

Inverse-photoemission study of hole-concentration dependence of the electronic structure in $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_8$ ($x=0.0-0.05$)

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(Received 17 January 1991; revised manuscript received 19 April 1991)

Inverse-photoemission spectroscopy has been performed on $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_8$ ceramics, where hole concentration is controlled by the atomic ratio between divalent Ca and trivalent Y atoms. It was found that hole doping does not cause a rigid shift of the density of states relative to the Fermi level, but creates additional electronic states in the vicinity of the Fermi level.

Photoemission spectroscopy has established the existence of a substantial density of states at the Fermi level in high- T_c superconductors¹⁻³ and angle-resolved photoemission measurements clearly reveal dispersive bands that cross the Fermi level.⁴⁻⁷ The nature of the electronic states near the Fermi level has been studied by x-ray-absorption⁸⁻¹⁰ and electron-energy-loss¹¹ spectroscopies, which show that the states near the Fermi level have a dominant O $2p_{x,y}$ character. The next step to approach the high- T_c mechanism is to elucidate the origin of the electronic states near the Fermi level. It is still unknown whether they are Kondo-like states as in heavy fermion systems, singlet A_1 -band states due to the strong electron correlation, impuritylike states as in heavily doped semiconductors, or normal one-electron states as predicted from the band-structure calculation.

In this paper we present the experimental result of inverse-photoemission spectroscopy on $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_8$ where the hole concentration is controlled by the atomic ratio between divalent Ca and trivalent Y atoms. We found that the change in the hole concentration does not necessarily cause a rigid shift of the density of states relative to the Fermi level, but brings about a change in the population of the states themselves; the hole doping produces additional electronic states in the vicinity of the Fermi level.

Ceramic samples used in this study were prepared by sintering a mixture of high-purity Bi_2O_3 , SrCO_3 , CaCO_3 , Y_2O_3 , and CuO powders with respective molar ratios. X-ray-diffraction measurement showed that they are all single phase. The T_c 's of the samples determined by resistivity and magnetic susceptibility measurements were 76, 88, and 47 K for $x=0.0, 0.3$, and 0.5 , respectively, in good agreement with the previous study.¹²

Inverse-photoemission measurement was done with an inverse-photoemission spectrometer constructed at our laboratory, which has a Pierce-type electron gun and a Geiger-Müller-type counter with a SrF_2 window and iodine gas in it. The energy and angular resolutions were 0.35 eV and 2° , respectively. A clean sample surface for measurement was obtained by scraping the sample with a diamond file under vacuum of 5×10^{-10} Torr in the spectrometer. All measurements were done at room temperature. The Fermi level was referred to that of a silver film

deposited on each sample.

Figure 1 shows inverse-photoemission-spectroscopy (IPES) spectra of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_8$ ($x=0.0, 0.3$, and 0.5), together with photoemission-spectroscopy (PES) spectra of $x=0.0$ and 0.5 for comparison.¹⁰ The intensity of the IPES spectrum is normalized at 5 eV. As shown in Fig. 1, the inverse-photoemission intensity in the vicinity of the Fermi level gradually decreases as the Y content increases, namely the hole concentration decreases. The change in hole concentration does not necessarily cause a rigid shift of the density of states relative to the Fermi level, but gives rise to a change in the population of the states near the Fermi level. It is useful to compare the present experimental result with a previous inverse-photoemission result on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ 2:2:1:2 and $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ 2:2:0:1 single crystals by Wagener *et al.*¹³ According to them, the inverse-photoemission intensity in the vicinity of the Fermi level is almost the same between the two compounds (Fig. 2 in Ref. 13), although the 2:2:1:2 compound is a superconductor with T_c of 85

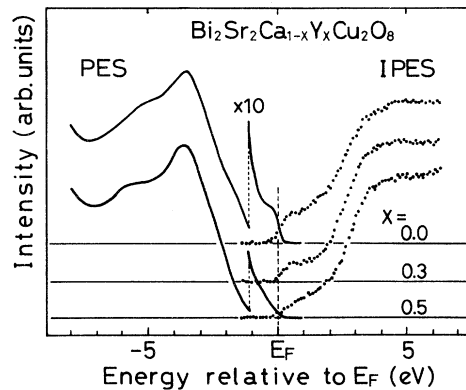


FIG. 1. Inverse-photoemission (IPES) spectra of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_8$ ($x=0.0, 0.3$, and 0.5), compared with photoemission (PES) spectra of $x=0.0$ and 0.5 (Ref. 10). The intensity of each inverse-photoemission spectrum is normalized at 5 eV. Note that the intensity in both photoemission and inverse-photoemission spectra at the Fermi level gradually decreases when Y content (x) increases, namely the hole concentration decreases.

K while the 2:2:0:1 compound is not a superconductor. It may imply that the magnitude of the density of states in the vicinity of the Fermi level has no direct relation to the occurrence of the high- T_c superconductivity. However, it is known that an as-grown 2:2:0:1 sample is in the so-called overdoped state¹⁴ and annealing it in reduced atmosphere recovers or increases the T_c . And further, when we take into account the fact that the 2:2:1:2 compound has two CuO_2 layers in a unit cell while the 2:2:0:1 compound has only one, the experimental result by Wagener *et al.* clearly indicates that the population of holes per CuO_2 layer in $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ is about twice as much as that in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and the overdoping of holes suppresses the superconductivity in $\text{Bi}_2\text{Sr}_2\text{CuO}_6$. Thus, the experimental result by Wagener *et al.* is consistent with the present result in that the density of the electronic states in the vicinity of the Fermi level increases with hole doping.

As shown in Fig. 1, no rigid transfer of the electronic states from occupied states (PES spectrum) to unoccupied states (IPES spectrum) or vice versa is observed even when the hole concentration is changed. The photoemis-

sion intensity near the Fermi level shows a similar behavior to that of inverse photoemission against the hole concentration. This suggests that the electronic states near the Fermi level are not simple one-electron states as predicted from the band-structure calculation, but are additional states produced in the gap by hole doping.

The present IPES and PES results seem consistent with observation of "midgap states" by optical-absorption spectroscopy,¹⁵⁻¹⁷ which found that an extra optical-absorption band arises in the mid-ir region upon hole doping. This mid-ir absorption is attributed to an optical transition from or to the additional electronic states produced by hole doping near the Fermi level. Thus, although the origin of the electronic states near the Fermi level is not fully understood at present, the present IPES study suggests that the electronic states near the Fermi level are electronic states introduced by carrier (hole) doping. This experimental fact should be taken into consideration when a high- T_c mechanism is constructed.

This work was supported by a grant from the Ministry of Education, Culture, and Science of Japan.

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