PHYSICAL REVIEW B VOLUME 48, NUMBER 21 1 DECEMBER 1993-I

Dielectric function of $BaPb_{1-x}Bi_xO_3$ investigated by ellipsometry

Y. Y. Wang
Department of Materials Science and Engineering, Science and Technology Center for Superconductivity, Northwestern University, Evanston, Illinois 60208

G. F. Feng
Coordinated Science Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

T. E. Sutto
Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

P. D. Han
Department of Materials Science and Engineering and Science and Technology Center for Superconductivity, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

(Received 22 October 1992; revised manuscript received 19 July 1993)

Dielectric functions of $BaPb_{1-x}Bi_xO_3$ $(0<x<0.4)$ are investigated by ellipsometry. A broad excitation, which was observed in the visible photon energy region, is quantitatively analyzed. As the material becomes a normal metal with doping of $x=0$, the oscillator strength of the excitation decreases to almost zero. In the Hubbard-band model, this indicates that in the normal metallic ($T_c<4$ K) doping regime, the density of the upper Hubbard state is reduced dramatically due to the screening of electron-electron Coulomb interaction. Based on that assumption, it is suggested that there might be a connection between the "upper Hubbard band" and the superconductivity.

I. INTRODUCTION

$BaPb_{1-x}Bi_xO_3$ (BPBO), which becomes superconducting at 13 K, was reported by Sleight and co-workers.[1,2] Since then, the material has been under extensive studies in different aspects, such as structural properties, electrical, and magnetic properties, and electronic structure. However, the recent discovery of high-T_c copper oxide materials, (Ba,K)BiO_3 (BKBO) (Ref. 3) and $Ba_4BiPb_2TiO_{12}$ (Ref. 4) has created a renewed interest in the electronic properties of $BaPb_{1-x}Bi_xO_3$, because of the general perception that it may carry a clue to the mechanism of high-temperature superconductivity.

In recent years, electron-energy-loss spectroscopy (EELS) and ellipsometry measurements indicate that in high-T_c copper oxide materials, there is a broad excitation centered at 2.7 eV, which is associated with copper oxide planes.[5-8] It is suggested that this excitation is due to the transition between the low Hubbard band to the "upper Hubbard band."[5,6,9] Because of the similar properties between $BaPb_{1-x}Bi_xO_3$ and high-T_c copper oxide materials—ranging from doping properties, the nonclassical relationship between the density of state and critical temperature,[10] as well as tunneling properties[11]—it is interesting to see whether the optical spectrum of $BaPb_{1-x}Bi_xO_3$ in the visible range has a similar excitation as that in Cu-O materials.

In the 1980s, Tajima and co-workers[12-14] reported optical properties of a different doping concentration of $BaPb_{1-x}Bi_xO_3$ from infrared photon energy to ultraviolet. Although their investigation of optical properties of $BaPb_{1-x}Bi_xO_3$ has provided important information of the electronic structure of this material, the reports did not provide quantitative analysis of the excitation in the visible photon energy region. In light of Hubbard-band excitation at ~2.7 eV in Cu-O material, quantitative information of the excitation in $BaPb_{1-x}Bi_xO_3$ becomes important for the understanding of this material.

In addition, most of the optical measurements on the oxide materials were investigated in the doping region at the transition between semiconducting and superconducting. We, however, believe that the doping region from the superconducting to normal metallic state would be equally important to understand these oxide materials.

In this paper, we investigate the dielectric function of $BaPb_{1-x}Bi_xO_3$ of different doping composition by using an ellipsometer covering the energy range between 1.5 and 5.0 eV and quantitatively analyze the broad excitation in the visible photon energy region with different doping. We compare the dielectric function of $BaPb_{1-x}Bi_xO_3$ with that of copper oxide high-T_c superconductor materials and suggest a Hubbard-band mechanism to interpret the optical data.

II. EXPERIMENT

$BaPb_{1-x}Bi_xO_3$ was prepared from 99.999% materials supplied by Aldrich. Stoichiometric amounts of powders were weighed out, ground and reacted at 800 °C for 20 h. The sample was then oven cooled and reground. The pellets were sintered at 820 °C under flowing air (5–10 cc/min) for 20 h and then cooled down to room temperature over a 12 h period. X-ray analysis was performed using a Scintag Powder Diffractometer over a 2θ range

0163-1829/93/48(21)/16006(5)/$06.00

from 5° to 85°, with the Cu $K_\alpha = 1.5406$ Å used as the incident radiation. A single phase was observed in all doped samples and unit cell parameters of different doping materials were consistent with the previously reported data.[15] Figure 1 shows the energy dispersive x-ray analysis of the materials, indicating the proper composition of the material.

The samples were mechanically polished with a 1200 grit aluminum oxide polishing paper prior to the measurement. Due to the residual surface roughness, the optical dielectric function is understood as a pseudodielectric function.[16] The sample color changes from black to dark blue as the composition changes from $x=0$ to 0.25. The superconducting transition temperature of all samples was determined magnetically prior to the ellipsometry measurement. For $x=0$ doped material, the superconductor state was not observed above 4 K. The superconductor transition temperatures for $x=0.10$ and 0.25 samples were determined as 7 and 13 K, respectively. The $x=0.40$ doped sample is a semiconductor.

The ellipsometry measurement was carried out on a spectroscopic ellipsometer modified from a single-wavelength rotating-analyzer ellipsometer. The incident beam from the monochrometer was collimated, polarized, and then reflected by the sample surface. The beam passing through the analyzer was recorded as intensity versus analyzer rotating angle, $I(\phi)$. The optical complex reflectivity ratio,

$$\rho = r_p / r_s \ , \tag{1}$$

where r_p and r_s are the complex reflectivity for p and s polarization, can be derived from the Fourier transformation of $I(\phi)$.[17] The complex dielectric function of the sample is then given by

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 = \sin^2\theta \left[1 + \left[\frac{1-\rho}{1+\rho} \right]^2 \tan^2\theta \right] \ , \tag{2}$$

where θ is the angle of incidence.

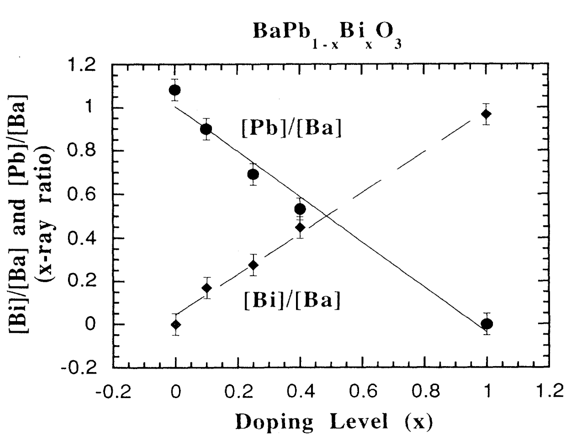

FIG. 1. [Bi]/[Ba] and [Pb]/[Ba] determined by energy dispersive x ray.

III. RESULT AND DISCUSSION

The dielectric functions of $BaPb_{1-x}Bi_xO_3$ with different compositions are shown in Fig. 2. For $x=0.4$, the material behaves as a semiconductor. The ε_2 spectrum has a broad excitation centered at 3.2 eV and an abrupt increase near 1.5 eV, which represents an excitation centered at lower energy.[12–14] This excitation at about 1.5 eV evolves from the excitation at 2.0 eV in the $BaBiO_3$.[12–14,18] At $x=0.25$ and 0.10, the material becomes superconducting. The excitation near 1.5 eV, which appears in the $x=0.4$ doping sample, disappears in the ε_2 spectra in the low-energy region and it is replaced by a slow rising of ε_2. The broad excitation at ~3 eV shifts toward the low-energy region. As $x=0$, the material becomes normal metal, and the strength of the broad excitation reduces substantially.

Since the broad excitation is superimposed on a smooth background, to quantify this excitation, it is necessary to subtract the background. We choose a polynomial function to fit the background at the low and high end of the energy region of the ε_2 spectrum. For $x=0.40$ doped material, because of the narrow excitation at about 1.5 eV, in addition to the polynomial function, a Gaussian function is added to obtain a proper background fitting. The fitted curves of the background are shown in Fig. 2(b) with the dashed lines. The background subtracted ε_2 spectra are shown as the dots in Fig. 3. A Gaussian model,

$$F(E) = \frac{A}{(2\pi\Gamma^2)^{1/2}} \exp\left[-\frac{1}{2} \left[\frac{E-\Omega}{\Gamma} \right]^2 \right] \ , \tag{3}$$

is used to fit these excitation and is shown with the solid lines in Fig. 3. The center, width, and amplitude of the excitations are listed in Table I for different compositions along with the material properties. The T_c of the material and the center and strength of the excitation are plotted against the doping level in Fig. 4.

Our result of the dielectric function of $x=0.25$ is close to Tajima *et al.*'s result of $x=0.17$ in the energy range of 1.5–6.0 eV.[14] Figure 5 shows the calculated reflectance spectra from our results and they are similar to those reported by Tajima *et al.*[14] on the single crystals in the energy range of 0–30 eV. Both Tajima's and our results indicate that the center of the broad transition in the visible range shifts toward low energy as x decreases. But, Tajima *et al.*[14] did not provide quantitative analysis of the oscillator strength of the excitation. Based on the currently acquired knowledge about the material, it is clear that information on the oscillator strength is equally important for the interpretation of the excitation.

The problem of $BaPb_{1-x}Bi_xO_3$ originates from the problem of $BaBiO_3$. Like undoped Cu-O materials, $BaBiO_3$ material, with an odd number of electron in the valence band, is a semiconductor despite the metallic prediction based on the band-structure calculation.[19] Early interpretation, also the most popular one, of the insulator phase in $BaBiO_3$ was that Bi tends to stay as Bi^{+3} and Bi^{+5}, forming a charge density wave (CDW). The experimental evidence of CDW is that there are two distinct

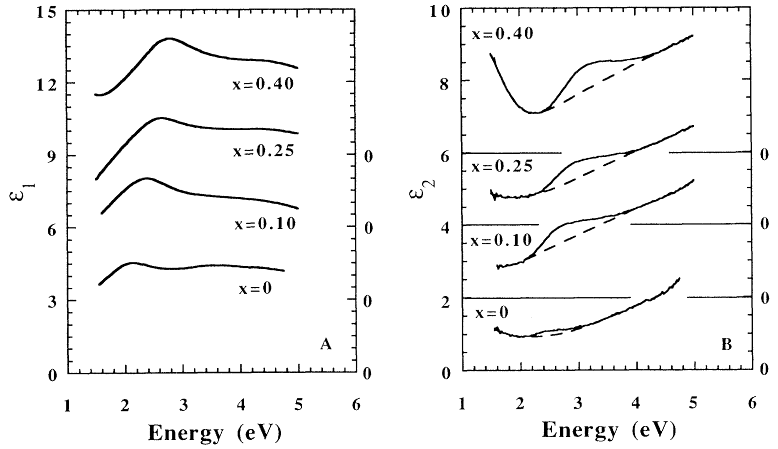

FIG. 2. (a) Real part of dielectric functions of $BaPb_{1-x}Bi_xO_3$. (b) Imaginary part of dielectric functions of $BaPb_{1-x}Bi_xO_3$. The dashed lines are the polynomial fitted curves of the background near the excitation energy region.

Bi-O bonds in $BaBiO_3$. However, the band-structure calculation with different bond length shows little charge fluctuation of Bi.[19] Furthermore, recent experiments indicate that some of the early evidence of CDW in $BaBiO_3$ and $Ba_{1-x}K_xBiO_3$ may be due to the radiation-induced damage in the material.[20–23]

Most of the earlier published optical spectra for this kind of material, including $Ba_{1-x}K_xBiO_3$, were interpreted by the CDW model.[12–14,24–26] In this model, the excitation at 2.0 eV in $BaBiO_3$, shown in Fig. 5, is interpreted as the excitation across the CDW band gap. However, because of the similarities between $BaPb_{1-x}Bi_xO_3$ (and BKBO) and Cu-O materials,[10,11] we suggest an alternative way to interpret the optical data of this material.[27]

In $BaBiO_3$, as shown in Fig. 6,[18] the 2.0 eV excitation is followed by a broad excitation at about ~3.5 eV, which is very similar to the optical spectrum of the Cu-O material. In the undoped Cu-O material, the narrow excitation at low energy is interpreted as an excitonic enhanced transition from the low Hubbard band to the "upper Hubbard band;" whereas, the broad excitation at ~2.7 eV is interpreted as the transitions from the low Hubbard band to the "upper Hubbard band."[5,6,9] This picture of Cu-O materials is consistent with the O *K*-edge absorption spectrum and EELS spectrum of $La_{2-x}Sr_xCuO_4$, in which two types of hole are discovered: one is associated with the "upper Hubbard band," and the other is associated with the low Hubbard band.[29–31] In addition, it is also discovered that in $La_{2-x}Sr_xCuO_4$, overdoping of Sr ($T_c < 4$ K) results in a dramatic reduction of the density of the state of the "upper Hubbard band."[28–30] It is worth mentioning that the O *K*-edge absorption spectrum of $BaPb_{1-x}Bi_xO_3$ (Refs. 31 and 32) is more like the one with electron-doped Cu-O materials[33] than that of hole-doped Cu-O materials.[28–30] ($La_{2-x}Sr_xCuO_4$ is hole-doped material.) This may be because that in $BaPb_{1-x}Bi_xO_3$, electron is its major carrier in the superconducting phase.[34] A Mott insulator model proposed by Eskes, Meinders, and Sawatzky[35] indicates that the energy position of the carrier is different between electron-doped and hole-doped oxide superconductors, but the energy position of the upper Hubbard state is the same for both.

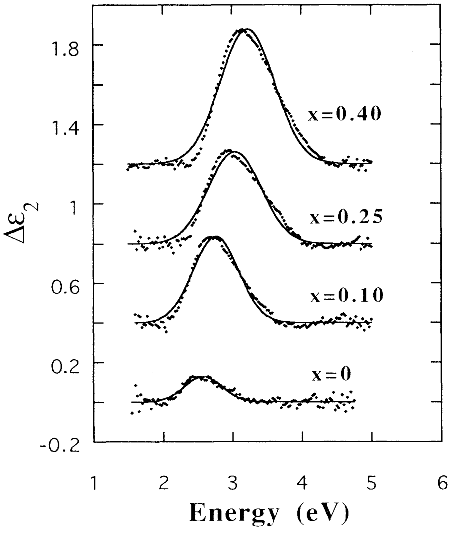

FIG. 3. The broad excitation of different compositions after the background subtraction. The dots are the experimental points, and the solid lines are the Gaussian fit of the data.

In the Hubbard-band picture, the narrow excitation at low energy in the semiconductor phase of $BaPb_{1-x}Bi_xO_3$ can be interpreted as an excitonic enhanced transition from the low Hubbard band to the upper Hubbard band. The broad excitation which follows the narrow excitation, as shown in Fig. 6, can be interpreted as the transitions from low Hubbard band to the upper Hubbard band.[18] By electron-energy-loss spectroscopy, it is

TABLE I. Gaussian fitting parameters of the broad excitation with different doping level.

$BaPb_{1-x}Bi_xO_3$	State	T_c (K)	*A* (eV)	Ω (eV)	Γ (eV)
$x = 0.40$	Semi-*c*	N.A.[a]	0.667	3.22	0.393
$x = 0.25$	Super-*c*	13	0.440	3.04	0.380
$x = 0.10$	Super-*c*	7	0.358	2.76	0.327
$x = 0.0$	Metal	<4	0.087	2.58	0.270

[a] Not applicable.

discovered that there is an optical forbidden transition near this broad excitation energy region in $BaBiO_3$.[36] When the material becomes a superconductor, the excitonic transition is replaced by a free carrier plasmon in the infrared energy region. This explains the reducing of the low-energy excitation [a reduction of the abrupt rising in ε_2 at ~ 1.5 eV, shown in Fig. 2(b)] from the semiconducting doping regime to the superconducting doping regime. The oscillator strength of the broad excitation at ~ 3 eV decreases slightly as the material becomes a superconductor. As soon as the material becomes a normal metal with the pure Pb doping ($BaPbO_3, T_c < 4$ K), the oscillator strength of the broad excitation is reduced to almost zero, as shown in Figs. 3 and 4. In the Hubbard-band picture, this result implies that the density of the upper Hubbard state is reduced to almost nothing (relatively speaking), due to the screening of the electron-electron Coulomb interaction with the pure Pb doping. This is similar to the overdoping phenomenon in $La_{2-x}Sr_xCuO_4$, mentioned in the previous paragraph, where the density of the upper Hubbard state reduces to undetectable level in the overdoping regime.[28–30] This indicates that there may be a connection between the upper Hubbard state and superconductivity.

It should be pointed out, however, that in Cu-O materials, $dp\sigma$ hybridization between Cu and O is more two

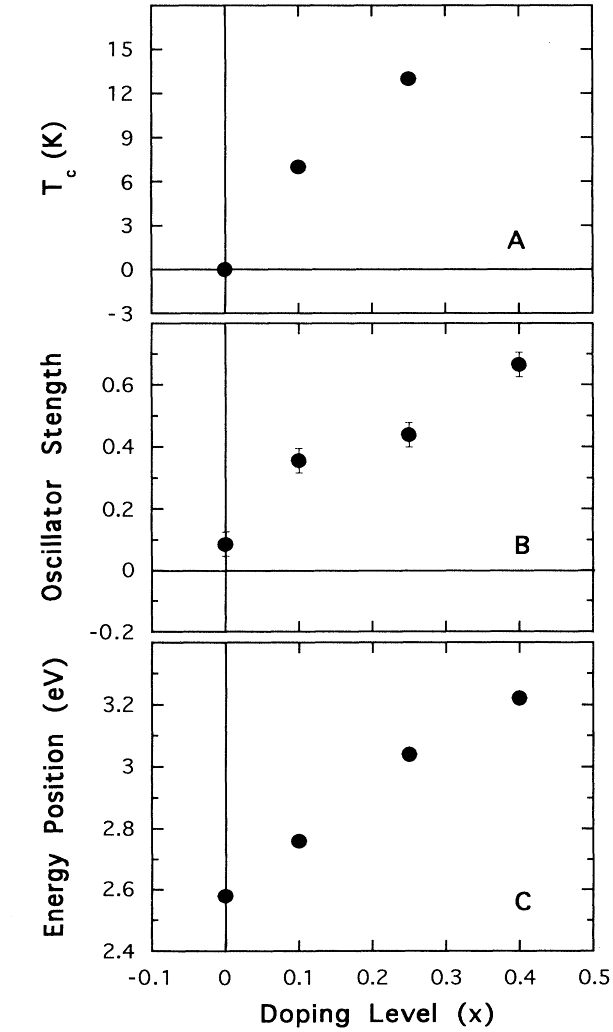

FIG. 4. (a) T_c vs the doping composition. (b) The area of the excitation vs Bi doping concentration. (c) Energy position of the excitation vs doping.

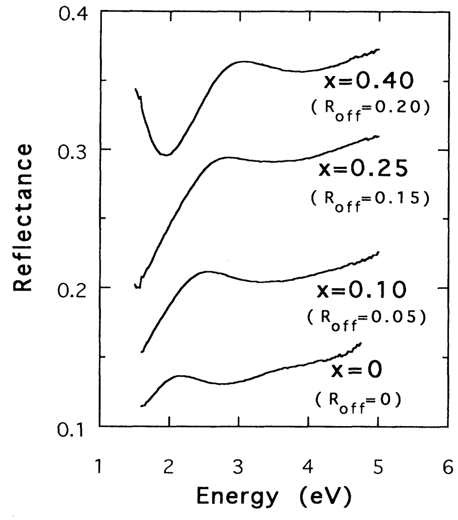

FIG. 5. The reflectance spectra calculated from the ellipsometry measurement. R_{off} is the offset value relative to the axis for the spectra.

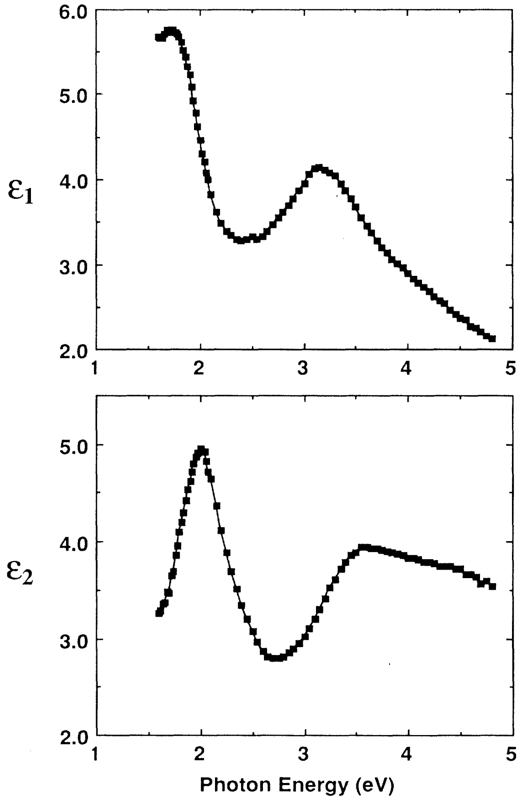

FIG. 6. Dielectric function of $BaBiO_3$, previously published in Ref. 18.

dimensional; whereas, in $BaPb_{1-x}Bi_xO_3$, $sp\sigma$ hybridization between Pb (or Bi) and O is more isotropic.

IV. CONCLUSION

The ellipsometry measurement of $BaPb_{1-x}Bi_xO_3$ with different doping shows that the oscillator strength of the broad excitation at ~ 3 eV is dramatically reduced from a superconductor state to a normal metallic state. In the scenario of the Hubbard model, this implies that the electron-electron Coulomb interaction is screened out by the pure Pb doping, resulting in the normal metallic properties of the material (no superconducting above 4 K). Based on that assumption, our result suggests that there may be a connection between the upper Hubbard state and superconductivity in this kind of material.

ACKNOWLEDGMENTS

The authors would like to thank B. A. Averill and V. P. Dravid for their support of this experiment and S. E. Schnatterly for the stimulating discussions. This work was partially supported by NSF-DMR through the Science and Technology Center for Superconductivity (STcS, NSF-DMR-8809854), by the National Science Foundation, the Solid State Chemistry Program, Grant No. DMR-8313252, and by the Electric Power Research Institute.

---

[1] A. W. Sleight, J. L. Gillson, and P. E. Bierstedt, Solid State Commun. **17**, 27 (1975).

[2] D. E. Cox and A. W. Sleight, Solid State Commun. **19**, 969 (1976).

[3] R. J. Cava, B. Batlogg, J. J. Krajewski, R. C. Farrow, L. W. Rupp, Jr., A. E. White, K. T. Short, W. F. Peck, Jr., and T. Y. Kometani, Nature **332**, 314 (1988).

[4] T. E. Sutto and B. A. Averill, Chem. Mater. **3**, 209 (1991).

[5] Y. Y. Wang, Ph.D. thesis, Virginia Polytechnic Institute and State University, 1990.

[6] Y. Y. Wang and A. L. Ritter, Phys. Rev. B **43**, 1241 (1991).

[7] M. K. Kelly, P. Barboux, J. M. Tarascon, and D. E. Aspnes, Phys. Rev. B **40**, 6797 (1989).

[8] M. Garriga, T. Humlicek, J. Burth, R. L. Johnson, and M. Cardona, Opt. Soc. Am. B **6**, 470 (1989).

[9] N. Nucker, H. Romberg, S. Nakai, B. Scheerer, J. Fink, Y. F. Yan, and Z. X. Zhao, Phys. Rev. B **39**, 12 379 (1989).

[10] B. Batlogg, *A Comparison Between Bi-O and Cu-O Based Superconductors Mechanism of High Temperature Superconductivity*, Vol. II of *Springer Series in Material Science* (Springer, Berlin, 1989), p. 324.

[11] F. Sharifi, A. Pargellis, and R. C. Dynes, Phys. Rev. Lett. **67**, 509 (1991).

[12] S. Tajima, S. Uchida, A. Masaki, H. Takagi, K. Kitazawa, and S. Tanaka, Phys. Rev. B **32**, 6302 (1985).

[13] S. Tajima, S. Uchida, M. Masaki, H. Takagi, K. Kitazawa, and S. Tanaka, Phys. Rev. B **35**, 696 (1987).

[14] S. Tajima, H. Ishii, I. Rittaporn, S. Uchida, S. Tanaka, K. Kitazawa, M. Seki, and S. Suga, Phys. Rev. B **38**, 1143 (1988).

[15] D. E. Cox and A. W. Sleight, Acta. Crytallogr. Sec. B **35**, 1 (1979).

[16] D. E. Aspnes and A. A. Studna, Appl. Opt. **14**, 220 (1975).

[17] D. E. Aspnes and A. A. Studna, Phys. Rev. B **27**, 985 (1983).

[18] Y. Y. Wang, G. F. Feng, T. E. Sutto, and Z. Shao, Phys. Rev. B **44**, 7098 (1991).

[19] L. F. Mattheiss and D. R. Hamann, Phys. Rev. B **28**, 4277 (1983).

[20] S. Pei, N. J. Zaluzec, J. D. Jorgensen, B. Dabrowski, D. G. Hinks, A. W. Mitchell, and D. R. Richards, Phys. Rev. B **39**, 811 (1989).

[21] S. Pei, J. D. Jorgensen, B. Dabrowski, D. G. Hinks, D. R. Richards, A. W. Mitchell, J. M. Newsam, S. K. Sinha, D. Vaknin, and J. Jacobson, Phys. Rev. B **41**, 4126 (1990).

[22] M. Verwerft, G. van Tendeloo, D. G. Hinks, B. Dabrowski, D. R. Richards, A. W. Mitchell, D. T. Marx, S. Pei, and J. D. Jorgensen, Phys. Rev. B **44**, 9547 (1991).

[23] J. P. Zhang (personal communication).

[24] H. Sato, S. Tajima, H. Takagi, and S. Uchida, Nature **338**, 241 (1989).

[25] S. H. Blanton, R. T. Collins, K. H. Kelleher, L. D. Rotter, Z. Schlesinger, D. G. Hinks, and Y. Zheng, Phys. Rev. B **47**, 996 (1993).

[26] M. A. Karlow, S. L. Cooper, A. L. Kotz, M. V. Klein, P. D. Han, and D. A. Payne, Phys. Rev. B **48**, 6499 (1993).

[27] Y. Y. Wang, H. Zhang, V. P. Dravid, D. Shi, D. G. Hinks, Y. Zheng, and J. D. Jorgensen, Phys. Rev. B **47**, 14 503, (1993).

[28] C. T. Chen, F. Sette, Y. Ma, M. S. Hybersten, 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).

[29] C. T. Chen, L. H. Tjeng, J. Kwo, H. L. Kao, P. Rudolf, F. Sette, and R. M. Fleming, Phys. Rev. Lett. **68**, 2543 (1992).

[30] H. Romberg, M. Alexander, N. Nucker, P. Adelmenn, and J. Fink, Phys. Rev. B **42**, 8768 (1990).

[31] F. M. F. De Groot, J. C. Fuggle, and J. M. van Ruitenbeek, Phys. Rev. B **44**, 5280 (1992).

[32] Z. X. Shen, P. S. P. Linderg, B. O. Wells, D. S. Dessau, A. Borg, I. Lindau, W. E. Spicer, W. P. Ellis, G. H. Kwei, K. C. Ott, J.-S. Kang, and J. W. Allen, Phys. Rev. B **40**, 6912 (1989).

[33] J. Fink, N. Nucker, M. Alexander, H. Romberg, M. Knupfer, M. Merkel, P. Adelmann, R. Claessen, G. Mante, T. Buslaps, S. Harm, R. Manzke, and M. Skibowski, Physica C **185-189**, 45 (1991).

[34] T. D. Thanh, A. Koma, and S. Tanaka, Appl. Phys. **22**, 205 (1980).

[35] H. Eskes, M. B. J. Meinders, and G. A. Sawatzky, Phys. Rev. Lett. **67**, 1035 (1991).

[36] Y. Y. Wang, H. Zhang, V. P. Dravid, and S. E. Schnatterly (unpublished).