Tuning High-$T_c$ Superconductors via Multistage Intercalation

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Multistage intercalation has been used to tune the interaction between adjacent blocks of CuO$_2$ sheets in the high-$T_c$ (high superconducting transition temperature) superconductor Bi$_2$Sr$_2$CaCu$_2$O$_y$. As revealed by atomic-resolution transmission electron microscopy images, foreign iodine atoms are intercalated into every nth BiO bilayer of the host crystal, resulting in structures of stoichiometry $\text{Bi}_{2n-2}\text{Sr}_2\text{Ca}_2\text{Cu}_{2n-2}\text{O}_{y}$ with stage index $n$ up to 4. An expansion of 3.6 angstroms for each intercalated BiO bilayer decouples the CuO$_2$ sheets in adjacent blocks. A comparison of the superconducting transition temperatures of the pristine host material and intercalated compounds of different stages suggests that the coupling between each pair of adjacent blocks contributes ~5 K to $T_c$ in Bi$_2$Sr$_2$CaCu$_2$O$_y$.

Although it is generally believed that the critical structural units in the highest $T_c$ superconductors are the CuO$_2$ planes, the significance of coupling between the planes is poorly understood. It was recently demonstrated that, like many other two-dimensional materials, Bi-based high-$T_c$ superconducting oxides can be intercalated with foreign species (1). For stage-1 iodine-intercalated Bi$_2$Sr$_2$CaCu$_2$O$_y$, guest iodine atoms are introduced between every pair of weakly bonded BiO bilayers, thus affecting the coupling between identical host blocks containing the double CuO$_2$ planes. In some intercalation compounds, higher stage structures are possible; a stage-$n$ structure has $n$ identical host layers or blocks sandwiched between each pair of intercalant layers. High-stage single-phase graphite intercalation compounds can be synthesized with $n$ as high as 8 (2), but in other layered compounds it is difficult to achieve single-phase intercalation with $n > 1$. The possibility of using intercalants to vary the strength of interlayer interactions and possibly modify microscopic charge transfer makes the intercalation of high-$T_c$ compounds attractive. Systematic investigation of the superconductivity mechanism and its relation to crystal structure is possible if different intercalants can be incorporated and higher stage compounds can be generated.

We here examine interblock interactions in the high-$T_c$ superconductor Bi$_2$Sr$_2$CaCu$_2$O$_y$ by using multistage iodine intercalation to "tune" the coupling between adjacent CuO$_2$-containing blocks. Atomic resolution real-space transmission electron microscopy (TEM) images identify stage structures with $n \leq 4$. Correlations between the crystal structure and $T_c$ allow us to determine the contributions to $T_c$ of interblock CuO$_2$ plane interactions and to evaluate various models for the superconductivity mechanism.

In the intercalation of pristine Bi$_2$Sr$_2$Ca-
Cu₂O₈ crystals we used a gas diffusion technique similar to that described elsewhere (1). For high-stage intercalation, iodine and Bi₂Sr₂CaCu₂O₈ crystals were placed in evacuated cells with a common connection for vapor transport. The iodine cell was held at 150°C and the sample cell at between 300°C and 350°C, for up to 2 weeks. Intercalated crystal structures were characterized by x-ray diffraction and by TEM. In general, intercalation resulted in a complete disappearance of the pristine phase. As with stage-1 materials, nearly phase-pure stage-2 materials could be produced. Stage-3 and stage-4 structures were obtained only as minority phases.

Figure 1, a through d, shows real-space TEM images, respectively, for pristine Bi₂Sr₂CaCu₂O₈ and stage-1, stage-2, and stage-3 iodine-intercalated crystals, all viewed along the [110] direction. In each case, pristine-like BiO bilayers are identified by bars and iodine-intercalated BiO bilayers by arrows. The image in Fig. 1a agrees with the established crystal structure of pristine Bi₂Sr₂CaCu₂O₈. For the stage-1 material (Fig. 1b), iodine is intercalated into every BiO bilayer; for the stage-2 material (Fig. 1c), iodine is intercalated into every other BiO bilayer; for the stage-3 material (Fig. 1d), iodine is intercalated into every third BiO bilayer. The resulting intercalated stage structures have stoichiometry Bi₂Sr₂Ca₂₋ₙCu₂+xO₈, where n is the stage index. Structures with n ≤ 4 have been identified in TEM images. In all cases, the iodine intercalation is epitaxial (the iodine is located between oxygen of the BiO layers) and results in two major structural changes. First, it expands each intercalated BiO bilayer by 3.6 Å along the c axis. Second, it changes the staggered Bi atom stacking sequence (between adjacent BiO bilayers) to a commonly registered stacking sequence. For example, the stacking sequence AB...BA...A/AB relevant to pristine Bi₂Sr₂CaCu₂O₈ changes in the stage-2 compound to AB...B...BA...A/AB...A and B represent BiO layers shifted by 1/2 a with respect to each other, the dotted lines represent the other elements inside the block, and the slash represents the iodine intercalant.

The ability to produce largely homogeneous stage-1 and stage-2 compounds of Bi₂Sr₂Ca₂₋ₙCu₂+xOₘ allows a direct comparison between structural and superconducting properties. Figure 2 shows the magnetic susceptibility, χₐc, as a function of temperature for pristine Bi₂Sr₂CaCu₂O₈, stage-1 Bi₂Sr₂CaCu₂+xOₘ, and stage-2 Bi₂Sr₂Ca₂₋ₙCu₂+xOₘ. Well-defined transitions to the superconducting state are visible in each case. Consistent with previous studies, Tc for stage-1 iodine-intercalated Bi₂Sr₂CaCu₂+xO₈ is 80 K, corresponding to a ~10 K depression in Tc compared to the pristine host material. Tc for stage-2 Bi₂Sr₂CaCu₂+xO₈ is 85 K, corresponding to a ~5 K depression in Tc.

It is unlikely that the shift in Tc is due to charge transfer between the iodine and host material. The iodine is only weakly bonded to the BiO layers, and the distance between the intercalated layers and the Cu₂O₈ layers is large. Transport measurements (3) on the stage-1 material have confirmed that the normal state behavior of the Cu₂O₈ planes remains unchanged by the intercalation. The shift in Tc for different intercalation stage structures can therefore be assumed to be a consequence of changes in the interblock coupling (4, 5). The dominant effect of intercalation is to reduce interblock coupling, which results from an increase in the distance between the Cu₂O₈-containing blocks. Stage-1 intercalation reduces the adjacent block coupling in both directions along the c axis, whereas stage-2 intercalation preserves the original coupling in one direction for each block. Because ΔTc for the stage-1 material is ~10 K while ΔTc for the stage-2 material is only ~5 K, empirically it appears as if next-block coupling contributes about 5 K to Tc for each neighboring block of pristine Bi₂Sr₂CaCu₂O₈.

Our results suggest that, independent of the specific pairing mechanism, interblock coupling should be incorporated into any realistic model of high-Tc superconductivity. Here we examine two prototypical layering models: both are capable of accounting for the behavior of Tc upon multistage intercalation. No specific microscopic mechanism is assumed, and the parameters in each model are determined here phenomenologically.

The simplest layer-coupling model is one in which Tc varies linearly with the interplane coupling. Each Cu₂O₈ plane is coupled to its neighbors in the c direction, but intraplane coupling is neglected. Wheatley, Hsu, and Anderson (6) used this type of model to discuss superconductivity due to spinon-holon scattering. Despite inconsistencies in the spinon-holon theory as a whole revealed by transport measurements (3), the layering model used by Wheatley et al. is non-mechanism-specific. Here we apply the layering scheme to the present experiment to discuss the effects of intercalation and exhibit the merits of this approach.

In the linear layering model, the superconducting amplitude in plane i, ηi, depends on ηi₋₁ and ηi₋₂ and the couplings between the planes, λi₋₁ and λi₋₂. For Bi₂Sr₂Ca₄Cu₁₀O₅, there are two different couplings, λ₀ and λ₁, for nearest and next nearest planes, respectively. The nearest planes are within a block, whereas the next nearest planes are in adjacent blocks. Because all the Cu₂O₈ planes are equivalent, all the η's are equal and the eigenvalue equation for Tc,
\[ \lambda_0 + \lambda_1 \eta = T_c \eta \] (1)

yields \( T_c \) (pristine) = \( \lambda_0 + \lambda_1 \).

For stage-1 \( \text{Bi}_2\text{Sr}_2\text{Ca}_x\text{Cu}_2\text{O}_y \), the model is the same but with \( \lambda_1 \) replaced by \( \lambda_1' \) because the next nearest plane coupling is assumed to be grossly affected by the intercalation. The predicted stage-1 \( T_c \) is then \( \lambda_0 + \lambda_1' \).

For stage-2 \( \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_{8+} \), the CuO2 planes are no longer equivalent; there are planes (a) coupled by \( \lambda_0 \) and \( \lambda_1 \) and planes (b) coupled by \( \lambda_0 \) and \( \lambda_1' \). The eigenvalue equation for \( T_c \) is then

\[ T_c \frac{\eta_a}{\eta_b} = \left[ \begin{array}{c} \frac{\lambda_1}{\lambda_0} \lambda_0 \lambda_1 \end{array} \right] \frac{\eta_a}{\eta_b} \] (2)

If we assume that intercalation completely destroys the next nearest plane coupling, then \( \lambda_1' \to 0 \), and the measured \( T_c \) (stage-1) yields \( \lambda_0 = 80 \) K. With \( T_c \) (stage-2) = 85 K, \( \lambda_0 = 80 \) K, and \( \lambda_1' = 0 \) K, we find \( \lambda_1 = 9.7 \) K. This is consistent with the results for the pristine material, where \( T_c \) is typically 90 K \( \approx (\lambda_0 + \lambda_1' \). It is possible to use the above analysis to predict the \( T_c \)'s for higher stage compounds. If \( \lambda_0 = 80 \) K, \( \lambda_1 = 10 \) K, and \( \lambda_1' = 0 \) K, the predicted \( T_c \)'s for stages 3, 4, 5, and 6 are 87, 88, 89, and 89 K, respectively. Although we have demonstrated that stage-3 and stage-4 structures exist for iodine-intercalated \( \text{Bi}_2\text{Sr}_2\text{Ca}_x\text{Cu}_2\text{O}_y \), we have not been able to reliably determine the \( T_c \)'s for these minority phases.

A second approach incorporates interplane interactions into a Bardeen-Cooper-Schrieffer (BCS)-like framework. Such a model has been advanced by Ihm and Yu (7), although they neglected interblock coupling. Because our experiments indicate that this coupling cannot be neglected, we incorporate such a coupling into a phenomenological model (which is essentially an extension of the original work of Ihm and Yu).

Solving the BCS-like gap equations, assuming a constant density of states per CuO2 plane (even after intercalation), one obtains

\[ F(\text{pristine}) = \left( \frac{1}{\lambda_0 + \lambda_1' + \lambda_s} \right) \] (3)

\[ F(\text{stage-1}) = \left( \frac{1}{\lambda_0 + \lambda_1'} \right) \] (4)

\[ F(\text{stage-2}) = \left( \frac{1}{\lambda_0 + \lambda_1} \right) \] (5)

\[ F(\text{Bi-2223}) = \left( \frac{1}{\lambda_s + \lambda_1 + \lambda_1'} \right) \] (6)

where \( F(\Delta_e) = \int_{e_0}^{\infty} \text{tanh}(e + \Delta_e^2) \frac{1}{2kT} \frac{1}{2} De \), is the gap function (\( h \) is Planck's constant divided by \( 2\pi \), \( \omega \) is frequency, \( \varepsilon \) is energy, \( k \) is Boltzmann's constant, \( \lambda_s(\varepsilon) = N(\varepsilon)\varepsilon \left[ N(\varepsilon)V_{\text{eff}} \right] \), the intraplane and nearest CuO2 plane couplings (7); and \( \lambda_s \) is \( N(\varepsilon)\varepsilon \), the next block coupling [\( N(\varepsilon) \) is the density of states at the Fermi level, and \( V \) is the strength of the interaction].

In this model, \( F \) determines \( T_c \) through \( kT_c = 1.14 \, \hbar \Omega \exp(-F) \). If we fit the coupling parameters \( \lambda_0, \lambda_1, \) and \( \lambda_1' \) for \( \hbar \Omega = 0.1 \) eV to the experimentally determined \( T_c \)'s of pristine \( \text{Bi}_2\text{Sr}_2\text{Ca}_x\text{Cu}_2\text{O}_y \) (Bi-2223) (\( T_c = 110 \) K) and the pristine and stage-1 \( \text{Bi}_2\text{Sr}_2\text{Ca}_x\text{Cu}_2\text{O}_y \) compounds, we obtain \( \lambda_0 = 0.2840, \lambda_1 = 0.0725, \) and \( \lambda_1' = 0.0156. \) Although \( \lambda_s \) is small (\( \approx 5 \%) \) of \( \lambda_0 \), it is over 20% of the size of \( \lambda_1' \) and not negligible. With these parameters, this model predicts the stage-2 \( T_c \) to be 84.9 K, in excellent agreement with the experimentally determined \( T_c = 85 \) K. Hence, with interblock coupling included, a BCS-like model accounts well for the intercalation-induced shift in \( T_c \) for the stage-2 material. The model can also be extended to predict the \( T_c \)'s of higher stage compounds, although the dependence of \( F \) on the coupling is much more complex than for lower stages.

In conclusion, we have shown that high-stage iodine intercalation of \( \text{Bi}_2\text{Sr}_2\text{Ca}_x\text{Cu}_2\text{O}_y \) is possible. The shifts in \( T_c \) of the intercalated materials demonstrate that interblock coupling is an important ingredient in describing high-\( T_c \) copper oxides. In \( \text{Bi}_2\text{Sr}_2\text{Ca}_x\text{Cu}_2\text{O}_y \), coupling between each pair of adjacent CuO2-containing blocks contributes \( \approx 5 \) K to \( T_c \).

REFERENCES AND NOTES
3. X.-D. Xiang et al., unpublished data.
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