Lattice dynamics and the spin-phonon interaction in $Bi_2Sr_2CoO_{6+\delta}$

H. L. Liu[A], H. C. Hsu[A,B], F. C. Chou[B,C], K. Koyama[D],
[A]*Department of Physics, National Taiwan Normal University, Taiwan*
[B]*Center of Condensed Matter Science, National Taiwan University, Taiwan*
[C]*National Synchrotron Radiation Research Center, Taiwan*
[D]*Institute for Materials Research, Tohoku University, Japan*

1. Introduction

$Bi_2Sr_2CoO_{6+\delta}$ has attracted attention because it is isostructural to the cuprate superconductor $Bi_2Sr_2CuO_{6+\delta}$. While $Bi_2Sr_2CuO_{6+\delta}$ is characterized by a network of CuO_2 planes and a transition temperature (T_c) of 10 K, $Bi_2Sr_2CoO_{6+\delta}$ contains CoO_2 planes with non-superconducting behavior. Furthermore, depending on the oxygen content, $Bi_2Sr_2CoO_{6+\delta}$ exhibits complicated magnetic properties [1]. When δ is close to 0.5, the Co ions have formal oxidation state 3+ and order antiferromagnetically at T_N ~ 250 K. The δ ~ 0.25 crystal has equal numbers of Co^{2+} and Co^{3+} and shows ferromagnetic behavior with a Curie temperature T_C ~ 100 K. For crystals with $0.25 < \delta < 0.5$, there is a strong tendency towards a phase separation in hole-rich Co^{3+} (antiferromagnetic) and hole-poor Co^{2+}-Co^{3+} (ferromagnetic) regions [1,2]. This phase separation is receiving great attention for its implications in the understanding of the ground state of strongly correlated electronic systems [3].

Despite much studies of the transport and magnetic properties[1,2], little is known about the phonon excitations in $Bi_2Sr_2CoO_{6+\delta}$. In this work, we investigate the temperature- and field-dependent X-ray powder diffraction (XRD) and optical reflectivity spectra of single-crystal $Bi_2Sr_2CoO_{6+\delta}$. We demonstrate that there is a strong interplay between lattice and spin degrees of freedom in this material.

2. Experimental

Single crystals of $Bi_2Sr_2CoO_{6+\delta}$ were grown by the traveling solvent floating zone method. The polycrystalline stoichiometry feed rod was prepared from a solid state reaction of Bi_2O_3, $SrCO_3$, and Co_3O_4 powders and the mixed powder was calcined at 850 ℃ for 12 h followed by a second anneal at 890 ℃ for 12 h. The final feed rod was annealed at 900 ℃ in air. A Bi_2O_3 rich flux was chosen at a molar ratio of 4:1 $Bi_2Sr_2CoO_6$ to Bi_2O_3. The oxygen content ($0.4 < \delta < 0.5$) of the crystal has been confirmed by the thermogravimetric analysis (TGA).

High magnetic field XRD experiments with Co $K\alpha$ radiation were carried at temperature between 10 K and 300 K using a Gifford-McMahon type cryocooler at the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University [4]. To accurately determine the structure of the sample and to avoid complications in the analysis due to the domain distribution and twinning, our measurements were performed on powder samples prepared by powdering single crystal. Near-normal incidence optical reflectance was measured by using a Bruker IFS 66v Fourier transform infrared spectrometer in the far-infrared and mid-infrared regions (80-6000 cm^{-1}). The near-infrared to near-ultraviolet regions (4000-55000 cm^{-1}) were covered using a Perkin-Elmer Lambda-900 spectrometer.

3. Results and Discussion

Figure 1 shows the magnetic dc-susceptibility of $Bi_2Sr_2CoO_{6+\delta}$ with the field applied along ab-plane as a function of temperature. One can identify an antiferromagnetic phase transition with T_N ~ 265 K. Figure 2 displays the zero-field temperature dependence

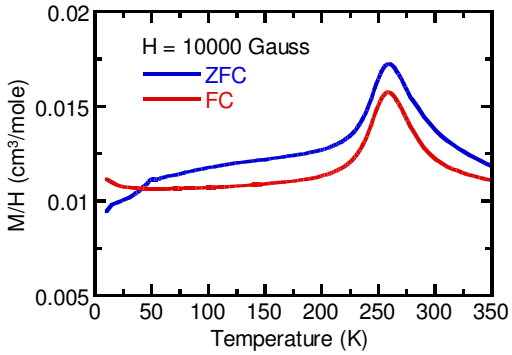

Fig. 1. Field-cooled (FC) and zero-field-cooled (ZFC) dc susceptibility vs. temperature in $Bi_2Sr_2CoO_{6+\delta}$.

of XRD profiles in the diffraction angle range of 29.0° < 2θ < 34.0° with step size of 0.01°. Here, *hkl* denotes the Miller indices. The XRD spectra do not change significantly with temperature, which implies there is no structural phase transition within the temperature range investigated. Only upon cooling below 300 K, $Bi_2Sr_2CoO_{6+\delta}$ show a decrease of the a- and c-axis lattice constants, mainly due to the thermal contraction effects. Notably, no field-induced changes of XRD peaks were found up to 5 Tesla. The absence of any field-induced effects indicates that the crystallographic structures of $Bi_2Sr_2CoO_{6+\delta}$ is robust against the external magnetic fields.

We now describe the temperature-dependent far-infrared conductivity spectra, shown in Fig. 3. According to a factor group analysis, $Bi_2Sr_2CoO_6$ has a tetragonal structure with space group *I4/mmm* in which a total of eleven infrared-active modes are expected; five

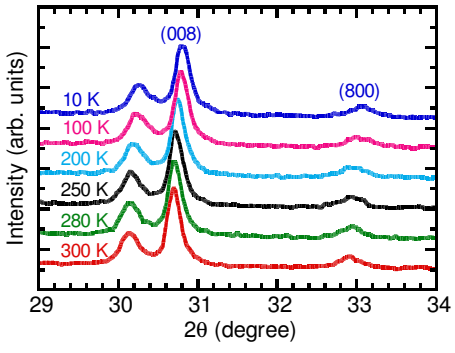

Fig. 2. Zero-field XRD profiles of $Bi_2Sr_2CoO_{6+\delta}$.at temperature between 300 K and 10 K.

A_{2u} mode along the *c* axis, and six E_u modes in the *ab* plane [5]. In our oxygen-doped sample, the *ab*-plane $\sigma_1(\omega)$ of $Bi_2Sr_2CoO_{6+\delta}$ exhibits eleven phonon resonances at about 80, 106, 144, 164, 203, 238, 341, 376, 457, 480, and 588 cm^{-1}. The greater number of phonon lines in the present sample implies that that assumption of tetragonal symmetry is good only as a first approximation. It is likely that oxygen doping destroys the inversion symmetry in the unit cell. This broken symmetry results in more general selection rules, so that vibrations in the undoped material which are active only along one polarization may become active in several in the doped material. A detailed assignment of the observed infrared phonon components was not attempted since the lattice dynamic computations are not presently available. Despite these limitations, there is agreement in the literature that the two low-frequency peaks at about 203 and 238 cm^{-1} correspond to the in-phase and out-of-phase Co-O bond-bending modes [6]. The highest-frequency peak at about 588 cm^{-1} is related to the in-plane oxygen stretching like vibration of the CoO_4 squares [7].

As the temperature is lowered, most of phonon peaks shift to higher frequency and become narrower. This hardening can be explained by means of thermal effects. However, upon crossing the antiferromagnetic phase transition, there are three important changes in certain modes below T_N: (i) a saturation of the softening of the 203 cm^{-1} mode; (ii) a gradual splitting of the 238 cm^{-1} mode, and (iii) .an asymmetric line shape of the 588 cm^{-1} mode. Since $Bi_2Sr_2CoO_{6+\delta}$ shows no drastic temperature dependence of a crystal structure and lattice parameters, the remarkable modifications of three phonon peaks below the magnetic ordering temperature must be due to spin-phonon interaction. The observed softening for the 203 cm^{-1} mode scales with the normalized square of the sublattice magnetization [1]. The phonon splitting of the 238 cm^{-1} mode suggests that a kind of spin-driven structural instability occurs. The asymmetric line shape of the 588 cm^{-1} mode derives primarily from an interaction between the lattice vibrations and a magnetic continuum.

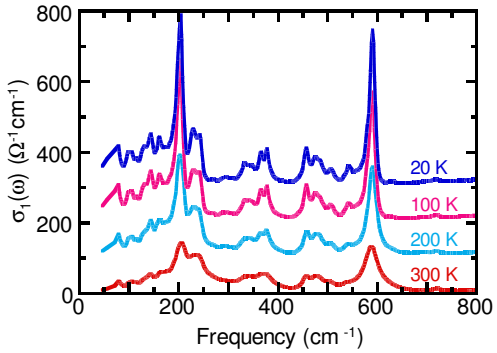

Fig. 3. The temperature dependence of far-infrared conductivity spectra of $Bi_2Sr_2CoO_{6+\delta}$. For clarity, the ordinate has been offset by 20% of the maximum of Y-axis for the successive spectra.

4. Conclusion

We have performed the temperature- and field-dependent XRD and optical reflectivity measurements of single-crystal $Bi_2Sr_2CoO_{6+\delta}$. The XRD profiles show temperature dependence that has no relationship to the antiferromagnetic phase transition. The crystal symmetry is retained up to 5 Tesla. Interestingly, three optical phonons are visibly affected by the magnetic ordering that could be attributed to a strong spin-phonon interaction.

Reference

[1] K. J. Thomas, Y. S. Lee, F. C. Chou, B. Khaykovich, P. A. Lee, M. A. Kastner, R. J. Cava, and J. W. Lynn, Phys. Rev. B **66**, 054115 (2002).

[2] Y. Nagao, I. Terasaki, and T. Nakano, Phys. Rev. B **76**, 144203 (2007).

[3] A. Moreo, S. Yunoki, and E. Dagotto, Science **283**, 2034 (1999), and references therein.

[4] K. Watanabe, Y. Watanabe, S. Awaji, M. Fujiwara, N. Kobayashi, and T. Hasebe, Adv. Cryog. Engin. **44**, 747 (1998).

[5] G. Burns, G. B. Chandrashekhar, F. H. Dacol, M.W. Shafer, and P. Strobel, Solid State Communications **67**, 603 (1988).

[6] A. A. Tsvetkov, D. Dulic, D. van der Marel, A. Damascelli, G. A. Kaljushnaia, J. I. Gorina, N. N. Senturina, N. N. Kolesnikov, Z. F. Ren, J. H. Wang, A. A. Monovsky, and T. T. M. Palstra, Phys. Rev. B **60**, 13196 (1999).

[7] M. A. Quijada, D. B. Tanner, F. C. Chou, D. C. Johnston, and S. -W. Cheong, Phys. Rev. B **52**, 15485 (1995).