,$$

where z is the oxygen content of the 1:2:3 sample. The average hole concentration p is connected with p_{pl} and p_{ch} by the relation

$$p=\tfrac{1}{3}(2p_{pl}+p_{ch}) \ .$$

For small p, all the holes resides on the CuO chain and these holes are localized. As p is increased, a threshold, i.e., p_c, is reached beyond which superconductivity occurs. At the threshold, i.e., $p=p_c$, p_{pl} is zero. Then p_{ch} is obtained by $p_{ch}=3p_c$. Consequently, p_{pl} is calculated from the relation

$$p_{pl}=3(p-p_c)/2 \ .$$

We discuss the pressure effect on T_c in the 1:2:3 system using the p_{pl} values. Figure 5 shows the relation between the pressure derivative dT_c/dP and p_{pl} for $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ samples, together with the T_c versus p_{pl} relation. Similar to the behavior in $(La_{1-x}Sr_x)_2CuO_4$,[2] T_c of $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ increases with an increase in p_{pl}, and levels off near its maximum T_c around 80 K at the optimum hole concentration of $p_{pl}\sim 0.18$. Beyond that, T_c decreases steeply with p_{pl}. It should be noted that dT_c/dP is positive in the region with $(dT_c/dp_{pl})>0$, whereas the sign of dT_c/dP changes to negative in the region with $(dT_c/dp_{pl})<0$, that is, above $p_{pl}\sim 0.2$. A recent neutron powder diffraction study of $YBa_2Cu_3O_z$ with $z=6.93$ and 6.60 under pressure by Jorgensen *et al.*[21] has revealed that charge transfer of holes from Cu(1) to Cu(2) is induced by pressure with the same transfer rate for both systems. Analogous to this study, beyond the optimum hole concentration in the CuO_2 plane, we expect T_c to decrease with increasing pressure. The results obtained here suggest that the application of pressure to the 1:2:3 system plays a role in hole doping of the CuO_2 plane. From a microscopic view-point, such a redistribution of holes may be governed by a difference between one-hole energy levels in different oxygen sites, the p_σ orbital in the in-plane oxygen and the p_z orbital in the apical oxygen. Thus, it would be concluded that the application of pressure causes a modification of the oxygen p-hole band structure, as pointed out in Ref. 22.

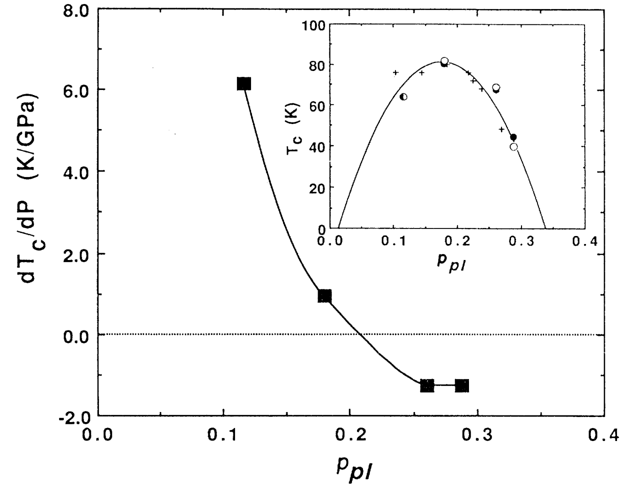

FIG. 5. The hole concentration p_{pl} vs the pressure derivative dT_c/dP for samples of $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$. The value of p_{pl} generally increases with the oxygen content. The solid squares denote the average value of dT_c/dP up to 2 GPa. The inset shows the p_{pl} vs T_c relation at 0.1 MPa. The solid and open circles show the midpoint of the resistive transition and the onset of the magnetic transition through dc magnetic susceptibility measurements, respectively. The crosses represent the value of T_c in $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ from Ref. 5. The lines drawn through the data are guides to the eye.

By the model discussed above, the magnitude of the pressure derivative dT_c/dP shows the predicted change in T_c in the region with $(dT_c/dp_{pl})>0$. However, the $(dT_c/dP$ for the region with $(dT_c/dp_{pl})<0$ remains constant. On the other hand, the relationship between T_c

and p_{pl} is symmetric near the optimum hole concentration in the $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$ system,[5] as shown in the inset of Fig. 5. The asymmetric behavior of dT_c/dP indicates that, even if the pressure application results in the increase of p_{pl}, dT_c/dP does not simply follow the behavior of the T_c versus p_{pl} diagram. To explain the difference between both regions, another factor may have to be taken into account.

A major change induced by pressure is the shortening of the bond lengths. Since the bond lengths are directly related to the hopping integrals and the magnetic exchange interaction, the shortening of the lengths in the *a* and *b* axes leads to an enhancement of such intraplane coupling. In the light of theoretical models for hole-doped copper-oxide superconductors,[22,23] the structural change along the *c* axis, i.e., decrease in the distance between the apical oxygen O(*A*) and CuO_2 plane, is expected to increase the intraplane coupling indirectly. Matsukawa and Fukuyama[22] reported that the decrease in the O(*A*)-Cu(2) distance leads to the enhancement of the long-range hopping integrals of Zhang-Rice singlets. Ohta and co-workers[23] revealed that the decrease in the O(*A*)-Cu(2) distance gives rise to two competitive effects: a decrease in the hopping integral *t* due to the destabilization of Zhang-Rice singlets, and an increase in *t* through an enhancement of the Madelung potential of O(*A*) relative to that of the CuO_2 plane. They explained the contribution from the latter may be more effective for the pressure effect on T_c as a whole. We expect that the pressure-induced enhancement of the intra-plane coupling favors an increase in T_c, irrespective of p_{pl}.

From these considerations, we could conclude that the large pressure derivative for the region with $(dT_c/dp_{pl})>0$ originates from the following two cooperative effects: the increase in the hole concentration p_{pl} and the enhancement of the intraplane coupling. The negative and relatively smaller values of dT_c/dP on the side with $(dT_c/dp_{pl})<0$ may be a result of compensation due to the above two effects.

The experimental results of dT_c/dP of $(La_{1-x}Sr_x)_2CuO_4$ still include some uncertainties.[8,9] A recent investigation by Pey *et al.*[24] on powder neutron-diffraction experiments under pressure, however, has also suggested a pressure-induced charge transfer as an explanation for the pressure effect on T_c in $La_{1.85}Sr_{0.15}CuO_4$. If simply so, T_c should decrease with increasing pressure for the region with $(dT_c/dp_{pl})<0$.

V. CONCLUSIONS

In conclusion, we found that, in $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_z$, the pressure derivative dT_c/dP shows decreasing positive values for the region with $dT_c/dp_{pl}>0$, and negative constant values for $(dT_c/dp_{pl})<0$: The sign and the magnitude of dT_c/dP depend on the hole concentration in the CuO_2 plane. These results indicate that the application of pressure plays a role in hole redistribution between the CuO chain and CuO_2 plane sites. In spite of the symmetric behavior of T_c versus p_{pl}, the relation of dT_c/dP versus p_{pl} is asymmetric, which might be due to the fact that the pressure-induced enhancement of intraplane coupling also contributes to the increase in T_c.

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