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2015 New J. Phys. 17 103004

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PAPER

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1 June 2015REVISED
6 September 2015ACCEPTED FOR PUBLICATION
9 September 2015PUBLISHED
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and DOI.H L Liu^{1,6}, T Y Ou-Yang^{2,3}, H H Tsai¹, P A Lin^{4,5}, H T Jeng⁴, G J Shu³ and F C Chou³¹ Department of Physics, National Taiwan Normal University, Taipei 11677, Taiwan² Department of Physics, National Taiwan University, Taipei 10617, Taiwan³ Center for Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan⁴ Department of Physics, National Tsing Hua University, Hsinchu 30013, Taiwan⁵ Center for Measurement Standards, Industrial Technology Research Institute, Hsinchu 31040, Taiwan⁶ Author to whom any correspondence should be addressed.E-mail: hliu@ntnu.edu.tw**Keywords:** strongly correlated electron system, optical properties, Raman and optical spectroscopy**Abstract**

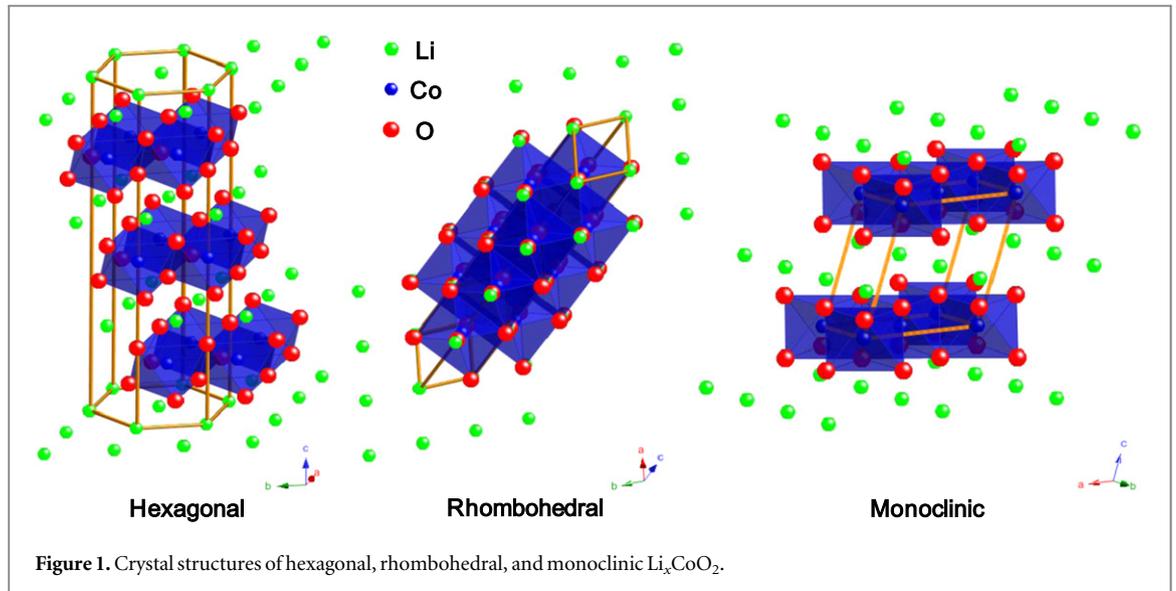
Spectroscopic ellipsometry and Raman scattering measurements of single-crystal Li_xCoO_2 ($x = 0.33, 0.43, 0.50, 0.53, 0.72$, and 0.87) are reported. The room temperature optical absorption spectra for x values in the range of 0.33 – 0.72 exhibit three bands near 1.60 , 3.35 , and 5.20 eV. On the basis of first-principles calculations, the observed optical excitations were appropriately assigned. The charge-transfer absorption bands shift to higher energies in $\text{Li}_{0.87}\text{CoO}_2$ because of symmetry-breaking-induced distortions of the hybridized Co-O orbitals with shifted oxygen $2p$ states. Furthermore, two Raman-active phonon modes, which display E_g and A_{1g} symmetry, are sensitive to lithium doping. Upon cooling across 200 K, which is the antiferromagnetic phase transition temperature of $\text{Li}_{0.50}\text{CoO}_2$, large splitting of the E_g mode and a discontinuous change in the frequency of the A_{1g} mode were observed. These results highlight the importance of spin-phonon coupling in $\text{Li}_{0.50}\text{CoO}_2$.

1. Introduction

Layered lithium cobaltites (Li_xCoO_2) have attracted considerable attention in recent years. The interest has been stimulated not only by their practical applications as rechargeable battery electrode materials and electrochromic displays [1, 2], but also by a need to understand the mechanism underlying their complex physical properties [3–9]. The fully lithiated compound with stoichiometry LiCoO_2 has a hexagonal structure belonging to the $R\bar{3}m$ space group. The building blocks are edges-sharing CoO_6 octahedra; the edges are linked to form CoO_2 sheets and they are separated by layers of lithium atoms, as shown in figure 1 [10]. During the oxidation of Li_xCoO_2 , the crystal structure can be described by a rhombohedral group. A monoclinic phase appears in the compound of $x = 0.50$ [7, 9, 10]. Furthermore, depending on the lithium content, Li_xCoO_2 exhibits various interesting electronic, magnetic, and thermoelectric properties [3, 5–9].

LiCoO_2 is an insulator with a band gap of 2.7 eV [11, 12]. Its magnetic susceptibility is low and shows weak temperature dependence because of the nonmagnetic low-spin state of Co^{3+} (t_{2g}^6) ions [6]. The delithiated compound Li_xCoO_2 contains Co^{4+} (t_{2g}^5) ions and shows hole doping in the t_{2g} orbitals. Li_xCoO_2 with $x \geq 0.94$ is semiconducting, whereas the highly Li-deficient phase ($0.75 \geq x \geq 0.25$) exhibits a metallic character [7, 13, 14]. At $x = 0.75$, unusually high thermoelectric power and metallic conductivity appear simultaneously [8]. In the ranges of $x \geq 0.94$ and $0.75 \geq x \geq 0.50$, Li_xCoO_2 shows Curie–Weiss behavior, whereas it becomes Pauli-paramagnetic for $x \leq 0.40$ [3, 5–8]. Notably, for $x = 0.50$ and 0.67 , a magnetic anomaly is observed near 175 K [6]. For $x = 0.40$, a susceptibility hump is detected at 30 K [6]. All these observations suggest that the physical properties of these materials are complex.

Despite intense research having been conducted on layered lithium cobaltites, their optical and phonon properties have remained relatively unexplored [11, 12, 15–18]. Moreover, previous studies on Li_xCoO_2 were limited to powder samples. Recently, we employed the electrochemical deintercalation method for synthesizing Li_xCoO_2 single crystals [9]. A- and chain-type antiferromagnetic orderings were observed for $x = 0.87$ and 0.50



at approximately 10 and 200 K [9]. For compounds with $x = 0.53, 0.50,$ and 0.43 , three phases with distinct physical properties were identified [9]. The peculiar magnetic anomaly observed near 175 K for powder samples could be associated with a minor phase preferentially formed on the surface or at grain boundaries [9].

In this study, we employed both spectroscopic ellipsometry and Raman scattering spectroscopy to elucidate the electronic and phononic excitations of Li_xCoO_2 , and we compared our results with the predictions of first-principles calculations. Understanding the intrinsic mechanisms governing the optical and phonon properties of Li_xCoO_2 is vital for device applications. Our overall objective was to identify the doping dependence of the crystal architecture, electronic structure, and lattice dynamics relationships of Li_xCoO_2 .

2. Technical details

2.1. Experiment

A series of single-crystal Li_xCoO_2 samples with $x = 0.33, 0.43, 0.50, 0.53, 0.72,$ and 0.87 were prepared through electrochemical deintercalation of pristine $\text{Li}_{0.87}\text{CoO}_2$. The details of sample preparation were reported elsewhere [9]. The crystals were thin platelets with dimensions of approximately $2 \times 2 \times 0.5 \text{ mm}^3$. Crystals of the same batch were characterized using synchrotron x-ray powder diffraction, dc resistivity, and magnetization measurements [9].

Spectroscopic ellipsometric measurements were performed for multiple angles of incidence between 60° and 75° by using a Woollam M-2000U ellipsometer over the spectral range 0.73–6.42 eV. The reproducibility of the spectra was confirmed at different regions on the sample surfaces by using a combination of focusing optics and spectroscopic ellipsometry for spot ($100 \times 100 \mu\text{m}^2$) measurements.

Micro-Raman scattering experiments were performed in a backscattering geometry by using a diode-pumped solid-state laser with an excitation wavelength of 532 nm. The linearly polarized light was focused on a $3 \mu\text{m}$ diameter spot on a sample surface, and the scattered light was collected and dispersed using a SENTERRA spectrometer equipped with a 1024 pixel wide charge-coupled detector. The polarizations of incident and scattered light were chosen so that they are parallel (parallel) or perpendicular (cross) to each other. The spectral resolution achieved using these instruments is typically less than 1 cm^{-1} . To avoid heating effects, the laser power was set to less than 0.2 mW. The sample was placed in a continuous-flow helium cryostat, which enabled measurements in the temperature range of 10–300 K.

2.2. Theoretical methods

We performed the first-principles calculations of electronic structure by using the full-potential projected-augmented-wave method as implemented in the VASP package within the generalized-gradient approximation (GGA) plus Hubbard U (GGA + U) scheme [19–22]. The material Li_xCoO_2 was simulated in the supercell approach under structure optimizations based on the experimental lattice structure [6]. The calculations were performed over 100 k -points in the irreducible Brillouin zones with a cutoff energy of 400 eV. On-site Coulomb energy $U = 4 \text{ eV}$ and exchange parameter $J = 1 \text{ eV}$ were used for cobalt to explore the correlation effects in $3d$ orbitals.

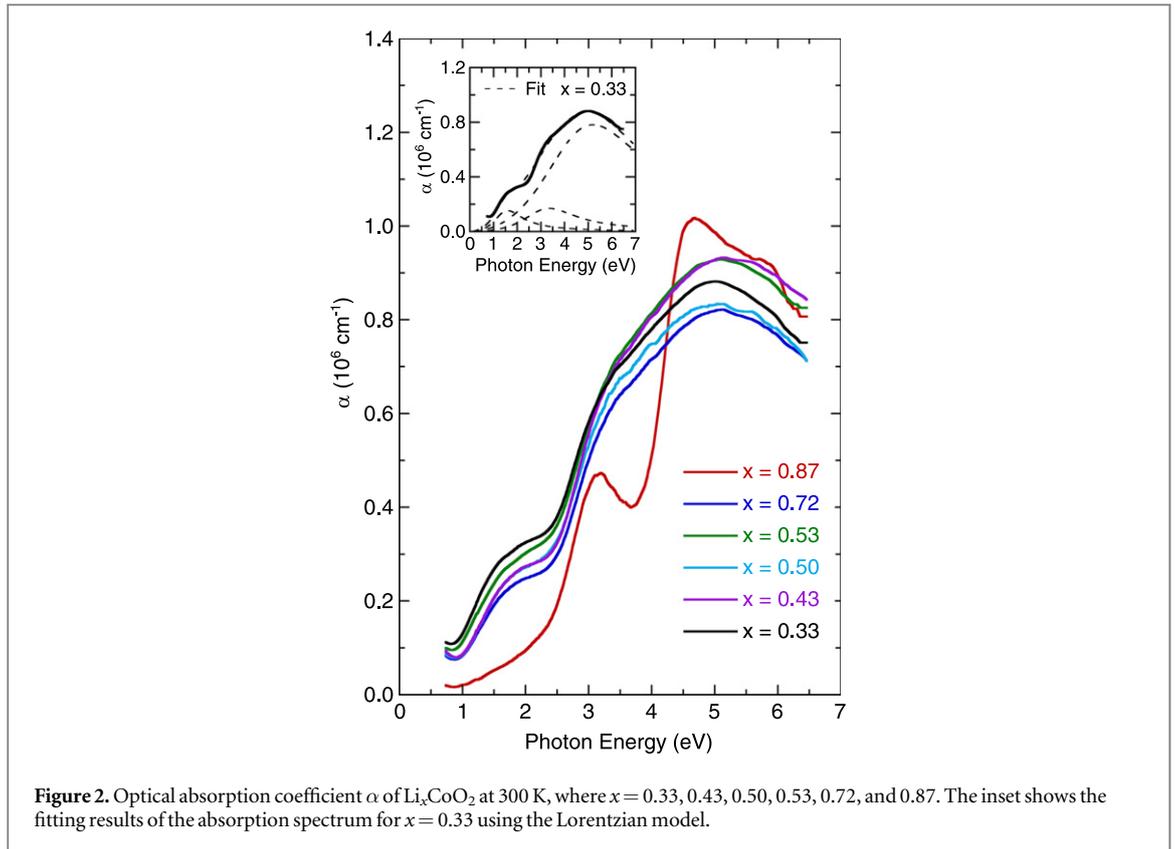


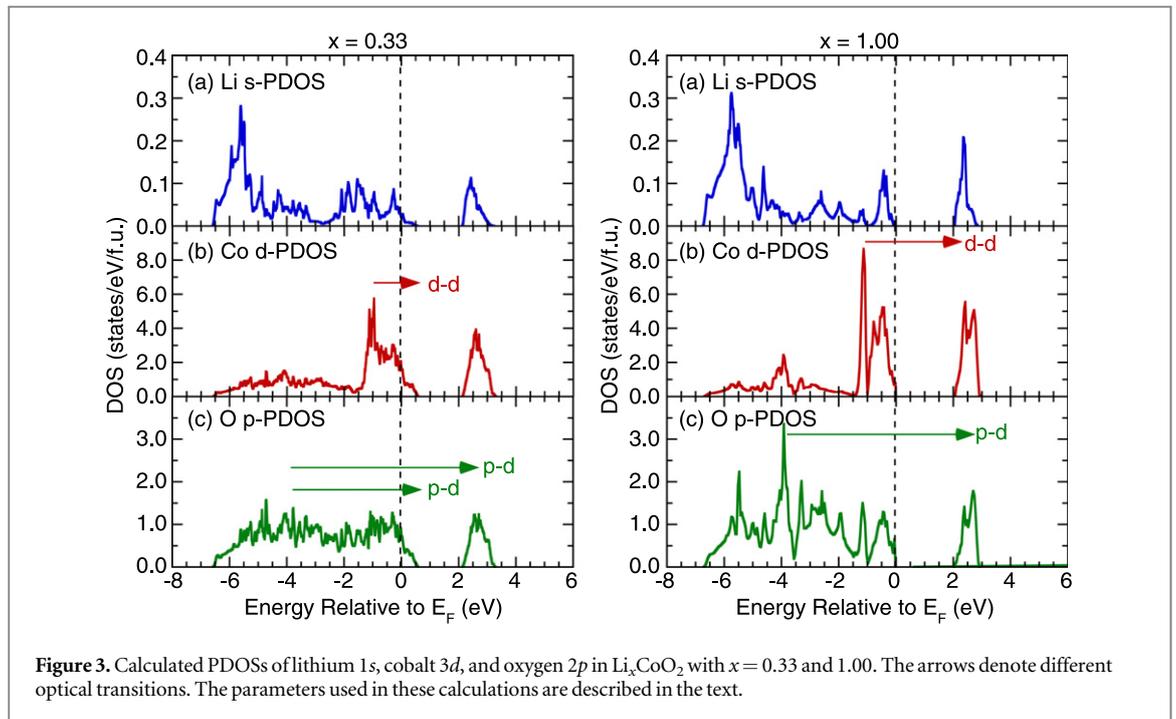
Figure 2. Optical absorption coefficient α of Li_xCoO_2 at 300 K, where $x = 0.33, 0.43, 0.50, 0.53, 0.72,$ and 0.87 . The inset shows the fitting results of the absorption spectrum for $x = 0.33$ using the Lorentzian model.

3. Results and discussion

3.1. Electronic excitations

Figure 2 shows the room temperature optical absorption spectra of Li_xCoO_2 obtained through spectroscopic ellipsometry analysis. These absorption spectra can be modeled reasonably well by using Lorentzian oscillators. For $x = 0.33$ – 0.72 , low-energy absorption shows a finite value. With an increase in the photon energies, the absorption gradually increases, manifests two bands near 1.60 and 3.35 eV, reaches a maximum value at approximately 5.20 eV, and then levels off. The positions of the three absorption peaks vary only slightly among the different lithium doping levels. By contrast, the low-energy absorption for $x = 0.87$ is low, and the first low-energy peak near 1.60 eV completely disappears. The three absorption bands are observed at approximately 3.08, 4.55, and 5.76 eV, reflecting changes in the electronic structure of the compound.

To assign the observed absorption peaks of Li_xCoO_2 , we calculated the partial densities of states (PDOSs) of lithium 1s, cobalt 3d, and oxygen 2p electrons for compounds with $x = 0.33$ and 1.00 (figure 3). Three crucial features can be observed in figure 3. First, the magnitude of PDOS of lithium 1s is considerably smaller than that of other atoms, and therefore, the PDOS has no influence on the absorption bands. Second, the PDOS for $x = 0.33$ exhibits nonzero electron density at the Fermi level, thereby reflecting metallic behavior. By contrast, the PDOS for $x = 1.00$ evidences insulating behavior with a band gap of 2.0 eV. Third, both the highest occupied and lowest unoccupied levels mainly show a cobalt 3d character, while oxygen 2p orbitals contribute to a much smaller extent. On the basis of these theoretical calculation results, we assigned the observed excitation near 1.60 eV to the on-site *d-d* transition between the occupied cobalt *d* states right below E_F and the unoccupied *d* states. Its energy scale is comparable to that of the band calculated for HoCoO_3 (~ 2.04 eV) and LaCoO_3 (~ 1.93 eV) [23]. In principle, optical excitations between *d* orbitals are forbidden because of the selection rule for electric dipole transitions. However, strong hybridization between oxygen 2p and cobalt 3d orbitals leads to the breaking of local symmetry, thereby enabling these transitions [24]. The absorption peaks near 3.35 and 5.20 eV were assigned to charge-transfer transitions from the occupied hybridized oxygen 2p with cobalt 3d states to the unoccupied cobalt 3d states [25, 26]. Our results also show great similarity with the local density approximation calculations of Na_xCoO_2 [27]. The observed 1.6 eV absorption peak in Na_xCoO_2 ($x = 0.25, 0.50, 0.70,$ and 0.75) [28, 29] corresponded to the transition from the occupied cobalt 3d t_{2g} to the empty cobalt 3d e_g states [27]. The higher energy absorption band at 3.1 eV observed in Na_xCoO_2 [28, 29] was assigned to the transitions from the fully occupied oxygen 2p states to the unoccupied cobalt 3d e_g states [27].

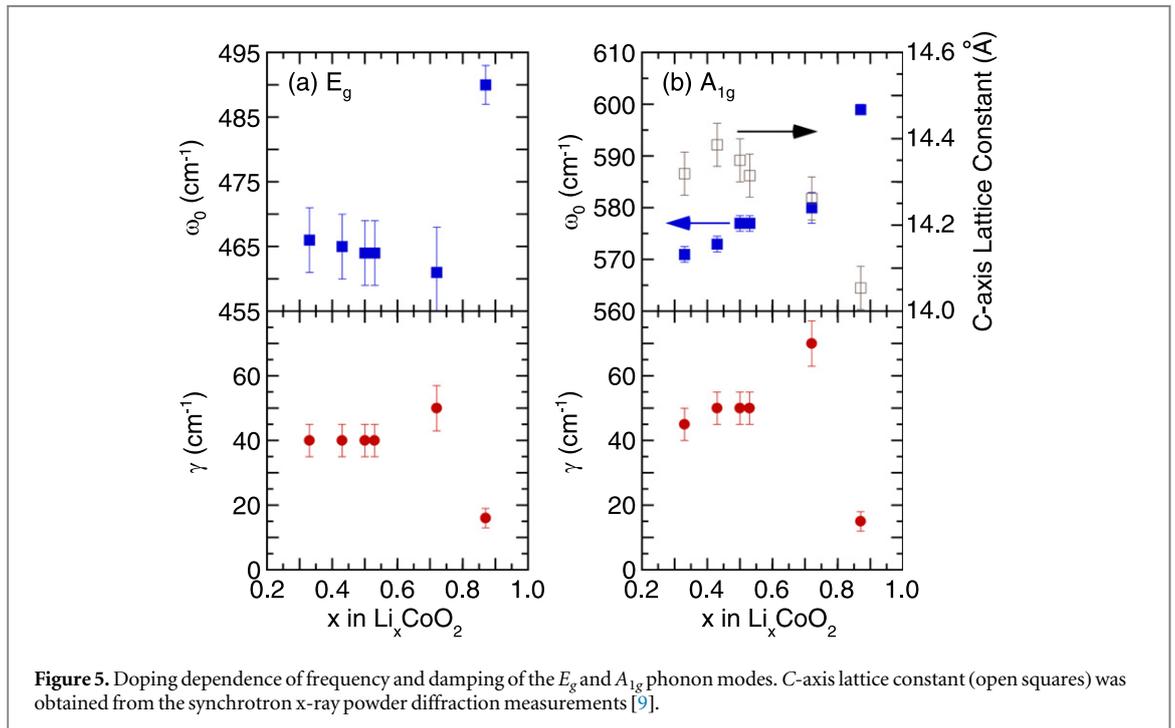
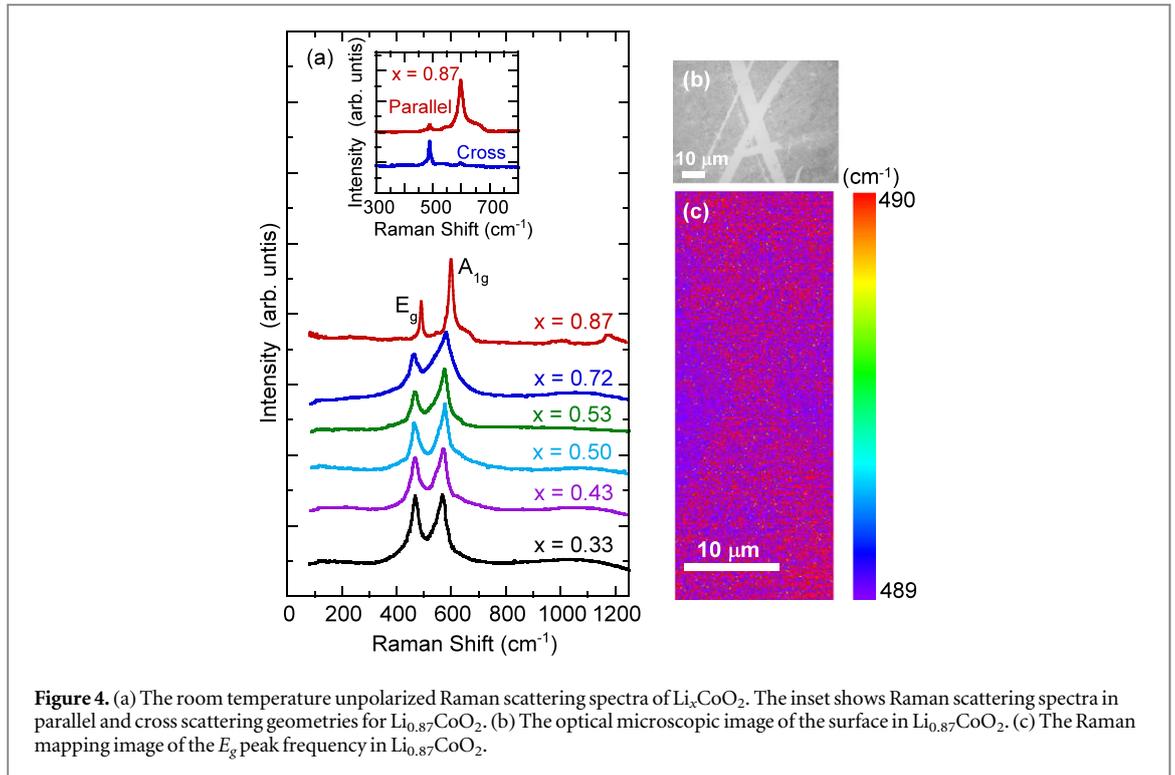


As mentioned, the absorption spectrum for $x = 0.87$ is different from that for other lithium doping levels. We assigned the observed peak near 3.08 eV to the on-site $d-d$ transition. Furthermore, the c -axis lattice parameter (14.057 Å) for $x = 0.87$ is lesser than that (14.319 Å) for $x = 0.33$ [9]. This modification splits the t_{2g} and e_g states of the cobalt 3d orbital. Accordingly, the PDOS of hexagonal LiCoO_2 (figure 3) reveals that the unoccupied cobalt 3d states show two peaks and that the highest occupied 3d states show three peaks. Strong peaks of the oxygen 2p states are farther from the Fermi level. The net effect is that the charge-transfer bands are shifted to higher energies.

3.2. Vibrational properties

Figure 4(a) shows the room-temperature Raman scattering spectra of Li_xCoO_2 with six different lithium contents. The spectra comprise two main first-order Raman phonon modes. We fitted these phonon peaks by using a standard Lorentzian profile (the inset of figure 6). The doping dependence of the fitting parameters is shown in figure 5. According to factor group analysis, the pristine sample with $x = 0.87$ has a hexagonal structure (space group $R\bar{3}m$) containing one formula unit per primitive cell. The Γ -point normal modes can be decomposed as $A_{1g} + E_g + 2A_{2u} + 2E_{2u}$ [15, 16]. These modes are classified as Raman-active ($A_{1g} + E_g$) and infrared-active ($A_{2u} + E_{2u}$). Thus, $\text{Li}_{0.87}\text{CoO}_2$ exhibits two strong Raman phonon modes at approximately 489 and 598 cm^{-1} . The inset of figure 4(a) shows Raman scattering spectra of parallel and cross measurements for $\text{Li}_{0.87}\text{CoO}_2$. The 598 cm^{-1} mode in cross geometry is much more suppressed than the other mode, indicating that it is of A_{1g} character. By contrast, the 489 cm^{-1} mode shows E_g symmetry. The E_g mode involves in-plane O-Co-O bending motions, whereas the A_{1g} mode results from out-of-plane Co-O stretching motions [15–18]. The low-intensity broad contributions of phonon modes around 1000 and 1175 cm^{-1} should be ascribed to multiphonon processes. Notably, spatial maps of the Raman frequency for the E_g mode (figure 4(c)) show uniform color contrast in each $\text{Li}_{0.87}\text{CoO}_2$ domain (figure 4(b)), confirming that the frequency of the E_g mode varies only slightly with location within a sample. This evidence indicates that our $\text{Li}_{0.87}\text{CoO}_2$ single crystal is in a purely hexagonal phase. This result differs from previous results indicating two coexisting hexagonal phases on the basis of observations of powder forms [16].

Upon a decrease in the lithium content, the positions of the E_g and A_{1g} mode shift toward lower frequencies and their linewidths broaden substantially. As indicated by the crystal structure analysis [5–7, 9], Li_xCoO_2 samples of $x = 0.33, 0.43, 0.53,$ and 0.72 have the rhombohedral space group and the phase with $x = 0.50$ belongs to the monoclinic system. Therefore, the frequency of the E_g mode observed for $x = 0.87$ (figure 5(a)) differs considerably from that for other doping levels. Furthermore, when lithium was deintercalated, the increase in the c -axis lattice constant resulted in red-shifting of the frequency of the A_{1g} mode (figure 5(b)). Our results are in reasonable agreement with recent first-principles calculations of phonon properties of LiCoO_2 and its delithiated state [30]. The broadening of the E_g and A_{1g} modes in compounds with low lithium doping could have been caused by an increase in the lattice disorder.



The temperature-dependent Raman scattering spectra of sample with $x = 0.50$ are presented in figure 6. The sample with $x = 0.53$ yielded qualitatively similar results. With a decrease in the temperature, the peak positions of the E_g and A_{1g} modes shifted to higher frequencies and the resonance linewidth narrowed. However, the positions of the two modes show peculiar behavior below 200 K. Figure 7 further illustrates the frequency, damping, and oscillator strength of the two modes as a function of temperature. First consider the E_g mode at approximately 464 cm^{-1} in figure 7(a); the phonon mode is associated with in-plane O-Co-O bending vibrations. As the temperature was lowered from 300 to 200 K, the phonon frequency of the E_g mode increased slightly, as expected for an anharmonic solid. Notably, splitting of the frequencies can be clearly observed below 200 K. The overall amount of splitting is approximately 18 cm^{-1} at 10 K. In figure 7(a), the damping is constant

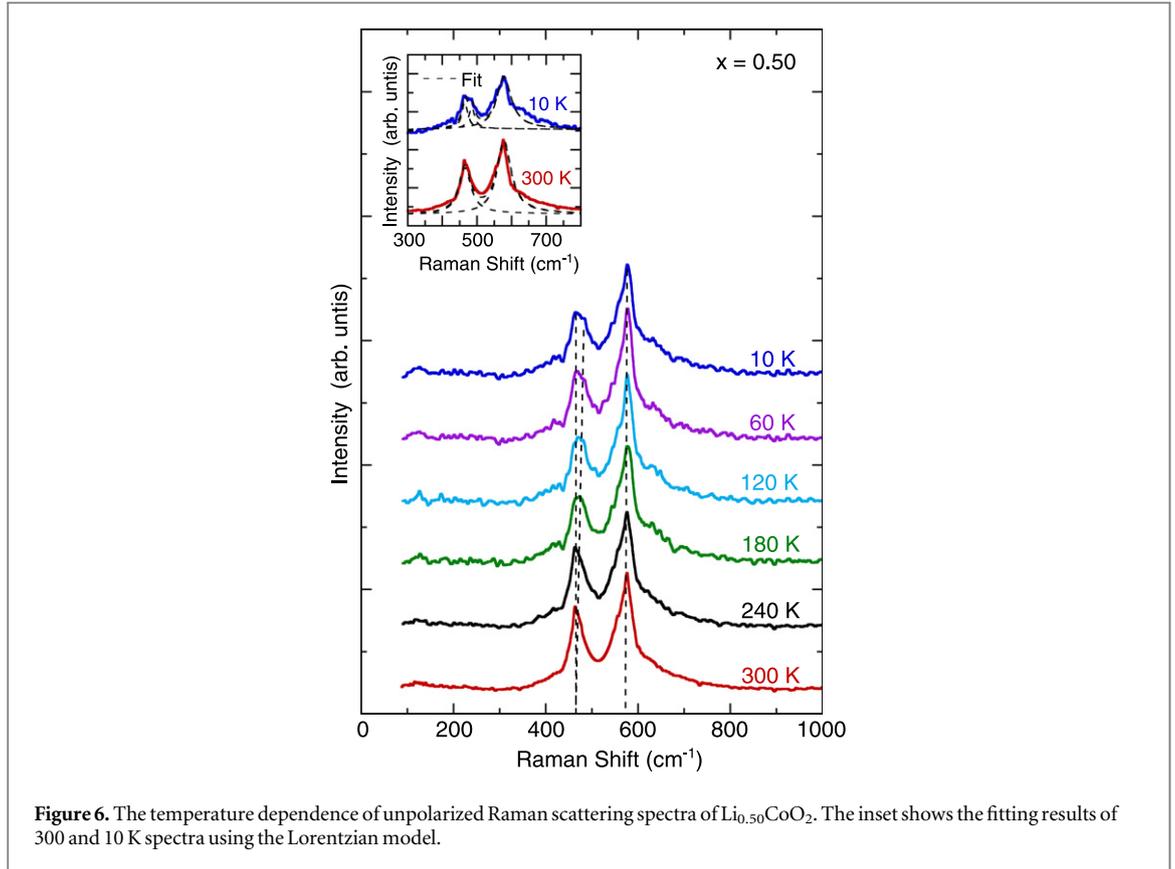


Figure 6. The temperature dependence of unpolarized Raman scattering spectra of $\text{Li}_{0.50}\text{CoO}_2$. The inset shows the fitting results of 300 and 10 K spectra using the Lorentzian model.

between 300 and 200 K, but decreases below 200 K. The oscillator strength decreases from 300 to 200 K, but exhibits little temperature dependence at lower temperatures.

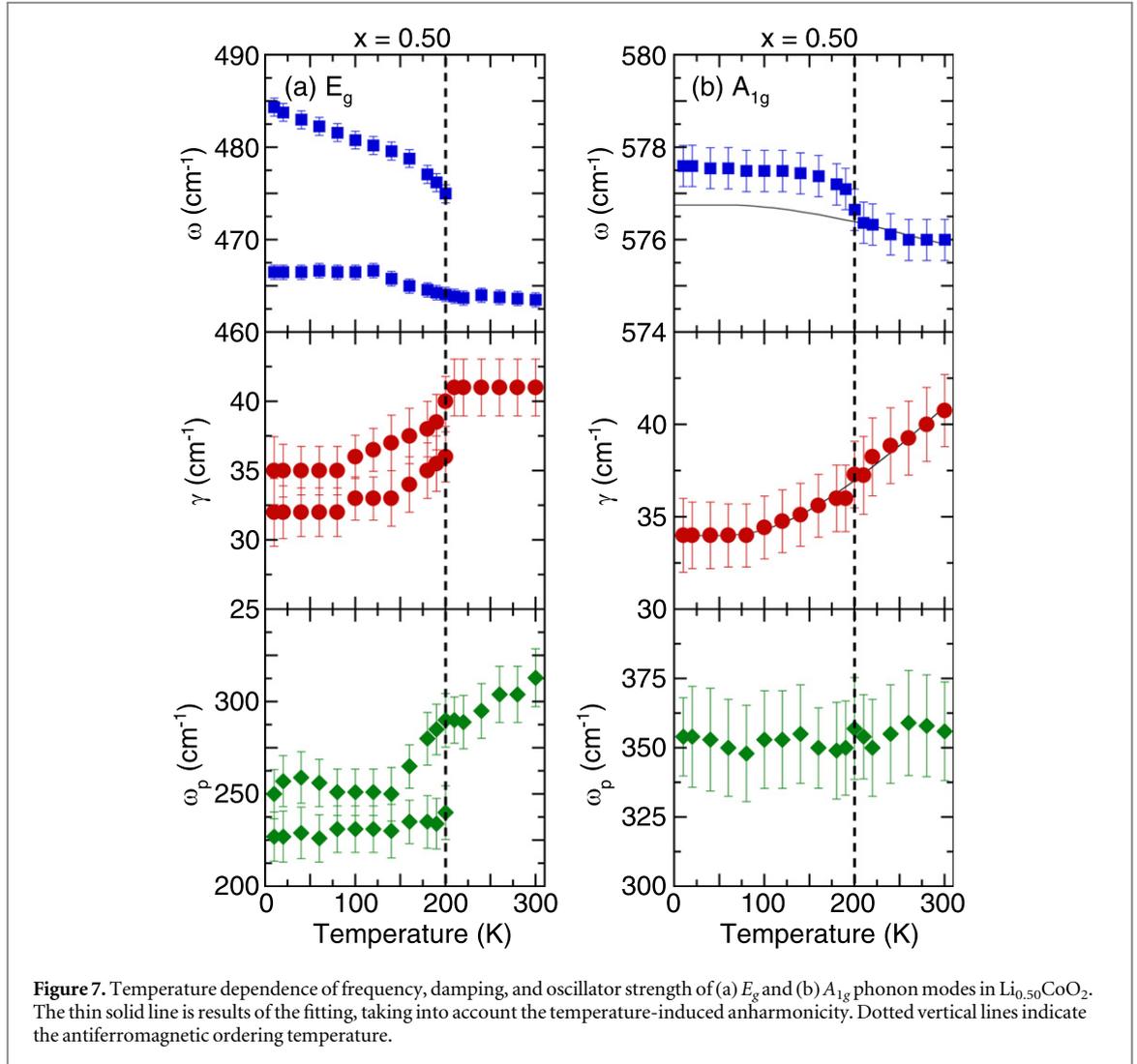
The most striking feature in figure 7(a) is the splitting of the E_g mode below 200 K, and at 10 K the amplitude of this splitting, which is approximately 4% of the mode frequency, is anomalously large. Since chain-type antiferromagnetic ordering has previously been detected in $\text{Li}_{0.50}\text{CoO}_2$ at approximately 200 K on the basis of magnetic susceptibility measurements [9], the observed large splitting of the E_g mode across the phase transition temperature should be closely related to the coupling between the lattice and spin degrees of freedom. Such phonon splitting behavior near T_N is similar to that of infrared-active phonon modes observed in antiferromagnetic transition metal oxides [26, 31, 32]. We speculate that the doubly degenerate in-plane E_g phonons are lifted because of strong spin-phonon interaction. Strong magnetoelastic coupling reflects the modulation of the Co-O-Co superexchange interaction by the E_g phonon in the antiferromagnetic phase and contributes to the anomalous behavior of this mode for $T < T_N$. Low-temperature high-resolution synchrotron x-ray diffraction experiments currently under way could facilitate acquiring conclusive evidence for magnetic-order-induced local symmetry breaking in $\text{Li}_{0.50}\text{CoO}_2$.

Finally, the temperature dependence of the A_{1g} mode at approximately 576 cm^{-1} is of particular interest (figure 7(b)). This phonon, related to out-of-plane Co-O stretching vibrations, gradually hardens as the temperature decreases from 300 to 200 K. However, the frequency of the A_{1g} mode changes discontinuously at T_N ; for $T < T_N$ the position of the mode continues to increase. In a normal anharmonic solid, with a decrease in the temperature, the phonon frequency should increase, while damping decreases. Anharmonic interactions are relevant to the high-order terms of atomic vibrations, beyond the traditional harmonic terms. The temperature-dependent phonon frequency and linewidth can be written as [33]

$$\omega(T) = \omega_0 + A \left(1 + \frac{2}{\exp(\hbar\omega_0/2k_B T) - 1} \right), \quad (1)$$

and

$$\gamma(T) = \gamma_0 + B \left(1 + \frac{2}{\exp(\hbar\omega_0/2k_B T) - 1} \right), \quad (2)$$



where ω_0 and γ_0 are the intrinsic frequency of the optical phonon mode and linewidth broadening because of defects. Parameters A and B are the anharmonic coefficients, and $\frac{1}{\exp(\hbar\omega_0/2k_B T) - 1}$ corresponds to the thermal population factor of acoustic modes. For the analysis of anharmonic contributions to the A_{1g} mode, the values of ω_0 ($\approx 577 \text{ cm}^{-1}$), γ_0 ($\approx 34 \text{ cm}^{-1}$), A (≈ -1.3), and B (≈ 9.1) were determined. The parameter A is negative, indicating that the peak shifts to a lower frequency with an increase in the temperature because of anharmonic phonon decay. By contrast, the parameter B is positive, reflecting linewidth narrowing with a decrease in the temperature. The solid lines in figure 7(b) are theoretical predictions based on equations (1) and (2), and they are in good agreement with the experimental data. Notably, the frequency of the A_{1g} mode deviates from the theoretical predictions below 200 K. We attribute this deviation mainly to spin-phonon coupling in the antiferromagnetic state of $\text{Li}_{0.50}\text{CoO}_2$.

4. Summary

We employed both spectroscopic ellipsometry and Raman scattering spectroscopy to investigate the doping dependence of electronic structure and lattice dynamics in Li_xCoO_2 single crystals. Furthermore, we characterized the optical transitions comprehensively by comparing experimental data and the results of first-principles calculations. The optical absorption spectra for x values in the range of 0.33–0.72 exhibit three features at approximately 1.60, 3.35, and 5.20 eV. The first peak was attributed to a transition between the occupied t_{2g} to the empty e_g states of cobalt $3d$ orbitals. The other two peaks were attributed to charge transfer transitions between oxygen $2p$ and cobalt $3d$ states. For the x value of 0.87, because of the symmetry-breaking-induced distortions of the hybridized Co-O orbitals with shifted oxygen $2p$ states, its charge-transfer excitations are blue-shifted. Moreover, characteristic changes were observed in the Raman phonon modes of E_g and A_{1g} symmetry with a change in the lithium concentration, and the changes were correlated with the crystal structure.

A decrease in the temperature leads to the E_g phonon mode splitting, and the frequency of the A_{1g} vibration changes discontinuously at 200 K, which is the antiferromagnetic transition temperature of $\text{Li}_{0.50}\text{CoO}_2$. These results suggest that the onset of antiferromagnetic ordering alters the character of atomic displacements, evidencing that strong spin–phonon coupling occurs in $\text{Li}_{0.50}\text{CoO}_2$.

Acknowledgments

HLL thanks technical support for the use of the laser Raman microscope (Raman-11) from Nanophoton Inc. HLL acknowledges financial support from the Ministry of Science and Technology of Republic of China under grant No. NSC 102-2112-M-003-002-MY3.

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