Title	Two effects of iodine intercalation on T_c in Bi_2Sr_2Ca_<1-x>Y_xCu_20_8 : Two-dimensionality and charge transfer
Author(s)	Fujiwara, Akihiko; Koike, Yoji; Sasaki, Keiichi; Mochida, Mitsunori; Noji, Takashi; Saito, Yoshitami
Citation	Physica C: Superconductivity, 208(1-2): 29-37
Issue Date	1993-04-01
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/4935
Rights	NOTICE: This is the author's version of a work accepted for publication by Elsevier. Changes resulting from the publishing process, including peer review, editing, corrections, structural formatting and other quality control mechanisms, may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Akihiko Fujiwara, Yoji Koike, Keiichi Sasaki, Mitsunori Mochida, Takashi Noji and Yoshitami Saito, Physica C: Superconductivity, 208(1-2), 1993, 29-37, http://dx.doi.org/10.1016/0921-4534(93)90665-D
Description	

(running title: Iodine Intercalation in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$)

TWO EFFECTS OF IODINE INTERCALATION ON T_c IN $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$: TWO-DIMENSIONALITY AND CHARGE TRANSFER

Akihiko FUJIWARA, Yoji KOIKE, Keiichi SASAKI, Mitsunori MOCHIDA, Takashi NOJI and Yoshitami SAITO

Department of Applied Physics, Faculty of Engineering, Tohoku University, Aramaki Aoba, Aoba-ku, Sendai 980, Japan

(Received 9 September 1992)

Effects of the stage-1 iodine-intercalation on T_c have been investigated in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$. The iodine intercalation causes two large effects; one is a change of the two-dimensionality due to an expansion of the crystal along the c-axis, and the other is an increase of conducting hole carriers due to charge transfer between intercalated iodine atoms and CuO_2 sheets in the host material. For the stage-1 iodine-intercalation compounds, it has been found that the former effect decreases T_c by about 10 K and that the latter effect shifts the x dependence of T_c to larger x values by about 0.05 because of the increase of conducting hole carriers by about 0.025 per CuO_2 unit. It has been concluded that the decrease in

T_c through iodine intercalation in $Bi_2Sr_2CaCu_2O_8$ is due to the both effects.

KEY WORDS:
high-T_c superconductivity,
$Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$,
intercalation,
electrical resistivity,
AC magnetic susceptibility.

1. Introduction

The compounds $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ (n = 1, 2, 3) are most anisotropic in not only crystallography but also physical properties among high-T_c superconductors with two-dimensional CuO_2 sheets in their crystal structures [1,2]. The large anisotropy in $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ appears to be attributed to the very weak coupling between BiO-BiO double layers, from an indirect evidence that the single crystals of n = 2 are easily cloven between the double layers. This very weak coupling enables the compounds to form intercalation compounds by taking guest atoms or molecules between the BiO-BiO double layers. In fact, it has been found by Xiang et al. [3,4] and the present authors [5-7] that $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ (n = 1, 2, 3) form iodine- and bromine-intercalation compounds, $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}I$ and $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}Br$, respectively. It has been confirmed from studies of the electron microscopy that both iodine [8-11] and bromine [12] atoms are intercalated between the BiO-BiO double layers.

In general, intercalation gives rise to two kinds of large effects on a host material: One effect is an expansion of the crystal along the c-axis, which changes the two-dimensionality of the crystal and also of its physical properties. The other effect is charge transfer between guest atoms or molecules and the host material, which changes the carrier number of the host material.

For lightly bromine-intercalated samples of $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}Br_x$ with $x \lesssim 0.3$, it has been found that the hole concentration in the conducting CuO_2 sheets increases through intercalation due to the latter effect of intercalation, namely, the charge transfer [5-7]. That is to say, intercalated Br atoms are almost all ionized as Br^- to supply the CuO_2 sheets with holes. As a result, both the electrical resistivity ρ and the superconducting transition temperature T_c decrease. The decrease in T_c through Br intercalation can reasonably be understood to be due to the overdoping of holes into the CuO_2 sheets, because the value of T_c in $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ strongly depends on the hole concentration in the CuO_2 sheets and the compounds $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ are situated in the overdoped region for n = 1 and 2 [13,14] or at the optimum hole concentration for n = 3 [5-7].

For stage-1 iodine-intercalated samples of $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}I$, T_c decreases only by about 10 K through intercalation. This has been explained as due to the former effect of intercalation, namely, an enhancement of the two-dimensionality [3,4,15]. However, it has recently been claimed from studies of the Hall effect and the X-ray photoemission spectroscopy that the hole concentration in the CuO_2 sheets slightly increases through the iodine intercalation due to the latter effect of intercalation, namely, the charge transfer and that consequently T_c decreases similarly to the case of Br-intercalated samples [16,17]. From one Raman scattering study, it has been concluded that intercalated iodine atoms are not ionized and exist like I_2 molecules [18]. From another Raman scattering study, on the contrary, it has been claimed that they are ionized as I_3^- molecular anions [19]. Therefore, at present, it is not clear which effect is dominant for the small decrease in T_c through iodine intercalation in $Bi_2Sr_2CaCu_2O_8$.

In this paper, we investigate the effects of stage-1 iodine-intercalation on T_c in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$, in order to elucidate the origin of the decrease in T_c through iodine intercalation in $Bi_2Sr_2CaCu_2O_8$. The system $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ has been well studied to clarify the hole-concentration dependences of physical properties including T_c in the $Bi_2Sr_2CaCu_2O_8$ phase, where the hole concentration is reduced through the partial substitution of the trivalent Y for the divalent Ca with little change in the crystal structure [13,14,20]. As shown by a solid line in fig. 1, T_c of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ increases, takes a maximum at $x \approx 0.2$ and decreases with increasing x, suggesting that $Bi_2Sr_2CaCu_2O_8$ is situated in the overdoped region. If the decrease in T_c through iodine intercalation in $Bi_2Sr_2CaCu_2O_8$ is due to the change of the two-dimensionality owing to the expansion along the c-axis, it is expected that the superconductivity is equally suppressed through the iodine intercalation for every sample with different x, as shown in fig. 1(a). On the other hand, if the decrease in T_c is due to the increase of conducting hole carriers owing to the charge transfer, it is expected that the superconducting region shifts to that of larger x values, as shown in fig. 1(b), because the maximum T_c is attained at the optimum hole concentration in the $Bi_2Sr_2CaCu_2O_8$ phase [13,14].

2. Experimental

Host samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ for the intercalation were prepared by conventional solid-state reaction for $0 \leqq x \leqq 0.6$. Raw materials of Bi_2O_3, $SrCO_3$, $CaCO_3$, Y_2O_3 and CuO powders were used in the molar ratio of Bi:Sr:Ca:Y:Cu = 2:2:1-x:x:2. The powders were mixed and prefired in air at 800°C for 12 h. After pulverization, the prefired materials were pelletized and sintered for 24 h at temperatures between 860°C and 880°C. This sintering process was carried out once again so as to obtain homogeneous samples. All products were characterized by powder X-ray diffraction to be of almost single-phase structures.

Iodine intercalation was done by vapor-phase reaction [3]. The host samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ and elemental iodine were sealed in an evacuated glass tube separately. In order to reduce oxygen release from the host samples during the intercalation process, the heat treatment was made at a low temperature of 150°C for 24 h [3,21]. The products were characterized by the weight change during the intercalation process and by powder X-ray diffraction to be stage-1 intercalation compounds of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$.

Resistivity measurements were carried out by the standard DC four-point probe method. Lead wires were attached to samples with silver paste. The AC magnetic susceptibility was measured with a small AC field (0.1 Oe, 333 Hz) by the conventional inductance method. Temperature measurements were made with a calibrated Si-diode thermometer.

3. Results and discussion

Figure 2 shows typical powder X-ray diffraction patterns for host samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ and iodine-intercalated ones of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$. The diffraction pattern changes through the iodine intercalation in the same way for every sample with different x. This suggests that iodine atoms are intercalated between the BiO-BiO double layers similarly for every sample with different x. The $hk\ell$ diffraction peaks with $h\neq0$ or $k\neq0$ for iodine-intercalated samples are broader than those of host samples, while the width of the 00ℓ peaks little changes through the iodine intercalation. This may be attributed to an imperfect change of the atomic stacking along the c-axis between the BiO-BiO double layers, from the staggered configuration of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ to the vertically aligned configuraion of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$.

Figure 3 displays variations of the lattice constants estimated from the powder X-ray diffraction with the Y concentration x. As for host samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$, the a-axis increases and the c-axis decreases with increasing x. A clear split of the a- and b-axes is observed at $x \geqq 0.45$, which is in agreement with the previous reports [14,20]. As iodine atoms are intercalated, the a-axis does not change so much, though detailed analyses can not be made due to the broadness of the $hk\ell$ peaks with $h\neq0$ or $k\neq0$. On the other hand, the c-axis drastically changes through the iodine intercalation. The value of the lattice constant c is reduced to about a half of that of the host sample, which is due to the stacking change along the c-axis between the BiO-BiO double layers, from the staggered configuration to the vertically aligned one. Therefore, c values for iodine-intercalated samples are plotted in fig. 3 with twice values for comparison with those of host samples. It is found that intercalated iodine atoms expand the spacing between the BiO-BiO double layers by about 3.5 Å similarly for every sample with different x. In addition, by looking more closely at the c value for iodine-intercalated samples, it tends to increase a little with increasing x. The reason is not clear.

Figure 4 shows the temperature dependence of the electrical resistivity ρ for host samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$. It is found that the value of ρ increases with increasing x. The value of T_c increases, takes a maximum at $x \approx 0.2$ and decreases with increasing x, and the superconductivity disappears at $x \geqq 0.6$. These behaviors, which are in agreement with the previous reports [14,20], suggest that the hole concentration decreases through the partial substitution of Y for Ca and that $Bi_2Sr_2CaCu_2O_8$ has too many holes to attain the maximum T_c, as mentioned in section 1. As for iodine-intercalated samples, the temperature dependence of ρ is shown in fig. 5. As clearly seen in fig. 6, the value of ρ increases by about two orders of magnitude due to the iodine intercalation for all x-values, in accordance with the report for sintered samples of $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}I$ [16]. It has, however, been reported for single-crystalline samples that the value of ρ in the a-b plane changes little through the iodine intercalation and that ρ along the c-axis becomes even metallic

[17,22]. Therefore, the increase in ρ through iodine intercalation for sintered polycrystalline samples is not considered to be an intrinsic property but is attributed mainly to the electrically poor connection between grains on account of the large expansion of the crystal along the c-axis through the intercalation. In spite of the large value, ρ tends to increase with increasing x, suggesting that the hole concentration decreases with increasing x for iodine-intercalated samples similarly to the case of host samples. This is also found from the x dependence of the resistivity ratio, ρ_{300K}/ρ_{100K}, which shows a tendency toward a metallic behavior, as shown in fig. 7 [23]. The fact that, ρ_{300K}/ρ_{100K} decreases with increasing x similarly for both host samples and iodine-intercalated ones suggests that the hole concentration decreases with increasing x in the same way for the both samples. From these results, it is concluded that the effects of iodine intercalation on the electrical properties are similar for all x-values, which may be natural because iodine atoms are intercalated between the BiO-BiO double layers similarly for all x-values.

Figure 8 displays the x dependences of T_c for host samples and iodine-intercalated ones, where the value of T_c is defined at the midpoint of the superconducting transition curve in the ρ vs T plot.

Measurements of the AC magnetic susceptibility have also been made as shown in figs. 9 and 10 for host samples and iodine-intercalated ones, respectively. The Meissner effect due to bulk superconductivity is observed for the both samples with

$0 \leqq x \lesssim 0.55$, though the Meissner signal is smaller for iodine-intercalated samples than for host ones. Figure 11 displays the x dependences of T_c for host samples and iodine-intercalated ones, where the value of T_c is defined as the temperature where χ changes from the normal-state value by 1 % of the value corresponding to the perfect diamagnetism. These values of T_c are approximately in agreement with those estimated from the resistivity measurements as shown in fig. 8, suggesting that the latter values are also based on the superconductivity of the bulk.

Here, we discuss the x dependence of T_c estimated from the resistivity measurements as shown in fig. 8, because the ambiguity in determining T_c is not large and the data are rather systematic compared with the estimation from the susceptibility measurements. It is found from fig. 8 that T_c decreases through the iodine intercalation for $0 \leqq x \leqq 0.3$ and that T_c changes little for $x \geqq 0.4$. What is most remarkable is that the maximum T_c is attained at $x \approx 0.3$ for iodine-intercalated samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$, while it is at $x \approx 0.2$ for host samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$. This shift from $x \approx 0.2$ to $x \approx 0.3$ means that the hole concentration in the conducting CuO_2 sheets increases through the iodine intercalation, because the maximum T_c is attained at the optimum hole concentration in the $Bi_2Sr_2CaCu_2O_8$ phase. The increase of the hole concentration in the CuO_2 sheets is understood to be due to the charge transfer between intercalated iodine atoms and the CuO_2 sheets resulting from the ionization of iodine. This is consistent with experimental results on the Hall effect of $Bi_2Sr_2CaCu_2O_8I$ that the Hall coefficient decreases a little through the iodine intercalation [16,17]. Considering the decrease of the maximum value of T_c through the iodine intercalation, on the other hand, there certainly exists an effect which suppresses the superconductivity regardless of hole concentration, namely, an effect of the change of the two-dimensionality due to the expansion of the crystal along the c-axis through the iodine intercalation, as mentioned in section 1. The change in T_c through iodine intercalation is explained by the both effects of the change of the two-dimensionality as shown in fig. 1(a) and of the increase of hole carriers in the conducting CuO_2 sheets due to the charge transfer as shown in fig. 1(b). After all, the T_c vs x curve for the iodine-intercalated samples in fig. 8 is regarded as a result of the shift of the T_c vs x curve for the host samples both to lower T_c values and to larger x values. Therefore, it is concluded that the decrease in T_c through iodine intercalation in $Bi_2Sr_2CaCu_2O_8$ is due to the both effects.

The above discussion can be made quantitatively. When data of T_c vs x for the host samples are modified so that the T_c values are equally decreased by 10 K and that the x values are equally increased by 0.05, they are roughly superposed on the T_c vs x curve for the iodine-intercalated samples, as shown in fig. 12. Consequently, it is found that the change of the two-dimensionality through iodine intercalation decreases T_c by about 10 K equally for all x-values. Concerning the T_c suppression, two mechanisms have been proposed from the viewpoint that the enhancement of the two-dimensionality through the intercalation is of importance [4,15]: one is based on the RVB model and is that the enhancement of two-dimensionality reduces the interlayer coupling between CuO_2 sheets which is effective for superconductivity [24,25]. The other is based on the BCS theory and is that the enhancement of two-dimensionality reduces the effective electron-phonon coupling which plays a role in the increase in T_c [26]. At present, however, it is not clear whether the physical properties including superconducting ones become more two-dimensional through the intercalation or not, though it may be said that the two-dimensionality is enhanced in crystallography. Moreover, there is an interesting report that the value of ρ along c-axis in single-crystal $Bi_2Sr_2CaCu_2O_8$ slightly decreases through the iodine intercalation and that its temperature dependence changes from a semiconductor-like behavior to a metallic one [17,22]. Therefore, it cannot be decided hastily that the enhancement of the two-dimensionality decreases T_c. It may be concluded that the two-dimensionality has close relation to the high-T_c superconductivity and that the change of the two-dimensionality through the iodine intercalation decreases T_c by 10 K. However, the mechanism on the decrease in T_c is not clear.

From fig. 12, it is also found that the hole concentration in the CuO_2 sheets increases through the iodine intercalation by about 0.025 per CuO_2 unit due to the charge transfer of about 0.05 holes per iodine. The quantity of the charge transfer is much less than that of Br-intercalated samples, about 1 hole per bromine [5-7], but is approximately in agreement with another experimantal result of $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}I$ (n = 1, 2, 3), 0.07 holes per iodine [17]. As to the state of intercalated iodine atoms, it is naively supposed that 5 % of iodine atoms are ionized as I^- and that 95 % of iodine atoms exist as I_2 molecules, assuming that the change of the carrier number is only due to the charge transfer between intercalated iodine atoms and the CuO_2 sheets. From some studies with the Raman spectroscopy [18,19] and the X-ray photoemission spectroscopy [17], however, it has been claimed variously that iodine atoms exist as I_2 molecules [18] or I_3^- molecular anions [19] or I^- and I^{7+} in part [17]. There has been also another supposition that the charge transfer is done between iodine atoms and the BiO-BiO double layers [4,17]. It is not settled which is correct, but in any case it appears to be true that iodine atoms are ionized in greater or less degree to supply the CuO_2 sheets with about 0.025 conducting holes per CuO_2 unit.

Lastly, it may be worth while discussing the change in oxygen contents during the intercalation process. As mentioned in section 2, the heat treatment was made at a temperature as low as possible, in order to reduce the effect of oxygen release from samples. However, the oxygen release may occur slightly during the intercalation process in spite of the careful treatment. The oxygen release in $Bi_2Sr_2CaCu_2O_8$ phase would cause the decrease of hole carriers, so that the superconducting region in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ would shift to that of smaller x values [27]. This is opposed to our experimental results that the superconducting region shifts through the iodine intercalation to that of larger x values. Therefore, it is not necessary to take into account the oxygen release at least in general studies. The slight oxygen release would only slightly revise the estimate of the carrier number in the CuO_2 sheets owing to the intercalated iodine atoms.

4. Summary

Effects of the stage-1 iodine-intercalation in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ have been investigated. From powder X-ray diffraction, it has been found that iodine atoms are intercalated between the BiO-BiO double layers so that the spacing between the double layers is expanded by about 3.5 Å similarly for every sample with different x.

From measurements of the electrical resistivity and the AC magnetic susceptibility, it has been found that T_c of the bulk decreases for $0 \leqq x \lesssim 0.3$ and changes little for $x \gtrsim 0.4$ through the iodine intercalation and that the Y concentration where the maximun T_c is attained shifts from $x \approx 0.2$ to $x \approx 0.3$ through the iodine intercalation. The change in T_c through iodine intercalation is explained by the two effects; one is the change of the two-dimensionality owing to the expansion of the crystal along the c-axis, and the other is the increase of conducting hole carriers owing to the charge transfer between intercalated iodine atoms and the CuO_2 sheets. For the stage-1 iodine-intercalation compounds, it has been found that the former effect decreases T_c by about 10 K for every sample with different x and that the latter effect shifts the x dependence of T_c to larger x values by about 0.05 because of the increase of conducting hole carriers by about 0.025 per CuO_2 unit. Therefore, it has been concluded that the decrease in T_c through iodine intercalation in $Bi_2Sr_2CaCu_2O_8$ is due to the both effects.

Acknowledgements

We thank Dr. M. Kato for helpful discussions. This work was supported by the Kurata Research Grant.

References

[1] Y. Koike, T. Nakanomyo and T. Fukase, Jpn. J. Appl. Phys. **27** (1988) L841.

[2] Y. Iye, S. Nakamura and T. Tamegai, Physica **C159** (1989) 433.

[3] X.-D. Xiang, S. McKernan, W.A. Vareka, A. Zettl, J.L. Corkill, T.W. Barbee III and M.L. Cohen, Nature **348** (1990) 145.

[4] X.-D. Xiang, A. Zettl, W.A. Vareka, J.L. Corkill, T.W. Barbee III and M.L. Cohen, Phys. Rev. **B43** (1991) 11496.

[5] Y. Koike, T. Okubo, A. Fujiwara, T. Noji and Y. Saito, Solid State Commun. **79** (1991) 501.

[6] T. Okubo, A. Fujiwara, Y. Koike, T. Noji and Y. Saito, Physica **C185-189** (1991) 847.

[7] Y. Koike, A. Fujiwara, T. Okubo, T. Noji, and Y. Saito, Jpn. J. Appl. Phys. **Ser.7** (1992) 29.

[8] N. Kijima, R. Gronsky, X.-D. Xiang, W.A. Vareka, A. Zettl, J.L. Corkill and M.L. Cohen, Physica **C181** (1991) 18.

[9] N. Kijima, R. Gronsky, X.-D. Xiang, W.A. Vareka, A. Zettl, J.L. Corkill and M.L. Cohen, Physica **C184** (1991) 127.

[10] B. Chenevier, S. Ikeda and K. Kadowaki, Physica **C185-189** (1991) 643.

[11] N. Kijima, R. Gronsky, X.-D. Xiang, W.A. Vareka, A. Zettl, J.L. Corkill and M.L. Cohen, Physica **C190** (1992) 597.

[12] N. Ohnishi, K. Hiraga, A. Fujiwara, Y. Koike and Y. Saito, unpublished.

[13] Y. Koike, Y. Iwabuchi, S. Hosoya, N. Kobayashi and T.

Fukase, Physica **C159** (1989) 105.

[14] A. Maeda, M. Hase, I. Tsukada, K. Noda, S. Takebayashi and K. Uchinokura, Phys. Rev. **B41** (1990) 6418.

[15] X.-D. Xiang, W.A. Vareka, A. Zettl, J.L. Corkill, T.W. Barbee III, M.L. Cohen, N. Kijima and R. Gronsky, Science **254** (1991) 1487.

[16] H. Nakashima, D.M. Pooke, N. Motohira, T. Tamura, Y. Nakayama, K. Kishio, K. Kitazawa and K. Yamafuji, Physica **C185-189** (1991) 677.

[17] D. Pooke, K. Kishio, T. Koga, Y. Fukuda, N. Sanada, M. Nagoshi, K. Kitazawa and K. Yamafuji, Physica **C198** (1992) 349.

[18] C.H. Qiu, S.P. Ahrenkiel, N. Wada and T.F. Ciszek, Physica **C185-189** (1991) 825.

[19] E. Faulques and R.E. Russo, Solid State Commun. **82** (1992) 531.

[20] T. Tamegai, K. Koga, K. Suzuki, M. Ichihara, F. Sakai and Y. Iye, Jpn. J. Appl. Phys. **28** (1989) L112.

[21] D. Pooke, K. Kishio, N. Motohira, T. Tamura, Y. Tomioka, T. Koga, K. Kitazawa and K. Yamafuji, in: Advances in Superconductivity IV, eds. H. Hayakawa and N. Koshizuka (Springer-Verlag, Tokyo, 1992) p.233.

[22] X.-D. Xiang, W.A. Vareka, A. Zettl, J.L. Corkill, M.L. Cohen, N. Kijima and R. Gronsky, Phys. Rev. Lett. **68** (1992) 530.

[23] Y. Koike, A. Kakimoto, M. Yoshida, H. Inuzuka, T. Noji and Y. Saito, Physica **B165&166** (1990) 1665.

[24] J.M. Wheatley, T.C. Hsu and P.W. Anderson, Nature **333** (1988) 121.

[25] J.M. Wheatley, T.C. Hsu and P.W. Anderson, Phys. Rev. **B37** (1988) 5897.

[26] J. Ihm and B.D. Yu, Phys. Rev. **B39** (1989) 4760.

[27] M. Nagoshi, T. Suzuki, Y. Fukuda, K. Terashima, Y. Nakanishi, M. Ogita, A. Tokiwa, Y. Syono and M. Tachiki, Phys. Rev. **B43** (1991) 10445.

Figure captions

Fig. 1. Schematic representation of the hole-concentration dependences of T_c in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ (solid lines) and $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$ (dashed lines), (a) in the case that the change of the two-dimensionality is dominant for the decrease in T_c through iodine intercalation in $Bi_2Sr_2CaCu_2O_8$, and (b) in the case that the increase of conducting hole carriers due to the charge transfer is dominant. Closed and open circles indicate $Bi_2Sr_2CaCu_2O_8$ and $Bi_2Sr_2CaCu_2O_8I$, respectively.

Fig. 2. Powder X-ray diffraction patterns using CuKα radiation for host samples of $y = 0$ and iodine-intercalated ones of $y = 1$ in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I_y$.

Fig. 3. Lattice constants a, b and c as a function of Y concentration x for host samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ (o) and iodine-intercalated ones of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$ (□). The c values of iodine-intercalated samples are plotted with twice values for comparison with those of host samples regardless of the stacking change along the c-axis between the BiO-BiO double layers.

Fig. 4. Temperature dependence of the electrical resistivity ρ for host samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$.

Fig. 5. Temperature dependence of the electrical resistivity ρ

for iodine-intercalated samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$.

Fig. 6. Variations with x of the electrical resistivity ρ at 100 K, ρ_{100K}, (open markes) and ρ at 300 K, ρ_{300K}, (closed marks) for host samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ (circle) and iodine-intercalated ones of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$ (square).

Fig. 7. Variations with x of the resistivity ratio, ρ_{300K}/ρ_{100K}, for host samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ (o) and iodine-intercalated ones of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$ (□).

Fig. 8. Variations of T_c with x for host samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ (o) and iodine-intercalated ones of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$ (□). The value of T_c is defined at the midpoint of the superconducting transition curve in the ρ vs T plot. Closed symbols indicate samples which are not superconducting above 4.2 K.

Fig. 9. Temperature dependence of the AC magnetic susceptibility χ for host samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$. Closed circles correspond to T_c's shown in fig. 11.

Fig. 10. Temperature dependence of the AC magnetic susceptibility χ for iodine-intercalated samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$. Closed circles correspond to T_c's shown in fig. 11.

Fig. 11. Variations of T_c with x for host samples of

$Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ (o) and iodine-intercalated ones of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$ (□). The value of T_c is defined as the temperature where χ changes from the normal-state value by 1 % of the value corresponding to the perfect diamagnetism, as shown by closed circles in figs. 9 and 10. Closed symbols indicate samples which are not superconducting above 4.2 K.

Fig. 12. Variations of T_c with x for host samples of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ (o) and iodine-intercalated ones of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$ (□), as shown in fig. 8. Data for host samples are modified as follows; the T_c values are decreased by 10 K and the x values are increased by 0.05 equally for all host samples.

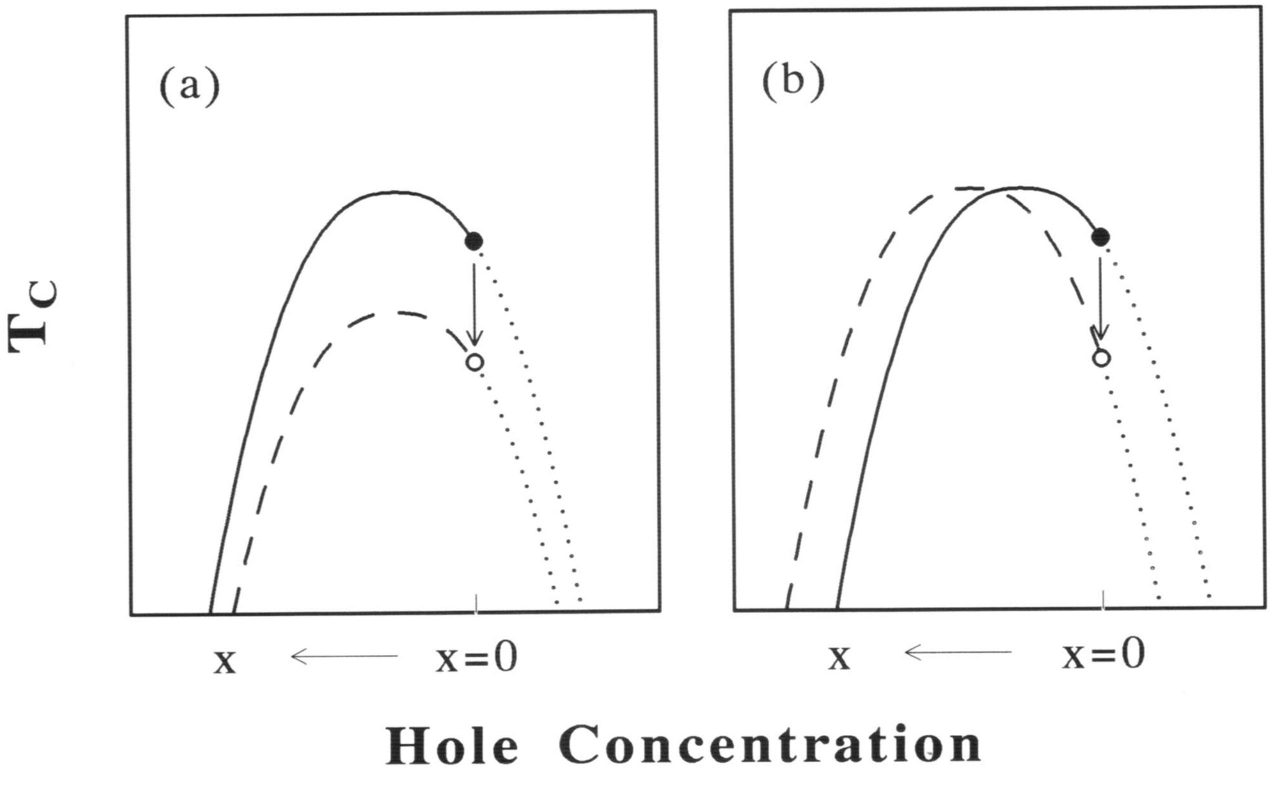
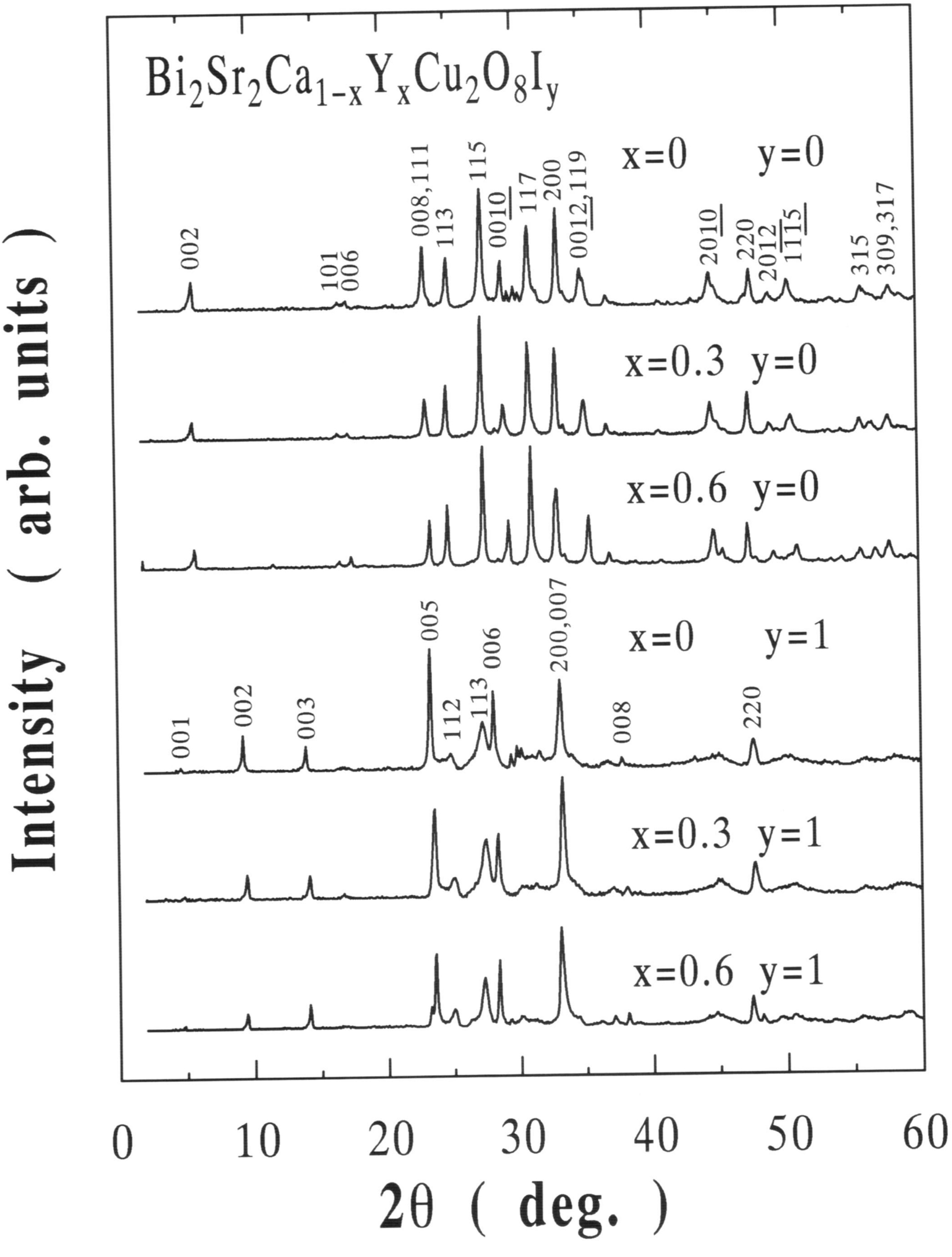


Fig. 1



Bi2Sr2Ca1-xYxCu2O8Iy
x=0 y=0
002
101
006
008,111
113
115
0010
117
200
0012,119
2010
220
2012
1115
315
309,317
x=0.3 y=0
x=0.6 y=0
x=0 y=1
001
002
003
005
112
113
006
200,007
008
220
x=0.3 y=1
x=0.6 y=1
Intensity (arb. units)
0
10
20
30
40
50
60
2θ (deg.)

Fig. 2

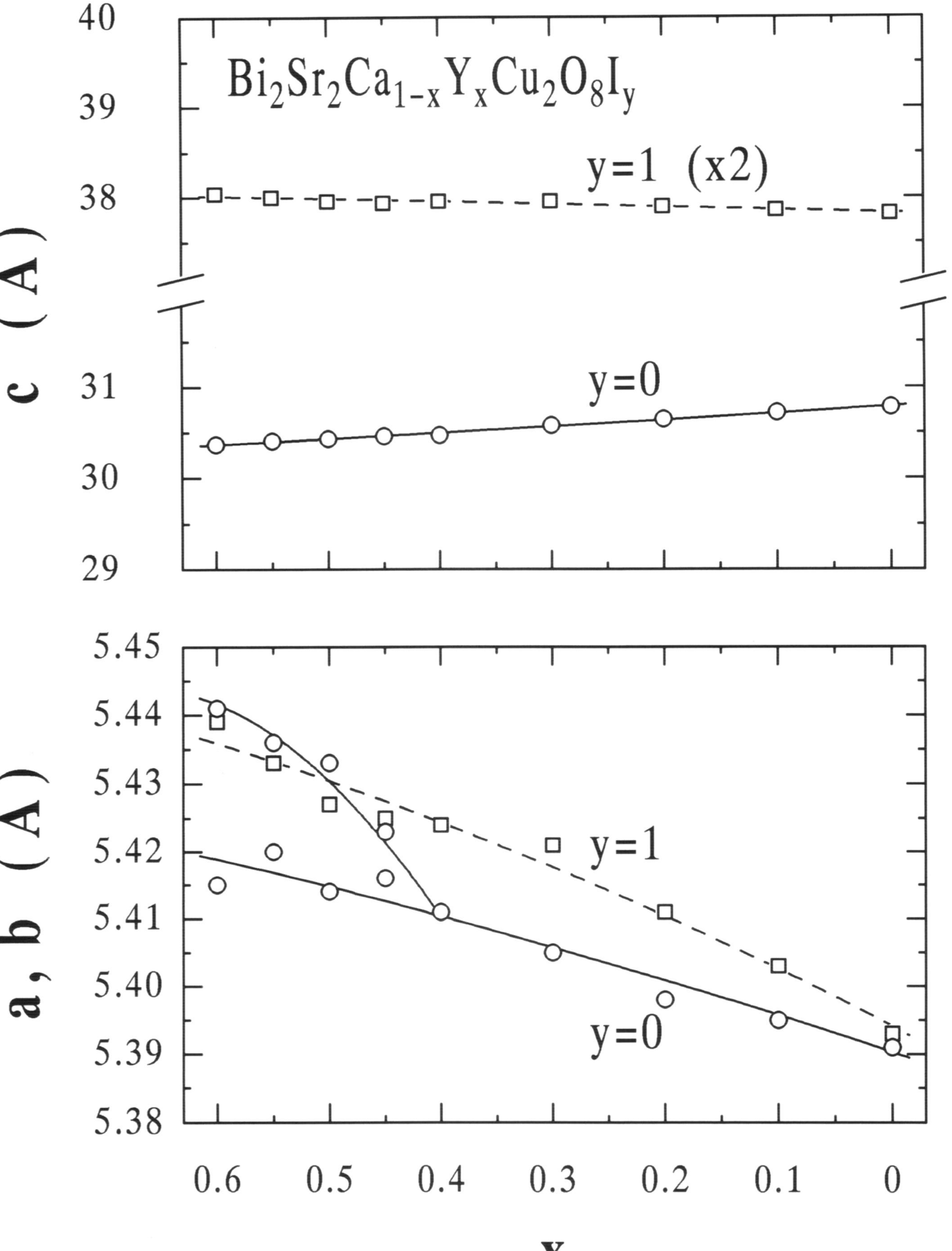
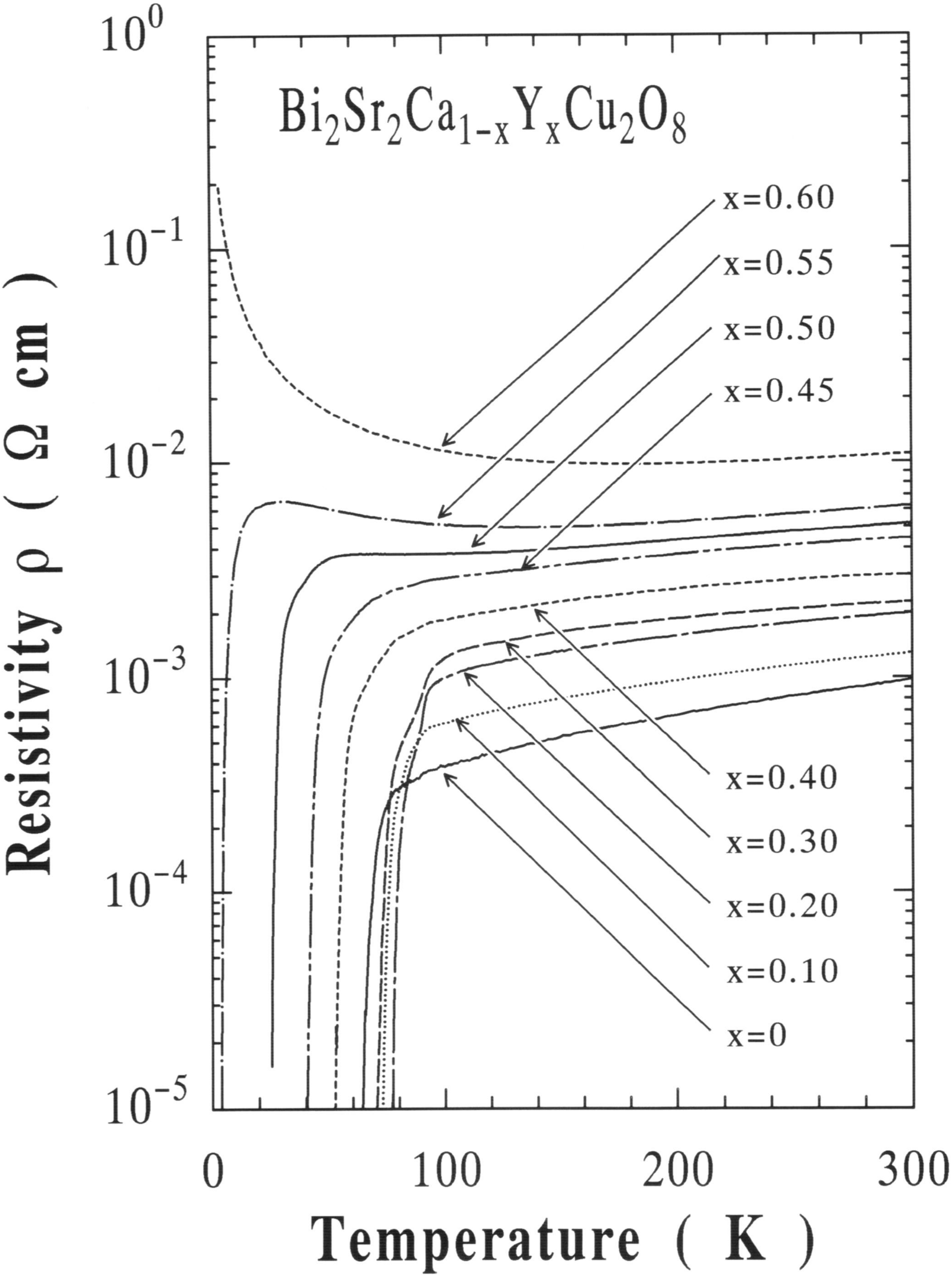
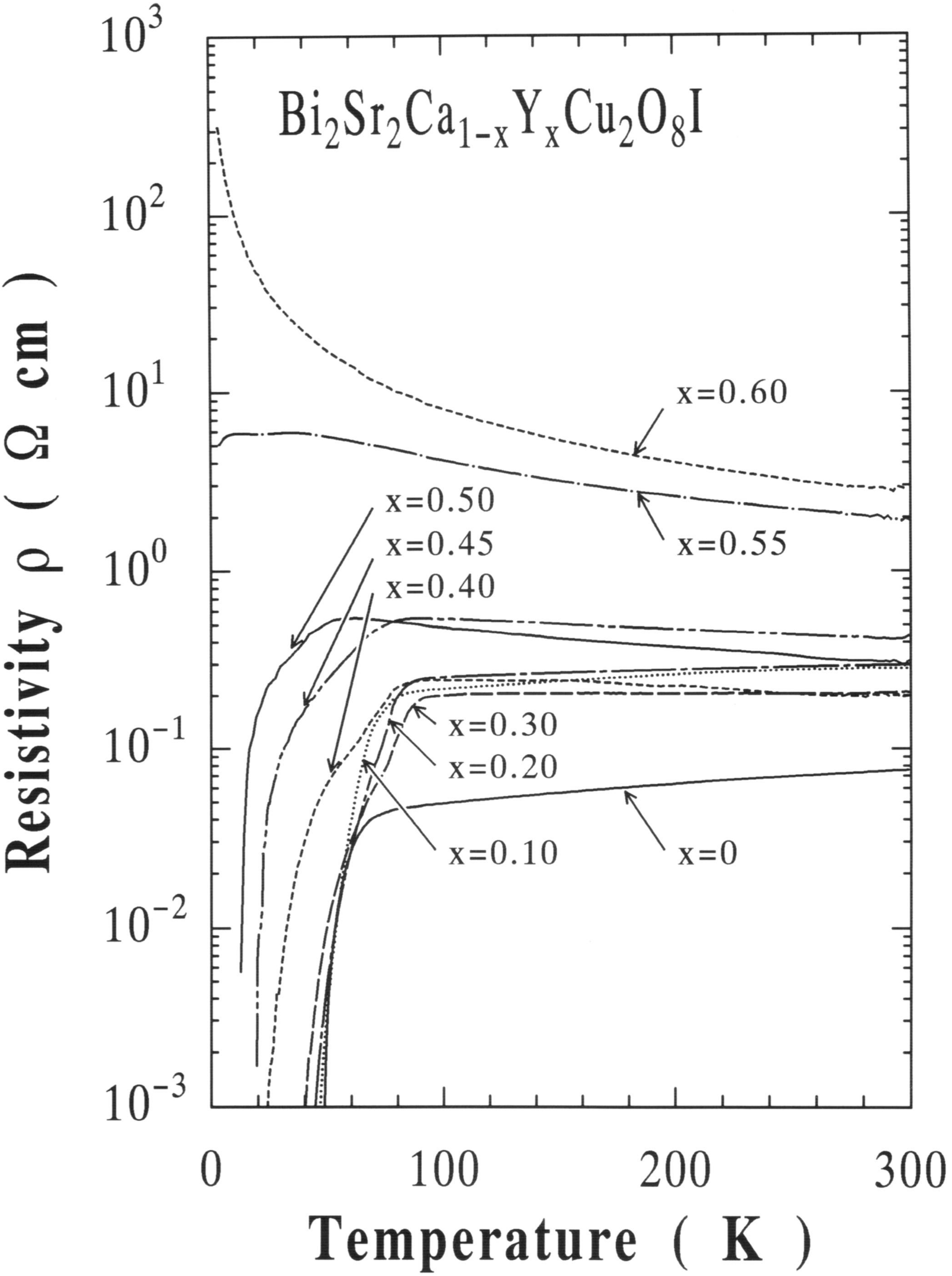

Bi2Sr2Ca1-xYxCu2O8Iy
y=1 (x2)
y=0
c (Å)
40
39
38
31
30
29
a, b (Å)
5.45
5.44
5.43
5.42
5.41
5.40
5.39
5.38
y=1
y=0
0.6
0.5
0.4
0.3
0.2
0.1
0
x

Fig. 3



$Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$
x=0.60
x=0.55
x=0.50
x=0.45
x=0.40
x=0.30
x=0.20
x=0.10
x=0
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
Resistivity ρ (Ω cm)
0
100
200
300
Temperature (K)

Fig. 4



$Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$
Resistivity ρ (Ω cm)
Temperature (K)
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
0
100
200
300
x=0.60
x=0.55
x=0.50
x=0.45
x=0.40
x=0.30
x=0.20
x=0.10
x=0

Fig. 5

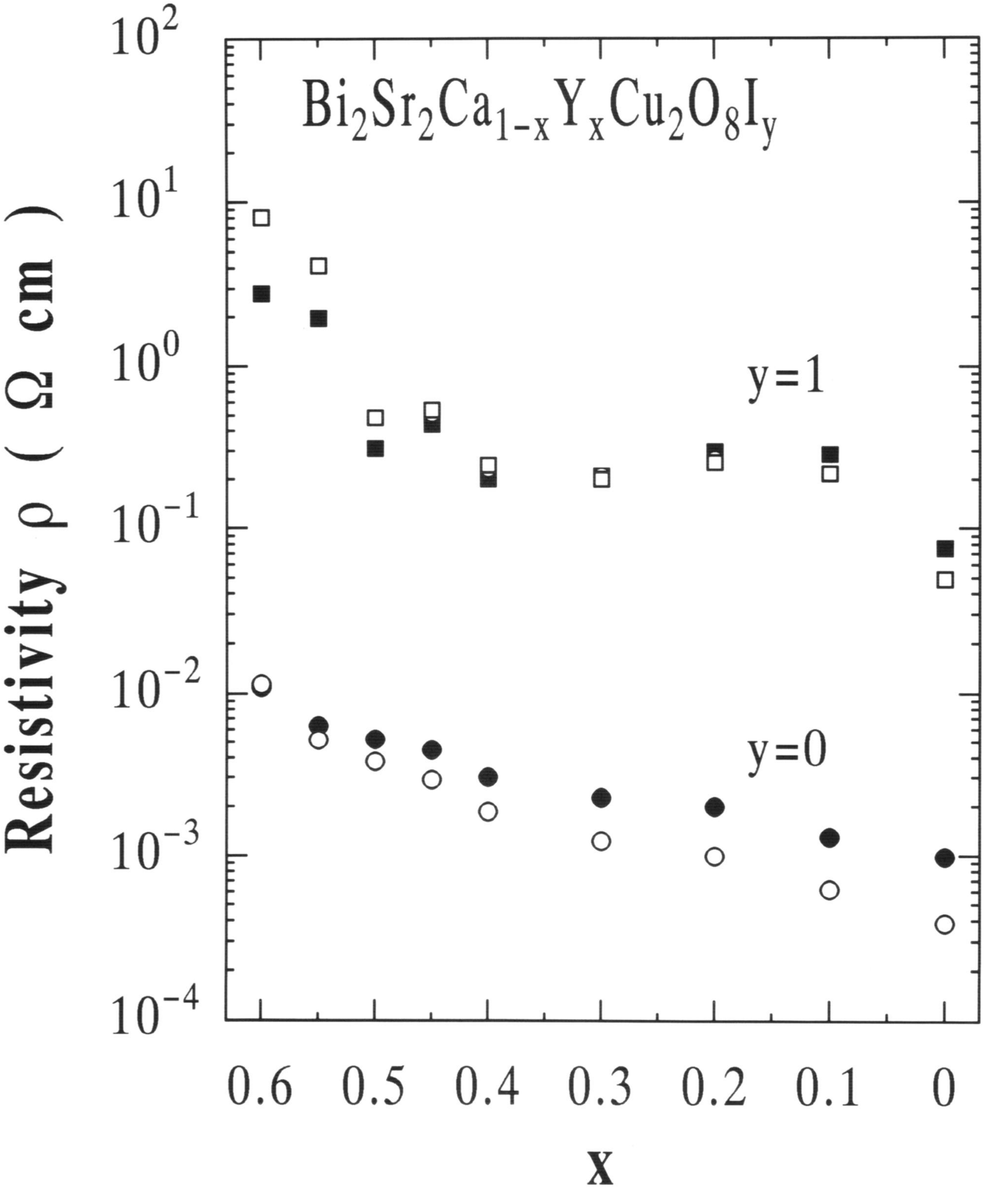

$Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I_y$
y=1
y=0
Resistivity ρ (Ω cm)
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
0.6
0.5
0.4
0.3
0.2
0.1
0
x

Fig. 6

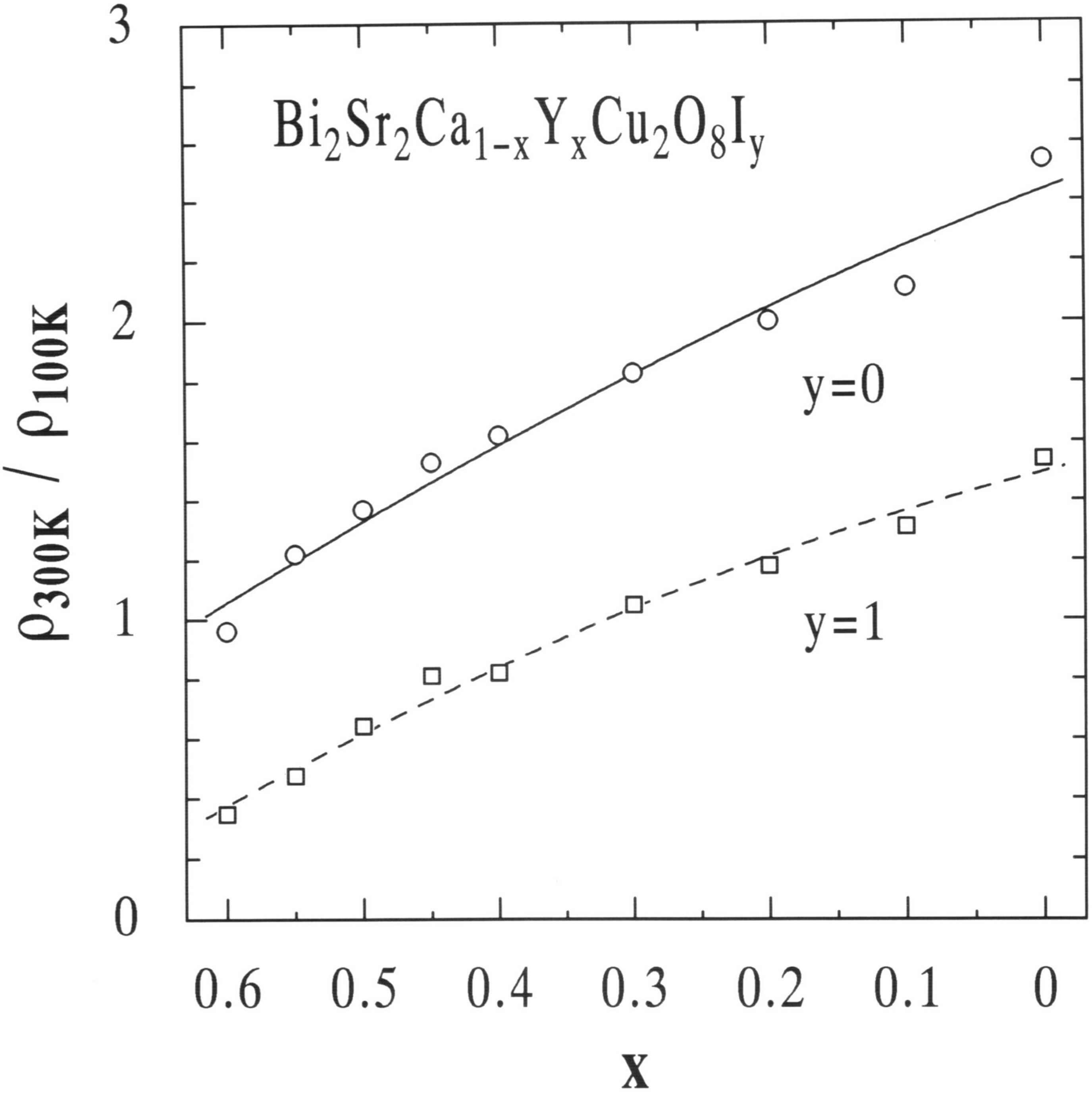

3
2
1
0
$Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I_y$
y=0
y=1
ρ_{300K} / ρ_{100K}
0.6
0.5
0.4
0.3
0.2
0.1
0
x

Fig. 7

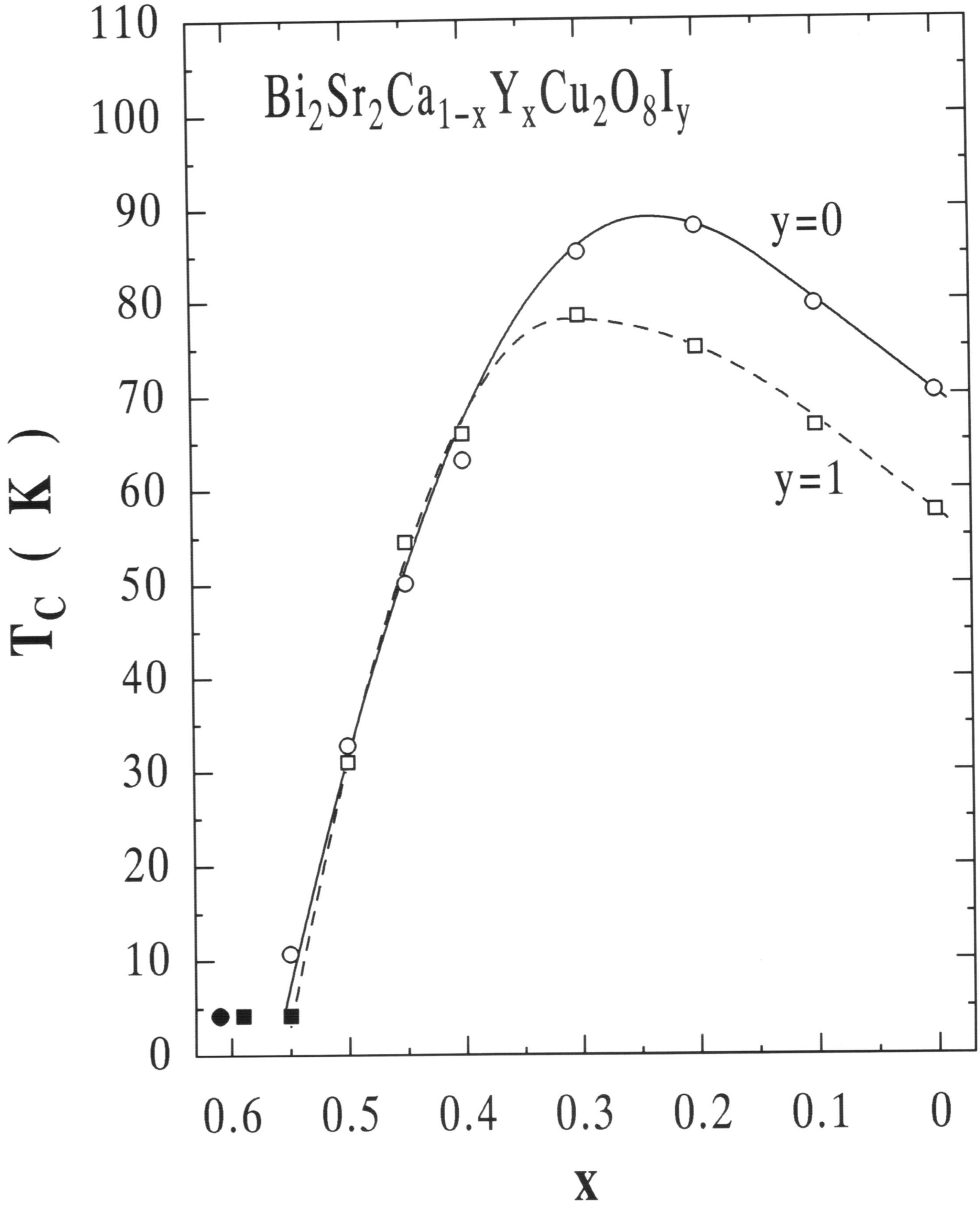

$Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I_y$
y=0
y=1
T_C (K)
x
110
100
90
80
70
60
50
40
30
20
10
0
0.6
0.5
0.4
0.3
0.2
0.1
0

Fig. 8

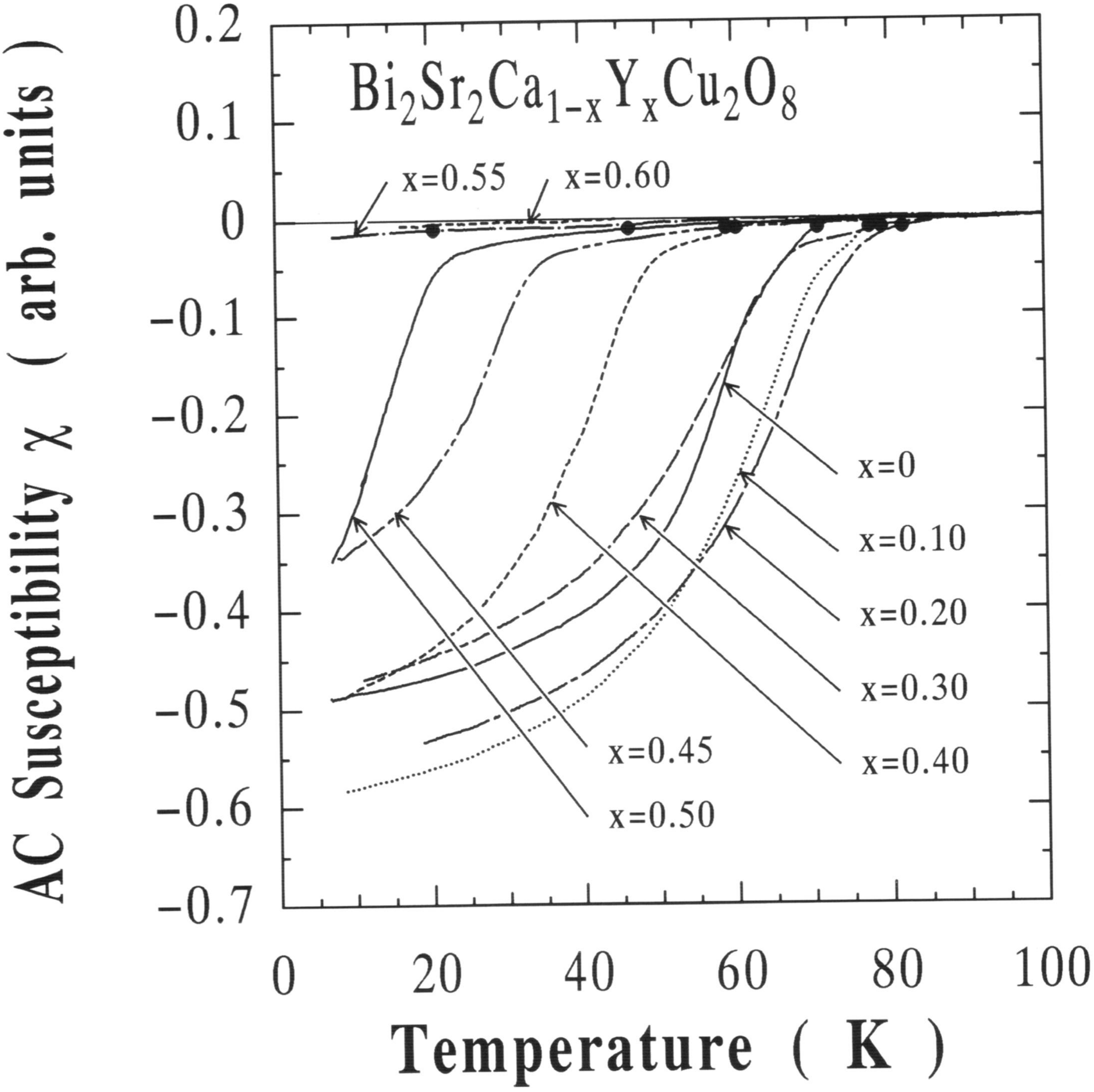

$Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$
x=0.55
x=0.60
x=0
x=0.10
x=0.20
x=0.30
x=0.40
x=0.45
x=0.50
AC Susceptibility χ (arb. units)
Temperature (K)
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
0
20
40
60
80
100

Fig. 9

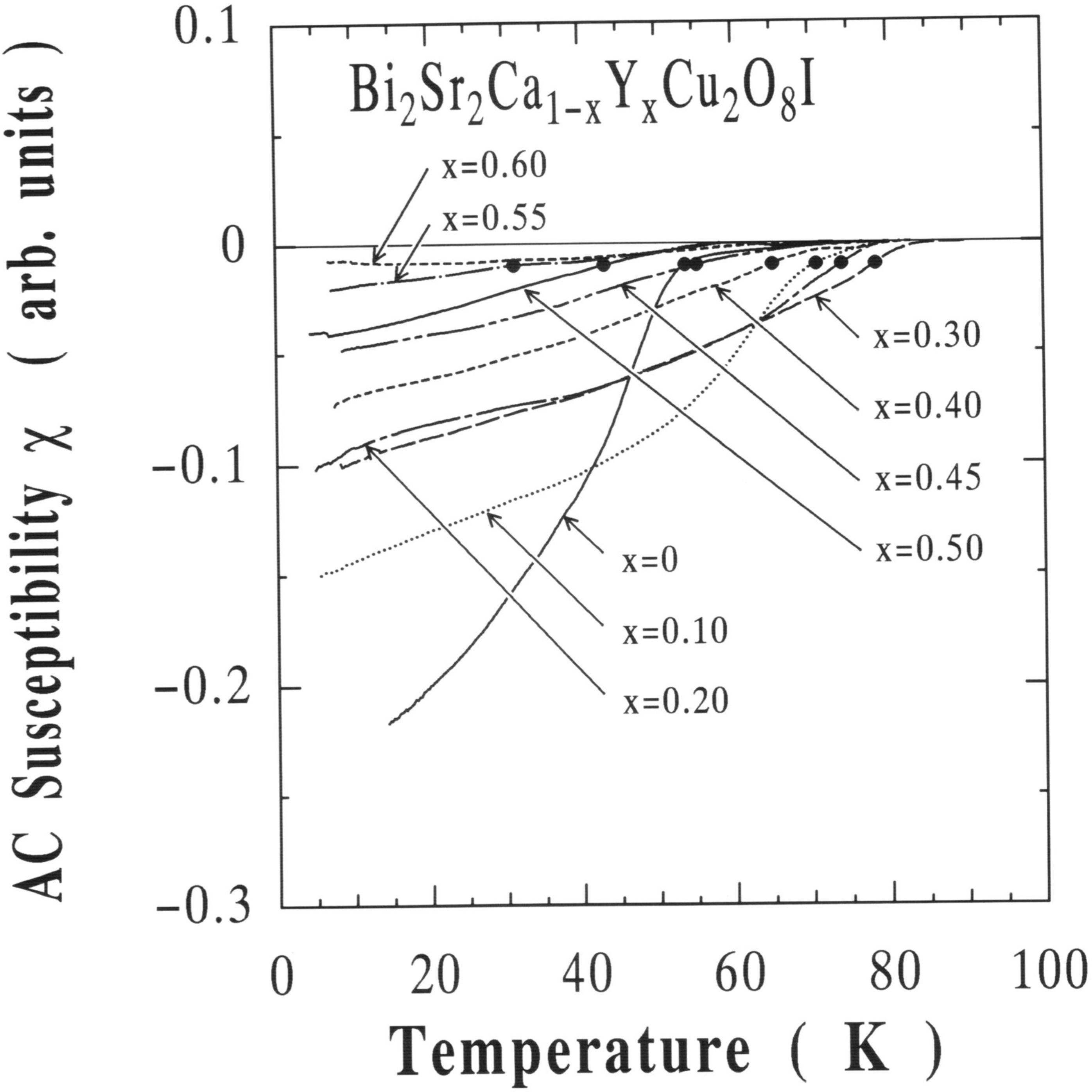

$Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I$
x=0.60
x=0.55
x=0.30
x=0.40
x=0.45
x=0.50
x=0
x=0.10
x=0.20
AC Susceptibility χ (arb. units)
0.1
0
-0.1
-0.2
-0.3
0
20
40
60
80
100
Temperature (K)

Fig. 10

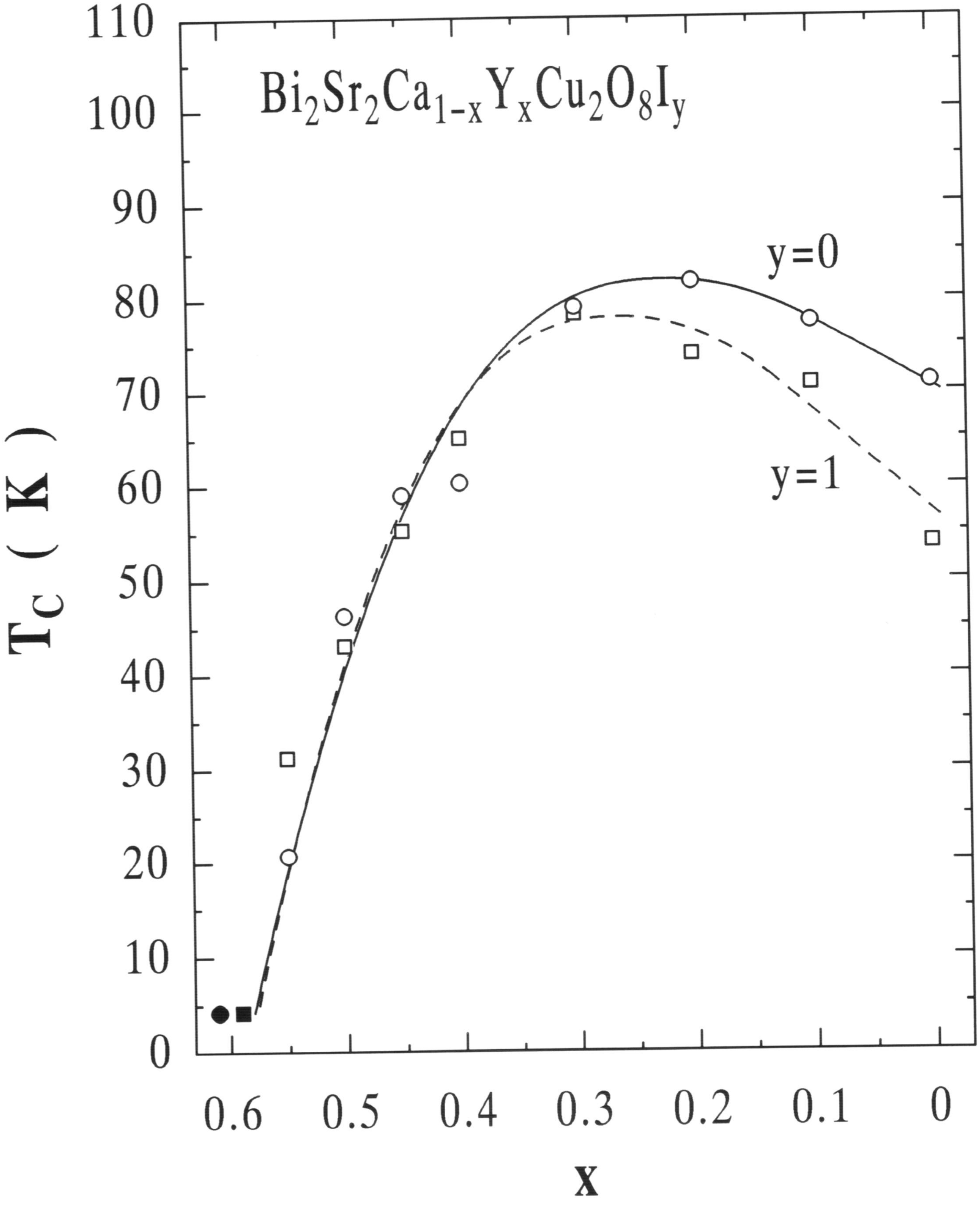
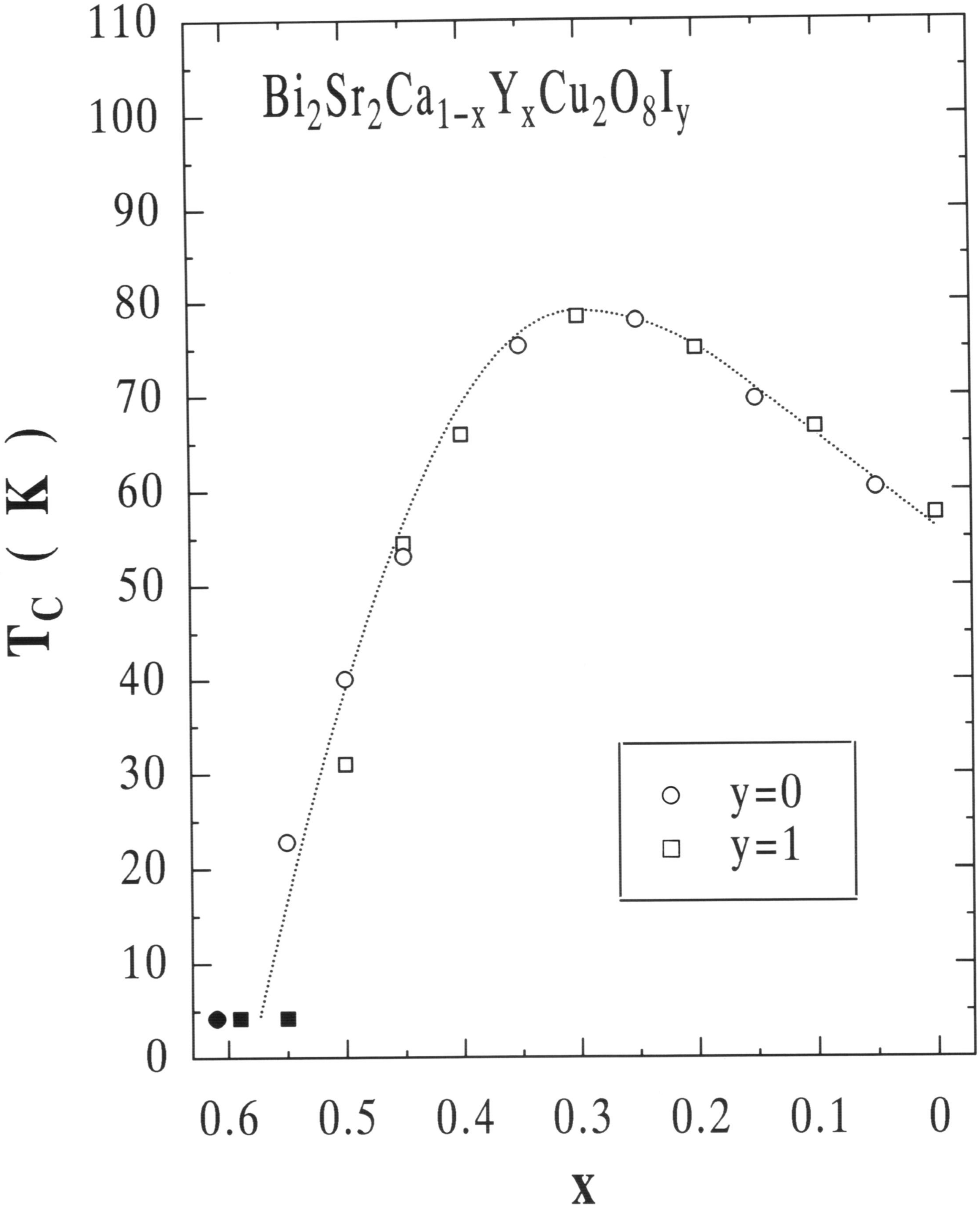

110
100
90
80
70
60
50
40
30
20
10
0
T_C (K)
0.6
0.5
0.4
0.3
0.2
0.1
0
x
$Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I_y$
y=0
y=1

Fig. 11



$Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8I_y$
T_C (K)
110
100
90
80
70
60
50
40
30
20
10
0
0.6
0.5
0.4
0.3
0.2
0.1
0
x
○ y=0
□ y=1

Fig. 12