INTERCALATING HIGH-T_c OXIDE SUPERCONDUCTORS

A. ZETTL, W.A. VAREKA, and X.-D. XIANG

Physics Department, University of California at Berkeley, and Materials Sciences Division of the Lawrence Berkeley Laboratory, Berkeley, California 94720 U.S.A.

Abstract. Intercalation can be used to insert guest atomic and molecular species between weakly-bonded slabs of a host structure. Intercalation of iodine into Bi-Sr-Ca-Cu-O results in a substantial expansion of the crystal along the c-axis direction, a modest depression in T_c, and changes in normal-state transport coefficients. The properties of the intercalated oxide superconductors can be used to evaluate the role of interlayer coupling and help establish suitable models for the anisotropic normal state transport and the unusual nature of the superconductivity.

Introduction

The microscopic theory of superconductivity developed by Bardeen, Cooper, and Schrieffer (BCS)[1] and subsequently extended by Eliashberg[2] and McMillan[3] has been phenomenally successful in accounting for the properties of most superconductors. In 1964, Marvin Cohen used BCS theory to predict[4] the first oxide superconductor, $SrTiO_3$, with a T_c of order 1K. The new class of high-T_c oxide superconductors introduced in 1986[5] and now displaying T_c's as high as ~135K (for $Hg_2Ba_2Ca_2Cu_3O_x$ under ambient pressure[6]) and ~160K (for $Hg_2Ba_2Ca_2Cu_3O_x$ under high pressure[7]) present new puzzles and new challenges. Despite tremendous experimental and theoretical effort devoted to these compounds over the past eight years, no consensus has been reached as to whether or not the superconductivity can be explained within the framework of the BCS formalism or if it necessitates a more exotic mechanism or a combination of mechanisms.

The high-T_c oxides are layered compounds where each unit cell contains one or more parallel CuO_2 conducting planes[8]. Each CuO_2 plane is built with one Cu atom bound with four O atoms. Generally the Cu atoms form a square lattice with the O atoms located midway between any two Cu's. Several materials like $YBa_2Cu_3O_{7-\delta}$ and $La_{2-x}Sr_xCuO_{4-\delta}$ undergo an orthorhombic distortion at low temperatures which distorts this geometry, but only slightly. In addition to the O in the plane, one or two O atoms sit above and below the Cu atoms along a direction which is essentially normal to the CuO_2 planes. The Cu-O bond length to these out-of-plane O atoms is generally greater than those in the plane. The CuO_2 planes are separated from each other by one or more intervening atomic layers. For all the high T_c oxides, this layered nature also carries over to the transport and magnetic properties which display large anisotropies between the in-plane and out-of-plane directions. Experimental results and band theory calculations indicate that the charge carriers are much more mobile parallel to the CuO_2 planes (the ab-plane) than in the normal direction (c-axis). For example, at room temperature $\rho_{ab}/\rho_c \sim 30$ for $YBa_2Cu_3O_{7-\delta}$[9] and up to ~10^4 for $Bi_2Sr_2CaCu_2O_x$[10]. The common layered nature of the high-T_c oxides and the large electrical anisotropy suggest that these features may play a key role in the superconductivity mechanism. We here explore

this possibility. Our focus shall be on intercalation effects in the Bi-Sr-Ca-Cu-O (BSCCO) superconductors.

Pristine Bi-Sr-Ca-Cu-O

The BSCCO family consists of three members with a pristine stoichiometry given by $Bi_2Sr_2Ca_nCu_{(1+n)}O_{(6+2n-\delta)}$ with n = 1, 2, or 3. The δ is included to explicitly represent the variable oxygen content found in these materials. These compounds are commonly referred to as Bi-2201, Bi-2212, and Bi-2223 for n = 1, 2, and 3, respectively. Fig. 1 shows the crystal structures[11] for these three compounds along with the associated T_c's. The unit cell consists of two identical perovskite-like blocks which have a shifted registry. Each block contains one, two, or three CuO_2 layers separated from each other by a Ca layer. These closely coupled CuO_2 planes are then sandwiched between a pair of SrO layers and finally two BiO layers. Therefore the bounding layers of these subunits or blocks are composed of BiO. When these blocks are stacked on top of each other there is a relative shift of a/2 which results in the Bi atoms of one block being coordinated with the O atoms in the adjacent block's BiO bounding layer. Therefore the unit cell consists of two of these blocks. As is common in all high T_c's the Cu atoms are either 4-fold, 5-fold, or 6-fold coordinated with O atoms. Careful examination[12] of the crystal structure also shows that there is a superlattice modulation along the a-axis with a wavelength
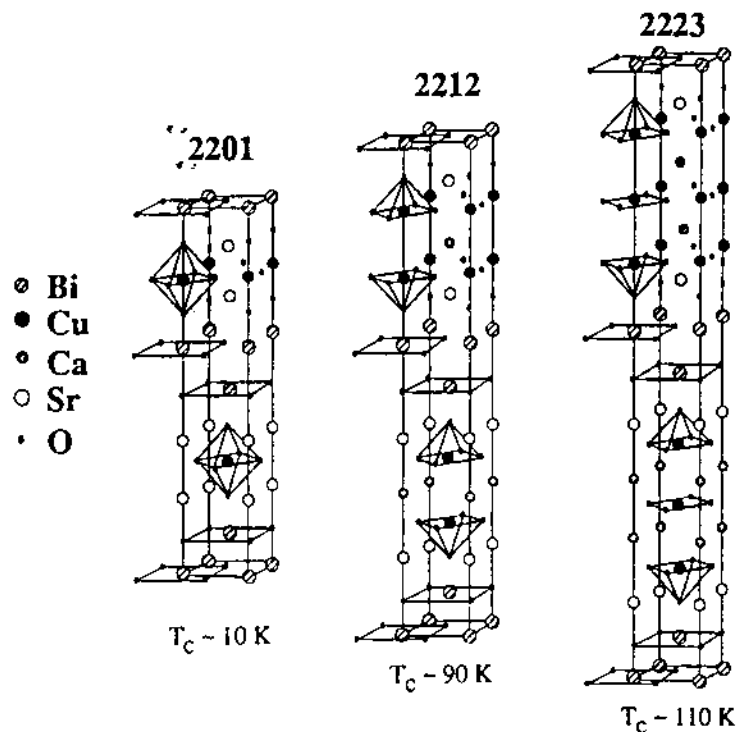

2223

2212

2201

⊘ Bi
● Cu
○ Ca
○ Sr
· O

$T_c \sim 10$ K

$T_c \sim 90$ K

$T_c \sim 110$ K

Fig. 1 Crystal structures and associated T_c's for the three members of the BSCCO family.

of ~ 26 Å. This modulation is believed to be mainly associated with the BiO bilayers and does not appear to be an important factor in the superconductivity. On the other hand, the striking differences between the T_c's of Bi-2201, Bi-2212, and Bi-2223 suggest that CuO_2 interlayer and interblock couplings are of critical importance in the superconductivity mechanism.

The superconducting transition temperature as well as the transport properties of BSCCO and other high-T_c oxide superconductors can also be dramatically affected by varying the oxygen content. In BSCCO, if the material is fully oxygenated by flowing pure oxygen over the sample as it is heated to 400-650°C, it is found to have a superconducting transition temperature of ~ 85 K. As the oxygen is removed from the sample T_c first increases to about 91-93 K and then rapidly decreases; the samples eventually becoming non-superconducting. In general, this is believed to be caused by a charge doping effect in the CuO_2 layers with the insertion or removal of oxygen. Similar behavior can be seen if instead one performs a substitutional doping on the constituents of some of the intervening layers. For example, again in BSCCO, if the trivalent Y is partially substituted[13] for the divalent Ca (which lies between the CuO_2 layers) there is little change in the crystal structure and yet one observes this same negative parabolic-like behavior in T_c vs. Y concentration. Hence charge doping into the CuO_2 layers also has a profound effect on T_c.

Intercalation in Bi-Sr-Ca-Cu-O

Intercalation is the insertion of guest atoms or molecules into a pre-existing host structure[14]. The guest species or intercalant migrates into voids or weakly bonded regions in the host structure thereby leaving intact the main structural features of the host. The interaction of the intercalant and host can result in a wide range of changes to the physical, chemical, electronic, and optical properties of the original host structure. The primary causes for electronic structural changes are charge transfer from the guest atoms to the host structure and changes in interlayer coupling for the host. Graphite and transition-metal dichalcogenides are classic examples of layered materials that can be easily intercalated by a variety of guest species, sometimes with dramatic consequences. For example, pristine graphite is a semimetal and is not superconducting, while intercalated graphite can be a superconductor[14].

Of all the high-T_c oxide structures, the BSCCO-family possesses the greatest degree of anisotropy. Since BSCCO compounds have a micaceous morphology cleaving easily between the BiO bilayers, BSCCO is a good candidate for intercalation between these bilayers. Intercalation can then be used to tune the anisotropy, allowing a systematic investigation of the role of anisotropy on the normal and superconducting state parameters. Many models of high-T_c superconductivity directly relate the anisotropy to the superconducting and normal state parameters, and hence intercalation can provide critical model constraints. In addition, intercalation might be an effective method to produce a variety of new high-T_c superconductors, ideally some with superior mechanical and/or electronic properties for applications purposes.

One class of common intercalants for graphite and the dichalcogenides is alkali-metals[14]. Attempts to intercalate similar guest species into the oxide superconductors have not yielded positive results[15]. For example, "intercalation" of K and Na into Bi-2212 crystals results in a drastic decrease in T_c and color change

of the crystals, but no significant change in the lattice parameters. This suggests that K and Na act as oxygen getters instead of intercalants. Similar problems most probably occur for Cu and Ag intercalation[16]. On the other hand, iodine can be cleanly and reproducibly intercalated into the entire BSCCO family[17-23]. Both stage-1 intercalation (where the iodine is inserted between each BiO bilayer), and higher stage structures (where stage-m means iodine is inserted into every mth BiO bilayer) have been produced and characterized.

STRUCTURAL PROPERTIES OF IODINE-INTERCALATED Bi-Sr-Ca-Cu-O

Iodine has been successfully intercalated into all members of the BSCCO family consisting of Bi-2201, Bi-2212, and Bi-2223; intercalated Bi-2212 is the most extensively studied. In all cases the iodine intercalates between the BiO double-layers, never within the tightly-bound CuO_2 layer-containing blocks. Fig. 2 shows schematically stage-1 and stage-2 iodine intercalation into Bi-2212. Stage-1 structures have been obtained for all three materials[18], and higher stage structures have been identified for Bi-2212[19,23]. The stage-1 compounds are air stable. Higher stage structures (stage 3 or greater) have been identified in Bi-2212 using high resolution transmission electron microscopy (TEM) only as minority phases. A significant number (≥ 5) of repeated units of stage-3 have been observed, and regions with a stage index up to 20 have also been imaged. At present all attempts to isolate these higher stages as majority phases have not been successful.

Table 1 is a summary of the lattice constants, space groups, and distances between the adjacent cation layers in the iodine intercalated BSCCO family. All of these data have been obtained using the results of high resolution TEM work except for the case of Bi-2201 where data were obtained from powder x-ray diffraction studies only. It should also be noted that the identification of Bi-2201 and Bi-2223 is ideal since the actual host material contains various dopants for structural stability (the pristine Bi-2201 is actually $Bi_{2.1}Sr_{1.5}La_{0.4}CuO_x$ and the pristine Bi-2223 is actually $Bi_{1.58}Pb_{0.32}Sb_{0.1}Sr_{1.75}Ca_{1.8}Cu_{2.75}O_x$).

The major structural effect of iodine intercalation into BSCCO is an increase in the c-axis lattice constant: each intercalated iodine layer expands the lattice by 3.6 Å. However, the actual lattice constant along the c-axis requires careful attention. At every intercalated BiO bilayer, the BiO layer stacking sequence of AB...BA...A in the pristine material is changed upon intercalation to a stacking sequence A/A...A/A...A. A and B refer to BiO layers with a/2 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. A similar change in the stacking sequence is commonly observed in graphite and the dichalcogenide intercalation compounds. Hence, intercalation shifts adjacent CuO_2 plane-containing blocks into common registry, thereby removing the staggered Bi sequence observed in, for example, pristine Bi-2212. As a consequence, the stage-1 material, though expanded along the c-axis direction, has a c-axis lattice constant which is *smaller* than that in pristine Bi-2212. This is because the intercalated material requires only a single building block of the host structure in addition to the iodine layer to form a unit cell, whereas the pristine material requires two building blocks due to the staggering of the BiO bilayers. In stage-2 iodine intercalated Bi-2212, each intercalated iodine layer again expands the lattice by 3.6 Å as observed for stage-1. The presence of iodine again changes the stacking sequence to a commonly registered one. Specifically, the stacking sequence
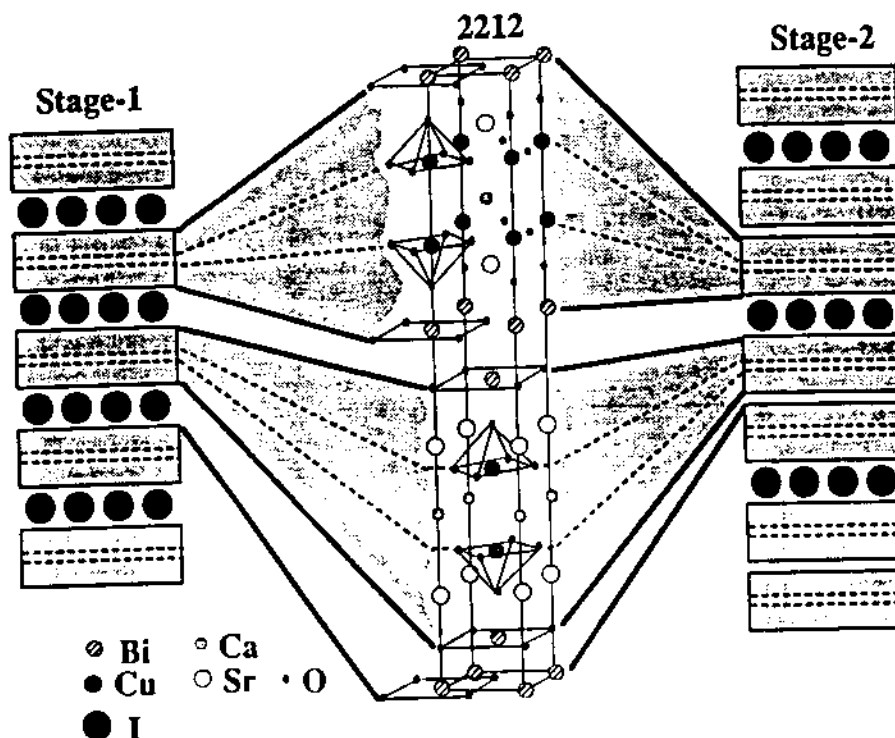
Fig. 2 Schematic of intercalation of Bi-2212 with iodine for both stage-1 and stage-2. The iodine intercalates between the weakly bonded Bi-O bilayers. The shaded regions represent the strongly bonded main structural units of the host and the dashed lines represent the CuO$_2$ layers.

AB...BA...AB relevant to pristine Bi-2212 changes in the stage-2 compound to AB...B/B...BA...A/A...AB. This implies that for stage-2 material the c-axis lattice parameter is significantly larger than in the pristine or stage-1 materials since it must include four building blocks of the pristine material in addition to the iodine layers to form the unit cell.

Comparison between TEM images recorded under [010] and [100] directions in stage-1 Bi-2212 demonstrates that the iodine is located between the oxygen atoms in the sandwiching layers, evidence that the iodine is perfectly epitaxially intercalated. TEM micrographs covering areas >1000 Å square are consistent with x-ray diffraction results of long range iodine order in the intercalated BiO bilayers. These images also confirm that the intercalation of iodine does not alter intra-block lattice parameters nor does it affect the b*-axis lattice modulation observed in the pristine host material[21]. Recently, Raman studies[24,25] have been performed on iodine intercalated Bi-2212, which interestingly indicate the presence of I$_3^-$. Assuming that the I$_3^-$ signature is originating from the iodine intercalated between the BiO bilayers, this suggests an additional modulation for the iodine layer. However, if an iodine trimer structure (perhaps linear) does exist, it must have a lattice match very close to that of the BiO surface in order to be consistent with the x-ray and TEM data. This is a subtlety that deserves further investigation.

	Pristine $Bi_2Sr_2CaCu_2O_x$	Stage-I $IBi_2Sr_2CaCu_2O_x$	Stage-II $IBi_4Sr_4Ca_2Cu_4O_x$	Stage-III $IBi_6Sr_6Ca_3Cu_6O_x$	Stage-n $IBi_{2n}Sr_{2n}Ca_nCu_{2n}O_x$
a	5.4	5.4	5.4	5.4	5.4
b	5.4	5.4	5.4	5.4	5.4
c	30.6	18.9	68.5	49.4	$m(3.6 + 15.3n)$ $m = 1$ when n is even $m = 2$ when n is odd
Space group	B_{bmb}	P_{ma2}	B_{bmb}	P_{ma2}	P_{ma2} when n is odd B_{bmb} when n is even
I-Bi	-	3.31	3.40	3.40	3.40
Bi-(I)-Bi	3.24	6.62	6.80	6.80	6.80
Bi-Sr	2.70	2.80	2.70	2.70	2.70
Sr-Cu	1.70	1.70	1.70	1.70	1.70
Cu-Ca	1.65	1.65	1.65	1.65	1.65

	Pristine $Bi_2Sr_2CuO_x$	Stage-I $IBi_2Sr_2CuO_x$	Pristine $Bi_2Sr_2Ca_2Cu_3O_x$	Stage-I $IBi_2Sr_2Ca_2Cu_3O_x$
a	5.4	5.4	5.4	5.4
b	5.4	5.4	5.4	5.4
c	24.2	15.8	36.9	22.0

Table 1 Comparison of lattice parameters (Å), space groups, and distances (Å) between adjacent cation layers in prisine BSCCO and iodine intercalated BSCCO. The distances between the layers are defined using the c-coordinates of the cations.

T_c OF IODINE-INTERCALATED Bi-Sr-Ca-Cu-O

The dramatic out-of-plane structural changes that result from intercalation might be expected to drastically affect the superconducting transition temperature T_c of BSCCO. On the other, if T_c is dictated soley by the internal structure of the CuO_2 containing blocks and intercalation causes no structural changes in and no charge transfer to the CuO_2 planes, then T_c may be completely insensitive to intercalation. Such an insensitivity to intercalation is observed in the layered superconductor TaS_2[26]. We here consider two trends in the intercalation dependence of T_c in BSCCO: how does T_c change for the different members of the BSCCO family on the intercalation of iodine, and what effect does stage index have on the superconducting properties of a particular member of the family?

T_c in pristine and intercalated samples of BSCCO can be determined using a number of techniques. One uses the ac susceptibility measured using an rf resonant magnetometer. Another method uses the dc susceptibility measured using a superconducting quantum interference device (SQUID) magnetometer. This method is particularly well suited for measuring the polycrystalline samples of the pristine and intercalated Bi-2201 and Bi-2223 materials. The temperature dependence of the resistivity of single crystals of Bi-2212 and IBi-2212 has also been measured using both contactless (eddy current) and direct 4-terminal techniques. Cross-checks indicate that all measurements methods yield reproducible and consistent T_c's.

T_c results for pristine and intercalated BSCCO materials are summarized in Table 2. Interestingly, all intercalated members of the BSCCO family remain

	Original T_c	Stage-1 T_c	ΔT_c	Stage-2 T_c	ΔT_c
2201	24	~22	~2	–	–
2212	~90	80	~10	85	~5
2223	~110	~100	~10	–	–

Table 2 T_c's (K) for all members of the BSCCO family as well as stage-1 and stage-2 iodine intercalated materials.

superconducting after iodine intercalation, but with a slight depression in T_c. The volume fraction of superconductivity, as determined from the Meissner fraction in dc magnetization measurements, is unchanged by the intercalation. The onset T_c of the stage-1 intercalated Bi-2201 compound is decreased by only 2 K with respect to T_c = 24 K for the (La doped) pristine material. The T_c of different pristine Bi-2212 samples is somewhat dependent on the details of the crystal synthesis, ranging from 85 to 92 K. However the stage-1 intercalated IBi-2212 structure always has a T_c of 78 - 80 K. Stage-2 intercalated Bi-2212 has a reproducible T_c of 85K. The T_c of the stage-1 Bi-2223 intercalated sample is again depressed by ~10 K with respect to T_c = 110 K for the pristine sample.

INTERLAYER COUPLING VERSUS CHARGE TRANSFER

The intercalation of iodine into the BSCCO structure could alter T_c in two obvious ways. The first is a modification of the inter-layer coupling of the CuO_2 sheets from one block of the host structure to the next, and the second is a potential charge transfer from the iodine layers to the CuO_2 layers. A number of studies on intercalated BSCCO have been performed to help determine the relative contribution of each effect to the observed shift in T_c. Several experiments indicate that there is little, if any, charge transfer from the iodine to the CuO_2 planes and the shift in T_c is attributed entirely to changes in inter-layer coupling. Other measurements have been interpreted as giving evidence that there is charge transfer.

If iodine intercalation results in charge-doping of the CuO_2 planes, this should be observable in in experiments that probe the electronic structure, including transport measurements, photoemission, and x-ray absorption. The ab-plane electrical resistivity is a relevant parameter, since the in-plane resistivity of pristine BSCCO is assumed to be dominated by conduction through the CuO_2 planes with essentially no contribution coming from conduction in the BiO and SrO planes. However, because intercalation expands the c-axis of Bi-2212 by 23%, an increase in ρ_{ab} upon intercalation is expected even in the absence of any change in the conduction properties of the CuO_2 planes. The relevant parameter to compare is the crystal sheet resistance, $R_\square = \rho/t$, where t is the thickness of the sample. This sheet
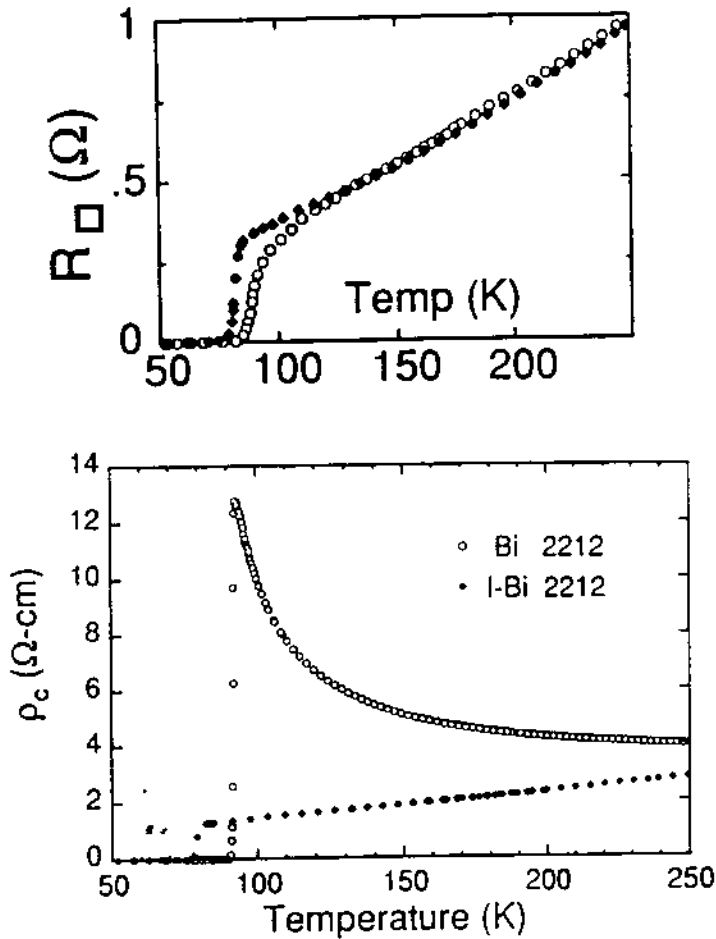
Fig. 3 (a) Normalized ab-plane resistance versus temperature for pristine Bi-2212 (open circles) and intercalated I-Bi-2212 (solid diamonds). (b) c-axis resistivity versus temperature for pristine Bi-2212 (open circles) and intercalated I-Bi-2212 (solid diamonds).

resistance effectively measures the conductivity per CuO_2 plane because intercalation only affects the spacing and not the number of planes. Fig. 3a shows for the same Bi-2212 sample the crystal sheet resistance before and after stage-1 intercalation[20]. Over much of the normal state temperature range, $R_\square$ is nearly identical for Bi-2212 and IBi-2212. Careful checks indicate that the magnitudes of $R_\square$ for Bi-2212 and IBi-2212 agree to within 1% at room temperature. These data suggest that conduction along the CuO_2 planes is virtually unaffected by the intercalation, and that iodine intercalation results in no significant charge transfer to the CuO_2 planes.

Another transport parameter sensitive to charge transfer is the Hall coefficient. Pooke et al[27] have compared the Hall coefficient of pristine Bi-2212 and stage-1 iodine intercalated Bi-2212 and find an apparent increase in carrier concentration with intercalation. Huang et al.[28] similarly interpret Hall effect and T_c measurements

under pressure, and suggest the number of holes transferred is 0.3 per iodine atom. It is difficult to reconcile these data with the ab-plane resistivity results just described.

The observation of I_3- in Raman measurements[24,25] suggests some charge transfer from the iodine layer to some part of the host structure, but not necessarily to the CuO_2 planes. There is clear evidence that there is some charge transfer between the iodine and the adjacent BiO bilayers. There is a significant shift in the x-ray-absorption near-edge structure[29] for the Bi L_3-edge in the iodine intercalated compound compared to the pristine material. Recent x-ray photoemission and angle-resolved ultraviolet photoemission spectra by Ma et al[30] show that while the electronic structure of the normal states near the Fermi level is strongly affected by iodine intercalation, the XPS Cu 2p core level data indicate that the hole concentration in the CuO_2 planes is essentially the same before and after intercalation in Bi-2212. Further evidence for charge transfer to the BiO bilayers comes from the observation[20,27,28] of a dramatic change in the temperature dependence of the c-axis resistivity upon intercalation, going from semiconductor-like to metallic-like, indicative of a change in the transport characteristics across these weakly bonded BiO bilayers. This behavior is shown in Fig. 3b. Although the temperature dependence of the resistivity tensor in intercalated Bi-2212 is metallic-like for both in-plane and out-of-plane transport, it is important to note that the in-plane to out-of-plane conduction anisotropy remains extreme. Indeed, as Fig. 3b demonstrates, the rough order of magnitude of ρ_c well above T_c is quite comparable for pristine and intercalated specimens. Near T_c the anisotropy is reduced by about one order of magnitude but still remains quite large. Iodine intercalation does not turn the BiO bilayers into good electrical conductors.

By measuring the x-ray-absorption near-edge structure corresponding to the Cu K-edge, Liang et al.[29] have determined that there is only a very small (0.03 holes per Cu) increase in the hole concentration on stage-1 iodine intercalated Bi-2212, consistent with the XPS findings of Ma et al.[30]. Fujiwara et al.[31] have measured the effect of hole doping in the iodine intercalated system by using the host structures $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ with differing values of x. Since the Y concentration directly affects the hole density in the CuO_2 layer, Fujiwara et al. were able to directly measure the T_c vs. hole doping curve by using host samples with different values of x. This study showed that there may be a charge doping of about 0.025 holes per Cu. It also explicitly separates the effects of charge transfer and inter-layer coupling since if the change in T_c is simply a charge doping effect then for some concentration of x the original T_c value should be obtained. The results indicate that the majority of the change in T_c upon intercalation is due to the modification of the inter-layer coupling and only a small amount is related to hole doping. Interestingly, other studies of La-doped[32] and Y-doped[33] Bi-2212 have been interpreted as giving evidence of substantial iodine-induced hole doping into the CuO_2 planes.

A comparison of ΔT_c for IBi-2212 and IBi-2223 is instructive; it argues against charge transfer to the CuO2 planes. The amount of charge transfer from the iodine to the CuO_2 planes would be expected to be the same in both cases. This assumption is based on the observation that the local environment of the iodine is the same in both systems and the x-ray and TEM studies show that the lattice expansion upon intercalation is also identical. If charge doping where the sole cause for the depression in T_c then one would expect that the IBi-2223 system would show a noticeably smaller change in T_c since the same amount of holes doped in must now be shared among three CuO_2 sheets whereas for IBi-2212 these extra holes would be

distributed over only two CuO_2 sheets.

Taking all the available data into account, it appears that charge doping to the CuO_2 layers cannot be ruled out as having some effect on the transition temperature. However, a significant body of evidence indicates that charge transfer is unlikely to be the major cause of the observed depression in T_c in intercalated BSCCO. If this is the case, then changes in interblock coupling of the CuO_2 planes dominate.

TESTING SOME INTERPLANE COUPLING MODELS

The shift in T_c upon intercalation and for different intercalation stage structures can be used to estimate the size of the adjacent block coupling in pristine and intercalated BSCCO. We assume that intercalation reduces the interblock coupling due to an increase in the distance between the CuO_2-containing blocks. Stage-1 intercalation reduces the adjacent block coupling in both directions along the c-axis, while stage-2 intercalation preserves the original coupling in one direction for each block. The coupling parameters for pristine and intercalated Bi-2212 are shown schematically in Fig. 4. Since ΔT_c for the stage-1 material is -10K while ΔT_c for the stage-2 material is only -5K, empirically it appears as if next-block coupling contributes about 5K to T_c for each neighboring block of pristine $Bi_2Sr_2CaCu_2O_x$.

Here we examine two prototypical layering models, both of which are capable of explaining the behavior of T_c upon multi-stage intercalation. No specific microscopic mechanism is assumed, and the parameters in each model are determined here phenomenologically.

The simplest layer coupling model is one where T_c varies linearly with the interplane coupling. Each CuO_2 plane is coupled to its neighbors in the c direction, and intraplane coupling is neglected. Wheatley, Hsu and Anderson (WHA)[34] have introduced and used this type of model to discuss superconductivity due to spinon-holon scattering. Here we apply the layering scheme to the effects of intercalation and exhibit the merits of this approach. Our analysis is not mechanism-specific.

In the linear layering model, the superconducting amplitude in plane i, η_i, depends on η_{i+1} and η_{i-1} and the couplings between the planes, $\lambda_{i,i+1}$ and $\lambda_{i,i-1}$. For $Bi_2Sr_2CaCu_2O_x$, there are two different couplings, λ_0 and λ_1, for nearest and next-nearest planes respectively. The couplings are shown schematically in Fig. 4. The nearest planes are within a block whereas the next-nearest planes are in adjacent blocks. Since all the CuO_2 planes are equivalent, all the η's are equal and the eigenvalue equation for T_c, $(\lambda_0 + \lambda_1) \eta = T_c \eta$, yields

$$T_c(\text{pristine}) = \lambda_0 + \lambda_1. \tag{1}$$

For stage-1 $IBi_2Sr_2CaCu_2O_x$, the model is the same but with λ_1 replaced by λ_1' since 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 $IBi_4Sr_4Ca_2Cu_4O_x$, the CuO_2 planes are no longer equivalent; there are planes (a) coupled by λ_0 and λ_1, and planes (b) coupled by λ_0 and λ_1'. The eigenvalue equation for T_c is then

Pristine   Stage-1   Stage-2

λ_0 λ_0 λ_1'

λ_1 λ_1' λ_0

λ_1

——— BiO_2
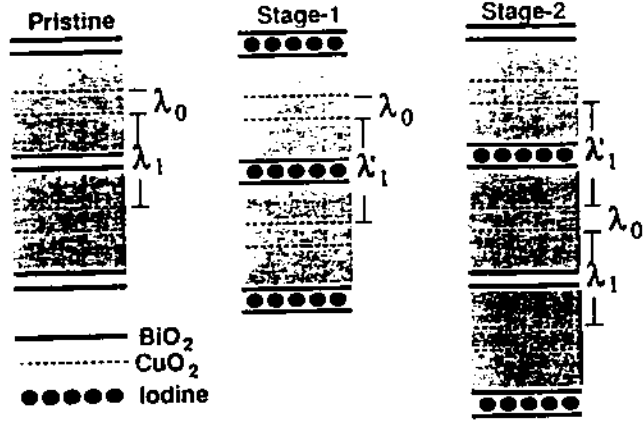············· CuO_2
●●●●● Iodine

Fig. 4 Schematic of interplane coupling parameters in pristine and intercalated Bi-2212.

$$T_c \begin{pmatrix} \eta_a \\ \eta_b \end{pmatrix} = \begin{bmatrix} \lambda_1 & \lambda_0 \\ \lambda_0 & \lambda_1 \end{bmatrix} \begin{pmatrix} \eta_a \\ \eta_b \end{pmatrix} \tag{2}$$

If we assume intercalation completely destroys the next-nearest plane coupling, then $\lambda_1' \to 0$, and the measured T_c(stage-1) yields $\lambda_0 = 80K$. With T_c(stage-2) = 85K, λ_0 = 80K, and $\lambda_1' = 0K$, we find $\lambda_1 = 9.7$ K. This is consistent with the results for the pristine material where T_c is typically 90K [= $(\lambda_0 + \lambda_1)$].

It is possible to use the above analysis to predict the T_c's for higher stage compounds. Assuming $\lambda_0 = 80K$, $\lambda_1 = 10K$, and $\lambda_1' = 0K$, the predicted T_c's for stages 2, 3, 4, and 5 are respectively 85, 87, 88, and 89K. With increasing stage number these rapidly approach the T_c for the pristine material, as expected. Although stage-3 and higher structures exist for iodine intercalated $Bi_2Sr_2CaCu_2O_x$, it has not been possible to reliably determine the T_c's for these minority phases.

Anderson and Zou (AZ)[35] have applied the layer model just described to the specific mechanism of spinon-holon scattering and used it to make predictions for the normal state transport. The experimental studies presented here can be used to examine these predictions and to provide information about microscopic interactions in these systems. Any viable model must account for both the small shift in T_c and the dramatic change in the out-of-plane conduction induced by intercalation.

The couplings λ_0 and λ_1 have the form $\lambda_{0,1} \sim |T_{\perp 0,1}|^2/J$, where $|T_{\perp}|$ is the interlayer hopping matrix element for nearest-neighbor planes (o) and next nearest-neighbor planes (1), and J is the spinon bandwidth. If $\lambda_1 \to 0$, then either $T_{\perp 1} \to 0$ or $J \to \infty$. J depends only on the structure of the spinon energy spectrum which in turn is determined solely by the CuO_2 planes. The condition $J \to \infty$ is not physical nor is it reasonable as will be shown in the discussion of ρ_{ab} below. Thus, we are left with the conclusion that $T_{\perp 1} \to 0$ or at least is greatly reduced upon iodine intercalation.

We examine the anisotropic electrical resistivity. In the AZ calculation[35], the resistivity in the ab-plane is caused by the scattering of holons by spinons. Thus, ρ_{ab} is a probe of the in-plane interaction and the densities of states of the spinons and

holons. Specifically,

$$\rho_{ab} = (m_B/n\ e^2 h)t^2 g_s g_b T \tag{3}$$

where m_B is the effective mass of the holons, n is the holon density, t is the in-plane scattering matrix element between holons and spinons, and g_s (g_b) is the spinon (holon) density of states. The value of ρ_{ab} for the intercalated samples demonstrates that the resistance of the CuO_2 planes is unchanged by the intercalation. Furthermore, the values of t, g_s, g_b, and J depend only on the spinon-holon local environment *in the CuO_2 planes*, and would remain constant unless the intercalation affected the structure of the material in those planes. The near-plane interlayer hopping matrix element ($T_{\perp0}$) also only depends on the local environment of the closest spaced CuO_2 planes. Thus, we can assume that t, J, g_s, g_b, and $T_{\perp0}$ are not affected by the intercalation. This supports the proposition that λ_0 is not altered by the intercalation, and that the observed depression in T_c is due to a reduction in λ_1 through a decrease in $|T_{\perp1}|$.

The out-of-plane resistivity ρ_c, however, poses a problem to an interpretation based on the AZ calculation. As shown in Fig. 3b, intercalated samples display a metallic-like ρ_c down to T_c. The AZ calculation for ρ_c in a single-plane system, following a similar development as for ρ_{ab}, gives

$$\rho_c = (h/e^2)(ab/c)[|T_\perp|^2 g_s g_b^2 T]^{-1} \tag{4}$$

where $T_\perp$ is the interlayer matrix element for the scattering of spinons and holons, ab is the area of the Cu-Cu square in the ab-plane, and c is the interlayer distance. Since in this interpretation Bi-2212 should have two types of c-direction tunneling -- from nearest neighbor planes and next nearest neighbor planes -- Eq. (4) is logically extended to give

$$\rho_c \sim (\alpha\lambda_0 T)^{-1} + (\beta\lambda_1 T)^{-1} \tag{5}$$

where α and β include factors of the densities of states, J, and the different c-axis spacings for next nearest neighbor and nearest neighbor CuO_2 planes.

In view of the T_c and ρ_{ab} measurements, if λ_1 decreases we would expect ρ_c for intercalated Bi-2212 to have a dramatically *increased* $1/T$-like behavior, whereas experiment shows no evidence for *any* $1/T$-like behavior (see Fig. 3b). In addition, the T_c measurements indicate that $\lambda_0 \sim 9\lambda_1$. Assuming the λ_1 term has been replaced by some other mechanism with the appropriate temperature dependence, one would *still* expect to see a small $1/T$ contribution to the resistivity from the λ_0 term near T_c. However, this is not observed experimentally.

Another approach to interplane coupling and T_c incorporates interplane interactions into a BCS-like framework. Such a model has been advanced by Ihm and Yu (IY)[36]. IY neglect interblock coupling. Since the intercalation results indicate that this coupling cannot be neglected, such a coupling may be incorporated[19] into a phenomenological model that is essentially an extension of the original IY work.

In the IY model the transition temperature is given by $kT_c = 1.14\hbar\omega\exp(-F)$ where $\hbar\omega$ is the range of the pairing mechanism and F is obtained by solving the following set of gap equations

$$\Delta_\ell \left[1 - \lambda_a F(\Delta_\ell) \right] = \sum_{\ell'} \Delta_{\ell'} \lambda_{cr} F(\Delta_{\ell'}) \qquad (6)$$

$$F(\Delta_\ell) = \int_0^{\hbar\omega} d\varepsilon \, \frac{\tanh\left[\left(\varepsilon^2 + \Delta_\ell^2 \right)^{1/2} \Big/ 2kT \right]}{\left(\varepsilon^2 + \Delta_\ell^2 \right)^{1/2}} \qquad (7)$$

where Δ_ℓ is the gap associated with a given layer ℓ, $F(\Delta_\ell)$ is the gap function, ε is energy, k is Bolzmann's constant, λ_a [λ_{cr}] is $N(\varepsilon_f)V_a$ [$N(\varepsilon_f)V_{cr}$], the intra-plane and nearest (within the same block) CuO_2 plane couplings, V is the strength of the interaction, and $N(\varepsilon_f)$ is the density of states at the Fermi level and is assumed to be the same for all CuO_2 planes. The smallest positive F produces the lowest free energy and hence the highest T_c so the desired solution is this value of F.

We extend the IY model by including the effects of the next-nearest plane coupling into the calculation. This introduces an additional coupling constant, λ_n corresponding to the next-nearest plane coupling, i.e., the coupling between the CuO_2 planes in adjacent blocks. Just as in the linear coupling model discussed above, we assume that the effect of intercalation is to change $\lambda_n \rightarrow \lambda_n' \approx 0$. That is to say, the coupling across an intercalated layer has been reduced so far that it can be treated as zero. Given this assumption, we derive[19] the following results,

$$F(\text{pristine}) = \left(\frac{1}{\lambda_a + \lambda_{cr} + \lambda_n} \right) \qquad (8)$$

$$F(\text{stage-1}) = \left(\frac{1}{\lambda_a + \lambda_{cr}} \right) \qquad (9)$$

$$F(\text{stage-2}) = \left(\frac{1}{\lambda_a + \lambda_{cr} + \dfrac{\lambda_n}{2}} \right) \qquad (10)$$

$$F(\text{Bi-2223}) = \left(\frac{1}{\lambda_a + \sqrt{2}\lambda_{cr} + \lambda_n} \right) \qquad (11)$$

Notice that the results of our calculation for stage-1 agree with the IY results for pristine Bi-2212 as they should since in both cases the effects of inter-plane coupling are ignored. If we fit the coupling parameters λ_a, λ_{cr}, and λ_n for $\hbar\omega = 0.1$ eV (from IY) to the experimentally determined T_c's of pristine Bi-2223 ($T_c = 110$ K) and the pristine Bi-2212 ($T_c = 90$ K) and stage-1 IBi-2212 ($T_c = 80$ K) compounds, we obtain $\lambda_a = 0.2840$, $\lambda_{cr} = 0.0725$, and $\lambda_n = 0.0156$. Although λ_n is small (~5% of

λ_a), it is over 20% of the size of λ_{er} and therefore not negligible. Inserting these parameters into Eq. (10), 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 the 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.

Therefore we conclude that the effects of interblock coupling are indeed important in determining the transition temperature in the BSCCO system. The microscopic mechanism giving rise to the unusual normal state transport, and ultimately the superconductivity, remains unclear.

Magneto-transport

The layered nature of the oxide superconductors is believed to play a role in the (unusual) magnetotransport. In YBCO the intrinsic anisotropy, though large, is not so great as to invalidate the three dimensional mean field treatment of Ginzburg-Landau (GL) theory[37], provided one is close to T_c. To accommodate this anisotropy, one replaces the original scalar effective mass m^* in the GL theory with an effective mass tensor $\tilde{m}$. This results in an anisotropic penetration depth and coherence length thereby distorting the Abrikosov flux lattice. In YBCO the measured anisotropy in the coherence length is $\xi_c(0) \sim 2$ Å and $\xi_{ab}(0) \sim 12$ Å[38]. Therefore, since the separation between the important CuO_2 layers is ~ 4.2 Å in the c direction, this approximation is only marginally justified except near T_c, where ξ diverges as $(1-t)^{-0.5}$, with $t \approx T/T_c$. For BSCCO the anisotropy is so extreme that "the three dimensional continuum picture is not a good approximation at all"[39]. In fact, defining the cross-over temperature, T_{co}, as the temperature at which $\xi_c(T)$ is equal to the separation between CuO_2 planes in adjacent blocks, one finds[40] $T_c - T_{co} \approx 0.3$ K!

We consider BSCCO not as a three dimensional system but as a series of two dimensional superconductors coupled together via weak Josephson coupling. This is the approach put forth in the Lawrence-Doniach (LD) model[41]. In this model the layers are in the ab-plane and the weak Josephson coupling occurs along the c direction. If the coherence length ξ_c perpendicular to the layers is greater than the separation of the layers d, this model essentially reproduces the results of the anisotropic GL model. If, however, $\xi_c \leq d$ then the results of this model differ significantly from the GL three-dimensional mean field approach.

One important prediction of the LD model is the possible coexistence of two different types of flux lattices[42]. For the field component along c the flux lattice is the standard Abrikosov lattice. However, for the field component along the planes there exists a Josephson vortex lattice. These Josephson vortices lie in the space between the superconducting sheets and have a width $= \Phi_0/H_{||}d$ where $H_{||}$ is the component of H along the planes and d is the separation between the superconducting planes. A Josephson vortex is uniquely different from an Abrikosov vortex in that the former does not have a normal core. Recently, evidence for these Josephson vortices has been observed in the c-axis I-V's for pristine Bi-2212[43]. In addition, Clem has proposed[44] that if the field is aligned at some angle out of the ab-plane

then the vortices must cut through the planes at some point producing "pancake vortices" in the CuO_2 planes.

If one accepts that the excess field-induced dissipation arises from flux motion induce by a Lorentz force JxH, then one would anticipate that the resistivity would vary as $\sin^2\Theta$, where Θ is the angle between the current J and the field H. Surprisingly, Iye et al.[45] and others have clearly shown that the dissipation in BSCCO is completely independent of Θ when H and J are both perpendicular to the c-axis. In contrast to this[46], YBCO shows some $\sin^2\Theta$ dependence and standard conventional flux flow superconductors show essentially a complete $\sin^2\Theta$ angular dependence. This would imply that the source of this discrepancy is coupled to the strong layered nature of YBCO and the *extreme* layered nature of BSCCO. To account for this behavior, Kes et al. have proposed[47] that the observed dissipation is due to an angular misalignment of less than 1° which would produce many "pancake vortices". These vortices then interact with the transport current to yield the Θ independent dissipation. Iye et al. argue that even without misalignment, there may be enough thermally activated pancake vortices to account for the dissipation. Finally, Kim et al. have proposed[48] an alternate explanation. In their model the dissipation is not due to fluxon motion, but instead it is the result of the reduction in the Josephson critical current between the layers cause by the field-induced depression of the order parameter in the grains. This reduced critical current then causes an increase in the dissipation. One must conclude that there is no true consensus on the physical cause of the field-induce dissipation (for all orientations of current and field) in the BSCCO system, and by analogy in any other oxide superconductor.

MAGNETORESISTANCE OF IODINE-INTERCALATED Bi-Sr-Ca-Cu-O

If we assume that dissipation in the BSCCO system is critically related to the two-dimensionality and in particular to the large separation of the CuO_2 layers, one is naturally led to the question of how the dissipation mechanism in BSCCO might be affected by increasing this separation via intercalation. By further decoupling the superconducting CuO_2 planes one may affect both the field penetration and the dynamics.

ab-plane Magnetoresistance

As shown in Fig. 3a, in zero applied magnetic field the ab-plane resistivity, ρ_{ab}, is essentially identical in pristine Bi-2212 and in the stage-1 iodine intercalated material , aside from the shift in the T_c of $\sim$ -10 K . We here investigate the effect of finite applied magnetic field H. The accuracy of the alignment of the sample with respect to the field is estimated to be < 1-2°.

Fig. 5 shows the ab-plane resistivity of pristine Bi-2212 for various magnetic field magnitudes and orientations with respect to the crystal axes and the direction of the transport current density J[49]. Fig. 6 shows analogous data for stage-1 iodine intercalated Bi-2212. If one focuses on the broadening of the transition defined here somewhat generally by looking at the 5% points of the magneto-resistance curves for the different fields compared to the 5% point for the zero field case, it is clear that the extent of the broadening has not been noticeably affected by the intercalation process. This would imply that the mechanism responsible for the anomalous resistive
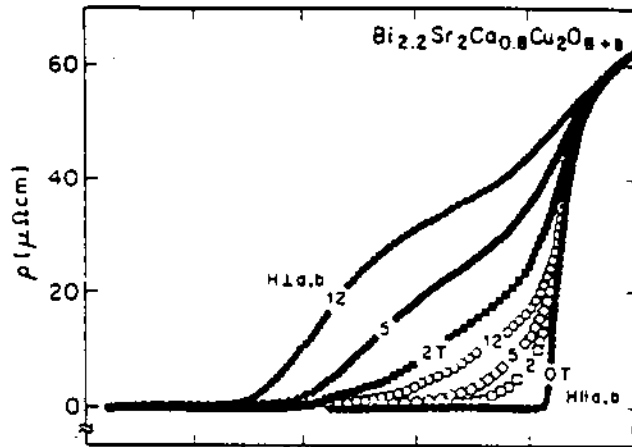
Fig. 5 ab-plane resistivity versus temperature in pristine Bi-2212, for different applied H-fields. Adapted from Palstra et al., ref. [49].

broadening is not closely coupled to the details of the spacer layers between the CuO_2 layers. This does not appear consistent with the model of Kim et al.[48] where the dissipation is due to changes in the Josephson critical current density between the CuO_2 layers and one would expect that the insertion of iodine between the BiO bilayers would modify this coupling. In addition, it has already been shown that the c-axis resistivity has been changed from a semiconducting-like to a metallic-like temperature dependence which also would also imply that a change in the dissipation behavior through this mechanism should be observed. On the other hand, these results are consistent with the models of Kes and Iye mentioned above since the dissipation in these models is due to pancake vortices in the CuO_2 layers and they are not expected to be significantly affected by the intercalation process.

Comparing Fig. 6a where the field geometry is such that there exists a macroscopic Lorentz force and Fig. 6b where there is no macroscopic Lorentz force, it is clear that the resistive broadening is still Lorentz force independent. This is consistent with the picture that the insensitivity to the angle Θ between the current density J and the field H is correlated with the two-dimensionality in this system. As mentioned previously, after intercalation the anisotropy in the resistivity ρ_{ab}/ρ_c is still on the order of 1000 at T_c and the transition temperature itself is still roughly comparable to that in the pristine Bi-2212, both of which when combined with the observation that IBSCCO still has a micaceous morphology strongly indicates that this material is still extremely two-dimensional.

Intercalating iodine into the BSCCO structure does not appear to significantly alter the extent to which the transition is broaden due to a magnetic field. In particular, it does not alter the angular independence of the dissipation for H and J in the ab-plane. This independence puts constraints on any theory that attempts to explain the anomalous magneto-resistance in the high T_c compound by constraining it to be insensitive to the physical spacing between the CuO_2 planes and to the magnitude and temperature dependence of the c-axis conductivity.
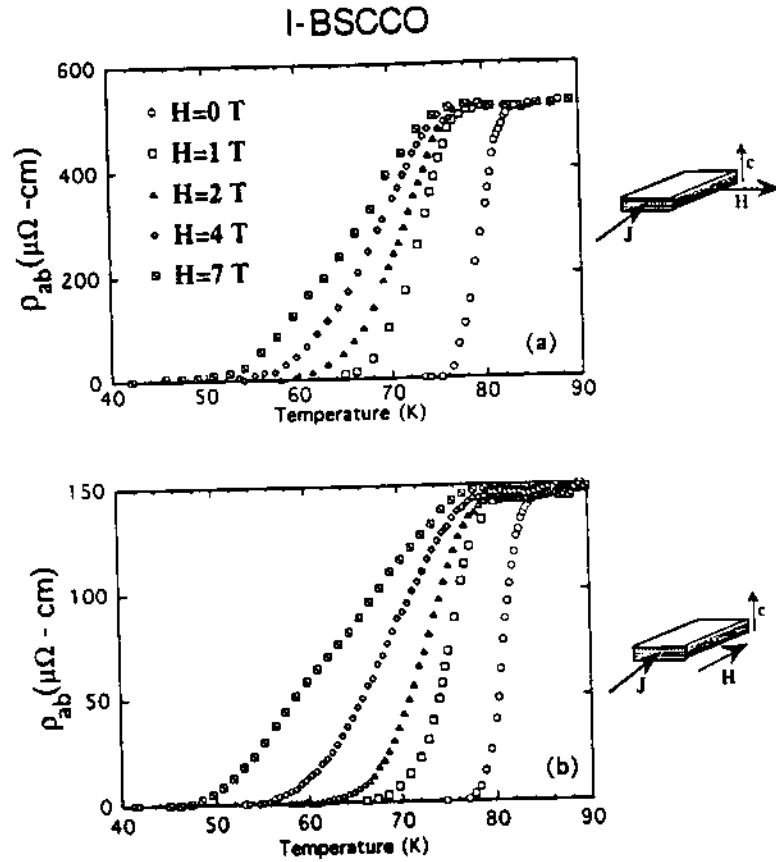
I-BSCCO

Fig. 6 ab-plane resistivity versus temperature in intercalated I-Bi-2212, for different applied H-fields.

c-axis Magnetoresistance

Fig. 7a shows the c-axis resistivity of a pristine Bi-2212 sample for various applied magnetic fields oriented in the ab-plane. Fig. 7b shows similar data for a stage-1 iodine intercalated crystal. For both sets of data the magnetic field is parallel to the ab-plane. Comparing Figs. 7a and 7b it is clear that there is a significant difference between the pristine and intercalated samples for fields $\leq$ 3.5 T. In the pristine Bi-2212 data the curve for H = 0.5 T is essentially identical with that for H = 0 T. If we again compare the points at which the resistance has fallen to ~5% of the value at the onset of the transition, then the difference in temperature of these 5% points for H = 0T vs. H = 0.5 T is $\Delta T_{5\%} < 0.5$ K. In contrast to this, the IBi-2212 data show that the H = 0.5 T is significantly different from the zero field case with a difference in the 5% points of approximately $\Delta T_{5\%} \approx 5$ K. Therefore, one sees an increase in the width of the transition for H = 0.5 T of more than one order of magnitude when compared to the pristine material. For H = 3.5 T the intercalated sample still shows a significantly broader transition but the difference in the 5%
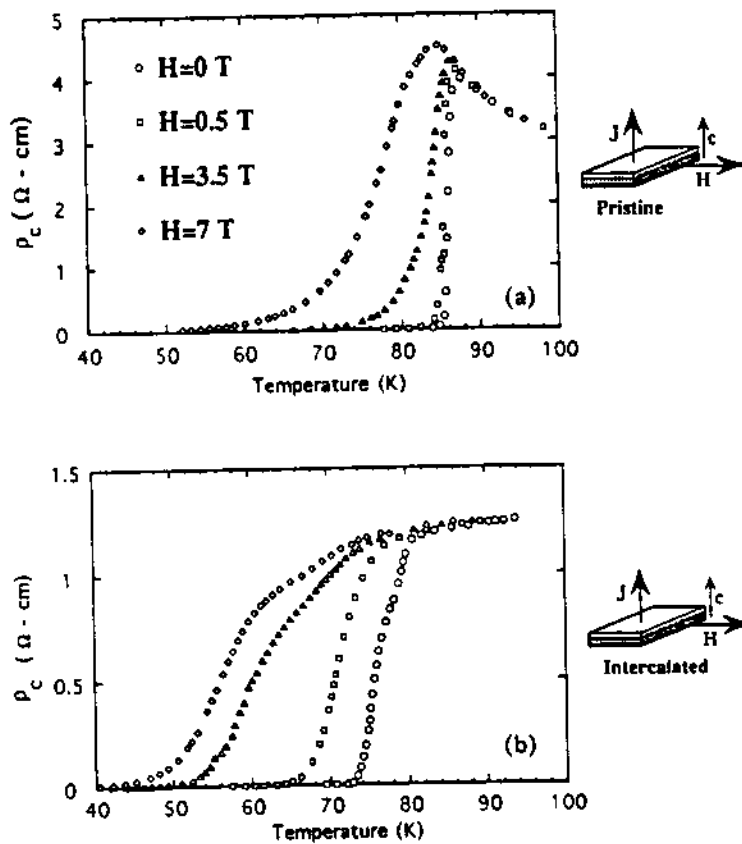
Fig. 7 c-axis resistivity versus temperature in (a) pristine Bi-2212 and (b) intercalated I-Bi-2212. H is perpendicular to J in both cases.

points between the pristine and intercalated samples is now somewhat less than one order of magnitude. When the field is increased still further this difference essentially disappears with both materials showing a $\Delta T_{5\%} \approx 20$-$25$ K for H = 7.0 T. This also may imply a very real difference in the field dependence at high fields (H > 7 T) in that for the pristine material the broadening is rapidly increasing with field whereas for the intercalated material it appears to be saturating. It is not clear, however, if for much larger fields the two sets of data would coalesce or if the pristine material would start to have broader transitions. One problem with interpreting the measured high field data is that the pristine material continues to show this normal-state-like upturn below the zero field onset temperature for these large fields. Since this tends to "pull" the whole curve up, it is not clear whether it is relevant to continue to look

at the width as defined by the 5% points of the onset temperature or instead one should look at the 5% points of the maximum resistivity value. One fact is clear, however, and that is that the low field (H ≤ 3.5 T) behavior is significantly affected by the intercalation of iodine into the structure.

It has been proposed[50] that the dissipation in ρ_c for H ⊥ c is due to the sliding of Josephson vortices along the ab-plane. In this picture each coreless Josephson vortex has a width $= \Phi_0/H_\parallel d$, where d is the distance between the superconducting layers and $H_\parallel$ is the component of H parallel to the ab-plane. The model interprets the threshold behavior seen in the I-V curves[50] as being due to the Josephson vortices remaining fixed for low currents because of a pinning potential. As the current is increased one reaches the point where the Lorentz force on the vortex overcomes the defect pinning force and the vortices slide in the direction of the Lorentz force, i.e., in the ab-plane. Using this model one would conclude that one effect of the intercalation of iodine into BSCCO would be to decrease the width of the Josephson vortices by ~23% since the separation of the CuO_2 planes is increased by this amount. In addition the character of the Josephson vortex may change because of a change in the Josephson coupling between the CuO_2 planes. Finally, the iodine may modify the distribution of pinning forces, especially in the neighborhood of the BiO bilayers. At present, this model is not sufficiently developed to be able to determine whether the pronounced increase in the low field resistive broadening in IBi-2212 is consistently explained. However, these data do provide fertile ground for future developments of this model.

The Future of Intercalation in Oxide Superconductors

Since the initial discovery[17] that iodine could be successfully intercalated into the BSCCO host structure yielding high-quality phase-pure compounds, numerous researchers have successfully repeated the intercalation process with iodine and have made some progress in intercalating other "guest" species into the oxide superconductors. We here briefly review these efforts and identify some promising directions for the future.

Several groups[51-54] have been pursuing electrochemical intercalation of the alkali-metals into BSCCO. One group also reported continuing efforts on electrochemical intercalation of Cu[55,56] Grigoryan et al.[57-61] have devoted considerable efforts towards intercalating ring-shaped organic molecules like benzene and the metal-phthalocyanines into BSCCO, but to date they have not been successful in obtaining uniformly pure materials. Numerous reports exist for intercalation attempts using other halogens. Evidence has been reported[56,62,63] for the successful intercalation of Br into BSCCO, but the resulting material is unstable in air and cannot be made phase pure since the reactivity of Br makes the samples too fragile for concentrations x ≥ 0.3, where x is defined by $Br_xBi_2Sr_2CaCu_2O_8$. Recently, Mochida et al.[55] reported the successful intercalation of the combination of IBr with a lattice constant expansion only slightly larger than that found for Br alone. Important new developments in BSCCO intercalation are the successful synthesis of AgI_x-Bi-2212 intercalation complexes. Kumakura et al.[64] have reported the insertion of AgI_2 into Bi-2212 with a resulting increase in the lattice constant of more than twice that found in the pure iodine intercalated Bi-2212 system. The intercalated AgI_2 compound is apparently very phase pure, displaying extremely sharp diffraction peaks. The resulting change in T_c for this material is reported to be $\Delta T_c \approx -26$ K, but at present it is unclear if

charge transfer effects are playing any role. Choy *et al*[65] have produced the related material AgI-Bi-2212. This material again has a dramatic expansion along the c-axis of 7.35Å, and the depression in T_c upon intercalation is about 10K, similar to that found for pure iodine intercalation.

To date, no other high T_c compound apart from BSCCO has been successfully intercalated. It would be desirable to examine the effects of intercalation on other high T_c compounds. The obvious choices are the closely related Tl- and Hg-based families. Unfortunately, the Tl-system differs from the BSCCO system in one important respect: the binding between the Tl bilayers is considerably stronger than in BSCCO. One simple way to see this is to compare the lattice spacing of these layers: in pristine BSCCO the BiO-BiO separation distance is 3.24 Å, whereas for the Tl compound the TlO-TlO separation distance is only ~2.0 Å which is comparable to all the other layer to layer spacings in this material. Therefore, the Tl compound does not have a micaceous morphology and therefore may be somewhat difficult to intercalate. Of course, the flip side is that if the Tl-based material could be intercalated there is no *a priori* reason for the intercalant to inject between the TlO bilayer and it may in fact locate much closer to the important CuO_2 layers. As for other high-T_c compounds, some claims of fluorine intercalation into $YBa_2Cu_3O_x$ were reported but subsequent studies showed that this was a substitutional effect where the apical oxygen atoms located above the Cu atoms in the BaO plane were being replace by fluorine.

The intercalation of oxide superconductors has become a growing sub-field in high T_c research and it shows the promise of not only generating novel materials but also in shedding light on the poorly understood mechanism of high-T_c superconductivity.

Acknowledgements

References

1. Bardeen J, Cooper LN, Schrieffer JR. Phys. Rev. 1957;108:1175
2. Eliashberg GM. Sov. Phys. JETP 1960;111:696
3. McMillan WL. Phys. Rev. 1968;167:331\
4. Cohen ML. Rev. Mod. Phys. 1964;36:240; Cohen ML. Phys. Rev. 1964;134:A511; Schooley JF, Hosler WR, Cohen ML. Phys. Rev. Lett 1964;12:474; Schooley JF et al. Phys. Rev. Lett. 1965;14:305
5. Bednorz G, Muller KA. Z. Phys. B 1986;64:189
6. Putilin SN et al. Nature 1993;362:226
7. Gao L et al. (preprint)
8. Shaked et al. Crystal Structure of the High-Tc Superconducting Copper-Oxides. Amsterdam: Elsevier Science B.V., 1994
9. Tozer SW, Kleinsasser AA, Penny T, Kaiser D, Holtzberg F. Phys. Rev. Lett. 1987;59:1768
10. Martin S et al. Phys. Rev. Lett. 1988;60:2194

11. Yvon K, Francois M. Z. Phys. B. 1989;76:413. See also Hazen RM. In Ginsberg DM, editor. Physical properties of high temperature superconductors, vol. 2. Teaneck, NJ: World Scientific, 1990
12. Matsui Y, Horiuchi S. Jpn J. Appl. Phys. 1988;27:L2306
13. Koike Y, Iwabuchi YH, Kobayashi N, Fukase T. Physica C 1989;159:105
14. See, for example, Whittingham MS. In Whittingham MS, Jacobson AJ, editors. Intercalation Chemistry. New York: Academic Press, 1982:1; Ubbelohde AR. In Levy F, editor. Intercalated Layered Materials, vol. 6. Boston: D. Reidel Publishing Co, 1979:1; Kirczenow G. Zabel H, Solin SA, editors. Graphite intercalation compounds I: Structure and dynamics, vol. 6. Berlin: Springer Verlag, 1990:59; Ecklund PC. In Dresselhaus MS, editor. Intercalation in layered materials, vol. 148. New York: Plenum Press, 1986:163; Issi JP. In Zabel H, Solin SA, editors. Graphite intercalation compounds II (Transport and Electronic properties), vol 18. New YorkL Springer Verlag, 1992:195
15. Vareka WA. University of California at Berkeley Ph.D. Thesis 1993
16. Scholz GA, Boswell FW. Solid State Commun. 1990;74:959
17. Xiang XD et al. Nature 1990;348:145
18. Xiang XD et al. Phys. Rev. B 1991;43:11496
19. Xiang XD et al. Science 1991;254:1487
20. Xiang XD et al. Phys. Rev. Lett. 1992;68:530
21. Kijima N et al. Physica C 1991;181:18
22. Kijima N et al. Physica C 1992;198:309\
23. Kijima N et al. Physica C 1992;190:597
24. Faulques E, Russo RE. Solid State Commun. 1992;82:531
25. Huong PV, Verma AL. Phys. Rev. B 1993;48:9869
26. Burk B. University of California at Berkeley Ph.D. Thesis, 1994
27. Pooke D et al. Physica C 1992;198:349
28. Huang T et al. Phys. Rev. B 1994;49:9885
29. Liang G et al. Phys. Rev. B 1993;47:1029; Choy JH et al. In Proceedings of International Conference on Science and Technology of Synthetic Metals, Seoul, 1994
30. Ma J et al. Physica C 1994;227:371
31. Fujiwara A et al. Physica C 1993;208:29
32. Muraoka Y et al. Physica C 1993;215:402
33. Muraoka Y et al. Physica C 1992;204:65
34. Wheatley JM, Hsu TC, Anderson PW. Nature 1988;333:121
35. Anderson PW, Zou A. Phys. Rev. Lett. 1988;60:132
36. Ihm J, Yu BD. Phys. Rev. B 1989;39:4760
37. Tinkham M. Introduction to Superconductivity. Malabar, Fl: Robert E. Krieger Publishing Co, 1980
38. Crommie MF. University of California at Berkeley Ph.D. Thesis, 1991
39. Tinkham M. Physica B1991;169:66
40. Kes PH, van der Beek CJ. Physica B 1991;169:80
41. Lawrence W, Doniach S. In Kanda, editor. Proceedings of the Twelfth International Conference on Low Temperature Physics. Kyoto: Academic Press, 1971:361
42. Theodorakis S. Phys. Rev. B 1990;42:10172
43. Briceno G, Crommie MF, Zettl A. Physica C 1993;204:389
44. Clem J. Bull. Am. Phys. Soc. 1990;35:260
45. Iye Y et al. Physica C 1990;167:278
46. Tinkham M. Physica B 1991;169:66

47. Kes PH, Aarts J, Vinokur VM, van der Beek CJ. Phys. Rev. Lett. 1990;64:1063
48. Kim DH, Gray KE, Kampwirth RT, McKay DM. Phys. Rev. B 1990;42:6249
49. Palstra TTM, Batlogg, B, Schneeyeyer LF, Waszczak JV. Phys. Rev. Lett 1988;61:1662; see also Briceno G, Crommie MF, Zettl A. Physica C 1993;204:389
50. Crommie MF, Briceno G, Zettl A. Phys. Rev. B 1992;45:13148
51. Fleischer NA et al. Physica C 1992;190:367
52. Fleischer NA, Manassen J, Coppens P, Lee P, Gao Y. Superconductivity and its Applications. 5th Annual Conference, Buffalo NY, 1991:366
53. Macklin WJ, Claude S, Brien V, Moseley PT. J. Mat . Chem. 1992;2:439
54. Ohashi M, Gloffke W, Whittingham MS. Sol. St. Ion. 1992;57:183
55. Mochida M et al. Physica C 1993;212:191
56. Koike Y et al. Solid State Commun. 1991;79:501
57. Grigoryan LS, Arutyunyan. Dok. Akad. Nauk. 1990;313:350
58. Grigoryan LS, Harutyunyan AR. In First International Conference, Strongly Correlated Electron States in Condensed Media, SCESCM-91, vol 17. Crimea USSR, 1991:1073
59. Grigoryan LS, Chakravarty N, Capri AZ. Mod. Phys. Lett. B. 1992;6:1843
60. Grigoryan LS et al. Physica C 1992;198:137
61. Grigoryan LS et al. Physica C 1993;205:296
62. Nakashima H et al. In International Conference on Materials and Mechanisms of Superconductivity, High Temperature Superconductors III, vol 1, Kanazawa Japan, 1991:677
63. Ijybi T et al. In International Conference on Materials and Mechanisms of Superconductivity, High Temperature Superconductors III, vol 2, Kanazawa Japan, 1991:847
64. Kumakura H et al. Jpn. J. Appl. Phys. 1993;32:L894
65. Choy JH. In Proceedings of the Fourth International Conference on Materials and Mechanisms of Superconductivity, High Temperature Superconductors. Grenoble, 1994