Optical phonons of superconducting infinite-layer compounds

\[ \text{Sr}_{0.9}\text{Ln}_{0.1}\text{CuO}_2 \ (\text{Ln} = \text{La, Gd, Sm}) \]

Mi-Ock Mun, Young Sup Roh, Kibum Kim, and Jae Hoon Kim

*Institute of Physics and Applied Physics and Department of Physics
Yonsei University, Seoul 120-749 Korea*

C. U. Jung, J. Y. Kim, Min-Seok Park, Heon-Jung Kim, and Sung-Ik Lee

*National Creative Research Initiative Center for Superconductivity
Department of Physics
Pohang University of Science and Technology
Pohang 790-784 Korea*

Abstract

We have identified the optical phonon modes of the superconducting infinite-layer compounds \( \text{Sr}_{0.9}\text{Ln}_{0.1}\text{CuO}_2 \) (\( \text{Ln} = \text{La, Gd, Sm}; \ T_c = 43 \text{ K for all} \)) from their infrared reflectivity spectra obtained with a Fourier-transform infrared spectrometer on high-quality high-purity samples synthesized under high pressure. The La- and the Gd-doped compounds exhibited only four (\( 2A_{2u}+2E_u \)) out of the five (\( 2A_{2u}+3E_u \)) infrared-active phonon modes predicted by a group theoretical analysis whereas the Sm-doped compound exhibited all five modes. We propose the atomic displacement pattern for each phonon mode based on reported lattice dynamics calculations and through comparison with the phonon modes of other single-layer high-\( T_c \) cuprate superconductors.

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I. INTRODUCTION

The superconducting infinite-layer cuprate Sr$_{1-x}$Ln$_x$CuO$_2$ ($Ln =$ Lanthanide element), which consists solely 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 of the CuO$_2$ planes without complications arising from complex crystal structures. For this reason, since its discovery in 1988 [1, 2], much effort was made to measure and understand the basic physical properties of this compound [3, 4, 5, 6, 7, 8]. 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. [9] and Tajima et al. [10] on Ca$_{0.86}$Sr$_{0.14}$CuO$_2$, a nonsuperconducting isostructural compound, and those by Zhou et al. [11] and Er et al. [12] on superconducting Sr$_{0.9}$Ln$_{0.1}$CuO$_2$ contradict one another in their mode assignments for the infrared-active phonons while the lattice dynamics calculations by Agrawal [13] and Koval [14] do not completely agree with experiment.

In this paper, we report on our infrared reflectivity measurements on high-quality high-purity samples of the superconducting infinite-layer compounds Sr$_{0.9}$Ln$_{0.1}$CuO$_2$ ($Ln =$ La, Gd, Sm; $T_c = 43$ K for all) synthesized under high pressure and propose our mode assignments for the optical phonons.

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 synthesis method [15, 16, 17]. 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 (Bruker IFS 113v) in the spectral range of 40 - 5000 cm\(^{-1}\) and with a grating spectrometer (Varian Cary 5G) from 4000 to 50000 cm\(^{-1}\).

III. RESULTS AND DISCUSSION

The reflectivity spectra of the infinite-layer compounds Sr\(_{0.9}Ln_{0.1}\)CuO\(_2\) (\(Ln = \text{La, Gd, Sm}\)) are shown in Fig. 1. 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. We calculated the optical conductivity via a Kramers-Kronig analysis to identify the transverse-optical phonon modes (Fig. 2). Our main objectives here are to determine the center frequencies of the optical phonon modes and to propose the atomic displacement patterns consistent with the available experimental and computational data.

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 \(\rightarrow D_{4h}^1\)) relevant to the tetragonal structure of the infinite-layer compound. 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 (\(\vec{E} \perp c\)) on \(\text{Ca}_{0.86}\text{Sr}_{0.14}\)CuO\(_2\) \[10\], which is a nonsuperconducting isostructural compound. The remaining \(E_u\) phonon is expected at about 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 \[18\]. Our mode assignments agree with the lattice dynamics calculation on \(\text{Ca}_{0.86}\text{Sr}_{0.14}\)CuO\(_2\) by Koval \textit{et al.} \[14\] at least in the symmetry of the modes although the actual frequencies and displacement patterns are not completely consistent. 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 and Fig. 2, 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 \(\text{Ca}_{0.86}\text{Sr}_{0.14}\)CuO\(_2\) (\(\vec{E} \perp c\)). \[10\]

Our assignment of the atomic vibration patterns for the infinite-layer compound (Fig. 3)
is based on the analogy with the case of $n$-type superconductors of the $T'$ structure [15], which also contain single CuO$_2$ planes without any apical oxygen. For Sr$_{0.9}$La$_{0.1}$CuO$_2$, the two $E_u$ modes at 354 cm$^{-1}$ and 559 cm$^{-1}$ 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 eigenfrequencies 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 remaining $E_u$ mode, which is detected only in the Sm-doped compound, is most likely to arise from the out-of-phase motion of Sr/Ln 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 $A_{2u}$ mode at 275 cm$^{-1}$ for Sr$_{0.9}$La$_{0.1}$CuO$_2$ 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. In Table I, we summarized our assignment of the phonon modes.

IV. CONCLUSION

The five optical phonons, $2A_{2u} + 3E_u$, of the high-purity high-quality 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.

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TABLE I: The phonon frequencies and the proposed atomic vibration pattern of the superconducting infinite-layer compound Sr$_{0.9}$Ln$_{0.1}$CuO$_2$.

| Mode   | Frequency (cm$^{-1}$) | Atomic Vibration Pattern                                      |
|--------|----------------------|----------------------------------------------------------------|
| $A_{2u}(1)$ | 152 148 161            | out-of-phase vibration of heavy ion against Cu along $c$ axis |
| $E_u(1)$    | - - 208               | in-plane external motion (CuO$_2$ plane against Sr/Ln sheet)  |
| $A_{2u}(2)$ | 275 275 280            | Cu-O dimpling motion along $c$ axis                           |
| $E_u(2)$    | 354 353 355            | in-plane Cu-O bending mode                                   |
| $E_u(3)$    | 559 562 561            | in-plane Cu-O stretching mode                                |
FIG. 1: The reflectivity of 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$_2$.

FIG. 2: The real part of the optical conductivity of Sr$_{0.9}$Ln$_{0.1}$CuO$_2$ obtained by a Kramers-Kronig analysis: 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$_2$.

FIG. 3: The atomic vibration patterns of Sr$_{0.9}$Ln$_{0.1}$CuO$_2$ with the tetragonal structure of P4/mmm(D$_{4h}^1$): black circle for Cu, white circle for O, and gray circle for Sr/Ln.
Fig. 1
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