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LETTER TO THE EDITOR

Unusual High Oxidation State of Iodine Intercalated in the $Bi_2Sr_2CaCu_2O_x$ Superconductor

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X-ray photoelectron spectroscopy (XPS) shows that iodine intercalated into the (Bi–O) layers of the oxide superconductor $Bi_2Sr_2CaCu_2O_x$ is present in a highly oxidized I(VII) state suggestive of the formation of strongly covalent I–O bonds as in KIO_4, not as in KIO_3. Electrons are transferred from the antibonding states of the covalent complex to the CuO_2 sheets, which lowers T_c. The core-level spectra also show the presence of residual iodine species at the surface of the samples. Ar-ion sputtering of the surface disintercalates iodine from the bulk to the surface.

Recently, it has been demonstrated that iodine molecules can be intercalated into Bi–Sr–Ca–Cu–O superconductors (*1*, *2*). Among these, the stoichiometry of the iodine derivative of the $Bi_2Sr_2CaCu_2O_x$ (2212) phase was found to be $I \cdot Bi_2Sr_2CaCu_2O_x$ ($I \cdot 2212$); the superconducting transition temperature ($T_c \simeq 70 \sim 80$ K) was slightly lower after iodine intercalation than the pristine 2212 phase ($T_c \simeq 82 \sim 90$ K).

According to the investigation of the Hall coefficient by Pooke, Kishio, and co-workers, a modest transfer of holes to the CuO_2 plane upon iodine intercalation has been postulated (*3*, *4*). Controversially, Xiang *et al.* speculated on an electron transfer from the iodine layers to the CuO_2 sheets based on the changes in T_c (*2*). But in general, the iodine bonding in the interlayer space of the 2212 phase is thought to be either van der Waals type or metallic.

In this paper, we report the preliminary results of X-ray photoelectron spectroscopy for the 2212 phase and its iodine derivative in order to aid understanding of the bonding state of iodine in the superconducting lattice.

The pristine 2212 phase was prepared by conventional solid-state reaction as reported previously (*5*). The iodine intercalate can be obtained by reacting iodine molecules with 2212 polycrystals directly at

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200°C for less than 1 hr in a vacuum-sealed pyrex tube. The iodine partial pressure (P_{I_2}) in the reaction cell at 200°C was estimated to be about 9.6 atm.

According to the X-ray diffraction analysis, the c-axis spacing for the iodine derivative was increased by about 6.9 Å compared to the pristine material due to the intercalation of iodine into the (Bi–O) layers by formation of the 1-stage intercalate, which is consistent with previous reports (*1*, *3*).

The stoichiometry of iodine in the 2212 phase was determined by thermogravimetric analysis (TGA); it indicates the formation of the I · 2212 phase.

The offset T_c of the pristine compound (72 K) and the iodine intercalate (62 K), which are lower than those reported previously, have been measured with a dc superconducting quantum interference device and also by the standard four-probe method. Though the T_c could be more or less changed, depending upon the oxygen content in the lattice, the decrease in T_c in this experiment may be explained by the fact that the hole concentration, i.e., the density of charge carriers, in the superconducting (Cu–O) planes is diminished.

X-ray photoelectron spectroscopy (XPS) experiments were performed in order to check for evidence of electron transfer from the iodine to the CuO_2 sheets. First, the XPS spectrum of the I 3d region for the I · 2212 phase was obtained at room temperature; in Fig. 1 it is compared with those for the standard samples of KIO_3 and KIO_4. The I 3d core-level spectra show two main peaks corresponding to the $3d_{5/2}$ and $3d_{3/2}$ levels. In the case of the I · 2212 phase, two additional peaks shifted by ca. 5 eV are observed. A surprising thing to note here is that the main peaks for the I · 2212 phase have almost the same binding energy (BE) as those for KIO_4. Such a high binding energy peak is only observed in core-level photoemission from a formal heptavalent iodine compound like KIO_4 (Fig. 1). No peaks corresponding to pentavalent iodine, like KIO_3, are found. The above experimental finding indicates that the superconducting 2212 phase contains the iodine ion mainly in the formal oxidation state of VII+; at least, the bonding nature of iodine in the interlayer appears to be as covalent as in KIO_4, which is also consistent with the chemical stability of the sample. We therefore believe that this result provides clear and direct evidence of electron transfer from the intercalated iodine to the 2212 lattice. Since only the (Bi–O) planes are strongly perturbed by the iodine intercalation, no significant perturbation of the $\sigma^*_{x^2-y^2}$ band (*6*) of the CuO_2 sheets is expected other than electron transfer to the band, which is consistent with the experimental variation of T_c.

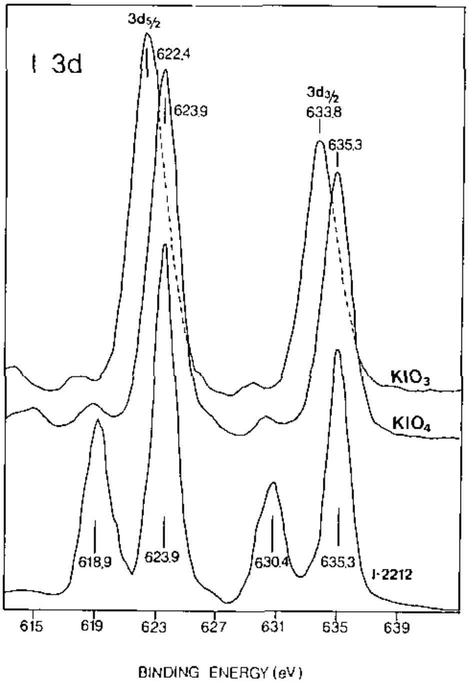

FIG. 1. Iodine 3d core-level XPS spectra for the I · 2212, KIO_3, and KIO_4.

The two peaks at lower BE are quite similar to those observed for KI and/or I_2 (*7*), which suggests that they come from reduced

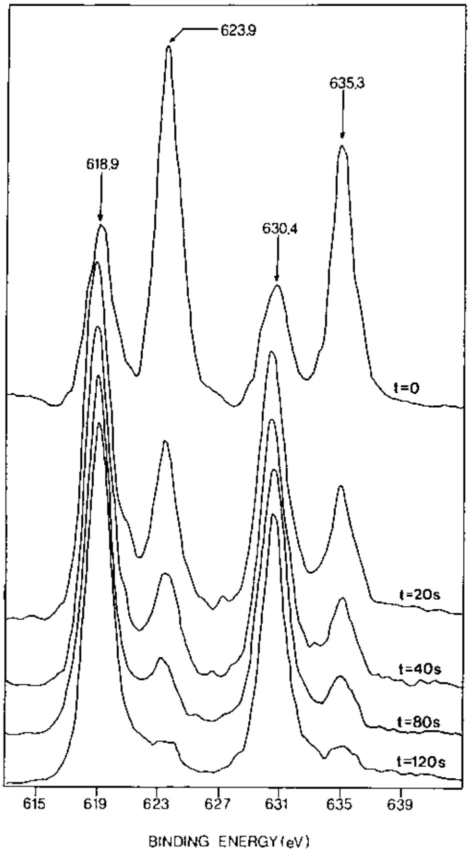

FIG. 2. Iodine $3d$ core-level XPS spectra for the I · 2212 at various sputtering times t = 0, 20, 40, 80, and 120 sec.

surface species. In order to check out this deduction, we investigated samples that were subjected to Ar-ion bombardment for different amounts of time. As can be seen from Fig. 2, there is a dramatic increase in the peaks at low BE and a decrease in the peaks at high BE. Since Ar-ion bombardment under ultrahigh vacuum ($\sim 10^{-9}$ Torr) can be expected to induce a reductive disintercalation of the iodine from the interlayer space of the (Bi–O) slabs, this result shows that the intercalated iodine is present in the unusually high VII+ oxidation state, whereas the peaks at lower BE belong to surface species that grow in concentration with disintercalation of iodine from the bulk.

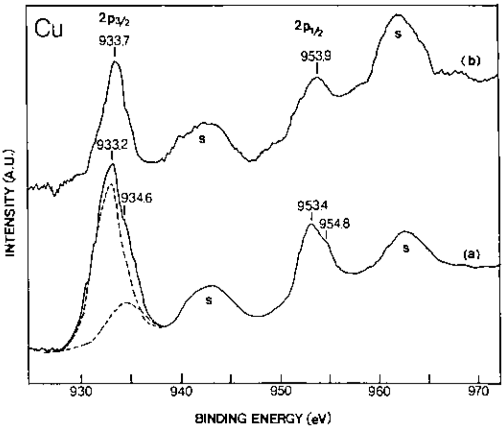

FIG. 3. Copper $2p$ core-level XPS spectra for the (a) 2212 and (b) I · 2212.

We note also that Ar-ion sputtering is not an appropriate procedure for cleaning the surface of such an intercalation compound; the guest species tend to be disintercalated from the host upon local heating by high-energy ion-beam sputtering under UHV, and also the high-T_c copper oxides like $YBa_2Cu_3O_{7-\delta}$ are easily reduced at the surface from Cu(III) to Cu(II) or Cu(I) as has been reported previously (*8, 9*).

Charging effects by Ar-ion sputtering could be ruled out in these measurements since the BEs for the core $4f$ electrons of the bismuth are identical before and after the Ar-ion sputtering.

The Cu $2p$ XPS spectra for the pristine 2212 and I · 2212 phases are compared in Fig. 3. The two main peaks corresponding to the $2p_{1/2}$ and $2p_{3/2}$ levels are accompanied by satellite peaks at about 9 eV higher binding energy than the main $2p$ peaks. Such satellites are frequently observed in core-level photoemission from divalent copper compounds (*10–13*) and are attributed to a ligand–metal charge transfer ($2p^63d^9 \rightarrow 2p^53d^{10}$) in the final state of the photoemission process (*14*) that effectively screens the excited core hole. The identification of these satellites for both samples strongly evidences the presence of Cu^{II} and Cu^{III}. The latter could be directly confirmed from the broad anisotropic Cu $2p$ peaks as represented in Fig. 3. The Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks of the pristine compound could be respectively separated into two peaks as follows: (1) Cu $2p_{3/2} \rightarrow$ 933.2 eV (Cu^{II}) and 934.6 eV (Cu^{III}), (2) Cu $2p_{1/2} \rightarrow$ 953.4 eV (Cu^{II}) and 954.8 eV (Cu^{III}). The observed BEs are consistent with those for Cu $2p$ in $YBa_2Cu_3O_{7-\delta}$ (*8*, *15*) and $Bi_2Sr_2CaCu_2O_x$ (*16*). After iodine intercalation, the higher (Cu^{III}) BE peaks are strongly depressed as is to be expected for electron transfer from the intercalated iodine to the CuO_2 sheets.

From these observations, we conclude that the iodine intercalated into the 2212 phase is highly oxidized, probably by the formation of strong I–O bonds with oxygen in the Bi–O planes. Electrons are transferred from the antibonding states of these bond to the CuO_2 sheets, and reduction of the CuO_2 sheets causes a lowering of T_c. The degree of charge transfer to the CuO_2 sheets depends upon the number of holes in the Bi–O charge reservoir of the pristine phase.

Acknowledgments

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