

Infrared Spectroscopy of the Charge Ordering Transition of $\text{Na}_{0.5}\text{CoO}_2$

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We report infrared reflectivity study of charge ordering in a $\text{Na}_{0.5}\text{CoO}_2$ single crystal. In comparison with $x = 0.7$ and 0.85 compounds, we found that the effective carrier density increases systematically with decreasing Na contents. The charge ordering transition only affects the optical spectra below 1000 cm^{-1} . A hump near 800 cm^{-1} develops below 100 K , which is accompanied by the appearance of new lattice modes as well as the strong antiresonance feature of phonon spectra. These observations signify a polaronic characteristic of charge carriers. Below T_{co} , an optical gap develops at the magnitude of $2\Delta \approx 3.5k_B T_{\text{co}}$ ($T \ll T_{\text{co}}$), evidencing an insulating charge density wave ground state.

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The recent discovery of superconductivity at 5 K in hydrated sodium cobaltate, $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ [1], has stimulated many studies on correlated electrons in a two-dimensional triangular lattice. The precursor host compound of this superconductor is unhydrated Na_xCoO_2 . It consists of alternate stacks of Na and CoO_2 layers with edge sharing CoO_6 octahedra. The physical properties of Na_xCoO_2 depend strongly on the Na concentration. Recent transport, magnetic, and structural studies on single crystals of Na_xCoO_2 for $0.3 < x < 0.75$ revealed a crossover from an unusual Curie-Weiss metal near $x = 0.7$ to a paramagnetic metal for x near 0.3 . The composition that separates the two metallic regimes at higher and lower Na concentrations, $\text{Na}_{0.5}\text{CoO}_2$, undergoes a transition into an insulating state at 53 K , accompanied by a giant increase of Hall coefficient. Electron diffraction studies revealed the presence of an orthorhombic symmetry of superlattice in $\text{Na}_{0.5}\text{CoO}_2$, which was attributed to Na ordering [2]. Neutron powder diffraction measurements further revealed an ordering of the Na ions into zigzag chains along one crystallographic direction, which decorates the chains of Co ions with different amounts of charges [3].

Charge ordering in Na_xCoO_2 is a subject of great interest. It was suggested to be a major instability in the narrow conduction band of the CoO_2 layer, in addition to the superconductivity [4]. Charge ordering at commensurate fillings $x = 1/4$ and $1/3$ were studied in detail and regarded as a competitor for the superconductivity observed in the range of $1/4 \leq x \leq 1/3$ in hydrated Na_xCoO_2 [4–6]. Possible charge ordered states at other commensurate fillings $x = 1/2$, $2/3$, and $3/4$ were also proposed [4–6]. Those charge ordered states are believed to be easily frustrated by the random potential from the neighboring Na layers, resulting in a glassy phase, which is likely responsible for the anomalous metallic behavior.

Experimentally, although NMR measurements point towards possible charge orderings in Na_xCoO_2 for $0.5 \leq x \leq 0.75$ [7,8], an unambiguous charge ordering state with localized electrons was observed only for $x = 0.5$, as we have mentioned above.

Infrared spectroscopy is a powerful tool to probe the charge excitations of an electronic system. Infrared investigations on metallic $\text{Na}_{0.5}\text{CoO}_2$ with different Na concentration have been reported by several groups [9–12]. In this work, we present the in-plane optical measurements at different temperatures on $\text{Na}_{0.5}\text{CoO}_2$ single crystals, focusing on the evolution of the electronic states across the charge ordering transition. In comparison with $x = 0.7$ and 0.85 compounds, we found that the spectral weight associated with the conducting carriers at high temperature increases systematically with decreasing Na contents. The charge ordering transition affects the conductivity spectrum only below 1000 cm^{-1} . A broad hump near 800 cm^{-1} develops below 100 K , with its intensity further enhanced at lower temperature. Upon entering the charge ordering state, a sharp suppression of the spectral weight is seen near 250 cm^{-1} , indicating the opening of a charge gap.

High-quality $\text{Na}_{0.5}\text{CoO}_2$ single crystals with size around $2\text{ mm} \times 2\text{ mm}$ were obtained by flux growing method and chemical deintercalation of Na in solutions of I2 dissolved acetonitrile. The actual Na concentrations were determined by inductively coupled plasma spectrometry analysis experiments, and by the energy-dispersive x-ray analysis (EDX) using scanning electron microscopy, respectively. The two methods give almost identical results as $x = 0.505$ and 0.499 , respectively. Detailed preparation and characterization of the samples will be published elsewhere [13]. The near-normal incident reflectance spectra were measured on the freshly cleaved surface by a Bruker 66v/S spectrometer in the

frequency range from 40 to 29 000 cm^{-1} , as described in our earlier report [10]. Standard Kramers-Kronig transformations were employed to derive the frequency-dependent conductivity spectra.

Figures 1(a) and 1(b) show the room temperature in-plane reflectance and conductivity spectra for $\text{Na}_{0.5}\text{CoO}_2$ together with two metallic Na_xCoO_2 crystals with higher Na concentrations $x = 0.7$ and 0.85 . Here, the spectra of $x = 0.7$ crystal were taken from our earlier measurement [10]. The crystal of $x = 0.85$ was grown by a floating zone optical image furnace. The transport and magnetic properties of this crystal were presented elsewhere [14]. The effective density of carriers per Co ion contributed to conductivity below ω can be obtained by the partial sum rule

$$\frac{m}{m_b} N_{\text{eff}}(\omega) = \frac{2mV_{\text{cell}}}{\pi e^2 N} \int_0^\omega \sigma(\omega') d\omega', \quad (1)$$

where m is the free-electron mass, m_b the averaged high-frequency optical or band mass, V_{cell} a unit cell volume, and N the number of Co ions per unit volume. Figure 1(c) displays $(m/m_b)N_{\text{eff}}$ as a function of frequency for the three samples. It shows clearly that the effective conducting carriers increase with decreasing Na contents, even though the $x = 0.5$ compound becomes insulating at low temperature. N_{eff} is related to an equivalent plasma frequency, after choosing a proper high-frequency limit ω_c , via the relationship $\omega_p^2 = 4\pi e^2 N_{\text{eff}}(\omega_c)/m_b(V_{\text{cell}}/N) =$

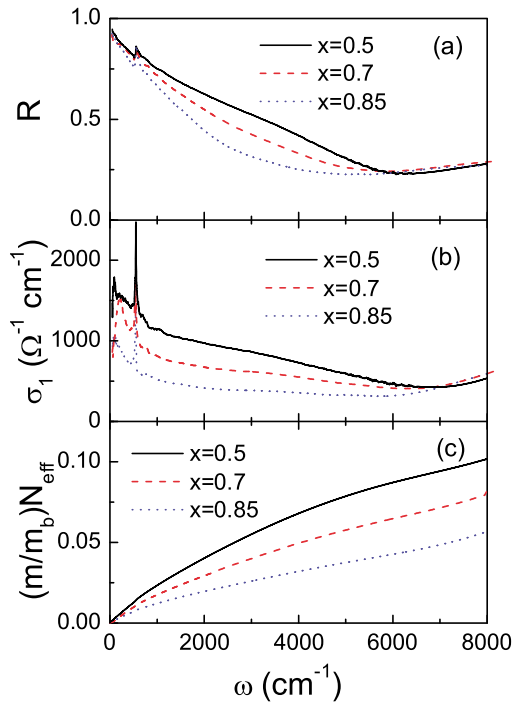


FIG. 1 (color online). Frequency dependences of the in-plane reflectance (a), conductivity (b), and effective density of carriers per Co ion (c) for Na_xCoO_2 with different Na concentrations at room temperature.

$8 \int_0^{\omega_c} \sigma(\omega') d\omega'$. Choosing $\omega_c \approx 6000 \text{ cm}^{-1}$, a frequency where $R(\omega)$ reaches its minimum but below the interband transition, we get the overall plasma frequency $\omega_p \approx 1.4 \times 10^4$, 1.2×10^4 , and $1.0 \times 10^4 \text{ cm}^{-1}$ for $x = 0.5$, 0.7 , and 0.85 compounds, respectively. In the Na_xCoO_2 system, the $x = 1$ end point member has a $t_{2g}^6 e_g^0$ (low spin state of Co^{3+}) electron configuration and is expected to be a band insulator with a completely filled t_{2g} band and an empty e_g band; the $x = 0$ end point member with $t_{2g}^5 e_g^0$ (Co^{4+}) configuration has a hole in the highest lying t_{2g} state and is anticipated to be a Mott insulator within the strong electron-correlation picture [5,6]. Then, the metallic Na_xCoO_2 with $0 < x < 1$ can be viewed either as a doped band insulator with a hole concentration of $(1 - x)$ or as a doped Mott insulator with an electron concentration of x . The optical measurement, which reveals an increase of carrier density with decreasing Na content, apparently supports the picture of a doped band insulator. Since the infrared spectra with higher Na concentrations $0.58 \leq x \leq 0.82$ have been reported, we shall focus our attention on the $x = 0.5$ sample in the rest of this paper.

The temperature dependent reflectance of the $\text{Na}_{0.5}\text{CoO}_2$ crystal is shown in Fig. 2. The inset shows the temperature dependent in-plane dc resistivity ρ_{ab} determined by the four-contact method, which is very similar to the result by Foo [2]. ρ_{ab} has a weak temperature dependence at high temperature but increases sharply near $T_{\text{co}} \approx 50 \text{ K}$, the characteristic temperature for the charge ordering transition. In accord with non-metallic dc resistivity behavior with a negative slope, we found that the low-frequency reflectance decreases with decreasing temperature. However, the reflectance in the midinfrared region increases with decreasing temperature. Upon entering the charge ordering state ($T < T_{\text{co}}$),

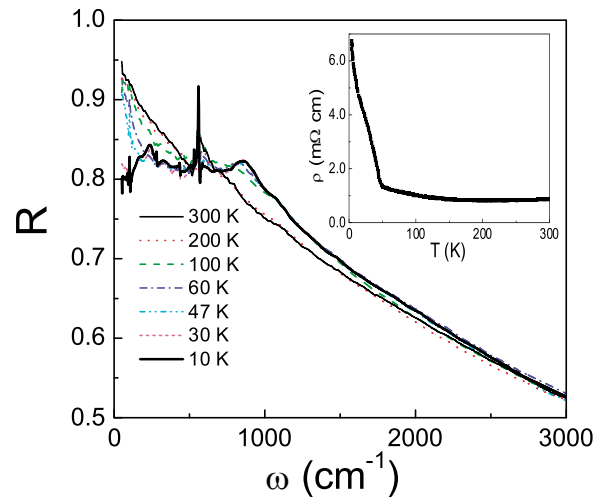


FIG. 2 (color online). Frequency dependences of the in-plane reflectance spectra for $\text{Na}_{0.5}\text{CoO}_2$ at different temperatures. The inset shows the curve of dc resistivity versus temperature of the $\text{Na}_{0.5}\text{CoO}_2$ crystal.

$R(\omega)$ below 250 cm^{-1} was further suppressed, leading to an energy gap in the extracted conductivity spectra.

Figure 3 shows the low-frequency conductivity spectra of $\text{Na}_{0.5}\text{CoO}_2$ at different temperatures. The room temperature spectrum is very similar to the measurement result of the $x = 0.7$ compound, except for a relatively higher magnitude of conductivity curve due to higher conducting carrier density. The low-frequency drop of $\sigma_1(\omega)$ is believed to have a common origin as in the $x = 0.7$ compound, an issue being addressed in our earlier work [10]. As the temperature decreases from 300 to 200 K, the spectral change is very small. However, at lower temperatures, a number of striking features manifest in $\sigma_1(\omega)$ spectra. First of all, a sharp suppression of the conductivity spectra below the charge ordering transition temperature T_{co} is seen near 250 cm^{-1} , indicative of the opening of a charge gap. The magnitude of the gap, 2Δ , defined as an onset energy of the steeply rising part of $\sigma_1(\omega)$ is roughly 125 cm^{-1} at our lowest measurement temperature, leading to the value of $2\Delta/k_B T_{\text{co}} = 3.5$, which is in good agreement with the predicted value for a mean-field charge density wave (CDW) transition. A peak could be seen just above the gap edge, which is also a predicted feature of CDW transition, and has been observed in many CDW materials. The observation provides convincing evidence for the formation of an insulating charge density wave ground state in the ordered phase.

Second, a broad hump near 800 cm^{-1} develops at low temperature. The feature is already evident at 100 K, a temperature much higher than T_{co} , but becomes further enhanced at lower temperature. The hump is a novel phenomenon for the $x = 0.5$ compound. It is absent for other x concentrations of the Na_xCoO_2 system [9–12]. The hump position sets up an energy scale where the charge carriers become frozen or bounded. At present, its origin is not clear. To some extent, the hump is related

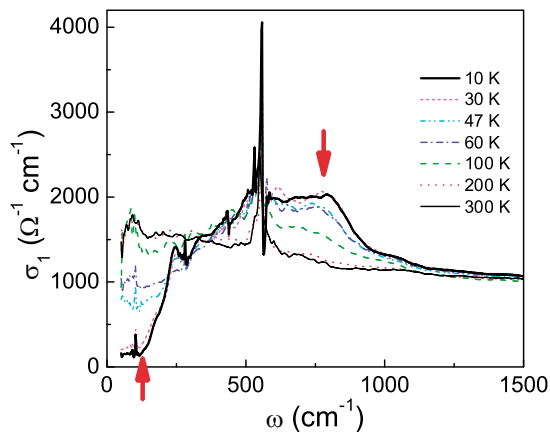


FIG. 3 (color online). The in-plane optical conductivity spectra of $\text{Na}_{0.5}\text{CoO}_2$. The arrow at the low-frequency side indicates the gap position; the arrow at the higher frequency side indicates a hump, which is enhanced at lower temperature.

to the charge ordering since its spectral weight comes from the missing area in the low-frequency part. On this account, its emergence above T_{co} may be explained as due to fluctuated charge ordering. However, the charge ordering itself does not necessarily cause such a hump feature. In many other charge ordering compounds, no such hump was observed. A favorable candidate for the hump is that it is caused by a polaronic characteristic of charge carriers due to the enhanced electron-phonon interaction at low temperature. The temperature dependence of the hump is in good agreement with the expected behavior of polarons [15,16]. Further support for this possibility comes from phonon spectra, as we shall discuss below.

Third, dramatic change appears in phonon modes. At high temperatures (above 200 K), only two infrared active phonons are present in the spectra: a stronger one at 551 cm^{-1} and a weaker one at a bit lower frequency 530 cm^{-1} . The two phonons are similar to the results seen in the $x = 0.7$ crystal at high temperature [10], both being close to the frequency of a hard E_{1u} mode as predicted by symmetry analysis [17]. However, below 100 K, three additional phonon modes at 102, 282, and 435 cm^{-1} could be seen clearly. The appearance of the new phonon modes suggests the change of the structure. Since the modes could already be seen at 100 K, being correlated with the above hump feature, the structural instability occurs at much higher temperature than the metal-insulator transition temperature. Electron diffraction measurements by Huang *et al.* on $\text{Na}_{0.5}\text{CoO}_2$ revealed extra diffraction spots at 100 K in comparison with diffraction pattern at room temperature, indicative of a structure distortion at low temperature [3]. We believe that the appearance of new phonon modes is correlated with this structure distortion, which could be ascribed to the ordering of Na ions. On the contrary, the metal-insulator transition at 50 K is associated with the charge ordering transition of Co ions. In addition to the appearance of new modes, another striking observation is that the phonons at low temperature exhibit extremely strong antiresonance feature or Fano line shape at the region where the electronic background is high. To the contrary, such a line shape is almost completely absent at high temperature. Such an antiresonance feature unambiguously indicates a strong electron-phonon coupling in $\text{Na}_{0.5}\text{CoO}_2$. As a result, it may cause the formation of localized bounded states of charge carriers, or small polarons.

The above experimental observation and analysis led us to arrive at the following picture for the evolution of the charge dynamics with temperature in the $\text{Na}_{0.5}\text{CoO}_2$ compound. The charge carriers at low temperature should be regarded as bounded small polarons due to the strong electron-phonon coupling. They start to form at around 100 K, leading to the hump feature in the conductivity spectra. At lower temperature T_{co} , a CDW order, perhaps a “small polaron CDW,” is further formed, which is

accompanied by a gap opening in the charge excitation spectrum.

We now discuss the implications of the optical data. From the comparison of $x = 0.5$ with $x = 0.7$ and 0.85 compounds, we have shown that the effective conducting carriers increase with decreasing Na contents, even though the $x = 0.5$ compound becomes insulating at low temperature. However, the available angle-resolved photoemission spectroscopy (ARPES) experiments seem to indicate that the “Fermi surfaces” of the $\text{Na}_{0.7}\text{CoO}_2$ compound [18] is larger than that of the $\text{Na}_{0.5}\text{CoO}_2$ compound [19]. In this case, the Luttinger theorem for enclosed volume of Fermi surface is apparently violated in a doped Na_xCoO_2 system. We believe that those seemingly contradicted results pose a strong constraint on a theory. One theoretical approach, which is capable of explaining the anomalous metallic properties at low temperature and unusual Fermi surfaces seen in ARPES for Na_xCoO_2 , was developed by Baskaran [4]. In this theory, the underlying charge ordering at commensurate filling is a key assumption. However, due to the random potential from the neighboring Na layers and the strong commensurability effects of the triangular lattice, the charge ordered states would be easily frustrated. Baskaran suggested that the metallic state of the Na_xCoO_2 system is a homogeneous quantum molten state of these ordered states, which he referred to as a quantum charge liquid.

Although charge ordering in the Na_xCoO_2 system was suggested to be a major instability in the narrow conduction band of the CoO_2 layer, static charge ordering with localized electrons was observed only for the $x = 0.5$ compound at low temperature. Our infrared data show that even for the $x = 0.5$ compound, the charge dynamics is affected only at very low frequencies (roughly below 1000 cm^{-1}). We emphasize that this energy scale is much lower than those found for many other systems. For example, in quasi-one-dimensional charge ordering systems BaIrO_3 or organic systems like $(\text{TMTSF})_2\text{X}$ salts (where TMTSF is tetramethyltetraselenafulvalene), the size of the optical gap (2Δ) is around $9k_B T_c$ [20,21]. In the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ system, the ratio of $2\Delta/k_B T_c$ could be as large as 30 for $x = 0.5$ [22]. The very small energy scale may explain why charge ordering is easily destroyed and not observed in other commensurate filling x in Na_xCoO_2 .

To conclude, we have measured the infrared spectra of $\text{Na}_{0.5}\text{CoO}_2$, which is known to have static charge ordering at low temperature. In comparison with the $x = 0.7$ and 0.85 compounds, we found that the spectral weight associated with the conducting carriers at high temperature increases systematically with decreasing Na contents. The charge ordering transition only affects the conductivity spectrum below 1000 cm^{-1} . A broad hump near 800 cm^{-1} develops below 100 K, which is correlated with the appearance of new lattice modes as well as the strong

antiresonance feature of phonon spectra. At lower temperature T_{co} , a CDW order, perhaps a small polaron CDW, is further formed, which is accompanied by the development of a gap in the charge excitation spectrum. Our work highlights the importance of charge ordering and strong electron-phonon interaction in the Na_xCoO_2 system.

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Note added.—After this work was completed, we learned about another infrared work on the Na_xCoO_2 system with insulating samples included [23]. Their experimental data, particularly for the $x = 0.25$ composition, further strengthen our viewpoint and conclusions.

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