

INTERCALATION OF OXIDE SUPERCONDUCTORS

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ABSTRACT

Iodine has been intercalated into the oxide superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. The iodine intercalates epitaxially between the double Bi-O sheets, and results in an expansion of the crystal in the c-axis direction and a shift in the registration of the CuO_2 -containing blocks. Both stage-1 and stage-2 intercalated structures have been synthesized and characterized. No significant charge transfer is observed from the iodine layers to the CuO_2 planes, yet T_c is slightly reduced by the intercalation, from 90K to 80K (stage-1) or to 85K (stage-2). In stage-1 structures, the functional form of the out-of-plane resistivity is changed from "semiconductor-like" to "metallic-like" upon intercalation. These results are compared to various layer models for high- T_c superconductivity.

1. Introduction

Intercalation, the insertion of foreign atomic or molecular species into an "open" or loosely bonded host structure, is a powerful and unique method by which interaction parameters in the host structure can be systematically explored. In a layered system such as graphite, for example, alkali metal atoms can be intercalated between the graphite sheets, leading to charge transfer to the sheets as well as a change in the physical separation of the sheets¹. These changes influence the anisotropic structural and electronic properties of the material. Intercalated graphite is a very low temperature superconductor, whereas unintercalated graphite is not.

The highest- T_c superconductors have in common two-dimensional CuO_2 planes incorporated in a loosely bonded matrix. For example, the 90K superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (Bi-2212) has closely spaced "double" CuO_2 planes in a common "block"; these blocks are separated by double Bi-O sheets. The CuO_2 planes are highly conducting, while the Bi-O sheets serve as insulating spacers. This leads to a highly anisotropic electronic structure, characterized by a metallic ab-plane resistivity and a c-axis resistivity that is large and has a "semiconductor-like" temperature dependence. Several models of high- T_c superconductivity are based on layer interactions, either intralayer, interlayer, or a combination of the two.

The ability to intercalate foreign species, such as iodine^{2,3}, between the van der Waals bonded Bi-O double sheets of Bi-2212 sets the stage for the following possibilities: 1) changes in the coupling between CuO_2 -containing blocks, 2) charge transfer from the iodine to the CuO_2 planes, 3) changes in the anisotropic transport and elastic properties, 4) changes in the superconducting properties such as transition temperature, flux pinning and critical current, 5) in-situ fabrication of devices, such as Josephson junctions, and 6) testing of models of high- T_c superconductivity. Here we investigate some structural and electronic changes resulting from iodine intercalation of Bi-2212. Two competing layer models of high- T_c superconductivity are explored.

2. Structural Changes Upon Intercalation

Iodine is intercalated into single crystals of Bi-2212 using a vapor transport method².

Depending on the temperature at which the reaction is carried out, different stage structures are obtained. In stage-1 material, iodine is intercalated between all the double Bi-O sheets. In stage-2 material, iodine is intercalated between every other set of double Bi-O sheets⁴. For iodine intercalated Bi-2212, structures up to stage-5 have been observed, but so far only stages 1 and 2 have been prepared in single-phase form.

Fig. 1 shows schematically the structures for pristine, intercalated stage-1, and intercalated stage-2 crystals. The drawings are based on x-ray diffraction and TEM structural studies⁵. Two notable structural changes result from intercalation. First, the (epitaxially situated) iodine atoms expand the crystal dimension along the *c*-axis, thereby increasing the distance between CuO_2 -containing blocks. Each intercalated iodine sheet separates the Bi-O double sheets by 3.6 \AA . For the stage-1 material, which has a stoichiometry $\text{I}_1\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$, this corresponds to an expansion of the crystal in the *c* direction by 23%, compared to the pristine material. In stage-2 material, every other Bi-O bilayer is intercalated, and the *c*-axis expansion is about 12%. The stoichiometry of stage-2 material is $\text{I}_{1/2}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$. It is important to note that in stage-1 material intercalation symmetrically alters coupling in both directions between adjacent CuO_2 -containing blocks, whereas for stage-2 material this symmetry is broken and the coupling is altered only in one direction.

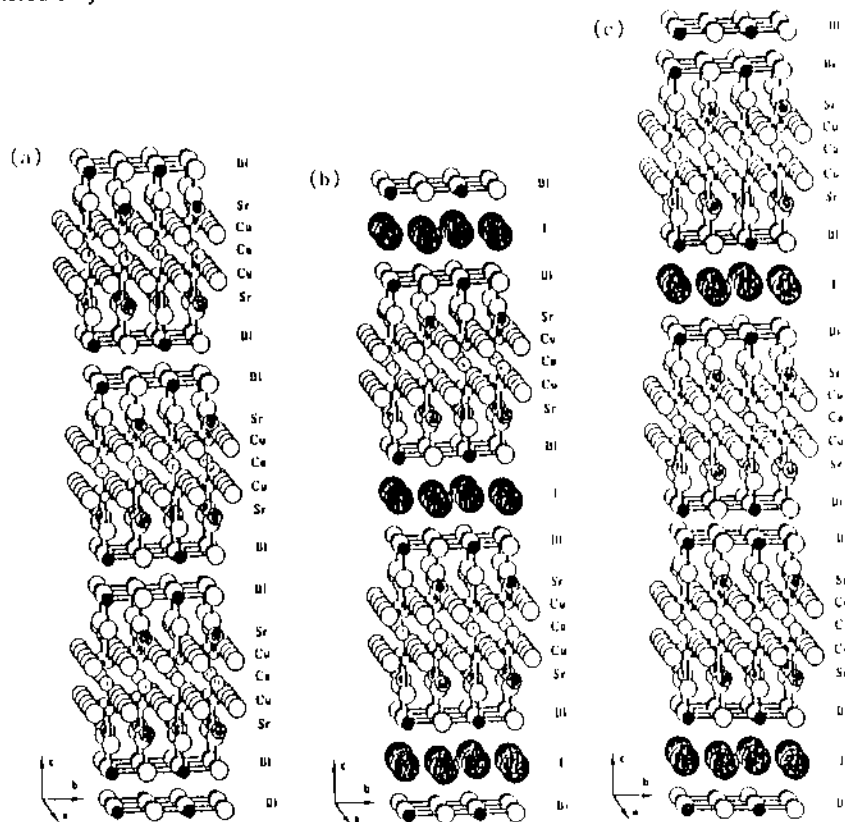


Fig. 1 Structure of (a) pristine, (b) stage-1 intercalated, and (c) stage-2 intercalated Bi-2212.

The second important structural change induced by intercalation is a shift in the registry of the CuO_2 blocks. In pristine material (Fig. 1a), the Bi atoms in adjacent Bi-O sheets are staggered, or in other words the blocks themselves are not lined up along the c-axis but rather they zig-zag back and forth. Intercalation shifts the blocks into registry by aligning the Bi atoms in adjacent Bi-O sheets. This shift necessitates a redefinition of the unit cell in the crystal. In stage-1 material, the improved registry at every Bi-O bilayer results in a *reduction* in the unit cell size along the c axis. So, even with the 23% crystal expansion, the unit cell dimension for stage-1 material is 18.9\AA , compared to 30.6\AA for the pristine material. In stage-2 material, the improved registry takes place at only every other Bi-O bilayer. From an electronic band structure point of view, the shifting of adjacent blocks into registry could have important consequences, for example in terms of electronic transport.

An additional structural feature concerns the well known in-plane superlattice modulation of pristine Bi-2212. Interestingly, intercalation appears to have no effect on this modulation, which suggests that the iodine induces a relatively minor elastic strain field perturbation. From a structural point of view, it thus appears that iodine intercalation simply changes the relative (ab-plane and c-axis) positions of CuO_2 -containing blocks, but leaves the internal structure of the blocks fully intact.

3. Electronic Changes

Iodine is strongly electronegative and thus a reasonable question is to what extent iodine intercalation changes the charge concentration in the host crystal. Indeed, one of the original motivations for performing iodine intercalation in Bi-2212 was to attempt injection of holes into the CuO_2 planes via iodine insertion between the CuO_2 planes themselves (not yet realized) or between the Bi-O sheets. Charge carrier concentration is most directly determined by transport measurements, for example Hall effect or electrical resistivity. Hall effect measurements have not yet been performed, but resistivity data are available.

Fig. 2a shows the ab-plane resistivity of a Bi-2212 crystal before and after stage-1 iodine intercalation. These data were obtained using a contactless eddy current loss measurement probe⁶. The advantage of this method (over the more conventional wire-bonded contact technique) is that it provides an accurate measurement of the resistivity of the same crystal before and after intercalation. The resistivity $\rho_{ab}(T)$ for the pristine material shows the well-known metallic functional form, with a drop to the superconducting state at $T_c \approx 90\text{K}$. The intercalated material has a slightly higher resistivity, but displays a similar temperature dependence. T_c for the intercalated

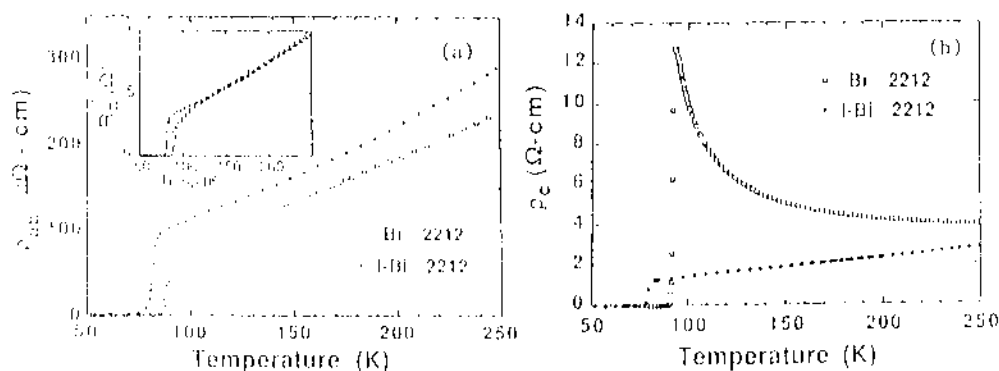


Fig. 2. In plane (a) and out-of-plane (b) resistivity of pristine and stage-1 intercalated Bi-2212. The inset in (a) shows the CuO_2 plane sheet resistance.

sample is about 80K. Stage-1 iodine intercalation thus depresses T_c by about 10K. Although intercalation appears to increase the ab-plane resistivity, it should be recalled that intercalation expands the crystal along the c-axis. Since the CuO_2 planes are believed to be the dominant charge transport channels along the ab-plane direction, we normalize the measured resistivity to resistance per CuO_2 plane. This is shown in the inset to Fig. 2a, for both the pristine and intercalated materials. As the inset shows, the resistance per CuO_2 plane is, throughout the entire temperature range above T_c , unaffected by intercalation. A careful calibration of the resistance measuring instrument at room temperature indicated identical sheet resistances for the CuO_2 planes to within 1%, the experimental error. From this we conclude that intercalation has no effect on the hole carrier density in the CuO_2 planes, and hence that there is no significant charge transfer taking place between intercalated iodine and the CuO_2 planes.

It is also interesting to note that the (weak) bonding properties between the Bi-O double sheets in the pristine material are not grossly affected by iodine insertion. Intercalated specimens are easily cleaved along the iodine layer, suggesting a weak (van der Waals) bond formed between the iodine and the adjacent Bi-O sheet. If significant charge transfer between the iodine and the close Bi-O sheet were taking place, a stronger ionic-like bond would form. Hence we conclude that the iodine is not to a very large extent electronically active in the host Bi-2212 structure.

From the above discussion, one might expect iodine intercalation to result in an increase in the out of plane electrical resistance. If transport across the insulating Bi-O sheets represented a hopping process, then increasing the thickness of the sheet structure could reduce the hopping probability and decrease the conductivity.

Fig. 2b shows the experimentally determined c-axis resistivity $\rho_c(T)$ for pristine and intercalated stage-1 Bi-2212 material, measured using a more conventional contact technique. $\rho_c(T)$ for the pristine crystal shows the typical "semiconductor-like" upturn with decreasing temperature. Close to room temperature, ρ_c for the intercalated specimen is *comparable* in magnitude to that for the pristine material. Hence at high temperature, intercalation neither significantly enhances nor impedes out-of-plane conduction. On the other hand, the temperature dependence of $\rho_c(T)$ for the intercalated crystal is absolutely *linear*, decreasing smoothly with decreasing temperature. The behavior is thus "metallic-like". However, the magnitude of the c-axis resistivity, before or after intercalation, is too large to be associated with a true metallic (i.e. coherent) transport across the blocks. In other words, if band theory were to apply, the high resistivity would imply a mean free path for the out of plane carriers less than the interplane separation. Interestingly, a similar argument applies to the c-axis conduction of other high- T_c layered cuprates. For the (slightly less anisotropic) material $\text{YBa}_2\text{Cu}_3\text{O}_7$, some specimens again show a linear "metallic-like" c-axis resistivity, despite the implied very short mean free path. These results suggest that the out-of-plane transport in these materials may be unconventional.

Figs. 2a and 2b show that T_c remains a scalar quantity for intercalated specimens, with a value of 80K for stage-1 material. We have performed dc and ac magnetization measurements on intercalated stage-1 and stage-2 crystals. The results are consistent with resistivity measurements. Fig. 3 shows the ac magnetic susceptibility, χ_{ac} , for pristine and iodine intercalated stage-1 and stage-2 crystals. The respective T_c 's are approximately 90K, 80K, and 85K. Hence the stage-2 crystal, which has only half of the Bi-O bilayers intercalated, has a T_c intermediate to that of the pristine and stage-1 material.

4. Relevance to Models of High- T_c Superconductivity

The dominant effect of intercalation in Bi-2212 appears to be a change in interblock coupling due to an increase in the physical separation of the blocks at the Bi-O sheets. Intra-block coupling is unaffected. A number of models have been proposed that may be relevant to high- T_c superconductors. In some descriptions, low dimensional effects are important.

The "rounding" of the in-plane resistivity $\rho_{ab}(T)$ just above T_c has been taken as strong

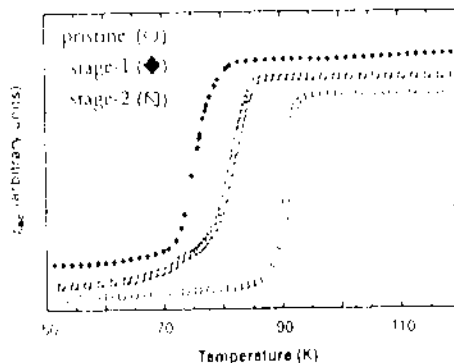


Fig. 3 Magnetic susceptibility of pristine, stage-1, and stage-2 intercalated Bi-2212

evidence for low dimensional superconducting fluctuations. It is instructive to compare the detailed $\rho_{ab}(T)$ behavior in pristine and stage-1 intercalated Bi-2212. Since intercalation is expected to decrease interblock coupling (and thus slightly depress T_c), a consequence might be an enhancement to 2D-like fluctuations above T_c .

Fig. 4a shows $\rho_{ab}(T)$ for pristine and stage-1 iodine intercalated Bi-2212. In Fig. 4b the T_c 's of the two samples have been artificially shifted into agreement and the resistivity magnitudes scaled so that the curves roughly align at the midpoint of the resistivity drop at T_c . Although some deviations are apparent between the data sets, Fig. 4b shows that intercalation does not significantly alter the rounding of $\rho_{ab}(T)$ above T_c ; hence any fluctuations that may be playing a role in the transport properties of the pristine material are relatively unaffected by intercalation.

Two detailed layer models have recently been proposed to account for superconductivity in the copper oxides. The first, by Ihm and Yu (IY)⁷, is a BCS-based model which includes in the calculation of T_c both intraplane CuO_2 coupling and nearest-neighbor interplane CuO_2 coupling. Next-nearest plane interplane coupling is neglected, so the interaction is limited to the presumed independent blocks containing the double CuO_2 planes.

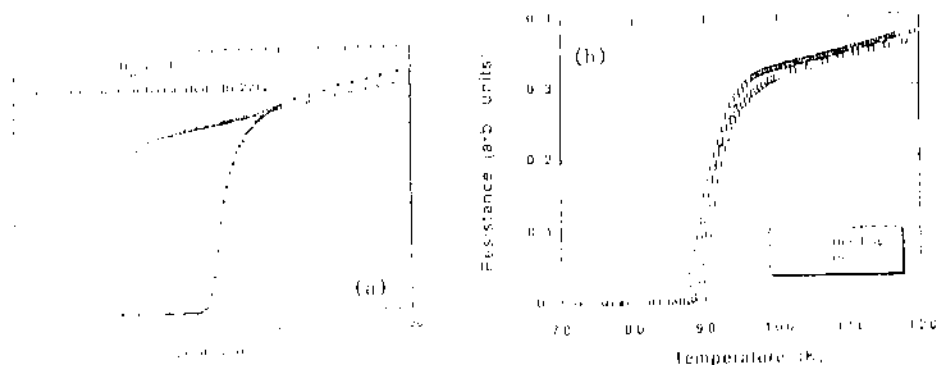


Fig. 4 (a) Resistivity of pristine and stage-1 intercalated Bi-2212. (b) Same data as (a) with T_c and resistivity magnitude normalized.

Since iodine intercalation affects only the interblock coupling, it should, according to the 1Y model, have no effect on T_c (on the other hand, if iodine had been intercalated between the double CuO_2 planes within the blocks, a large negative change in T_c would be expected). Thus the 1Y model cannot account for the experimental findings of Fig. 3, where T_c does depend on the strength of the interblock coupling. Interblock (or equivalently, next-nearest neighbor coupling) can be incorporated into the 1Y framework. The extended model⁴ has been analyzed and it can self-consistently account for a stage-2 T_c of 85K, using as input parameters $T_c=90\text{K}$ for pristine material and $T_c=80\text{K}$ for stage-1 material. The strength of the interblock coupling parameter is found to be 22% of the nearest-neighbor plane coupling. The model does not address transport properties.

A second model is based on the RVB state. Wheatley, Hsu, and Anderson (WHA)⁸ neglect intraplane interactions and assume contributions from both nearest neighbor interactions (between the double CuO_2 planes) and next-nearest neighbors (interblock coupling). Without modification, this model accounts for the T_c 's of pristine, stage-1, and stage-2 materials, (and predicts⁴ T_c 's of 87K, 88K, and 89K for stages 3, 4, and 5, respectively) using as fitting parameters 80K for nearest-neighbor coupling and 10K for next-nearest neighbor in the pristine material (reducing to zero in stage-1 intercalated material). If these same parameters are used in the RVB holon-spinon transport model of Anderson and Zou (AZ)⁹, predictions can be made for the anisotropic electrical resistivity of pristine and intercalated material. While rough agreement is found for the experimentally determined resistivity tensor of pristine material, the linear temperature dependence of $\rho_c(T)$ of stage-1 Bi-2212 shown in Fig. 3b is in apparent conflict⁶ with the model (the model predicts a very strong $1/T$ -like temperature dependence for material with a reduced interblock coupling).

5. Conclusion

Intercalation can be applied to the layered cuprates to generate new superconducting crystal structures and to test models of superconductivity. It would be worthwhile to test further the physical properties of the intercalated Bi-based superconductors. In particular, one might expect changes in elastic, thermal, magnetic, and superconducting properties. It should also be possible to intercalate, with various foreign species, other layered high- T_c superconductors, such as thallium-based materials, infinite-layer structures, and "123" and "214" compounds.

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7. References

1. See, for example, F. Levy, ed. *Intercalated Layered Materials* (Reidel, Dordrecht, 1979)
2. X.-D. Xiang et al *Nature* **348** (1990) 145
3. X.-D. Xiang et al *Phys. Rev. B* **43** (1991) 11496
4. X.-D. Xiang et al *Science* **254** (1991) 1487
5. N. Kijima et al *Physica C* **181** (1991) 18
6. X.-D. Xiang et al *Phys. Rev. Lett.* (1992)
7. J. Ihm and B.D. Yu, *Phys. Rev. B* **39** (1989) 4760
8. J.M. wheatley, T.C. Hsu, and P.W. Anderson *Nature* **333** (1988) 121
9. P.W. Anderson and Z. Zou *Phys. Rev. Lett.* **60** (1988) 132