

Pressure dependence of the superconducting transition temperature and the Hall coefficient in $\text{IBi}_{2.2}\text{Sr}_{1.8}\text{CaCu}_2\text{O}_{8+y}$ single crystals

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The superconducting transition temperature T_c and the Hall coefficient have been measured on $\text{IBi}_{2.2}\text{Sr}_{1.8}\text{CaCu}_2\text{O}_{8+y}$ single crystals under hydrostatic pressure. The T_c linearly decreases at the rate $dT_c/dP \sim -3.5$ K/GPa, indicating the facts that the charge transfer occurs between intercalated iodine atoms and CuO_2 layers, and the hole concentration situates in the overdoped region. The facts have been further identified by our Hall-coefficient measurements at ambient pressure, showing an increase of the hole concentration after intercalation. The number of holes transferred from intercalated iodine atoms was calculated to be 0.3 per iodine atom. The pressure derivative of the Hall coefficient is $-0.39 \times 10^{-3} \text{ cm}^3 \text{ C}^{-1} \text{ GPa}^{-1}$, which is approximately twice as large as the value on the pristine crystal, indicating the valence change of the intercalated iodine under pressure.

I. INTRODUCTION

The structure of the high- T_c copper oxide superconductor is anisotropic along the ab plane and the c -axis direction. It was believed that the electrical transport anisotropy is derived from the structural anisotropy. Although the mechanism of high- T_c superconductors is still a mystery today, it is generally considered that the two dimensionality of the structure is important for high- T_c superconductors. Among all high- T_c copper oxide superconductors discovered at present, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ (Bi-2:2:1:1) is markedly anisotropic in its structure and easy to be intercalated. Xiang *et al.*^{1,2} intercalated iodine in Bi-2:2:1:2, yielding a new stage-1 compound $\text{IBi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ (IBi-2:2:1:2). The crystal structure of stage-1 iodine-intercalated superconducting $\text{IBi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ has been determined by x-ray-diffraction analysis³ and transmission electron microscopy,⁴ showing that the iodine atoms intercalate between the weakly bound (Bi-O) bilayers with a corresponding expansion along the c -axis direction by 0.36 nm for each Bi-O bilayer. The intercalation of iodine not only affects the crystal structure of Bi-2:2:1:2, but its electrical properties as well. It has been reported^{1,2} that the superconducting transition temperature T_c is depressed by about 10 K and the temperature dependence of the resistivity along the c -axis direction changes from a semiconductor-like behavior to a metal-like one after intercalation, indicating that the electrical transport anisotropy is greatly reduced.

To explain the decrease of T_c through the intercalation of iodine, two main effects were considered.^{1,3,5-7} One is due to the expansion of the crystal along the c -axis direction; namely, the enhancement of the distance between CuO_2 layers in adjacent blocks affects interblock coupling and leads to the change T_c . The other is an increase of the conductive hole carriers due to the charge transfer between intercalated iodine atoms and CuO_2 layers.

On the other hand, the valence state of the intercalated iodine has been investigated, based on the assumption

that charge transfer exists between intercalated iodine atoms and CuO_2 layers. From one Raman-scattering experiment,⁸ it has been claimed that the intercalated iodine atoms are not ionized and exist like I_2 molecules. Another Raman-scattering study,⁹ on the contrary, has shown that the iodine are ionized as I_3^- molecular anions. In addition, a coexistence of I^- and I^{7+} valence states has also been reported⁶ by x-ray-photoemission spectroscopy (XPS). However, the above results have not been confirmed by other experiments.

Since the hole concentration CuO_2 layers could be varied under pressure,^{10,11} the pressure effect is thought to be favorable for studying the decrease of T_c through iodine intercalation. The study of the variation of T_c with hole concentration under pressure has been reported. Kosuge *et al.*¹² suggested that the sign of dT_c/dP principally depends on where the hole concentration is located; i.e., dT_c/dP is positive in the underdoped region, zero if optimally doped, and negative for samples in the overdoped region. Furthermore, Neumeier and Zimmermann¹³ claimed that another type of mechanism will affect T_c under pressure for Y-Ba-Cu-O system superconductors, besides the effect of the hole concentration. In the present study, we crudely assume that the variation of T_c is mainly influenced by the hole concentration in the CuO_2 layers. Therefore, if the hole concentration in the pristine sample is situated in the underdoped region, a positive value dT_c/dP is expected because of the increase of the hole concentration in the CuO_2 layers under pressure. After intercalation, if the hole concentration is still located in the underdoped region—i.e., the charge transfer between intercalated iodine atoms and CuO_2 layers is small³ or does not occur—the value of dT_c/dP should be the same as that in the pristine sample. On the contrary, if the sample becomes overdoped, the pressure derivative of T_c would show a negative value. In addition, the hole concentration in the sample can be directly detected by Hall-coefficient measurements. Accurate measurement of the Hall coefficient under pressure can show the variation of the hole concentration and thus the

valence change of iodine in IBi-2.2:1:2; if charge transfer does occur.

Generally, the hole concentration of Bi-2.2:1:2 is situated in the overdoped region,^{14,15} whereas Bi_{2.2}Sr_{1.8}CaCu₂O_{8+y} (Bi-2.2:1.8:1:2) (Ref. 16) is located in the underdoped region, since the small amount of Bi substitution for Sr causes a decrease of holes in the CuO₂ layers. Thus IBi_{2.2}Sr_{1.8}CaCu_{8+y} (IBi-2.2:1.8:1:2) single crystals, it seems, are suitable for studying whether or not charge transfer occurs between intercalated iodine atoms and CuO₂ layers. Here, besides the XPS spectra, we mainly present the results of resistance and Hall-coefficient measurements under pressure on IBi-2.2:1.8:1:2 single crystals. Some results are compared with the pristine ones to show the change of physical properties after the iodine intercalation.

II. EXPERIMENTAL DETAILS

Pristine single crystals of Bi-2.2:1.8:1:2 were prepared by the traveling-solvent floating-zone (TSFZ) method. Raw materials of Bi₂O₃ (99.99%), Sr(NO₃)₂ (99.9%), CaCO₃ (99.9%), and CuO (99.99%) powders were used in a molar ratio of [Bi]:[Sr]:[Ca]:[Cu]=2.2:1.8:1:2 for the feed rod and 2.4:1.5:1:1.8 for the solvent rod, respectively. Details are given in Ref. 16. The grown crystals have a sheet shape which can be easily laminated along the *ab* plane. The composition of the single crystal was determined by inductive coupled plasma (ICP) (SEIKO model SPS1500) spectrometry, and the ratio was [Bi]:[Sr]:[Ca]:[Cu]=2.2:1.8:1:2.

The iodine-intercalated single crystal used in this work were made by a gas-diffusion method. High-quality single crystals of Bi-2.2:1.8:1:2 ($T_c > 83$ K), and elemental iodine were encapsulated in a Pyrex tube under a vacuum of $< 10^{-3}$ torr. Iodine intercalation was carried out at 200°C for 10 days in a uniform-temperature furnace. The lattice parameters, examined by x-ray diffraction, are $a = b = 0.513 \pm 0.007$ nm, $c = 3.054 \pm 0.05$ nm for the pristine crystals and $a = b = 0.513 \pm 0.007$ nm, $c = 3.710 \pm 0.007$ nm for the iodine-intercalation ones, respectively, indicating that the structure of the intercalated crystals is stage 1.

The temperature dependence of the electric resistance along *ab* plane and *c*-axis direction was measured on two crystals (with typical dimensions of $6 \times 2 \times 0.02$ mm³) by dc standard-four-probe and pseudo-four-probe techniques.¹⁷ Copper wires (0.03 mm diameter) were connected by indium onto the crystals as lead wires. The measuring current was chosen to be 1 mA, which corresponds to a current density of $\sim 2.5 \times 10^4$ A m⁻² in the *ab* plane and $\sim 10^2$ A m⁻² along the *c*-axis direction, respectively. Hydrostatic pressure was generated by a CuBe piston-cylinder cell, and the pressure in the cell between 60 K and room temperature was monitored by a manganin resistance.¹⁸ The temperature of the crystal was determined by a Chromel-Constantan thermocouple adjacent to the sample, and the error of temperature induced by pressure was checked¹⁹ within the accuracy of the thermocouple.

The pressure dependence of the Hall coefficient was

detected at room temperature in the *ab* plane. The measured crystal was carefully cut into a cross shape with a thickness of 0.02048 mm, which was accurately measured by laser microscopy (Lasertec Corp. model 1LM21). High pressure was applied by the same device used for the resistance measurement. The electric current and magnetic field were chosen to be 8.00 mA and 1.2 T, respectively. The magnetic field was produced by an electromagnet and checked within an error of 5% in the high-pressure cell. The Hall emf was measured with the current parallel to the *ab* plane and the magnetic field applied perpendicular to the plane.

The electron binding energy of the iodine 3*d* core levels was measured in an IBi-2.2:1.8:1:2 crystal by XPS (SHIMADZU ESCA-850) at room temperature, and the binding energy was corrected by the peak of Au 4*f*_{7/2}.

III. RESULTS AND DISCUSSION

The temperature dependence of the electric resistance along the *c*-axis direction at various pressures is shown in Fig. 1(a) for an IBi-2.2:1.8:1:2 single crystal. The pressures given in the figure are the values at the superconducting transition temperature. Here we give the resis-

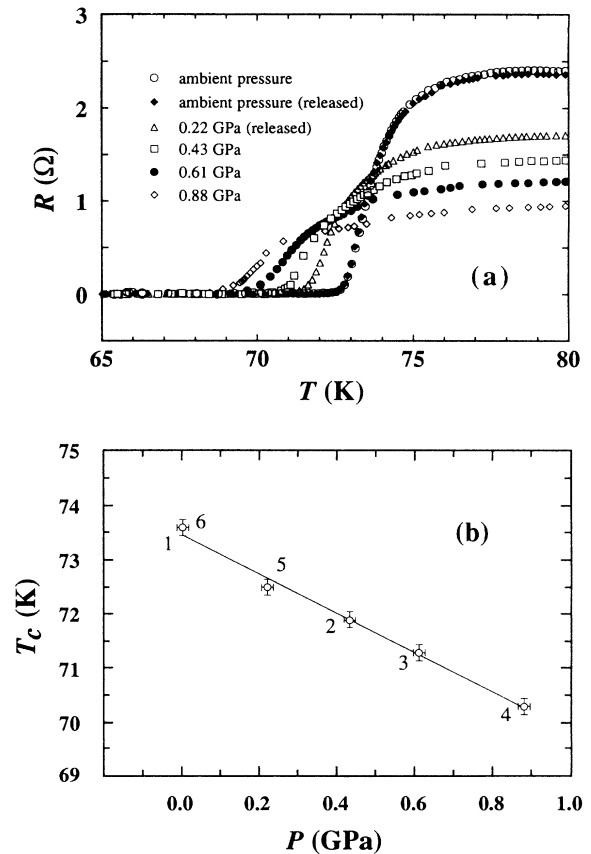


FIG. 1. (a) Resistance along the *c*-axis direction for an IBi-2.2:1.8:1:2 single crystal at various pressures. Pressures in the figure indicate the values at the superconducting transition temperature. (b) Superconducting transition temperature T_c obtained from (a) as a function of pressure. The numbers give the order of measurements, and the solid line is obtained by the least-squares method.

tance instead of the resistivity, since the geometrical factors for the measurement along the c -axis direction are poorly known. It is evident from Fig. 1(a), contrary to the results for the pristine crystal, that T_c decreases with increasing pressure, indicating that the hole concentration is located in the overdoped region. Here we assume, and later show, that the hole concentration of the intercalated compound increases with pressure. It is also evidence that the charge transfer between intercalated iodine atoms and CuO_2 layers does occur through iodine intercalation. The symbols (triangles and solid diamonds) in the figure show the resistance measured under released pressures in order to check whether or not intercalated iodine escapes from the crystal with increasing pressure. The very small deviation from the circles (ambient pressure) and solid diamonds (released ambient pressure) implies intercalated iodine is stable in the applied pressure range. Figure 1(b) shows the pressure dependence of the T_c obtained from Fig. 1(a). Here the T_c in the figure is defined as the temperature at which the resistance drops to half of its extrapolated normal-state value. That the T_c decreases from 83.0 K (Ref. 16) to 73.6 K through intercalation at ambient pressure is in agreement with the results of others.^{3,7} Under pressure, the T_c drops almost linearly with increasing pressure, with a large negative pressure derivative $dT_c/dP = -3.6$ K/GPa, obtained by the least-squares method.

Figure 2(a) shows the temperature dependence of the electric resistance in the ab plane at various pressures for another IBi-2.2:1.8:1:2 single crystal. The pressures in the figure, as in Fig. 1(a), are the values at T_c which has been defined as above. Clearly, the T_c in the ab plane, having the same tendency as that along the c -axis direction, shifts to lower temperatures with pressure. The linear variation of the T_c with pressure is given in Fig. 2(b). The value $dT_c/dP = -3.5$ K/GPa, which was obtained by the least-squares method, is similar to the value in the c -axis measurement, although these values were obtained from two measurements on two different crystals.

One possible explanation for the negative pressure derivative is that after iodine intercalation the hole concentration in the CuO_2 layers increases, placing the sample in the overdoped region. It seems that the only possible origin of the increased hole content is from the intercalated iodine, since oxygen is not evolved at 200°C in this system.²⁰ If oxygen loss did occur at this temperature, however, the hole concentration would decrease²⁰ and the pressure derivative dT_c/dP would remain positive, contrary to our result. From the above considerations, the valence state of intercalated iodine should be negative, as inferred from the increase of the hole concentration in the CuO_2 layers.

In Fig. 3 we present the I 3d core level XPS spectra, showing both I 3d_{5/2} and I 3d_{3/2} states, on an IBi-2.2:1.8:1:2 crystal, compared with KI, KIO₃, and KIO₄, in order to determine the valence state of iodine in the crystal. No energy shift of the iodine main peaks was observed after a long-term etching by Ar⁺, indicating that the valence state of iodine is invariant through the crystal. Detailed values of the binding energy for these

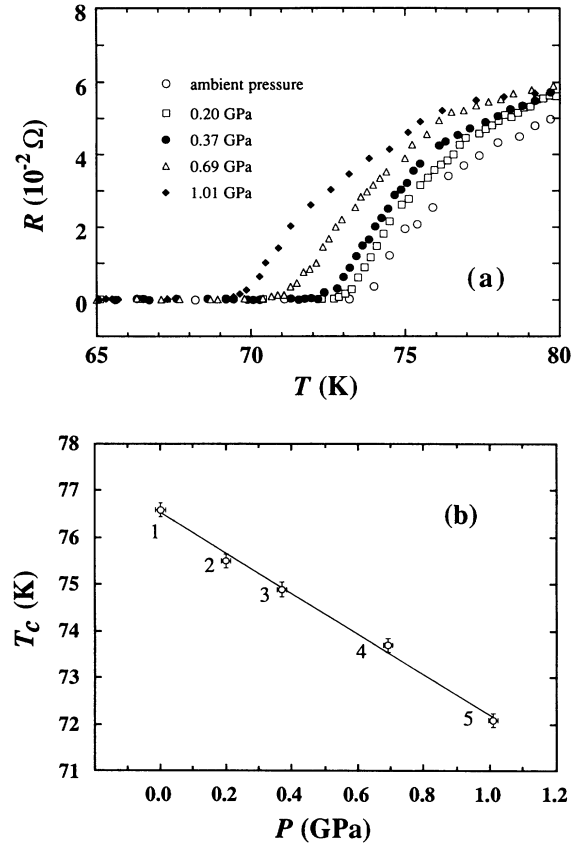


FIG. 2. (a) Resistance in the ab plane for an IBi-2.2:1.8:1:2 single crystal at various pressures. Pressures in the figure indicate the values at the superconducting transition temperature. (b) Superconducting transition temperature T_c obtained from (a) as a function of pressure. The numbers give the order of measurements, and the solid line is obtained by the least-squares method.

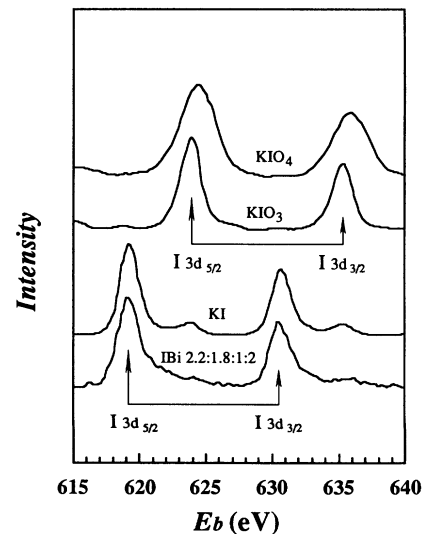


FIG. 3. XPS iodine 3d spectra for an IBi-2.2:1.8:1:2 single crystal and KI, KIO₃, and KIO₄ samples.

TABLE I. Binding energies of I $3d$ core level and valence of iodine.

Material	$3d_{5/2}$ (eV)	$3d_{3/2}$ (eV)	Valence
IBi-2.2:1.8:1:2	619.2	630.4	?
KI	619.2	630.9	-1
KIO ₃	623.7	635.2	+5
KIO ₄	624.3	635.9	+7

samples are listed in Table I. From the figure and table, it is clear that the binding energy of I $3d_{5/2}$ and I $3d_{3/2}$ peaks for IBi-2.2:1.8:1:2 is close to that in KI. On the other hand, there are two small peaks (636.3 and 624.2 eV) in IBi-2.2:1.8:1:2, which closely correspond to the binding energies found in KIO₄. One explanation of these peaks⁶ is the existence of a small proportion of I⁷⁺. However, our XPS spectra on KI (with a purity of 99.5%) also show these peaks at 635.2 and 624.2 eV, respectively, with stronger relative intensity. It seems we cannot naively conclude the existence of I⁷⁺ in IBi-2.2:1.8:1:2 only from the above unknown peaks.

To determine the variation of the hole concentration in the CuO₂ layers, the Hall coefficient in the ab plane was measured under various pressures for an IBi-2.2:1.8:1:2 crystal. Of course, the Hall coefficient of IBi-2.2:1.8:1:2, as the other superconductors,¹¹ is temperature and pressure dependent. Here, however, only the data at room temperature were given and the result of the iodine intercalated crystal was compared with that of the pristine crystal which has been reported.¹⁶ The measurement of the dependence of the Hall coefficient with pressure for pristine and iodine intercalated crystals at low temperature is being prepared. In Fig. 4 the dependence of the Hall coefficient with pressure is shown for IBi-2.2:1.8:1:2, compared with that for Bi-2.2:1.8:1:2.¹⁶ At ambient pressure, a decrease of the Hall coefficient after intercalation

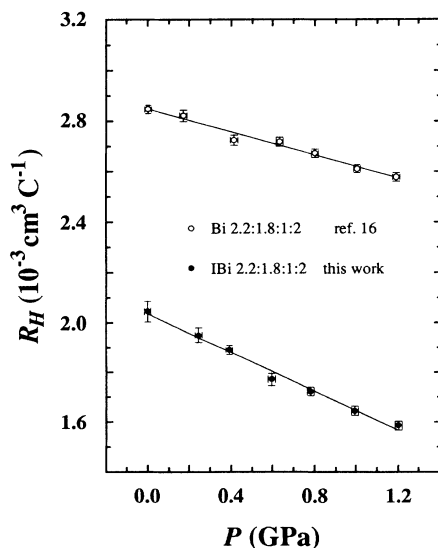


FIG. 4. Pressure dependence of the Hall coefficient in the ab plane for an IBi-2.2:1.8:1:2 single crystal, compared with the results of the pristine crystal. The solid lines are obtained by the least-squares method.

indicates an increase of the hole concentration in the ab plane. If the Hall coefficient R_H and the hole concentration n_p satisfy the relation $R_H = 1/en_p$, the number of holes per formula unit is 0.44 and 0.74 for pristine and intercalated crystals, respectively. As discussed previously, the increase of the hole concentration is only due to the charge transfer from the intercalated iodine; thus, the number of holes donated by one intercalated iodine atom is 0.3. On the other hand, the Hall coefficient decreases linearly with pressure for both crystals, and the pressure derivative of the Hall coefficient is -0.23×10^{-3} and $-0.39 \times 10^{-3} \text{ cm}^3 \text{ C}^{-1} \text{ GPa}^{-1}$ for pristine and intercalated crystals, respectively. After intercalation, the negative derivative value became nearly twice as large as that of the pristine crystal. The increase of the negative derivative value can be explained by two reasons. One is the difference of compressibility in the intercalated and pristine crystals. In fact, the expansion of the c axis after iodine intercalation will probably increase the compressibility of the lattice and lead to an increase in the negative derivative value. The other is the transfer of the holes from the intercalated iodine to the ab plane. As mentioned above, the valence state of the intercalated iodine has been investigated by several groups. According to the present result, neutral molecular iodine (I₂) seems impossible because it cannot explain the increase of holes in the CuO₂ layers at ambient pressure and, thus, the negative pressure derivative of T_c . In addition, if the valence state of iodine were a coexistence of I⁻ and I⁷⁺, a possible direction of the valence change under pressure, from the viewpoint of the crystal structure, is from I⁻ to I⁷⁺ due to their different ionic radii [I⁻ \sim 0.2 nm, I⁷⁺ \sim 0.06 nm (Ref. 21)], and thus the pressure derivative of the Hall coefficient for the iodine intercalated crystal will be smaller than that on the pristine one, if the compressibility in both the crystals is assumed to be the same, which is contrary to our Hall-coefficient result under pressure. The valence state of iodine in IBi-2.2:1.8:1:2 is probably an I₃⁻ molecular anion state as considered in Ref. 9, since the mean valence of I₃⁻ fits our Hall-coefficient result within experimental accuracy. At high pressure, the I₃⁻ molecular anion probably decomposes as follows: $\text{I}_3^- \rightarrow 3\text{I}^- + 2p$ (p is the hole). This assumption, however, still needs to be further verified, e.g., an experiment of Raman scattering under high pressure.

The Hall-coefficient dependence of T_c for pristine and intercalated Bi-2.2:1.8:1:2 single crystals is presented in Fig. 5. The shape of the curve is bell like, which is in agreement with that reported recently by Klotz and Schilling,²² if our linear relation between Hall coefficient and pressure is still satisfied until 5 GPa. The bell-like dependence of T_c on pressure is reported both in the bismuth-based superconductor and the yttrium-based one as well.²³ On the other hand, the T_c as a function of the oxygen content for Bi-2.2:1:2 was shown to be an inverted parabola.^{24,25} Here it is necessary to point out the difference between the Hall concentration in the ab plane and that in the CuO₂ layer. In the present study, the Hall coefficient was measured on the ab plane, not only on the CuO₂ layers. For a Bi-2.2:1:2 superconductor, besides the CuO₂ layers, the Bi₂O₂ layers can be thought of as

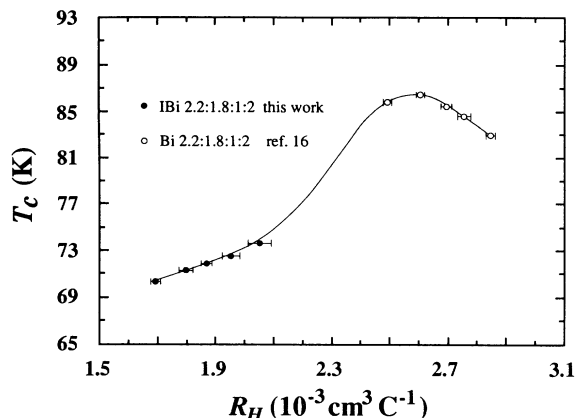


FIG. 5. Superconducting transition temperature T_c vs Hall coefficient for pristine and intercalated single crystals. The lines are guides to the eye.

another type of conductive layer.²⁶ The total measured Hall concentration may come from both layers. For the intercalated crystal, similarly, we cannot naively consider that the intercalated iodine only provide carriers to the CuO_2 layers. The observed change of the conductive behavior along the c -axis direction is an indication that some charge is transferred between the intercalated iodine and the Bi_2O_2 layers. In Fig. 6, we show the pressure dependence of the resistivity ratio $\rho(300 \text{ K})/\rho(100 \text{ K})$ on the c -axis direction. It is clear from the figure that the conductive behavior is semiconductor like and metal like for pristine and intercalated crystals, respectively. Under pressure, the ratio for the pristine crystal is nearly pressure independent, whereas for the intercalated crystal it increases markedly with pressure.

Last, we have to mention here whether the expansion of the c axis is unfavorable for T_c is still unknown from our experiments, because the pressure-induced charge transfer plays an important role in our samples. Xiang *et al.* suggested³ that the decrease of T_c was directly proportional to the expansion of the crystal along the c -axis direction; i.e., T_c decreases 10 and 5 K for stage-1 and 2 samples, respectively. Using the same values of the compressibility on the Bi-2.2:1:2 crystal,²⁷ we can evaluate the increase in T_c under pressure according to the above suggestion. The increase in T_c is too small (< 0.7 K under 1 GPa) to compare with the decrease in T_c induced by charge transfer under pressure.

IV. CONCLUSION

The superconducting transition temperature T_c and the Hall coefficient have been measured on

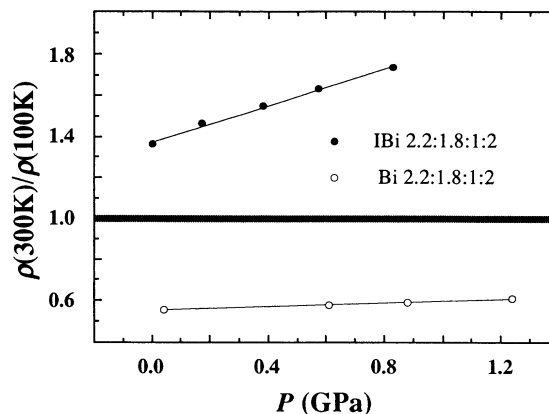


FIG. 6. Pressure dependence of the resistivity ratio $\rho(300 \text{ K})/\rho(100 \text{ K})$ along the c -axis direction for pristine and intercalated single crystals. The shaded line separates two regions representing semiconductorlike and metal-like regions, respectively.

$\text{IBi}_{2.2}\text{Sr}_{1.8}\text{CaCu}_2\text{O}_{8+y}$ single crystals under hydrostatic pressure as high as 1.2 GPa. In our pressure region, the iodine is stable in the crystal. The T_c of the intercalated crystals, contrary to the pristine ones, shows a linear decrease at the rate $dT_c/dP = -3.5 \text{ K/GPa}$ in the ab plane for one sample and $dT_c/dP = -3.6 \text{ K/GPa}$ along the c -axis direction for another sample, respectively. This result indicates that a positive charge transfer occurs between intercalated iodine and the CuO_2 layers, leaving the hole concentration in the overdoped region. This conclusion has been further confirmed by our Hall-coefficient measurement at ambient pressure, which shows a decrease of the Hall coefficient, i.e., an increase of the hole concentration, after intercalation. The number of holes transferred from the intercalated iodine atoms was estimated to be 0.3 per iodine atom, which is in quantitative agreement with one of the Raman-scattering studies in which the iodine is ionized as an I_3^- molecular anion. The pressure derivative of the Hall coefficient is $-0.39 \times 10^{-3} \text{ cm}^3 \text{ GPa}^{-1}$, which is approximately twice as large as the value for the pristine crystal, indicating a valence change of intercalated iodine under pressure.

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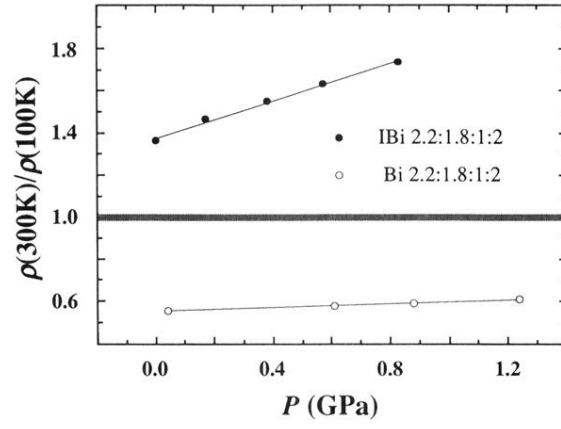


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