Progress in Superconductivity Vol.3 No.1 pp13-16 31 October 2001

Optical Properties of Infinite-Layer Superconductors $Sr_{0.9}Ln_{0.1}CuO_2$ (Ln=La, Gd, Sm)

Mi-Ock Mun[a], Young Sub Rho[a], Kibum Kim[a], and Jae H. Kim*,[a]
A. B. Kuz'menko[b] and D. van der Marel[b]
C.U. Jung[c], J. Y. Kim[c], M. S. Park[c], H. J. Lee[c], and Sung-Ik Lee[c]
[a] *Institute of Physics and Applied Physics and Department of Physics, Yonsei University, Seoul 120-749, Korea*
[b] *Material Science Center, University of Groningen,Nijenborgh 4, 9747 AG Groningen, The Netherland*
[c] *National Creative Research Initiative Center for Superconductivity and Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Korea*

무한층 초전도체 $Sr_{0.9}Ln_{0.1}CuO_2$ (Ln=La, Gd, Sm)의 광학적 성질

문미옥[a], 노영섭[a], 김기범[a], 김재훈*,[a]
A. B. Kuz'menko[b] and D. van der Marel[b]
정창욱[c], 김지연[c], 박민석[c], 이헌정[c], 이성익[c]

Abstract

We have measured the reflectivity of superconducting infinite-layer compounds $Sr_{0.9}Ln_{0.1}CuO_2$ (Ln=La, Gd, Sm) with T_c = 39 K using a Fourier-transform infrared spectrometer. We have identified the optical phonon modes from their infrared reflectivity and conductivity spectra and have proposed possible displacement patterns. The La- and the Gd-doped compounds exhibited only four ($2A_{2u}+2E_u$) out of the five ($2A_{2u}+3E_u$) infrared-active phonons predicted by a group theoretical analysis whereas the Sm-doped compound exhibited all five modes. For the La-doped sample, we investigated the temperature dependence of the optical response functions in a wide temperature range of 7 – 300 K. In FIR region, the reflectivity is apparently enhanced below ~120 cm^{-1} as temperature decreases across T_c. The value of $2\Delta/k_BT_c$ is about 4.5, which is consistent with maximum gap value of d-wave high-T_c cuprates.

keywords : optical property, phonon, infinite-layer superconductor, FTIR, superconducting gap

I. Introduction

The infinite-layer superconductor $Sr_{0.9}Ln_{0.1}CuO_2$ (Ln = Lanthanide element), which consists only of CuO_2 planes separated by metal ions, embodies the essential and minimal structure underlying all high-T_c cuprate superconductors. It provides us with a good opportunity to understand the mechanism of high-T_c superconductivity by isolating the intrinsic properties

---

*Corresponding author. Fax: +82 2 392 1592
e-mail: jaehkim@phya.yonsei.ac.kr

of the CuO_2 planes from complications due to complex crystal structures [1]. For this reason, since its discovery in 1988 [2,3], much effort was made to measure and understand the basic physical properties of this compound [4-7]. However, the difficulties in obtaining high-quality infinite-layer compounds so far, mostly due to impurities and/or multiphases, have made it hard to obtain reliable experimental data and to test currently available theoretical models. This is also the case with the infrared spectroscopic measurement, which is one of the basic probes of the electrons and phonons in solids. Previous reports by Burns *et al.* [8] and by Tajima *et al.* [9] on a isostructural non-superconducting $Ca_{0.86}Sr_{0.14}CuO_2$, and those by Zhou *et al.* [10] and Er *et al.* [11] on superconducting $Sr_{0.9}Ln_{0.1}CuO_2$ contradict one another in their phonon mode while the lattice dynamics calculations by Agrawal [12] and Koval [13] do not completely agree with experiment. For the fundamental optical responses of this compound, no studies have been reported.

In this paper, we report on our infrared reflectivity measurements on high-quality high-purity samples of the infinite-layer superconductor $Sr_{0.9}Ln_{0.1}CuO_2$ (Ln=La, Gd, Sm; T_c = 39 K for all). We proposed our mode assignments for the optical phonons and presented the optical response functions above and below T_c.

II. Experimental

Our samples of the superconducting infinite-layer compounds $Sr_{0.9}Ln_{0.1}CuO_2$ (Ln=La, Gd, Sm) were synthesized by a high-pressure method [14]. The zero-field-cooled measurement of the magnetic susceptibility clearly showed a sharp transition at T_c and indicated the Meissner fraction greater than 80 %. The T_c's are 43 K for all the samples studied, where the transition temperature was determined by the criterion of 10 % onset of superconductivity in the low-field magnetization measurements.

Normal-incidence reflectivity measurements were carried out with a Fourier-transform spectrometer in the spectral range of 40 – 6000 cm^{-1} and with a ellipsometry from 6000 to 37000 cm^{-1}. For low temperature measurement, we used the optical cryostat in which temperature was controlled from 7 to 300 K. Absolute reflectivity calibration is made by *in-situ* Au deposition on sample.

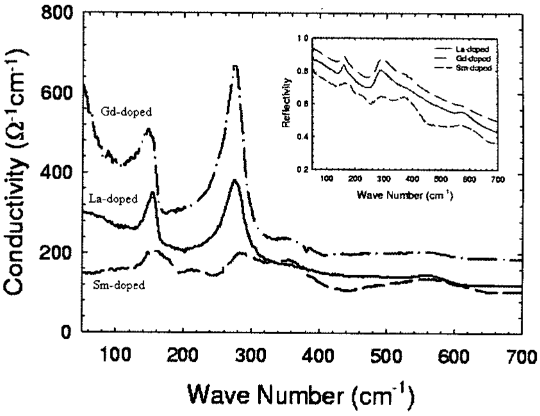

Fig. 1. The real part of the optical conductivity of $Sr_{0.9}Ln_{0.1}CuO_2$ obtained by a Kramers-Kronig analysis. Inset shows the reflectivity $Sr_{0.9}Ln_{0.1}CuO_2$ measured at normal-incidence. (solid line for $Sr_{0.9}La_{0.1}CuO_2$, dash-dot line for $Sr_{0.9}Gd_{0.1}CuO_2$, and dashed line for $Sr_{0.9}Sm_{0.1}CuO_2$)

III. Results and Discussion

Infrared-active optical phonon modes

The reflectivity spectra and the optical conductivity of the infinite-layer compounds $Sr_{0.9}Ln_{0.1}CuO_2$ (Ln=La, Gd, Sm) are shown in Fig. 1. Our Kramers-Kronig calculation was anchored to the ellipsometric data [15]. At low frequencies, the reflectivity curves show typical metallic response of the free carriers and the infrared-active phonon modes appear as peaks in the 50 - 700 cm^{-1} range. A group theoretical analysis predicts five infrared-active optical phonons, two A_{2u} modes and three E_u modes, for the space group (P4/mmm; D_{4h}^1) relevant to the tetragonal structure of the infinite-layer compounds.

In $Sr_{0.9}La_{0.1}CuO_2$, only four modes were detected at 152, 275, 354, and 559 cm^{-1}. The highest two modes at 354 and 559 cm^{-1} were assigned to E_u modes in view of previous polarized measurements (**E // ab**) on a non-superconducting isostructural compound $Ca_{0.86}Sr_{0.14}CuO_2$ [8]. The remaining E_u phonon is expected at ~ 230 cm^{-1} but is not detected most probably due to screening by free carriers. The two lowest modes at 152 and 275 cm^{-1} of $Sr_{0.9}La_{0.1}CuO_2$ must then be A_{2u} modes. It is quite natural for the A_{2u} modes to dominate the reflectivity spectra of polycrystalline samples [16].

$Sr_{0.9}Gd_{0.1}CuO_2$ shows similar phononic behavior with its second E_u mode more pronounced. As can be seen in Fig. 1, the $Sr_{0.9}Sm_{0.1}CuO_2$ sample is of relatively poor quality, showing in lower and more smeared reflectivity compared to $Sr_{0.9}La_{0.1}CuO_2$ and $Sr_{0.9}Gd_{0.1}CuO_2$. Nevertheless, all the five phonon modes were observed at 161, 208, 280, 355, and 561 cm^{-1}, respectively. The lowest E_u mode, not detected in the La- and the Gd-doped compounds, now appears at 208 cm^{-1}, which is consistent with the aforementioned polarized data on $Ca_{0.86}Sr_{0.14}CuO_2$ [9].

Our assignment of the atomic vibration patterns for the infinite-layer compound is based on the analogy with the case of *n*-type superconductors of the T' structure [17], which also contain single CuO_2 planes without any apical oxygen. The two E_u modes are assigned to the Cu-O bending and the Cu-O stretching motions in the **ab**-plane, respectively. These two planar vibrations are commonly observed in other cuprates at similar eigen-frequencies because they are associated with the CuO_2 plane itself and hence are not largely affected by the nature of the insulating or charge-reservoir blocks. The lowest E_u mode, which is detected only in the Sm-doped compound, is most likely to arise from the out-of-phase motion of $Sr_{0.9}Ln_{0.1}CuO_2$ metal ion sheets against CuO_2 planes in the planar direction (the external mode). The lowest A_{2u} mode is assigned to the out-of-phase vibration of metallic Sr/*Ln* ions against Cu ions along the **c** axis. This mode shifts more or less with *Ln* replacement. The second A_{2u} is assigned to the dimpling motion of oxygen and copper ions along the **c** axis without involving the motion of heavy metallic ions, which is consistent with the robustness of this mode against ion substitution.

Estimation of energy gap

The temperature dependent reflectivity spectra of $Sr_{0.9}La_{0.1}CuO_2$ were shown in Fig. 2. In the mid-infrared region, the reflectivity does not vary much while the temperature changes. In the far-infrared region, the reflectivity spectra show a highly metallic behavior including phonon contributions. According to decreasing temperature, the reflectivity apparently enhances its intensity below T_c for $\omega < \sim 120$ cm^{-1}. However, the reflectivity does not reach the value of unity even if the temperature goes down far below T_c. This may be the finite absorption induced from the impurities in the sample or from the quasi-particle excitations below the superconducting gap.

To see the enhancement of the reflectivity clearly, in Fig. 3, the temperature dependence of the reflectivity ratio normalized by the intensity reflected at 70 K is plotted. At ~ 120 cm^{-1}, the reflectivity ratio starts to increase apparently below T_c indicating the energy gap opening in the density of state. The value of $2\Delta/k_BT_c \sim 4.5$ indicates strong-coupling limit similar to high- T_c cuprate superconductor.

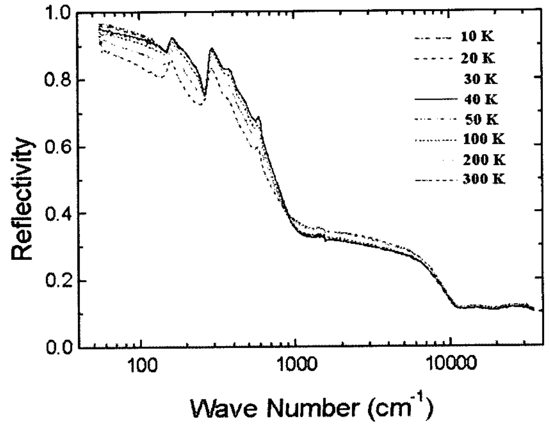

Fig. 2. The temperature dependent reflectivity spectra of $Sr_{0.9}La_{0.1}CuO_2$.

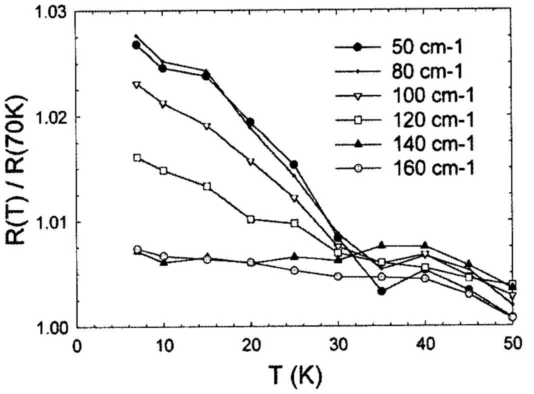

Fig. 3. The reflectivity ratio normalized by the reflectivity at 70 K as a function of temperature at low frequencies of $Sr_{0.9}La_{0.1}CuO_2$.

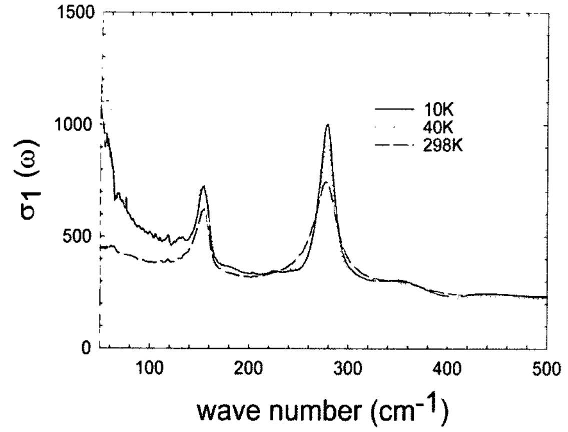

Fig. 4. The real part of the optical conductivity of $Sr_{0.9}La_{0.1}CuO_2$ measured at different temperatures.

The gap opening accompanies the decrease of the real part of optical conductivity resulting from the condensation of charge carriers into pairs (Fig. 4). The conductivity at low frequencies increases according to deceasing temperature from room temperatures. It decreases again as temperatures cross T_c. However, the conductivity does not reach the zero value below the superconducting gap in the superconducting state. This is consistent with the response of the reflectivity in the superconducting state.

III. Conclusion

The five infrared-active optical phonons, $2A_{2u} + 3E_u$, of the superconducting infinite-layer compounds $Sr_{0.9}Ln_{0.1}CuO_2$ were identified and assigned on the basis of a group theoretical analysis, reported lattice dynamics calculations and comparison with other single-layer cuprate materials. Across T_c, the reflectivity enhancement below $\omega \sim 120$ cm^{-1} gives a signature of superconducting gap suggesting a strong coupling limit superconductivity.

Acknowledgements

JHK was supported by BK21 Project of Ministry of Education. MOM was supported by Basic Research Program for the Women Scientists of the Korea Science & Engineering Foundation for this work. SIL was supported by the Creative Initiative Research Program of the Ministry of Science and Technology of Korea and KOSEF (Contract Number 95-0702-03-03-3).

References

[1] D.B. Tanner and T. Timusk, "Optical properties of high-temperature superconductors" in *Phiscal Properties of High Temperature Superconductors*, III, eds. D.M Ginsberg, Singapore: World Scientific, 363-469 (1991).
[2] T. Siegrist, S.M. Zahurak, D.W. Murphy, and R.S. Roth, Nature, 334, 231 (1988).
[3] M.G. Smith, A. Manthiram. J. Zhou, J.B. Goodenough, and J.T. Markert, Nature, 351, 549 (1991).
[4] Y.Y. Wang, H. Zhang, V.P. Dravid, P.D. Han, and D.A. Payne, Phys. Rev. B, 48, 9810 (1993).
[5] N. Ikeda, Z. Hiroi, M. Azuma, M. Takano, Y. Bando, and Y. Takeda, Physica C, 210, 367 (1993).
[6] R. Feenstra, T. Matsumoto, and T. Kawai, Physica C, 282-287, 105 (1997).
[7] T. Matsumoto and T. Kawai, Appl. Phys. A, 68, 687 (1999).
[8] G. Burns, M.K. Crawford, F.H. Dacol, E.M. McCarron III, and T.M. Shaw, Phys. Rev. B, 40, 6717 (1989).
[9] S. Tajima, T. Ido, S. Ishibashi, T. Itoh, H. Eisaki, Y. Mizuo, T. Arima, H. Takagi, and S. Uchida, Phys. Rev. B, 43, 10496 (1991).
[10] X. Zhou, M. Cardona, W. Ko"nig, J. Zegenhagen, and Z. X. Zhao, Physica C, 282-287, 1011 (1997).
[11] G. Er, S. Kikkawa, M. Takahashi, F. Kanamaru, M. Hangyo, K. Kisoda, and S. Nakashima, Physica C, 290, 1 (1997).
[12] B.K. Agrawal and S. Agrawal, Phys. Rev. B, 48, 6451 (1993).
[13] S. Koval and R. Migoni, Physica C, 257, 255 (1996).
[14] C.U. Jung, J.Y. Kim, Mun-Seog Kim, S.Y. Lee, Sung-Ik Lee, and D.H. Ha, accepted by Current Applied Physics (2001).
[15] J.W. van der Eb, A.B. Kuz'menko, and D. van der Marel, Phys. Rev. Lett., 86, 3407 (2001)
[16] J. Hemlicek, J. Kircher, H.-U. Harbermeier, M. Cardona, and A. Roseler, Physica C, 190, 383 (1992).
[17] E.T. Heyen, G. Kliche, W. Kress, W. Konig, M. Cardona, E. Rampf, J. Prade, U. Schroder, A.D. Kulkarni, F.W. de Wette, S. Pinol, D. McK. Paul, E. Moran, and M.A. Alario-Franco, Solid State Commun., 74, 1299 (1990).