Infrared spectroscopy of the charge ordering transition in Na\(_{0.5}\)CoO\(_2\)

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We report infrared spectra of a Na\(_{0.5}\)CoO\(_2\) single crystal which exhibits a sharp metal-insulator transition near 50 K due to the formation of charge ordering. 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 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 anti-resonance feature of phonon spectra. At lower temperature \(T_{co}\), an optical gap develops at the magnitude of \(2\Delta \approx 3.5k_B T_{co}\), evidencing an insulating charge density wave ground state. Our experimental results and analysis unequivocally point towards the importance of charge ordering instability and strong electron-phonon interaction in Na\(_{0.5}\)CoO\(_2\) system.

PACS numbers: 78.20.-e, 71.27.+a, 74.25.Gz, 74.25.Kc

The recent discovery of superconductivity at 5K in hydrated sodium cobaltate, Na\(_x\)CoO\(_2\)·yH\(_2\)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\(_x\)CoO\(_2\). It consists of alternate stacks of Na and CoO\(_2\) layers with edge sharing CoO\(_6\) octahedra. The physical properties of Na\(_x\)CoO\(_2\) depend strongly on the Na concentration. Recent transport, magnetic and structural studies on single crystals of Na\(_x\)CoO\(_2\) for 0.3 < \(x < 0.75\) revealed a crossover from an unusual Curie-Weiss metal near \(x=0.7\) to a paramagnetic metal for \(x < 0.3\). The composition that separates the two metallic regimes at higher and lower Na concentrations, Na\(_{0.5}\)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 Na\(_{0.5}\)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\(_x\)CoO\(_2\) is a subject of great interest. It was suggested to be a major instability in the narrow conduction band of 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 < \(x < 1/3\) in hydrated Na\(_x\)CoO\(_2\).\(^4\)\(^5\)\(^6\) Possible charge ordered states at other commensurate fillings \(x=1/2\), 2/3 and 3/4 were also proposed.\(^4\)\(^5\)\(^6\) Those charge ordered states were 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\(_x\)CoO\(_2\) for 0.5 ≤ \(x\) ≤ 0.75,\(^2\)\(^7\)\(^8\) an unambiguous charge ordering state with localized electrons was only observed 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 Na\(_x\)CoO\(_2\) with different Na concentration have been reported by several groups.\(^9\)\(^10\)\(^11\)\(^12\) In this work, we present the in-plane optical measurements at different temperatures on Na\(_{0.5}\)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 only affects the conductivity spectrum 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 Na\(_{0.5}\)CoO\(_2\) single crystals with size around 2mm×2mm were obtained by flux growing method and chemical deintercalation of Na in solutions of I\(_2\) dissolved acetonitrile. 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 cm\(^{-1}\) to 29000 cm\(^{-1}\), as described in our earlier report.\(^10\) Standard Kramers-Kronig transformations were employed to derive the frequency-dependent
conductivity spectra.

Fig. 1(a) and (b) show the room temperature in-plane reflectance and conductivity spectra for Na_{0.5}CoO_{2} together with two metallic Na_{x}CoO_{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. The crystal of x=0.85 was grown by a floating zone optical image furnace. The transport and magnetic properties of this crystal was presented elsewhere. The effective density of carriers per Co ion contributed to conductivity below ω can be obtained by the partial sum rule

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

where m is the free-electron mass, m_b the averaged high-frequency optical or band mass, V_{cell} a unit cell volume, N the number of Co ions per unit volume. Fig. 1(c) displays N_{eff} as a function of frequency for the three samples. It shows clearly that the effective conducting carriers increases with decreasing Na contents, even though x=0.5 compound becomes insulating at low temperature. N_{eff} can be related to an equivalent plasma frequency, after choosing a proper high-frequency limit ω_{c}, via the relationship $ω_{p}^2 = 4πe^2N_{eff}(ω_c)/m_b(V_{cell}/N)$. Choosing $ω_{c}≈6000$ cm$^{-1}$, a frequency where R(ω) reaches its minimum but below the interband transition, we get the overall plasma frequency $ω_\rho ≈ 1.4×10^4$ cm$^{-1}, 1.2×10^4$ cm$^{-1}$ and $1.0×10^4$ cm$^{-1}$ for x=0.5, 0.7 and 0.85 compounds, respectively. The results strongly suggest that metallic Na_{x}CoO_{2} should be considered as a doped band insulator with the hole concentration of (1-x), rather than as a doped Mott insulator with the electron concentration of x. Since the infrared spectra with higher Na concentrations 0.58≤x≤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 Na_{0.5}CoO_{2} crystal is shown in Fig. 2. The inset shows the temperature dependent in-plane dc resistivity $ρ_{ab}$ determined by four-contact method, which is very similar to the result by Foo. $ρ_{ab}$ has a weak temperature dependence at high temperature but increases sharply near $T_{co}≈50K$, the characteristic temperature for the charge ordering transition. In accord with nonmetallic dc resistivity behavior with a negative slope, we found that the low-frequency reflectance decreases with decreasing temperature. However, the reflectance in the mid-infrared region increases with decreasing temperature. Upon entering the charge ordering state ($T<T_{co}$), R(ω) below 250 cm$^{-1}$ was further suppressed, leading to an energy gap in the extracted conductivity spectra.

Fig. 3 shows the low frequency conductivity spectra of Na_{0.5}CoO_{2} at different temperatures. The room temper-
a sharp suppression of the conductivity spectra below the gap. The magnitude of the gap, \(2\Delta\), defined as an onset of striking features manifest in the spectra increases from 300 K to 200 K, the spectral change to have a common origin as in \(x=0.7\) compound, an issue of charge ordering since its spectral weight comes from the carrier density. The low frequency drop of \(\sigma_1(\omega)\) is believed to have a common origin as in \(x=0.7\) compound, an issue of polarons. Further support for this possibility comes from phonon spectra, as we shall discuss below.

Thirdly, 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 \(x=0.7\) crystal at high temperature,[10] both being close to the frequency of a hard \(E_{1u}\) mode as predicted by symmetry analysis.[12] 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 \(Na_{0.5}CoO_2\) revealed extra diffraction spots at 100 K in comparison with diffraction pattern at room temperature, being 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 lineshape at the region where the electronic background is high. By contrary, such lineshape is almost completely absent at high temperature. Such antiresonance feature unambiguously indicates a strong electron-phonon coupling in \(Na_{0.5}CoO_2\). As a result, it may cause the formation of localized bounded states of charge carriers, or small polarons.

The above experimental observation and analysis lead us to arrive at following picture for the evolution of the charge dynamics with temperature in \(Na_{0.5}CoO_2\) compound. The charge carriers at low temperature should be regarded as bounded small polarons due 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.

![FIG. 3: The in-plane optical conductivity spectra of Na_{0.5}CoO_2. The arrow at low frequency side indicates the gap position, the arrow at higher frequency side indicates a hump, which is enhanced at lower temperature.](image)
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 increases with decreasing Na contents, even though x=0.5 compound becomes insulating at low temperature. However, the available ARPES experiments indicated that the "Fermi surfaces" of Na$_{0.7}$CoO$_2$ compound[16] is larger than that of Na$_{0.5}$CoO$_2$ compound[17]. In this case, the Luttinger theorem for enclosed volume of Fermi surface is apparently violated in doped Na$_x$CoO$_2$ system. We believe that those seemingly contradicted results pose a strong constraint on a theory. One theoretical approach, which is capable to explain the anomalous metallic properties at low temperature and unusual "Fermi surfaces" seen in ARPES for Na$_x$CoO$_2$, 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 Na$_x$CoO$_2$ system is a homogeneous quantum molten state of these ordered states, which he referred to as a quantum charge liquid.

Although charge ordering in Na$_x$CoO$_2$ system was suggested to be a major instability in the narrow conduction band of CoO$_2$ layer, static charge ordering with localized electrons was only observed for 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 (TMTSF)$_2$X salts, the size of optical gap (2$\Delta$) is around 9kBT$_{co}$.[18, 19] In La$_{1-x}$Ca$_x$MnO$_3$ system, the ratio of the 2$\Delta$/kBT$_{co}$ could be as large as 30 for x=0.5.[20] The very small energy scale may explain why charge ordering is easily destroyed and not observed in other commensurate filling x in Na$_x$CoO$_2$.

To conclude, we have measured the infrared spectra of Na$_{0.5}$CoO$_2$ which is known to have static charge ordering at low temperature. 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 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 anti-resonance 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 Na$_x$CoO$_2$ system.

We acknowledge helpful discussions with J. L. Luo, T. Xiang, and G. M. Zhang. This work is supported by National Science Foundation of China (No. 10025418, 10374109), the Knowledge Innovation Project of Chinese Academy of Sciences.

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