

Electronic Band Structure of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$ ($x = 0.4$ to 1.0) Determined by Infrared-Induced Intersite Transitions

Masayuki Sato, Ryuichirou Horiba, and Keigo Nagasaka

Department of Physics, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162, Japan
(Received 21 September 1992)

To investigate the band structure of nonmetallic $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$ ($x = 0.4-1.0$), photon-induced hopping has been employed as a new method, in which transmission spectroscopy has been carried out from 10 to 12000 cm^{-1} . The photon-induced-hopping conduction edge has been found at 5200 cm^{-1} . This edge does not shift with x ($x = 0.4-1.0$), whereas the absorption is proportional to $1-x$. The charge-transfer absorption edge at 12000 cm^{-1} also does not shift with x . Using this method, the bandwidth has been determined to be 5200 cm^{-1} . Obvious midgap states have not been observed.

PACS numbers: 78.50.Ge, 71.25.Tn, 74.72.Hs, 78.30.Er

An explanation of the optical conductivity of cuprate superconductors above T_c by means of a generalized Drude model with frequency-dependent scattering time has been proposed [1]. This phenomenon was discussed in terms of a model of the motion of carriers with antiferromagnetic spin fluctuations [2,3]. However, the electronic band structure which dominates the conduction remains a controversial problem. On the basis of infrared reflection spectroscopy [4] and photoemission spectroscopy [5] (PES), it has been reported that there should be a midgap state. Recently, however, it was reported that no midgap state could be found in an x-ray-absorption (XAS) spectrum [6]. Infrared (IR) and far-infrared (FIR) transmission spectroscopies are crucial in the study of electronic states in which holes contribute to the conduction as successive intersite transitions. First, when a specimen of suitable thickness is used, IR and FIR

transmission spectra can give much more direct information on the intersite transition than can IR and FIR reflections, the analysis of which requires the use of the Kramers-Kronig transformation. Second, IR and FIR studies give higher-resolution spectra than do high-energy spectroscopic studies.

Free-carrier conduction gradually disappears and hopping conduction appears in $\text{Bi}_2\text{Sr}_2\text{Ca}_x\text{Y}_{1-x}\text{Cu}_2\text{O}_y$ crystals in the region $x \geq 0.4$ under the influence of a random potential which is introduced into the CuO_2 plane by the partial substitution of Y^{3+} for Ca^{2+} ions, as shown in Figs. 1(a) and 1(b). In the temperature dependence of the dc resistivity, one can observe variable-range-hopping (VRH) conduction in which holes hop between occupied and unoccupied localized $\text{O-}2p$ orbitals by means of thermal activation [7-9]. As the impurity conduction in germanium [10], we have observed the photon-induced-hopping (PIH) conduction from occupied to unoccupied localized $\text{O-}2p$ orbitals in the random potential as well as low-lying phonons in the range from 10 to 100 cm^{-1} , as shown in Fig. 2 [9]. In addition, the so-called charge

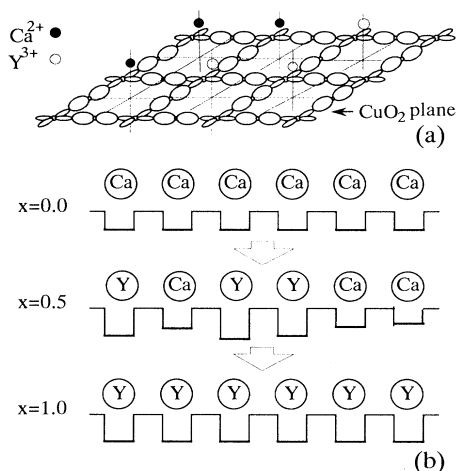


FIG. 1. (a) Sketch of CuO_2 and Ca-Y planes of $\text{Bi}_2\text{Sr}_2\text{Ca}_x\text{Y}_{1-x}\text{Cu}_2\text{O}_y$. Ca^{2+} and Y^{3+} ions are randomly located in the Ca-Y plane. (b) Schematic diagrams of the potential of the CuO_2 plane due to Ca^{2+} and Y^{3+} ions. As shown in the second diagram, the random potential is introduced by the partial substitution of Y^{3+} for Ca^{2+} ions.

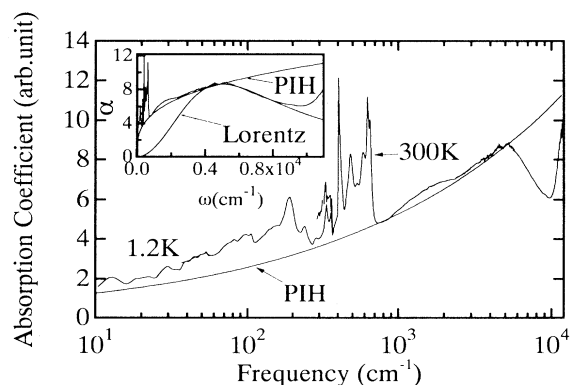


FIG. 2. Absorption spectrum of nonmetallic $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.6}\text{Y}_{0.4}\text{Cu}_2\text{O}_y$ crystal measured at 1.2 K ($10-350\text{ cm}^{-1}$) and 300 K ($300-12000\text{ cm}^{-1}$), and a calculated PIH absorption spectrum, Eq. (1). Inset: No Lorentz oscillator like mid-IR absorption can be fitted to the experimental spectrum.

transfer (CT) absorption has been observed above 12000 cm^{-1} , which has been ascribed to the intersite transition from an occupied O site to an unoccupied Cu site in the upper Hubbard band.

The intersite optical transitions, i.e., the PIH and CT, are quite different from typical optical transitions between two states of an atom. However, we can induce a transition between the same O-2*p* orbitals on two sites by optical excitation. The intersite transition probability should be much smaller than the transition probability between two states of an atom. However, the present PIH probability should have a finite value as does the well-established CT. Consequently, the transition between two O-2*p* orbitals, which corresponds to a charge transfer from one site to the other, can be observed. The momentum conservation rule holds even in the intersite transition. However, this rule is not exact because the initial and final states are composed of wave functions specified by various crystal momenta for their localization.

The absorption of PIH conduction is given by a simple equation,

$$\alpha = \alpha_0 \omega^s, \quad (1)$$

where α_0 and s are constants and ω is the frequency [11]. The frequency exponent s is determined to be 0.3 from the absorption spectrum in the range of 10 to 100 cm^{-1} [9]. From the neutron inelastic scattering experiment, the phonon frequencies lie below 700 cm^{-1} [12]. We therefore presume that the absorption coefficients at and above 700 cm^{-1} are caused only by an electronic conduction such as PIH conduction and CT absorption. The constant α_0 has been chosen to fit the curve of Eq. (1) to the experimental absorption coefficient at 700 cm^{-1} . We see that the curve shows fairly good agreement with the experimental spectrum even from 700 up to about 5000 cm^{-1} , as shown in Fig. 2. However, no Lorentz oscillator like mid-IR absorption [4] can be fitted to the line shape at around 5200 cm^{-1} , as shown in the inset of Fig. 2. As expected from Eq. (1), the transition probability of PIH conduction should increase with the energy difference between the initial and final states [11]. The experimental absorption spectrum starts deviating from the curve of Eq. (1) at around 5200 cm^{-1} and makes an edge in the spectrum. We call this the PIH conduction edge [9]. The PIH conduction edge indicates a decrease of the joint density of states and yields a bandwidth. Observation of the PIH conduction employing seven samples of crystal $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$ ($x=0.4-1.0$) will help pave the way to estimate the characteristics of the conductive band even in metallic $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ and $\text{Ba}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$. In this study, we confirm, with the present method, the existence of a narrow conductive band and the lack of obvious evidence of the midgap state in all seven nonmetallic $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$ crystals ($x=0.4-1.0$).

The crystals were prepared by the flux method [9]. In

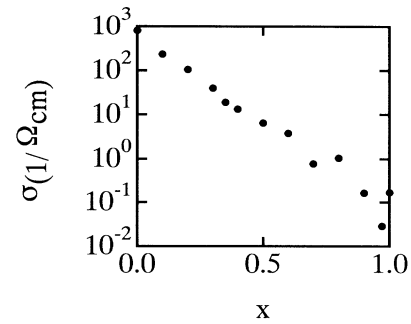


FIG. 3. dc conductivity of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$ at 300 K as a function of x .

this paper, the samples are designated by the value of x of the Y content of the starting materials. In the $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$ system, the carrier concentration should be determined by the yttrium content x and oxygen content y , and there are some reports of y being dependent on x [13]. However, there is evidence which indicates that the carrier concentration is mainly determined by x . From our experimental results, first, the dc conductivity at 300 K decreases with x , as shown in Fig. 3. Second, the resistivities are given by a function of temperature as $R = R_0 \exp(T_0/T)^{1/4}$, which shows the behavior of VRH conduction. The constant T_0 monotonously increases with x in the range from 0.4 to 1.0. Therefore, the carrier concentration is mainly determined by $1-x$. On the other hand, the critical value of x of the metal-nonmetal transition, which was studied by a solid reaction method, is about 0.5 [8,14], while that of ours is about 0.4. This discrepancy may arise from the fact that Y atoms are more easily substituted than Ca atoms in the case of the flux method. In addition, Tamegai *et al.* have reported that the crystal structure is orthorhombic in all ranges of x [8]. We have found the same structure in our seven samples using an x-ray diffractometer. Tamegai also reported that the lattice constant along the c axis decreases with x [8]. We have observed the same phenomenon. Consequently, we are convinced that the true Y content is almost proportional to x ; however, the true Y content may be slightly larger than x .

The transmission of samples was measured in the ranges of 10 to 400 cm^{-1} at 1.2 K ($\hbar\omega/k_B T = 12-480$) and of 50 to 12000 cm^{-1} at 300 K ($\hbar\omega/k_B T = 0.24-57$). The conduction in the a - b plane is responsible for these absorption spectra because radiation passes along the c direction. Absorption coefficients described by Eq. (1) have been observed for seven samples from $x=0.4$ to 1.0 in the range of 10 to about 5000 cm^{-1} . We are convinced that the PIH conduction also plays an important role in all samples from $x=0.4$ to 1.0.

The absolute value of absorption coefficients could not be obtained because the thickness of specimens could not be determined. However, the total phonon absorption coefficient should be unchanged in all nonmetallic sam-

ples. Therefore we employed each total phonon absorption coefficient as the reference absorption of each spectrum. Absorption spectra normalized by each total phonon absorption coefficient are shown in Fig. 4.

To summarize our results, intersite transitions are clearly observed in all seven nonmetallic $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$ crystals in the range of 10 to 12000 cm^{-1} , as follows.

(1) The PIH conduction between O sites dominates the absorption spectra from 10 to 5200 cm^{-1} . This PIH conduction attains the maximum value at 5200 cm^{-1} and drastically decreases above 5200 cm^{-1} . The edge yields the bandwidth to be 5200 cm^{-1} . The edge and shape of PIH conduction do not change with x , while the absorption intensity is almost proportional to $1-x$, as shown in the inset of Fig. 4.

(2) The CT absorption due to the intersite transition between O and Cu sites increases at 12000 cm^{-1} . The CT absorption edge does not shift with x .

To discuss the above experimental results, we must know at which band the Fermi level lies. From the calculation of the Madelung potential [15] and measurements of PES [16], the energy level of the Cu-3d upper Hubbard optical is thought to be about 2 eV (16000 cm^{-1}) higher than that of the two O-2p orbitals. From the measurements of electron energy loss spectroscopy (EELS), it has been reported that electrons are extracted from the O-2p band [17]. There have been some theoretical studies concerning the hybridization between O-2p and Cu-3d orbitals [18]. Thus the O-2p band or O-2p and Cu-3d hybridized band should contain the Fermi level. (We will use the term O-2p band to express either the hybridized band or the O-2p band.)

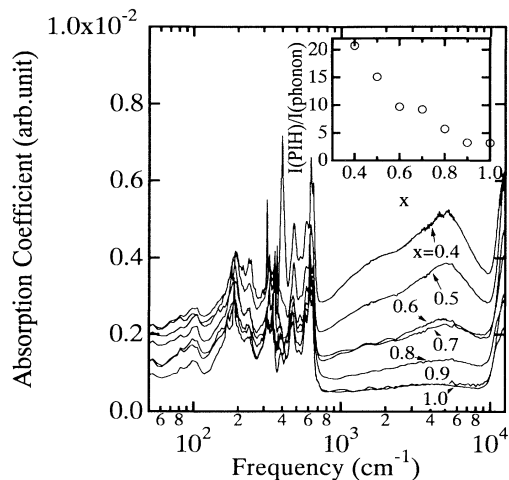


FIG. 4. Absorption spectra of nonmetallic $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$ ($x=0.4-1.0$) from 50 to 12000 cm^{-1} at 300 K. Absorption coefficients were normalized by each total phonon absorption coefficient. Inset: Integrated intensities of the PIH absorption, which are normalized by each total phonon absorption coefficient, as a function of x .

Holes are localized on O sites in the random potential, as shown in Figs. 1(a) and 1(b). The carrier absorption is dominated by only two types of intersite transitions, the PIH conduction giving rise to a transition between two adjacent O-2p orbitals on one hand, and the CT yielding a transition between O-2p and Cu-3d orbitals, on the other. Because the O-2p bandwidth is as narrow as 5200 cm^{-1} , based on the PIH absorption edge, this band must have a high density of states. As x of the Y content is decreased from $x=1.0$ to 0.4, the hole concentration increases with $1-x$. The PIH transition probability of holes is proportional to the number of O sites not occupied with electrons, which is proportional to $1-x$, as shown in Fig. 4. However, we see that the PIH absorption edge does not shift. The lack of shift in the PIH absorption edge indicates that the bandwidth is almost constant and that the Fermi level also shows a negligibly small shift with increasing carrier concentration due to the substitution of Y^{3+} for Ca^{2+} . Therefore, the O-2p band should have a high density of states. Based on the Hall effect, the hole concentration has been determined to be $3 \times 10^{21} \text{ cm}^{-3}$ even for metallic $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ [8], and the O-2p band must be almost filled with electrons for the nonmetallic $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$ ($x \geq 0.4$). Moreover, we see in Fig. 4 that the CT absorption edge does not shift by even as much as 1000 cm^{-1} among the seven spectra. Therefore, it can be considered that the energy difference between the Fermi level and the lowest energy level in the Cu orbitals of the upper Hubbard band does not change largely with x . From the behavior of the two types of optical transition, as schematically shown in Fig. 5, the O-2p band is thought to have a high density of states.

Recently, Murayama and Nakajima investigated the electronic states of hole-doped high- T_c cuprates using a $d-p$ model [18]. They predicted that the O-2p orbitals split into two energy levels: The lower band is broader than the very narrow upper band having the Fermi level. They did not introduce a new state in the CT gap. However, they have not yet taken into account the random po-

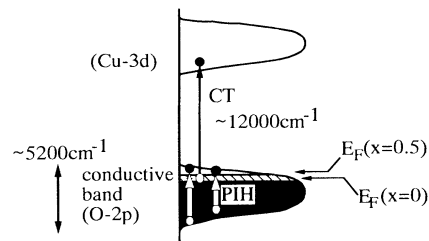


FIG. 5. Schematic band structure of nonmetallic $\text{Bi}_2\text{Sr}_2\text{Ca}_x\text{Y}_{1-x}\text{Cu}_2\text{O}_y$. The width of the conductive band is about 5200 cm^{-1} . The Fermi level makes a negligibly small shift with x . The PIH conduction is indicated by vertical lines, which exhibit the electronic transition from occupied to unoccupied states of the conductive band. The CT transition from O-2p to Cu-3d states is also shown.

tential.

There have been several reports on the midgap state. The midgap state was observed by means of PES and inverse photoemission spectroscopy (IPES) [19], while it cannot be found in the XAS [6] or EELS [20] spectra. By means of PES and IPES, one can determine the energy differences between electronic states of a solid and the state of a free electron in vacuum. In these cases one observes the various energy differences due to the distribution of Y^{3+} ions. In principle, the electronic state seems to be a broader band than the intrinsic width in both PES and IPES spectra. Consequently, the so-called midgap state seems to appear in the CT gap. On the other hand, with XAS and EELS, one can determine the energy difference between two states at one site. Therefore, one should observe a sharp energy difference between two states at the same site. There is no evidence of the midgap state in the XAS and EELS spectra. This aspect has been already mentioned by Chen *et al.* [6] and is also consistent with the results of our IR and FIR studies. Of several spectroscopic methods, IR and FIR transmission spectroscopies have much higher resolution than the others and are able to supply the most reliable information concerning intersite transitions in a solid. It is noted that there is no obvious evidence of a midgap state in our IR and FIR absorption spectra.

As x was decreased from 0.4 to 0.0, the carrier concentration increased by a factor of about 1.7, and the dominant conduction mechanism changed from hopping to free-carrier conduction, where the conductivity also increased continuously with x , as shown in Fig. 3. In both conduction mechanisms, however, carriers should pass through one path from among two candidates, $O-2p \rightarrow Cu-3d \rightarrow O-2p$ or $O-2p \rightarrow O-2p$ without passing through the Cu sites. In our IR and FIR transmission spectra, there is no obvious evidence of the midgap state in the seven samples, and the Drude absorption has been observed at 122 K in a metal [21]. Therefore, it can be speculated that the carriers pass mainly through $O-2p$ states. Thus, the one-body approximation may be employed for the metallic materials. In the superconducting state, it can be considered that the magnon cannot be greatly related to the formation of a Cooper pair.

In conclusion, we propose a band structure of nonmetallic $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ crystals as follows.

(1) The width of the band which has the Fermi level should be as narrow as 5200 cm^{-1} because photon-induced-hopping conduction is scarcely observed above 5200 cm^{-1} . Furthermore, the narrow band supplies a high density of states to the conduction holes. This should contribute to the high T_c .

(2) As the carrier concentration is increased from the CT insulator, the appearance of the midgap state is not obvious in our spectra and the CT gap of 12000 cm^{-1}

does not change.

- [1] E. Schlessinger, L. D. Rotter, R. T. Collins, F. Hertzberg, C. Feild, U. Welp, G. W. Crabtree, J. Z. Liu, Y. Fang, and K. G. Vandervoort, in *Physics of High-Temperature Superconductors*, edited by S. Maekawa and M. Sato (Springer-Verlag, Berlin, 1991).
- [2] C. L. Kane, P. A. Lee, and N. Read, *Phys. Rev. B* **39**, 6880 (1989).
- [3] T. Moriya, Y. Takahashi, and K. Ueda, *J. Phys. Soc. Jpn.* **59**, 2905 (1990).
- [4] S. Uchida, T. Ido, H. Takagi, T. Arima, Y. Tokura, and S. Tajima, *Phys. Rev. B* **43**, 7942 (1991).
- [5] T. Kusunoki, T. Takahashi, S. Sato, and H. Katayama-Yoshida, *Physica (Amsterdam)* **185-189C**, 1045 (1991).
- [6] C. T. Chen, F. Sette, Y. Ma, M. S. Hybertsen, E. B. Stechel, W. M. C. Foulkes, M. Schluter, S-W. Cheong, A. S. Cooper, L. W. Rupp, Jr., B. Batlogg, Y. L. Soo, Z. H. Ming, A. Krol, and Y. H. Kao, *Phys. Rev. Lett.* **66**, 104 (1991).
- [7] R. Yoshizaki, Y. Sato, Y. Abe, and H. Ikeda, *Physica (Amsterdam)* **152C**, 408 (1988).
- [8] T. Tamegai, K. Koga, K. Suzuki, M. Ichihara, F. Sakai, and Y. Iye, *Jpn. J. Appl. Phys.* **28**, L112 (1989).
- [9] M. Sato and K. Nagasaka, *Jpn. J. Appl. Phys.* **31**, 227 (1992).
- [10] R. C. Milward and L. J. Neuringer, *Phys. Rev. Lett.* **15**, 664 (1965); S. Narita and M. Kobayashi, *Philos. Mag. B* **42**, 895 (1980); G. A. Thomas, M. Capizzi, F. DeRosa, R. N. Bhatt, and T. M. Rice, *Phys. Rev. B* **23**, 5472 (1981).
- [11] N. F. Mott and E. A. Davis, in *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979), Chap. 2; M. Pollak and T. H. Geballe, *Phys. Rev.* **122**, 1742 (1961); I. G. Austin and N. F. Mott, *Adv. Phys.* **18**, 41 (1969).
- [12] B. Renker, F. Gompf, D. Ewert, P. Adelman, H. Schmidt, E. Gering, and H. Mutka, *Z. Phys. B* **77**, 65 (1989).
- [13] F. Munakata, K. Matsuura, K. Kubo, T. Kawano, and H. Yamauchi, *Phys. Rev. B* **45**, 10604 (1992).
- [14] N. Fukushima, H. Niu, and K. Ando, *Jpn. J. Appl. Phys.* **27**, L1432 (1988).
- [15] Y. Ohta, T. Tohyama, and S. Maekawa, *Phys. Rev. B* **43**, 2968 (1991).
- [16] A. Fujimori, S. Takekawa, E. Takayama-Muramochi, Y. Uchida, A. Ono, T. Takahashi, Y. Okabe, and H. Katayama-Yoshida, *Phys. Rev. B* **39**, 2255 (1989).
- [17] N. Nücker, H. Romberg, X. X. Xi, J. Fink, B. Gegenheimer, and Z. X. Zhao, *Phys. Rev. B* **39**, 6619 (1989).
- [18] Y. Murayama and S. Nakajima, *J. Phys. Soc. Jpn.* **60**, 4265 (1991).
- [19] T. Watanabe, T. Takahashi, S. Suzuki, S. Sato, and H. Katayama-Yoshida, *Phys. Rev. B* **44**, 5316 (1991).
- [20] N. Nücker, in *Physics of High-Temperature Superconductors* (Ref. [1]).
- [21] M. Sato, K. Nagasaka, M. Ihara, and T. Kimura, *J. Phys. Soc. Jpn.* **60**, 4337 (1991).