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Epitaxial intercalation of the Bi-Sr-Ca-Cu-O superconductor series

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We have successfully intercalated epitaxial iodine spacers between BiO bilayers of the oxide superconductors $Bi_2Sr_2CuO_x$ (Bi 2:2:0:1), $Bi_2Sr_2CaCu_2O_x$ (Bi 2:2:1:2), and $Bi_2Sr_2Ca_2Cu_3O_x$ (Bi 2:2:2:3), thereby forming new c-axis-expanded stage-I superconducting structures. Although the guest iodine layer expands each BiO bilayer by about 3.6 Å for all three compounds, the materials remain bulk superconductors with transition temperatures T_c as high as 100 K. The respective shifts in T_c upon intercalation of the different materials allow examination of the superconductivity mechanism in terms of the role of interplanar and intraplanar Cu-O coupling.

One of the most interesting aspects of the high-temperature superconducting oxides is that subtle changes in the crystal structure can have dramatic effects on the superconducting transition temperature T_c. Common to the high-T_c materials are conducting two-dimensional CuO_2 sheets. Although the superconductivity mechanism in these materials has not yet been established, it is generally believed that the CuO_2 sheets are the critical structural units. Carrier doping in the sheets, and the strength of the coupling between adjacent (and possibly more distant) sheets, may to a large extent dictate the T_c for a given material. In Y-Ba-Cu-O-based and Bi(Tl)-Sr(Ba)-Ca-Cu-based materials, for example, slight changes in oxygen content lead to large shifts in T_c.[1,2] In Bi(Tl)-Sr(Ba)-Ca-Cu-O structures, T_c is a function of the number of adjacent CuO_2 sheets per unit cell.[1,2] Also, in recent studies of epitaxial $YBaCu_3O_{7-x}/PrBa_2Cu_3O_{7-x}$ alternating thin films, it has been demonstrated that T_c can be drastically modified by the separation of the CuO_2 sheets.[3,4]

The highly anisotropic structural and electronic properties of these oxide superconductors are reminiscent of those of other layered materials such as graphite and transition-metal dichalcogenides. In the latter materials, guest atomic or molecular species can be introduced between two weakly bonded identical host layers or building blocks without dramatic changes in their in-plane or inner block structures. The resulting intercalation compounds can be made in forms that consist of an alternating sequence of n host layers (or blocks) and a monolayer of foreign atoms or molecules (the intercalant), where n is called the "stage" of the compound. The insertion of different foreign species usually leads to a drastic expansion of the interlayer (or interblock) dimension and consequent changes in the interlayer coupling constant. In many cases intercalation leads to charge transfer between the intercalant and the host layers. Since physical properties of the host materials can be tuned over a wide range by intercalation, it is a powerful means of systematically investigating the roles of both interlayer coupling and doping in the mechanism of high-T_c superconductivity.

One class of common intercalants for graphite and the dichalcogenides is the alkali-metal group.[5] Attempts to intercalate similar guest species into the oxide superconductors have not yielded positive results. For example, "intercalation" of K and Na into $Bi_2Sr_2CaCu_2O_x$ crystals results in a drastic decrease in T_c and color change of the crystals, but no significant change in the lattice parameters.[6] This suggests that K and Na act as oxygen getters instead of intercalants. Similar results are obtained for attempted Cu and Ag intercalation.[7] On the other hand, it was recently demonstrated[8] that iodine successfully intercalates into $Bi_2Sr_2CaCu_2O_x$ crystals with a dramatic change in the c-axis lattice parameter, yielding the stable stage-I compound $IBi_2Sr_2CaCu_2O_x$, with $T_c = 80$ K.

We here explore iodine intercalation in the Bi-based oxide superconductor series $Bi_2Sr_2CuO_x$ (Bi 2:2:0:1), $Bi_2Sr_2CaCu_2O_x$ (Bi 2:2:1:2), and $Bi_2Sr_2Ca_2Cu_3O_x$ (Bi 2:2:2:3). We find that iodine intercalates into the BiO bilayers of all three compounds with a large expansion of about 3.6 Å for each BiO bilayer. The intercalated iodine layers are epitaxial with respect to the adjacent BiO sheets, and the staggered stacking of the basic building blocks of the pristine host material is changed to a commonly registered stacking sequence (with a single basic block per new unit cell). The new intercalation compounds are bulk superconductors with relatively small shifts (2–10 K) in T_c compared to the pristine host materials.

Specimens of the pristine materials were prepared using standard methods. Single-phase Bi 2:2:0:1 and Bi 2:2:2:3 polycrystalline samples were synthesized by doping La for Sr in Bi 2:2:0:1, and (Pb,Sb) for Bi in Bi 2:2:2:3, with nominal compositions $Bi_{2.1}Sr_{1.5}La_{0.4}CuO_x$ and $Bi_{1.58}Pb_{0.32}Sb_{0.1}Sr_{1.75}Ca_{1.8}Cu_{2.75}O_x$, respectively.[9] For Bi 2:2:1:2, both polycrystalline samples and single-phased single crystals were used. Intercalation was accomplished for all three materials using a gas diffusion method described earlier.[8]

The pristine structures of the different Bi-based superconductors are very similar. Each unit cell is composed of two identical basic building blocks shifted by $\frac{1}{2}a$ with respect to each other. In each basic building block, one, two, and three CuO_2 sheets are sandwiched by SrO and further by BiO layers for Bi 2:2:0:1, Bi 2:2:1:2, and Bi 2:2:2:3, respectively.[10,11]

Figures 1(a)–1(c) show x-ray powder-diffraction pat-

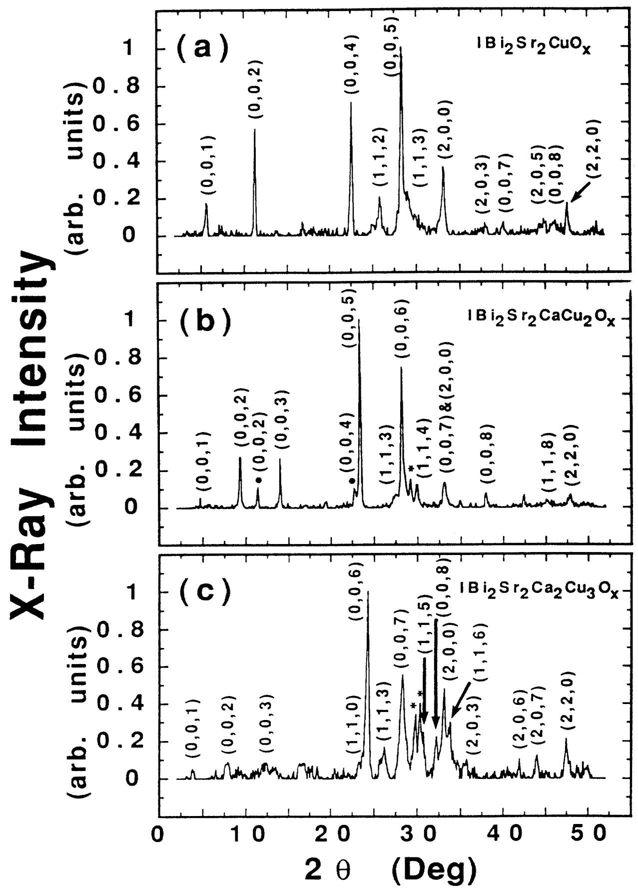

FIG. 1. X-ray powder-diffraction patterns for intercalation compounds (a) I-Bi 2:2:0:1 ($c=15.76$ Å, $a=5.40$ Å, $\delta=3.67$ Å; for pristine Bi 2:2:0:1 $c/2=12.09$ Å, $a=5.40$ Å); (b) I-Bi 2:2:1:2 ($c=19.02$ Å, $a=5.40$ Å, $\delta=3.59$ Å; for pristine Bi 2:2:1:2 $c/2=15.43$ Å, $a=5.40$ Å); and (c) I-Bi 2:2:2:3 ($c=22.01$ Å, $a=5.40$ Å, $\delta=3.53$ Å; for pristine Bi 2:2:2:3 $c/2=18.48$ Å, $a=5.4$ Å). δ is the expansion of BiO bilayers. Solid circles identify the I-Bi 2:2:0:1 phase, and asterisks identify an impurity phase also present in the pristine material.

terns for the iodine-intercalated structures I-Bi 2:2:0:1, I-Bi 2:2:1:2, and I-Bi 2:2:2:3, respectively. The changes in diffraction angle 2θ for the Miller index $(00l)$ peaks indicate respective expansions of 3.67, 3.59, and 3.53 Å per basic building block, compared to dimensions of the pristine, unintercalated host structures Bi 2:2:0:1, Bi 2:2:1:2, and Bi 2:2:2:3. For all three systems, the intensity patterns of the $(00l)$ peaks are consistent with x-ray diffraction computer simulations assuming one iodine per two Bi (in stoichiometry) sandwiched between two basic building blocks with BiO as adjacent layers. All three intercalated materials are thus stage-I, i.e., the stage index $n=1$. The stability of the positions for $(hk0)$ peaks upon intercalation indicates that the in-plane lattice of the building blocks is not disturbed by the intercalants. The (hkl) peaks can only be indexed if we assume the BiO layer stacking sequence of $AB\ldots BA\ldots A$ is changed upon intercalation to a stacking sequence $A/A\ldots A/A\ldots A$. A and B refer to BiO layers with $\frac{1}{2}a$ shift with respect to each other, the dotted line "..." refers to the rest of the elements in the basic building block, and "/" refers to the iodine layer. This assumption is also consistent with x-ray diffraction computer simulations. A similar change in the stacking sequence is commonly observed in graphite and the dichalcogenide intercalation compounds. Because of preferred crystallite orientation in the diffraction specimens, enhancement of the $(00l)$ peaks with respect to the (hkl) peaks is observed in the powder-diffraction patterns of Fig. 1. No effort has been made to determine the exact position of iodine atoms in the a-b plane. The exact stoichiometry of I (I:Bi = 1:2) determined by weight change and scanning electron microscope x-ray fluorescence of I-Bi 2:2:1:2 single crystals, along with the stability of all three intercalation compounds and the x-ray diffraction data, indicate that iodine layers are *epitaxially* intercalated between BiO bilayers. However, a small amount of peak broadening of (hkl) diffraction peaks with $h,k\neq 0$ indicates a slight imperfection in a-b plane ordering of the iodine.

Superconducting transition temperatures of the pristine and intercalated compounds were measured using a dc superconducting quantum interference device magnetometer and/or an ac rf resonant magnetometer (operated at 10 MHz). Figure 2 shows the dc susceptibility of a pristine Bi 2:2:0:1 specimen and the complementary iodine intercalated sample as functions of temperature. The onset T_c of the intercalated compound is decreased by only 2 K with respect to $T_c=24$ K for the (La-doped) pristine ma-

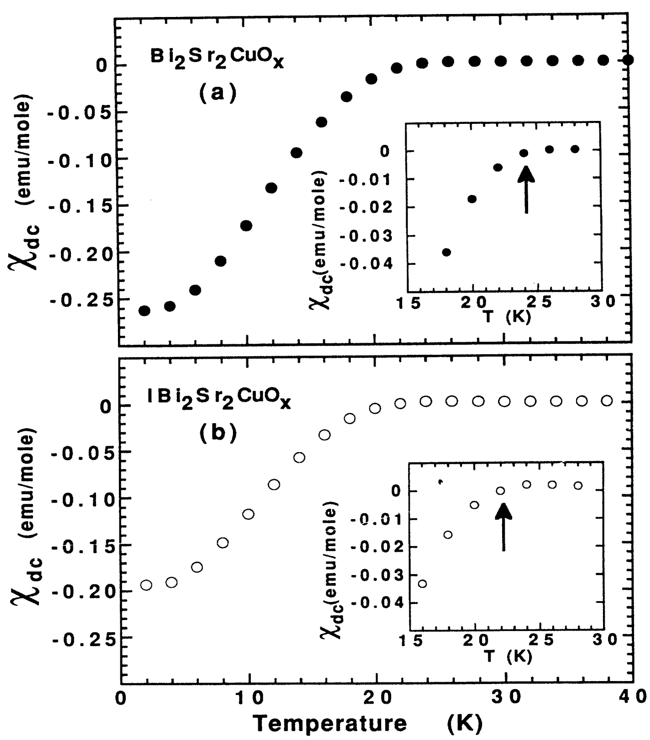

FIG. 2. dc magnetic susceptibility of (a) pristine Bi 2:2:0:1 and (b) intercalated I-Bi 2:2:0:1 polycrystalline samples. The insets show detailed behavior near the onset critical temperature, identified by a vertical arrow.

terial. Figure 3(a) shows the ac susceptibility of a Bi 2:2:1:2 single crystal before and after intercalation. The onset T_c is 90 K for the pristine sample and 80 K for the sample after intercalation. (The T_c of different pristine Bi 2:2:1:2 samples is somewhat dependent on the details of the crystal synthesis, ranging from 82 to 90 K. However, the intercalated I-Bi 2:2:1:2 structure always has a T_c of 80 K.) Figure 3(b) shows the ac susceptibility of pristine Bi 2:2:2:3 and an intercalated polycrystalline I-Bi 2:2:2:3 sample. The T_c of the intercalated sample is depressed by 10 K with respect to $T_c = 110$ K for the pristine sample. In all cases, there is clear evidence that all three intercalation compounds are bulk superconductors with Meissner effect magnitudes similar to those of pristine compounds.

Using the observed changes in crystal structure and superconducting transition temperature upon iodine intercalation of the series of materials, we can evaluate some current theoretical models that may apply to layered high-T_c oxides. A model proposed by Wheatley, Hsu, and Anderson[12] (WHA) is based on the coherent hopping of valence-bond pairs between CuO_2 planes. The dominant contribution is from hopping between planes within a block (intrablock coupling) with an enhancement from hopping between planes in adjacent blocks (interblock coupling). On the other hand, a model by Ihm and Yu (IY),[13] based on a Bardeen-Cooper-Schrieffer formalism, includes only coupling within each CuO_2 plane (intraplane coupling) along with intrablock coupling. IY ignore interblock coupling.

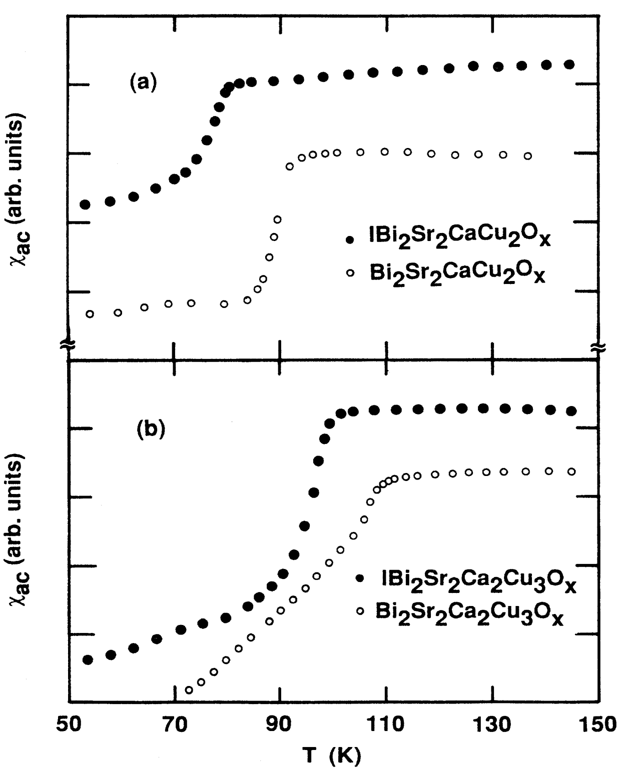

FIG. 3. ac magnetic susceptibility of (a) pristine (open circles) and intercalated (solid circles) Bi 2:2:1:2 single crystals; (b) pristine (open circles) and intercalated (solid circles) Bi 2:2:2:3 polycrystalline samples.

Since intercalation of the type discussed here may primarily affect interblock coupling by changing the distance between CuO_2 layers in adjacent blocks, we first focus on the WHA model.

The changes in T_c's up to 10 K for Bi 2:2:1:2 and Bi 2:2:2:3 intercalation compounds suggest that the contribution of next block coupling to T_c is on the order of 10 K, which is consistent with the WHA model calculation. The variation in T_c for different pristine Bi 2:2:1:2 samples compared to the same T_c in all the intercalated samples suggests that this next-block-coupling contribution could be different in pristine samples (possibly related to the subtle differences in their oxygen configuration). This could also explain the small change of T_c in the Bi 2:2:0:1 intercalation compound, i.e., the next-block-coupling contribution is small to begin with in the pristine sample due to subtle differences in its crystal structure with respect to two and three plane structures.

The above reasoning is further supported by results from a study of stage-II iodine intercalated Bi 2:2:1:2 crystals.[14] In stage-II compounds, iodine molecules intercalate into *every other* BiO bilayer with an expansion of 5.8 Å for each iodine molecular layer. The large expansion is due to the insertion of large size I_2 molecules with their bond perpendicular to the $\hat{c}$ axis of host materials. With this rearrangement, the next-block coupling is preserved in one (and only one) direction for each block. The T_c's in stage-II compounds decrease by about 5 K with respect to those of the pristine samples. This is consistent with the previous discussion. However, T_c in the stage-I intercalated Bi 2:2:0:1 remains as high as 22 K, indicating that the intraplane interaction stressed in IY's model may be responsible for this contribution. Doping in the Bi 2:2:0:1 sample may well enhance this interaction, so the corresponding effect may not be as large in Bi 2:2:1:2 and Bi 2:2:2:3 samples. Similar enhancement of T_c by doping SrO layers in the Bi 2:2:1:2 phase materials has also been observed.[13]

Our findings do not rule out the relevancy of either the WHA or IY models to superconductivity in these materials, but suggest that elements of both models are needed to explain it in detail.

It is helpful, at this point, to compare our results with studies on $YBa_2Cu_3O_7$ structures. In $YBa_2Cu_3O_7$, the inner cell CuO_2 sheets are presumably coupled strongly by Cu-O chains sandwiched between the CuO_2 sheets even though the sheets are about 8.3 Å apart. However, the closest distance between two CuO_2 sheets in adjacent cells is only about 3.2 Å, in contrast to 12 Å in the Bi(Tl)-based structures. Therefore, when insulating blocks of $PrBa_2Cu_3O_7$ are inserted between $YBa_2Cu_3O_7$, the drastic decrease of T_c by as much as 60 K may be attributed to the decoupling of CuO_2 sheets in adjacent cells (separated by Y).[3,4] With regard to intracell coupling in $YBa_2Cu_3O_7$, it has been suggested that the disruption of the Cu-O chains due to O_2 deficiency could be the reason that the 90-K $YBa_2Cu_3O_7$ compound converts to a 60-K superconductor as CuO_2 sheets in the cell decouple.[13]

An important question concerning iodine intercalation in the Bi-based materials is the possibility of charge transfer from iodine intercalant layers to the host layers. The fact that stage-I compounds are very stable at room temperature in air (in contrast to the stage-II compounds where nearly neutral I_2 molecules can easily diffuse out of the host material[14]) suggests that iodine atoms in stage-I compounds form a relatively strong (possibly metallic) bond with BiO layers between which they are sandwiched. Since it is well known that carrier doping in the CuO_2 layer can affect T_c, the observed changes in the transition temperature could be due in part to charge transfer from the iodine layers to the CuO_2 layers. However, in view of the large distance between the intercalant layer and the CuO_2 sheets, it is unlikely that there is a significant charge transfer to the CuO_2 sheets, though some charge transfer to the BiO layers is possible. The analysis in this paper assumes that the effect of charge transfer between the iodine and CuO_2 layers is small compared to that of changing the interlayer distances. This hypothesis could be tested by measuring the carrier density in the CuO_2 layers of the intercalated compounds via the Hall effect.

An interesting possibility is the intercalation of other oxide superconductor structures where intercalants might be located closer to the CuO_2 layers, resulting in a significant change in T_c due to charge transfer to the CuO_2 sheets.

In conclusion, iodine layers have been epitaxially intercalated between Bi-O layers in the Bi-based high-T_c superconductors. Changes in T_c's for the new structures imply that both next cell coupling and intraplane coupling are not negligible for superconductivity in these systems.

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