Raman spectroscopic evidence on molecular mercuric bromide in the two-dimensional lattice of $(HgBr_2)_{0.5}Bi_2Sr_2CaCu_2O_y$

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Polarized Raman spectroscopic experiments have been carried out for the mercuric bromide intercalated $Bi_2Sr_2CaCu_2O_y$ single crystal in order to investigate the evolution of electronic and geometric structures of host and guest upon $HgBr_2$ intercalation. All the present spectra indicate the presence of the symmetric linear $HgBr_2$ molecule in the interlayer space of the intercalate together with an interaction between the intercalated $HgBr_2$ and host lattice, which confirms clearly the previous extended x-ray-absorption fine structure/x-ray-absorption near-edge structure results. [S0163-1829(97)06209-7]

I. INTRODUCTION

Since the intercalation reaction makes it possible to hybridize various kinds of chemical species into the same crystal lattice, it provides an effective method not only to develop an interstratified compound but also to study the chemical and physical properties of low-dimensional materials. Recently its application has been extended to high-T_c superconducting materials, especially to Bi-based cuprate superconductors with extreme anisotropic crystal structures.[1–11]

Previously we have performed systematic Raman studies on iodine-intercalated $Bi_2Sr_2CaCu_2O_y$ and $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_y$, and found that the guest iodine is stabilized as a tri-iodide ion, acting as an electron acceptor.[6,7] Based on this finding, an attempt has been made to intercalate various guest species with Lewis acidity. Recently we have successfully developed a type of high-T_c superconducting compound of M-X-Bi-Sr-Ca-Cu-O (M=Hg and Ag; X=Br and I), where a superconducting layer and an insulating/superionic conducting one are regularly interstratified.[1–5] According to x-ray-diffraction (XRD) analysis and magnetic-susceptibility measurement, the HgX_2 intercalates are all superconducting with slightly lowered T_c (ΔT_c=5–7 K) relative to the iodine intercalate (ΔT_c=13 K), in spite of their remarkable basal increment (Δd=6–7 Å) which is almost twice as large as that for the first staged iodine intercalate (Δd=3.6 Å).[1–3] In previous studies on the iodine-intercalated $Bi_2Sr_2CaCu_2O_y$ compound, it has been argued that T_c evolution upon intercalation is likely dependent on one of two factors or both: the doped hole concentration[6,7] and/or interblock coupling.[8] But an insignificant T_c depression upon HgX_2 intercalation seems not to be comparable with the interblock coupling model.[8] Therefore, we have turned our attention to an interaction between guest and host, giving rise to the modification of the superconducting block and, thereby, T_c evolution.

In this study, we have performed Raman spectroscopic studies on the $HgBr_2$ intercalate of a single crystalline $Bi_2Sr_2CaCu_2O_y$ compound to investigate its chemical bonding nature and crystal structure, because this spectroscopy is a very effective method to investigate the electronic and crystal structures of high-T_c superconducting materials.[6,7,9–20] Moreover, this method has also been usefully applied to characterize the mercuric halide species in various states such as gas, solid, and molten salt, and to probe the local structure and bond strength of (Hg-X).[21–24]

II. EXPERIMENTAL

A single crystal of pristine $Bi_2Sr_2CaCu_2O_y$ was synthesized by the traveling-solvent floating-zone method. The intercalation of $HgBr_2$ into the $Bi_2Sr_2CaCu_2O_y$ single crystal was performed by using the vapor transport reaction between the guest $HgBr_2$ and the pristine $Bi_2Sr_2CaCu_2O_y$. The first staged $HgBr_2$ intercalate was prepared by heating a vacuum-sealed Pyrex tube containing $Bi_2Sr_2CaCu_2O_y$ single crystal and mercuric bromide (mole ratio of 1:5) at 230 °C for five days in a uniform temperature furnace.

The formation of a single phasic intercalate was confirmed by the x-ray-diffraction pattern as shown in Fig. 1. According to least-squares refinement, the c-axis unit-cell parameters were determined to be 30.6 Å for the single crystalline $Bi_2Sr_2CaCu_2O_y$ and 43.2 Å for its $HgBr_2$ intercalate. Since there are two intercalated layers of $HgBr_2$ for each unit cell of $Bi_2Sr_2CaCu_2O_y$,[1–3] each mercuric halide layer expands the c axis by about 6.3 Å, which is well consistent with the basal increment for the first staged $HgBr_2$ intercalate of the polycrystalline $Bi_2Sr_2CaCu_2O_y$.[1–3]

On the basis of the (00l) reflection intensities in the present XRD pattern, we have calculated a one-dimensional electron density map along the c axis, as shown in Fig. 2. Alternatively, we have obtained the other Fourier map from the suggested crystal structure where the intercalated $HgBr_2$ is stabilized as a linear molecule with a tilting orientation with respect to the basal plane. As can be seen from the figure, there is good agreement between both electron density maps, confirming the fitness of the present structure.

The Raman measurement was carried out at room temperature using a Jobin-Yvon/Atago Bussan T64000 triple
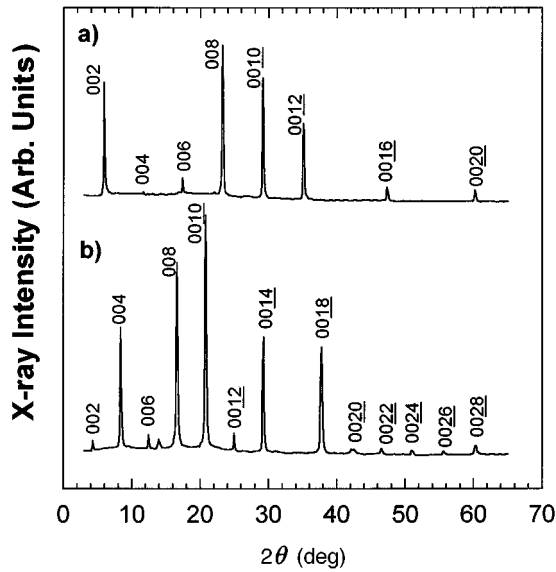
FIG. 1. X-ray-diffraction patterns for (a) the pristine $Bi_2Sr_2CaCu_2O_y$ single crystal and (b) its $HgBr_2$ intercalate. All reflections could be indexed on the basis of the double-slab tetragonal unit cell.

spectrometer equipped with micro-optics. The samples were excited with the 514.5 nm line of the Ar laser. All the present spectra were obtained by backscattering from freshly cleaved surfaces of a single crystal with various scattering geometries. In order to prevent possible thermal damage of the sample, the power of incident laser light was maintained at less than 20 W. The resolution of the present spectra was $3–4$ cm^{-1}. The Raman measurements for a different area of

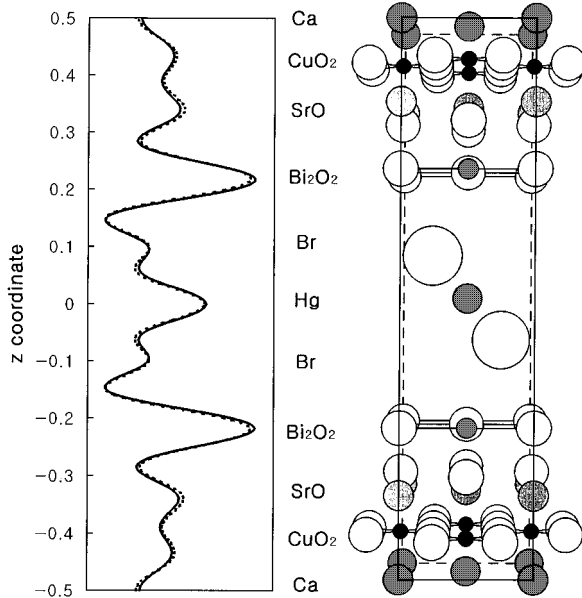FIG. 2. Crystal structure of the tetragonal $(HgBr_2)_{0.5}Bi_2Sr_2CaCu_2O_y$, together with one-dimensional electron density maps along the c axis. The dotted and solid lines represent the calculated electron density based on the observed XRD patterns and that on the basis of the present crystal structure, respectively.
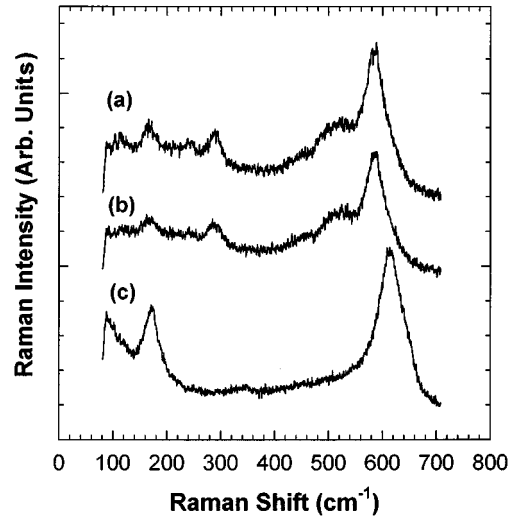

FIG. 3. The polarized Raman spectra for the $HgBr_2$ intercalate of $Bi_2Sr_2CaCu_2O_y$ single crystal with scattering geometry of (a) $z(x\bar{x})\bar{z}$, (b) $z(y\bar{y})\bar{z}$, and (c) $x(z\bar{z})\bar{x}$

the cleaved surface gave identical spectra, indicating the homogeneity of the intercalate.

III. RESULTS AND DISCUSSION

The group-theoretical analysis based on the space group $I4/mmm$ of tetragonal structure predicts six Raman-active A_{1g} modes for the pristine $Bi_2Sr_2CaCu_2O_y$ under the present experimental geometries, those which correspond to the symmetric c-axis vibrations of Bi, Sr, Cu, O_{Bi}, O_{Sr}, and O_{Cu}.[12,15] Among these Raman-active modes, the phonon modes of Bi and O_{Sr} appear at 65 and 634 cm^{-1} in the $x(z\bar{z})\bar{x}$-polarized spectra.[12,13] According to the previous Raman study of the La-substituted $Bi_2Sr_{2-x}La_xCuO_y$ phase,[14] the latter peak is found to be quite sensitive to the modification of the SrO plane. On the other hand, the other four A_{1g} modes relating to the c-axis vibrations of Sr, Cu, O_{Cu}, and O_{Bi} are observed at 116, 145, 409, and 466 cm^{-1} in the $z(x\bar{x})\bar{z}$- and $z(y\bar{y})\bar{z}$-polarized spectra, respectively.[12,13] Especially, the phonon line at 466 cm^{-1} is expected to provide a sensitive probe to the variation of the Bi_2O_2 layer that may be drastically affected by the intercalation reaction. In addition to these peaks, there are several weak bands originated from orthorhombic distortion and incommensurate superstructural modulation.[12,15]

Figure 3 exhibits the polarized Raman spectra of the $HgBr_2$-intercalated $Bi_2Sr_2CaCu_2O_y$ single crystal with the scattering geometries of $z(x\bar{x})$, $z(y\bar{y})\bar{z}$, and $x(z\bar{z})\bar{x}$. Regardless of scattering configuration, a characteristic Raman peak with considerable intensity is observed at around 170 cm^{-1}. Since there is no intense Raman feature in this frequency region for the pristine compound, this peak should be attributed to the phonon mode of the intercalated $HgBr_2$ species. Polarization-independent occurrence of this peak allows us to confirm the above assignment, because the intercalated $HgBr_2$ species have a tilted orientation to the basal plane as shown in Fig. 2, resulting in considerable Raman activity of the (Hg-Br) vibration for all the scattering geometries.[1–3]

The group-theoretical calculation based on the triatomic symmetric linear structure of point group $D_{\infty h}$ predicts one Raman-active mode (ν_1) and two Raman-forbidden but infrared-active ones (ν_2 and ν_3). In fact, the free $HgBr_2$ vapor with linear structure exhibits only one Raman peak at 225 cm^{-1}, corresponding to the symmetric vibration mode (ν_1).[21–23] However, a slight deviation from linear symmetric structure in the molten salt of $HgBr_2$ makes the Raman-forbidden ν_3 mode visible at 271 cm^{-1}.[22] For the $HgBr_2$ vapor with isotropic components of ^{79}Br and ^{81}Br where the ν_3 vibration mode is Raman active, the corresponding phonon line is observed at 293 cm^{-1}.[23] But the present spectra of $HgBr_2$ intercalate exhibit only a peak corresponding to the symmetric stretching (ν_1) vibration of (Hg-Br) but no peak corresponding to the Raman-forbidden mode (ν_3) around 270–290 cm^{-1}, indicating the presence of a linear symmetric $HgBr_2$ molecule as in the gaseous state. This symmetric stretching mode is remarkably softened from 225 cm^{-1} for the vapor to 170 cm^{-1} for the intercalate.[21–23] Moreover, its frequency is smaller for the intercalate than even for the $HgBr_2$ solid (186 cm^{-1}).[24] Since this mode is quite sensitive to environmental effects as found in the marked solvent shift,[22] its frequency difference among the vapor, solid, and intercalated states reflects different interaction with the neighboring chemical species in each state. In the case of the vapor state, the $HgBr_2$ exists as a linear molecule without any significant interaction with the other molecules, whereas, in the solid state, the $HgBr_2$ is stabilized as a CdI_2-type structure where the $HgBr_2$ species interact slightly with the other one in the adjacent layer.[25] In contrast, there is a significant electrostatic interaction between the electronegative bromine and electropositive bismuth in the $HgBr_2$ intercalate. Since enhanced interaction with the environment gives rise to the weakening of the competing (Hg-Br) bond, the observed order of peak frequency, ν (vapor)$>\nu$ (solid)$>\nu$ (intercalate), is well consistent with the expected order of interaction with the neighboring chemical species.

In addition to this peak, several Raman features corresponding to the phonon modes of the host lattice are also observed. In order to assign these peaks, we have carried out factor-group analysis on the basis of the structural model suggested from the previous XRD and extended x-ray-absorption fine-structure (EXAFS) analyses (Fig. 2).[3] For the sake of simplicity, we have taken the $HgBr_2$ molecule as an atomic species located in the position of mercury ion, since this treatment hardly perturbs the phonon modes of the host lattice. From this factor-group analysis, it is found that the intercalate has six Raman-active A_{1g} modes, corresponding to the c-axis vibrations of Bi, Sr, Cu, O_{Bi}, O_{Sr}, and O_{Cu}, those which are the same as the pristine's.

As can be seen in Fig. 3, the most prominent change induced by intercalation is the appearance of intense features at 520 and 585 cm^{-1} in the $z(x\bar{x})\bar{z}$- and $z(y\bar{y})\bar{z}$-polarized spectra. Judging from their frequencies, they are likely to be attributed to one of two phonon modes, A_{1g} vibrations of O_{Bi} or O_{Sr}.[12,13] However, their polarization dependence allows us to interpret them as the c-axis vibration of O_{Bi}, which is completely absent in the $x(z\bar{z})\bar{x}$ spectrum, rather than as that of O_{Sr} with a strong zz polarization. Therefore, this phonon line shifts upward from 466 to 520–585 cm^{-1} upon intercalation, which indicates the stiffening of the $(Bi^{3+}-O_{Bi}^{2-})$ bond

due to the electrostatic interaction with $(Br^{1-}-Hg^{2+})$ pair. In fact, the in-plane bond distance of (Hg-Br) calculated from XRD and EXAFS results is well consistent with the in-plane $(Bi-O_{Bi})$ bond length, which makes the effective interaction between two bonding pairs possible.[26] Such a hardening of the O_{Bi} mode is partially due to the oxidation of the Bi_2O_2 layer, which was found from the previous x-ray-absorption near-edge structure (XANES) spectroscopic study.[3] In fact, this phonon line is affected very drastically by modification of the Bi_2O_2 layer, as can be seen in the Raman spectra of Pb-substituted $Bi_{2-x}Pb_xSr_2CaCu_2O_y$ compounds where this phonon line is replaced by a wide band extending from 450 to 570 cm^{-1} upon Pb substitution.[17] On the other hand, the splitting of this phonon line into two peaks at 520 and 585 cm^{-1} indicates two kinds of oxygen sites in the Bi_2O_2 layer of intercalate, that is, a Hg-coordinates site and an uncoordinated one.

Another intense Raman peak is observed at 614 cm^{-1} with the $x(z\bar{z})\bar{x}$ scattering configuration, which is reasonably assigned to the c-axis vibration of O_{Sr} on the basis of polarization dependence. Contrary to the spectra for the pristine compound where this peak is split into two features at 630 and 660 cm^{-1},[12,15,16] the present spectra for the intercalate exhibit only a single peak as observed for the other intercalation compounds of iodine and IBr.[9–11] Such a splitting for the pristine has been understood as a result from a distribution of O_{Sr}-Bi-O_{Bi} force constants induced by the incommensurate superstructural modulation.[12,15,16] In fact, only a single peak corresponding to the A_{1g} vibration of the apex oxygen (O_{Sr}) is observed at 580 cm^{-1} for the $BiSr_2CaCu_2O_y$ phase with BiO monolayer where there is no O_{Sr}-Bi-O_{Bi} interaction.[19,20] In the case of the present intercalation compound, a collapse of two peaks into a single peak is explained by the weakening of the $(Bi-O_{Bi})$ interaction, since the interlayer distance of Bi_2O_2 layers is much elongated upon intercalation. It was also found that this phonon mode is softened upon intercalation as observed in the iodine intercalate, suggestive of the interaction between host lattice and guest molecule.[9,10]

There remain some weak peaks at 104, 114, and 288 cm^{-1} in the $z(x\bar{x})\bar{z}$ and $z(y\bar{y})\bar{z}$ spectra, those which are assigned to the tetragonal-forbidden mode of Bi/Sr, A_{1g} mode of Sr, and the tetragonal-forbidden mode of O_{Bi}/O_{Sr}, respectively.[12] Up to this point, three modes of the expected six A_{1g} ones are observed and assigned, but the remaining three are not detected in the present spectra. Among them, the A_{1g} mode of Bi cannot be observed in the present measuring range (80–700 cm^{-1}) due to its lower frequency. On the other hand, two peaks corresponding to the Cu and O_{Cu} vibrations seem to be concealed in the noise. Since the increase of hole concentration gives rise to an enhanced metallic screening within and between adjacent CuO_2 layers, resulting in the weakening of peak intensity,[18] the disappearance of peaks relating to the CuO_2 layer is well consistent with the previous XANES/EXAFS results where the CuO_2 layer is oxidized upon intercalation due to the charge transfer.

IV. CONCLUSION

In this study, we have performed a systematic polarized Raman experiment for the $HgBr_2$ intercalate. A clear obser-

vation of the symmetric vibration mode of (Hg-Br) indicates that the intercalated $HgBr_2$ molecule is stabilized as a symmetric linear molecule as in the vapor state. The softening of this mode upon intercalation is well understood on the basis of our structural model. On the other hand, there are remarkable variations of the Raman peaks relating to the phonons of host lattice, indicating a host-guest interaction, which is well consistent with previous EXAFS/XANES results. Compared to the O_{Sr} phonon line, the O_{Bi} one is more strongly influenced upon intercalation, confirming again our structural model where the intercalant layer is stabilized in between the Bi_2O_2 layers but far from the SrO one.

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