

Iodine intercalation in $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-z}\text{Co}_z)_2\text{O}_{8+\delta}$ with different δ values

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The effects of iodine intercalation have been investigated for the Co-substituted Bi-2212 phase $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-z}\text{Co}_z)_2\text{O}_{8+\delta}$ with different δ values in the overdoped regime. Whereas in the pristine samples T_c depends on z and δ , in the intercalated ones T_c is independent of δ . This indicates that the hole concentration p in the Bi-2212 phase has an upper limit and becomes saturated by the transfer of holes from the intercalated iodine. $T_c(z)/T_c(z=0)$ of the intercalated samples differs from that of the pristine ones. This suggests that the intercalation of iodine decreases T_c not only through an increase in p , but also through a structural change, probably the interlayer decoupling between adjacent blocks of the CuO_2 planes. [S0163-1829(96)05125-9]

I. INTRODUCTION

High- T_c cuprates are mostly described in terms of Josephson-coupled two-dimensional CuO_2 planes. It is widely known that the superconducting transition temperature T_c increases with the number of CuO_2 planes per unit cell, n , at least for $n \leq 3$. To explain this, several models have been proposed,¹⁻³ taking into account both intraplane properties and interplane coupling. In the $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ ($n=1,2,3$) system, it is known that the intercalation of atoms or molecules between the weakly coupled BiO-BiO double layers increases the c axis considerably, leaving the intraplane lattice parameters unchanged.^{4,5} In particular, intercalation of iodine into the Bi-2212 phase has been well established.^{4,6,7} Then, the question has been raised whether the resulting decrease in T_c through iodine intercalation is due to decoupling of the CuO_2 planes^{8,9} or due to transfer of holes from the intercalated iodine to the CuO_2 planes.^{10,11}

Formerly, Fujiwara *et al.*⁷ approached this problem by mapping the T_c - x diagram of the intercalation compound $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+\delta}\text{I}_y$ on that of the pristine compound $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+\delta}$. They concluded that the change of the interlayer coupling leads to an overall decrease in T_c , while the transfer of holes leads to a shift of the maximum T_c^{max} towards lower x values.

In this paper, to approach the above problem in another way, we investigate the effects of iodine intercalation for the Co-substituted Bi-2212 phase $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-z}\text{Co}_z)_2\text{O}_{8+\delta}$ with different δ values. Among possible substituents for Cu, Co has been chosen because of the comparatively large solubility.^{12,13}

II. EXPERIMENTAL DETAILS

Polycrystalline samples of $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-z}\text{Co}_z)_2\text{O}_{8+\delta}$ have been prepared by a conventional solid-state reaction method. Powders of Bi_2O_3 , SrCO_3 , CaCO_3 , CuO , and CoO have been mixed in a stoichiometric ratio and were pre-fired at 800 °C. After pulverization, the pre-fired samples were pelletized and sintered in air for 24 h at 850 °C. The last step was repeated to obtain homogeneous samples. All

samples were characterized by powder x-ray diffraction (XRD). We could not detect impurity phases due to the Co substitution for $z \leq 0.02$. The oxygen content of the sintered samples was changed by subsequent annealing in flowing gas of N_2 and O_2 at 600 °C. From iodometry analysis and weight change, the oxygen content of the unsubstituted samples ($z=0$) was estimated to be $\delta \approx 0.25$ (as sintered), $\delta \approx 0.19$ (N_2 annealed), and $\delta \approx 0.28$ (O_2 annealed), respectively.

The intercalation of iodine was carried out by vapor-phase reaction in an evacuated glass tube,⁶ at an iodine temperature T_i and a sample temperature T_s of $T_i = T_s = 150$ °C.

T_c was determined from resistivity measurements, choosing a 50% value of the normal resistivity at the superconducting transition as a criterion.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show typical XRD patterns of $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-z}\text{Co}_z)_2\text{O}_{8+\delta}\text{I}_y$ with $y=0$ and 1. It is found that the c -axis lattice parameter increases due to the intercalation from $c/2 = 15.4$ Å to $c = 19.0$ Å by 3.6 Å for all z values, while the a -axis parameter remains constant at 5.41 Å. With increasing $z > 0.02$, growth of impurity peaks is observed in the XRD patterns. In the pristine samples, the main impurity peak is hidden underneath the (117) peak, virtually increasing its magnitude in comparison with the (115) and (200) peaks. The structural change through the intercalation shifts the (00 l) peaks, so that the main impurity peak is no longer superposed in the intercalated samples.

From the weight change through intercalation, the iodine content y was determined to be $y = 1.0 \pm 0.03$ for $z \leq 0.02$, as shown in Fig. 2. Regardless of the oxygen content, y decreases with increasing z for $z > 0.02$. This is consistent with the growth of impurity phases for $z > 0.02$, supposing that iodine can only enter the Bi-2212 phase, but not the impurity phases.

Figure 3 shows T_c vs z for pristine and intercalated samples with different oxygen contents. For pristine samples, $T_{c0} \equiv T_c(z=0)$ decreases with increasing δ and hence with increasing hole concentration per Cu, p . This demonstrates that these samples are located on the overdoped side of the

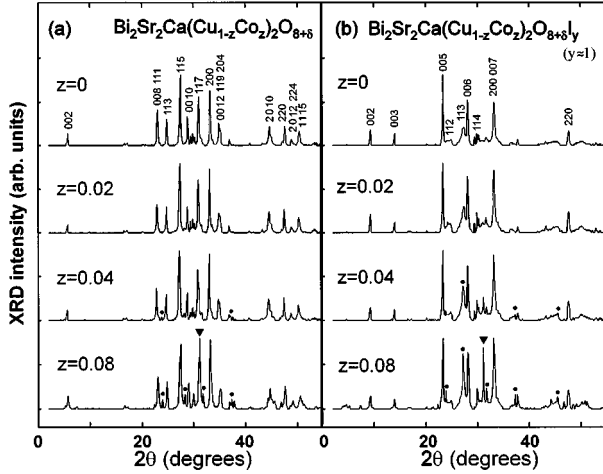


FIG. 1. Powder x-ray diffraction patterns for as-sintered samples of $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-z}\text{Co}_z)_2\text{O}_{8+\delta}$ before (a) and after (b) iodine intercalation. For $z \geq 0.04$, impurity phases (marked by dots and a triangle) appear. In pristine samples, the main impurity peak (marked by a triangle) is hidden underneath the (117) peak of the Bi-2212 phase.

T_c - p diagram, where T_c decreases upon hole doping.

With increasing z , T_c decreases linearly until $z = 0.02$ for all samples with different δ and y values. At this concentration a kink appears and the slope of T_c suppression decreases slightly. Since the growth of impurity phases is observed for $z > 0.02$, above this concentration Co atoms are concluded not to be fully incorporated into the Bi-2212 structure. Note that the slope $|dT_c/dz|$, as well as T_{c0} , is carrier dependent and decreases with increasing p for the pristine samples.

After intercalation, we find almost the same T_c for each concentration z , regardless of the δ value. For example, $T_{c0} = 51.1 \pm 0.6$ K after intercalation for all three types of pristine samples with $z = 0$. To examine the oxygen loss dur-

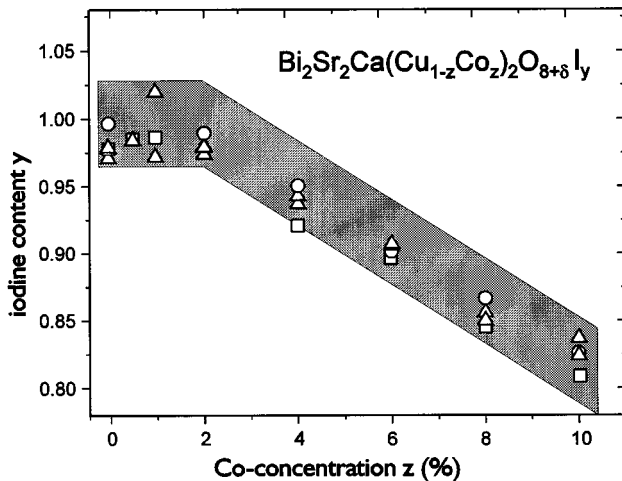


FIG. 2. Iodine content y in $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-z}\text{Co}_z)_2\text{O}_{8+\delta}\text{I}_y$, determined from the weight change through intercalation: Δ , samples as sintered; \square , N_2 annealed; \circ , O_2 annealed. Above $z = 0.02$, y decreases with increasing z . This is in agreement with the appearance of impurity phases seen in the powder x-ray diffraction patterns.

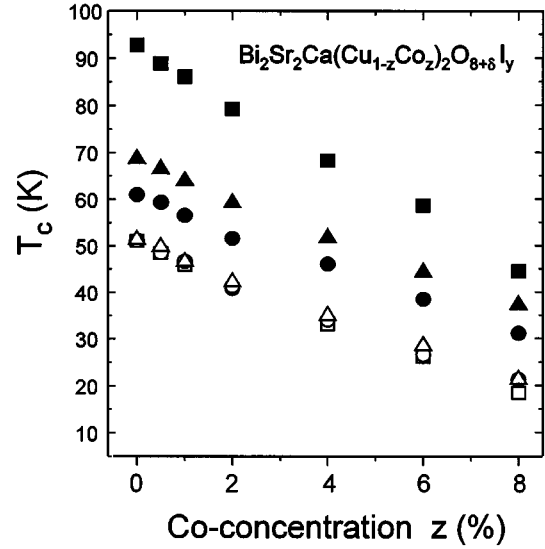


FIG. 3. T_c vs z in $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-z}\text{Co}_z)_2\text{O}_{8+\delta}\text{I}_y$ with different δ values: \square , samples N_2 annealed; Δ , as sintered; \circ , O_2 annealed. Solid and open symbols indicate pristine ($y = 0$) and iodine-intercalated ($y \approx 1$) samples, respectively. For each concentration z , the pristine samples with different δ values yield almost the same T_c after intercalation.

ing the intercalation process, we treated the pristine samples with $z = 0$ and different δ values under intercalation conditions, omitting, however, iodine. We observed an increase in T_c due to the oxygen loss, for the oxidized sample from $T_{c0} = 61.1$ K to 73 K and for the as-sintered sample from $T_{c0} = 68.9$ K to 80 K, while T_c remains unchanged for the oxygen-reduced samples as $T_{c0} = 92.9$ K. Although the samples clearly lose some oxygen during the intercalation process, this loss is insufficient to account for the observed δ independence of T_c after intercalation. A possible explanation is that the transfer of holes from the intercalated iodine to the CuO_2 planes is lower for samples with higher δ values, keeping the value of p constant.¹⁴ That is, the value of p in the Bi-2212 phase seems to have an upper limit and becomes saturated by the transfer of holes from the intercalated iodine, leading to the same T_c . Such a behavior has already been observed for samples of the Bi-2212 phase, annealed under high pressures of O_2 , where oxygen is considered to enter the samples as O_2 instead of O^{2-} above $\delta \approx 0.3$.¹⁵

Figure 4 shows replotted data of T_c as $T_c(z)/T_{c0}$ vs z . For the pristine samples, all data points are located on a single curve, which is independent of δ , namely, p . The intercalated samples, however, show a small but clear deviation towards stronger suppression. This can be seen even at low concentrations $z \leq 0.02$, where effects of the impurity phases can be excluded. The same deviation has been found using the diamagnetic onset of the ac susceptibility as a criterion for T_c .

Recently, we reported on the existence of a scaling law, observed in overdoped high- T_c cuprates.¹³ It was demonstrated that data with different p values, replotted as $T_c(z)/T_{c0}$, fall onto a single curve for each substituent. That is, assuming that p does not change with z , it was found that $T_c(z)/T_{c0} \equiv T_c(p, z)/T_c(p, 0) = g(z)$, where $g(z)$ is the

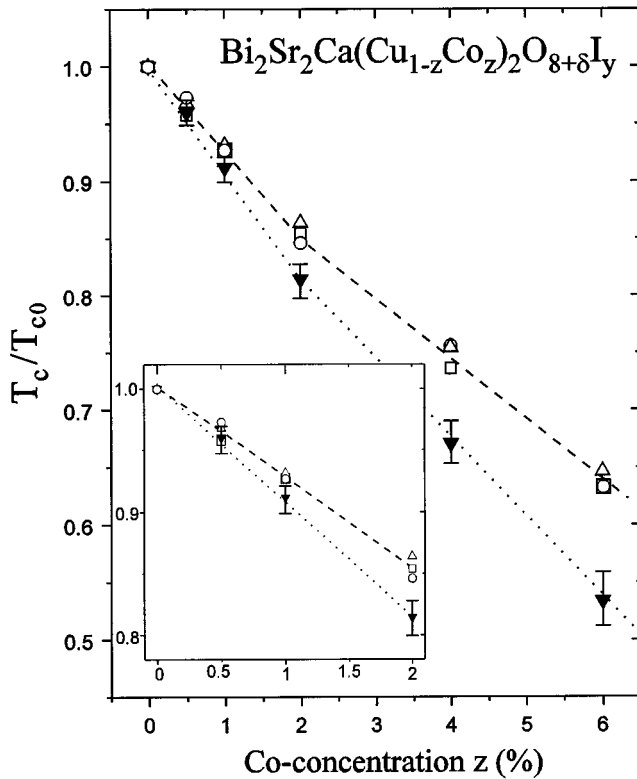


FIG. 4. Dependence of T_c/T_{c0} on z for $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-z}\text{Co}_z)_2\text{O}_{8+\delta}\text{I}_y$ with different δ values. Open symbols represent the pristine samples ($y=0$) of Fig. 3, and solid symbols represent averages over the intercalated samples ($y \approx 1$) of Fig. 3 with different δ values. The inset shows a range of low Co concentrations. The dashed line represents the scaling function $g(z)$ of the pristine samples. The dotted line of the intercalated samples shows a deviation from $g(z)$.

p -independent scaling function depending only on the crystal structure and the substituent.

In the case of trivalent substituents such as Co^{3+} , p might decrease with increasing z . We believe, however, that extra charges of the trivalent substituents are compensated by an increase of δ in the overdoped Bi-2212 phase. This is supported from measurements of the thermoelectric power $S(290\text{ K})$,¹⁶ which is sensitive to p .¹⁷ Even if there remain

uncompensated extra charges, the effect will be absorbed into an effective suppression function $g(z)$.

For Co-substituted pristine samples, as a matter of fact, the scaling holds good. Accordingly, the deviation of the intercalated samples from $g(z)$ of the pristine ones means that the decrease in T_c through intercalation cannot be explained as being due to only the transfer of holes from the intercalated iodine to the CuO_2 planes. It is said that the structural change through intercalation also affects T_c .

Here, from a theoretical point of view, we discuss the deviation from $g(z)$ for the intercalated samples. The scaling law in the overdoped regime has been understood,¹³ based on the Abrikosov-Gorkov pair breaking theory¹⁸ with slight modifications for superconductors with anisotropic gap symmetries like extended s wave and d wave. For these gaps, even nonmagnetic impurities are pair breaking¹⁹⁻²¹ and T_c/T_{c0} is given for small z values by

$$\frac{T_c}{T_{c0}} \equiv g(z) = 1 - \chi \frac{\pi}{4k_B} \frac{\Gamma_N}{T_{c0}}, \quad (1)$$

where $\chi \leq 1$ is related to the gap anisotropy and $\Gamma_N \propto z$ is the scattering parameter. The scaling law in the overdoped regime has been understood as being due to the compensation of the p dependence of T_{c0} by the p dependence of Γ_N .¹³ Then the deviation towards stronger suppression for the intercalated samples is simply explained as being due to a decrease in T_{c0} on account of the structural change, probably the interlayer decoupling between adjacent blocks of the CuO_2 planes, though we cannot rule out that Γ_N is also affected by the structural change.²²

In conclusion, both charge transfer and decoupling of the CuO_2 planes have to be taken into account to understand the T_c suppression through iodine intercalation, which is consistent with former reports.^{7,23}

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