

Infrared Probe of the Electronic Structure and Charge Dynamics of $\text{Na}_{0.7}\text{CoO}_2$

N. L. Wang, P. Zheng, D. Wu, and Y. C. Ma

*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences,
Beijing 100080, People's Republic of China*

T. Xiang

*Institute of Theoretical Physics and Interdisciplinary Center of Theoretical Studies, Chinese Academy of Sciences,
Beijing 100080, People's Republic of China*

R. Y. Jin and D. Mandrus

Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

(Received 24 December 2003; published 1 December 2004)

We present measurements of the optical spectra on $\text{Na}_{0.7}\text{CoO}_2$ single crystals. The optical conductivity shows two broad interband transition peaks at 1.6 eV and 3.1 eV, and a weak midinfrared peak at 0.4 eV. The intraband response of conducting carriers is different from that of a simple Drude metal. A peak at low but finite frequency is observed, which shifts to higher frequencies with increasing temperature, even though the dc resistivity is metallic. The origin of the interband transitions and the low-frequency charge dynamics have been discussed and compared with other experiments.

DOI: 10.1103/PhysRevLett.93.237007

PACS numbers: 74.25.Gz, 71.27.+a, 74.70.-b, 78.30.-j

The recent discovery of superconductivity at ~ 5 K in hydrated sodium cobaltate [1] has attracted much attention, as it might be a new system other than cuprates where a doped Mott insulator becomes a superconductor. The host compound Na_xCoO_2 consists of alternate stacking of Na and CoO_2 layers in which edge sharing CoO_6 octahedra lead to a two-dimensional (2D) triangular lattice of Co ions.[2,3] Superconductivity occurs when Na content x is near 0.3 and sufficient water is intercalated between the CoO_2 layers. This material provides a model system

for studying the physics of correlated electrons in a 2D triangular lattice. It is also believed that the study of Na_xCoO_2 system may shed new light on high-temperature superconductivity in cuprates.

To understand the mechanism of superconductivity in this material, great effort has been paid to the investigation of its electronic structure. As the first step, attention has been given to the host compound. A detailed band structure calculation for $x = 0.5$ compound has been performed by Singh [4]. Within the local density approximation (LDA), it was found that the O $2p$ bands are located well below the Fermi level and there is little hybridization between O $2p$ and Co $3d$ bands. The splitting between the Co $3d$ e_g and t_{2g} bands is very large. The conduction electrons are mainly from the t_{2g} band and the e_g band is about 2.5 eV above the Fermi level. In the rhombohedral crystal field, the t_{2g} manifold is further split into two a_{1g} and four e'_g bands. The a_{1g} bands contribute a large cylindrical hole Fermi surface centered at Γ . This large Fermi surface was confirmed by the angle-resolved photoemission spectroscopy (ARPES) measurements [5–7]. However, the six Fermi pockets

from the e'_g bands, predicted by the LDA, were not observed by the ARPES. On the other hand, if the effects of spin polarization were included, an itinerant ferromagnetic state was predicted to exist for $x = 0.3$ to 0.7 [4,8,9]. There was no report on the existence of distinct magnetic order in this material, but a Curie-Weiss-like susceptibility $\chi(T)$ was found when $x \approx 0.7$. This suggests that Co ions have local moments associated with the exchange splitting [1,10,11], but strong quantum fluctuations suppress the long-range ferromagnetic ordering in Na_xCoO_2 [8].

In this Letter, we report the in-plane optical response over broad frequencies on single crystals with $x = 0.7$. Our measurements yield two broad interband transition peaks at 1.6 eV and 3.1 eV. The interband transition energies are significantly different from the energy difference between the occupied t_{2g} and empty e_g bands (~ 2.5 eV) as predicted by the LDA. The physical origin for this difference will be discussed. Moreover, our experiments also revealed a weak midinfrared peak at 0.4 eV and unusual charge dynamics at low frequencies.

High-quality $\text{Na}_{0.7}\text{CoO}_2$ single crystals with size around 3×3 mm were grown using the flux method [12]. Figure 1 shows the in-plane dc resistivity ρ_{ab} measured by four-contact method. The temperature dependence of ρ_{ab} is typically metallic and agrees with those reported in Ref. [6,13,14] with similar Na concentration.

The crystals could be readily cleaved to obtain a fresh and shiny surface. The near-normal incident reflectance spectra were measured by a Bruker 66 v/S spectrometer in the frequency range from 40 to 29 000 cm^{-1} . The sample was mounted on an optically black cone in a cold-finger flow cryostat. An *in situ* overcoating tech-

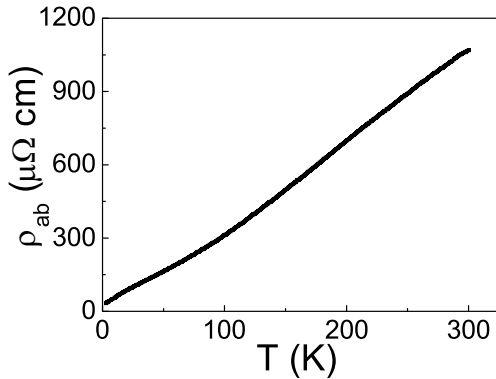


FIG. 1. The in-plane dc resistivity of $\text{Na}_{0.7}\text{CoO}_2$ single crystal as a function of temperature.

nique was employed for reflectance measurements [15]. The optical conductivity spectra were obtained from a Kramers-Kronig transformation of $R(\omega)$. We use Hagen-Rubens' relation for the low-frequency extrapolation, and a constant extrapolation to $100\,000\text{ cm}^{-1}$ followed by a well-known function of ω^{-4} in the higher-energy side.

Figure 2 shows the in-plane reflectance spectra measured at different temperatures between 10 and 300 K. In accord with the metallic dc resistivity behavior with a positive slope, we found that the low-frequency reflectance increases with decreasing temperature. However, the reflectance in the midinfrared region decreases with decreasing temperature and $R(\omega)$ at different temperatures cross at about 1300 cm^{-1} . The main spectral change caused by temperature variation is roughly below 4000 cm^{-1} . The reflectance reaches an edge (or a minimum) near 6000 cm^{-1} . This frequency is close to the so-called screened plasma frequency. We note that this frequency is significantly lower than that of optimally doped cuprates like $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$, suggesting that the conducting carrier density is lower in the present compound.

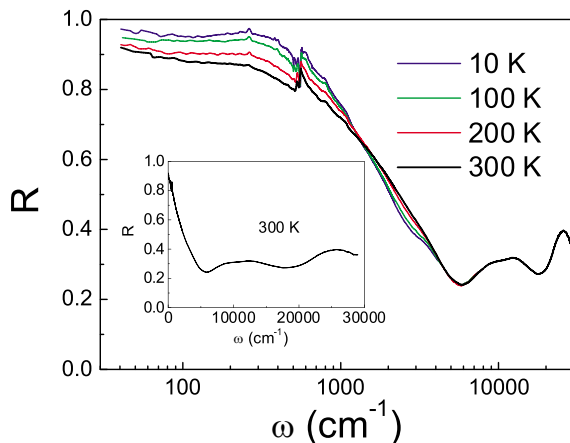


FIG. 2 (color online). Frequency dependences of the in-plane reflectance spectra at different temperatures. The inset is the room temperature reflectance in a linear frequency scale.

Figure 3 shows the conductivity spectra over broad frequencies. Corresponding to the reflectance edge, the optical conductivity also exhibits a minimum at similar frequency. The low-frequency part is mainly contributed by the conducting carriers. A sum of the spectral weight up to 6000 cm^{-1} yields approximately the overall plasma frequency of $\sim 1.2 \times 10^4\text{ cm}^{-1}$, which is apparently lower than the values for optimally doped cuprates obtained by the same method.[16] At the high-frequency side, two prominent interband transition peaks centered at $25\,000\text{ cm}^{-1}$ (3.1 eV) and $13\,000\text{ cm}^{-1}$ (1.6 eV) are observed and labeled as α and β . Lupi *et al.* observed a peak near 9000 cm^{-1} for a $\text{Na}_{0.57}\text{CoO}_2$ crystal [17], but it appears only as a weak shoulder for the β peak here. The peak strengths, especially the α one, could be affected by the high-frequency extrapolation in the Kramers-Kronig transformation, but their shapes and positions are less affected. In fact, as shown in the inset of Fig. 2, two interband transition peaks in the measured reflectance in the above mentioned energy scales can be clearly seen.

According to the band structure calculation [4], the O $2p$ bands are much below the Fermi level, and the transition between the O $2p$ bands and Co $3d$ bands is beyond our measurement frequencies. A most probable interband transition relevant to our observation is from the occupied Co $3d t_{2g}$ to the empty Co $3d e_g$ bands due to the octahedral crystal field splitting. However, the LDA result for the energy difference between the t_{2g} and e_g bands is 2.5 eV [4], which lies between those two peaks. We suggest that the difference could be due to the neglect of the spin polarization effect in the simple LDA calculation. Within spin-polarized local density approximation, $\text{Na}_{0.5}\text{CoO}_2$ is expected to be a ferromagnetic half metal [4], and the ferromagnetic instability is robust with respect to doping [8,9]. It is predicted that the exchange splitting of the t_{2g} states is about 1.5 eV for $\text{Na}_{0.3}\text{CoO}_2$ [9].

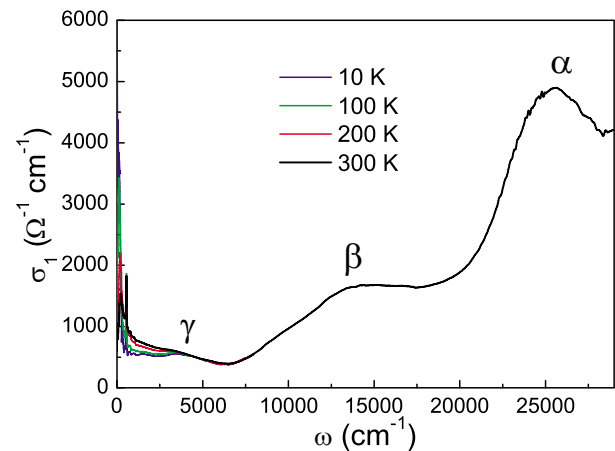


FIG. 3 (color online). The in-plane optical conductivity spectra of $\text{Na}_{0.7}\text{CoO}_2$ over broad range of frequencies. α and β represent two interband transitions; γ is a weak absorption feature in the midinfrared region.

Experimentally, although no long-range ferromagnetic ordering was observed, a Curie-Weiss-like temperature dependence of susceptibility $\chi(T)$ was found for x near 0.7 [1,10,11]. Recent neutron inelastic scattering also indicated ferromagnetic spin fluctuations within the cobalt-oxygen layers for $\text{Na}_{0.75}\text{CoO}_2$ [18]. Therefore, the exchange splittings for the spin-up and spin-down energy levels of t_{2g} and e_g are still expected to exist. However, due to spin fluctuations, the actual effect of the exchange splitting would be a broadening of the t_{2g} and e_g band widths. On one hand, it reduces the minimum excitation gap between the t_{2g} and e_g bands (leading to the β peak); on the other hand, it leads to further increase of the largest energy separation between the t_{2g} and e_g bands (α transition). So, the two peaks resemble the respective transitions between spin minority and spin majority DOS as observed in ferromagnetic materials, such as CrO_2 [19,20].

In addition to the interband transition, there is a weak absorption feature (labeled as γ in Fig. 3) in the midinfrared region around $\sim 3300 \text{ cm}^{-1}$ (0.4 eV). This feature is already present at room temperature, but becomes more pronounced at low temperatures. There are several possibilities for the origin of this absorption feature. A simple explanation is that the weak peak is due to the interband transition between different t_{2g} states. The ARPES experiments along the Γ -K direction revealed the existence of a nearly flat band at 0.16–0.2 eV below Fermi energy and an extended flat band just above E_F [7]. However, the transition between them is unlikely to be responsible for this feature, since the excitation energy is smaller than 0.4 eV. Thus it is more likely that this weak peak is due to a transition from occupied e_g' bands to some partially unfilled a_{1g} bands within t_{2g} manifold. An alternative explanation is that the weak midinfrared feature is due to strong correlation effects. Recent theoretical study based on a fermion-spin theory of the t - J model on a triangular lattice [21] shows that, besides a Drude-like peak at lower frequencies, a midinfrared peak exists in this material. In this picture, the midinfrared peak results from the competition between the kinetic and magnetic exchange energies. It is also possible that this peak results from spin polarons induced by magnetic fluctuations.

Figure 4 shows the conductivity spectra below 1500 cm^{-1} . The low-frequency conductivity increases with decreasing temperature, consistent with the metallic behavior of the dc resistivity shown in Fig. 1. The increase of the spectral weight at low frequencies comes from the region below the midinfrared peak. At room temperature, two in-plane phonons could be seen clearly at 525 and 553 cm^{-1} . With decreasing temperature, they shift slightly towards higher frequencies, and two additional phonons become visible at 505 and 575 cm^{-1} . In Na_xCoO_2 , Na ions have two possible sites, leading to two kinds of structural geometries [22]. Symmetry analysis for each geometry reveals two infrared-active in-plane

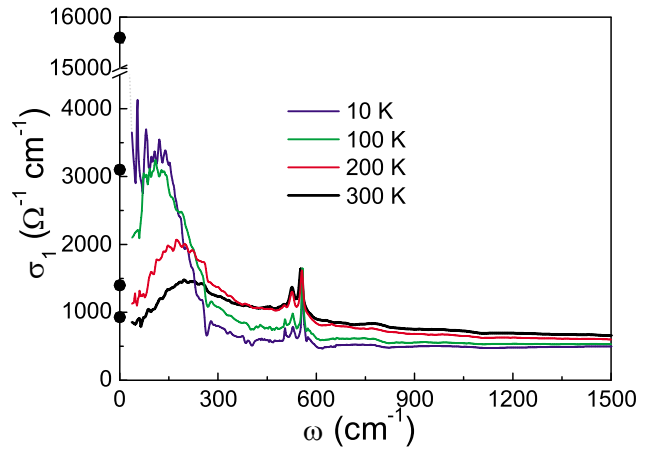


FIG. 4 (color online). The low- ω optical conductivity spectra of $\text{Na}_{0.7}\text{CoO}_2$ at different temperatures. The filled circles represent the dc conductivity values at 300, 200, 100 and 10 K (from bottom to top). The sharp increase indicated by the gray dash-dot line at 10 K is beyond our lowest measurement frequency.

phonon modes $2E_{1u}$ [23]. The respective mode frequencies are somewhat different for the two geometries. The observation of two in-plane phonon modes at room temperature, which are all close to the frequency of hard E_{1u} mode, may indicate that the two structural geometries, or both Na sites occupations, are present in the sample. The appearance of additional phonon modes might be due to a structural change with temperature. However, a complete understanding of the infrared-active phonons requires further efforts.

The most striking feature is that the intraband response of conducting carriers is rather different from the simple Drude behavior. The conductivity drops at very low frequencies, resulting in a low-frequency peak. The peak shifts toward lower frequency with decreasing temperature. Such peak has been observed by Bernhard *et al.* on $\text{Na}_{0.82}\text{CoO}_2$ single crystals in a very recent report [24]. Similar finite-energy peaks that shift to lower energies with decreasing T are predicted for Raman scattering in correlated systems near metal-insulator transition on the metallic side [25]. Usually, the drop of optical conductivity at low frequency is considered as a signature of charge localization. For Na_xCoO_2 , however, this drop is unlikely to be due to the weak localization effect, since the dc resistivity is purely metallic and does not show any sign of localization in the whole temperature range measured.

More information about the low-frequency charge dynamics could be obtained by comparing the dc resistivity with infrared conductivity at zero frequency limit. We found that, at room temperature, the optical conductivity in the low-frequency limit agrees well with the dc data within experimental errors. However, with decreasing temperature, the dc conductivity data appear to have higher values. In particular, at 10 K, the dc conductivity is as high as $15600 (\Omega \text{ cm})^{-1}$, 4 times higher than the

low-frequency optical conductivity data. This implies that there should exist a sharp increase in the optical conductivity below the frequency limit of our measurements. In this case, the conductivity drop tends to disappear due to the emergence of the new component at extremely low frequencies.

We believe that the temperature dependent behavior of the low-lying excitations observed in optical conductivity has close relationship with the quasiparticle dynamics observed in ARPES experiments. For $\text{Na}_{0.7}\text{CoO}_2$ single crystals, a well-defined quasiparticle was observed only at low temperature where the resistivity is linear in T [6]. The quasiparticle weight decreases to almost zero on raising temperature to above 100 K. In a study on $\text{Na}_{0.5}\text{CoO}_2$ crystals, Valla *et al.* [5] also found that the in-plane quasiparticles exist only at low temperature where the c -axis transport becomes metallic. If we compare the infrared data with ARPES results, it becomes clear that the low- ω drop in optical conductivity of Na_xCoO_2 correlates with the incoherent electronic states in which the quasiparticle picture breaks down. It also turns out that the positive slope of dc transport does not necessarily mean the existence of well-defined quasiparticles. The high-temperature transport in Na_xCoO_2 is incoherent in nature. It is worth pointing out that the finite-energy peak has also been observed in other strongly correlated systems [26]. The coexistence of the “metallic” dc resistivity with a finite-energy peak in optical conductivity and the absence of well-defined quasiparticles in ARPES is a great challenge to our understanding of the charge transport.

Our results also imply that the development of an extremely narrow and sharp Drude component at low temperature corresponds to the well-defined quasiparticles in ARPES. Note that the occurrence of a sharp and narrow resonance mode at $\omega = 0$ in a broad spectral background at low temperature was widely observed in heavy Fermion compounds, which was explained in terms of the renormalization of both the effective mass and scattering time of quasiparticles in the many-body picture [27]. Because this component actually exists below our measurement frequency here, its spectral weight (or correspondingly, renormalized plasma frequency) cannot be determined. The very narrow Drude peak was also inferred in the very recent work by Bernhard *et al.* [24] from the ellipsometry measurement on $\text{Na}_{0.82}\text{CoO}_2$. From the decrease of the real part of dielectric function at very low frequency, they estimated the plasma frequency for this narrow Drude carriers of roughly 1300 cm^{-1} . This value is almost 10 times smaller than that the overall plasma frequency obtained from the sum rule in the present work. Such difference also reflects the enhanced effective mass of quasiparticle at low temperature [27]. In fact, a moderate mass enhancement in Na_xCoO_2 was observed in the specific heat measurement [3].

To conclude, the electronic structure and charge dynamics have been investigated for $\text{Na}_{0.7}\text{CoO}_2$ by means of

optical spectroscopy probe. The optical conductivity spectra show two broad interband transition peaks at 1.6 eV and 3.1 eV, and a weak midinfrared peak at 0.4 eV. The former two peaks were explained as transitions between occupied t_{2g} to empty e_g bands by invoking the effect of exchange splitting. The midinfrared peak is attributed either to the interband transition within the t_{2g} manifold or to the electronic correlation effect. The intraband response of conducting carriers is different from that of a simple Drude metal. The optical conductivity exhibits a peak at finite frequency, which shifts slightly towards higher frequencies with increasing temperature. Our analysis suggests that the peak is not due to the carrier localization but represents the incoherent electronic states where the quasiparticle picture breaks down.

We acknowledge helpful discussions with Z. Fang, S. P. Feng, J. L. Luo, Y. Wang, L. Yu, and G. M. Zhang. This work is supported by the National Science Foundation of China, the K. C. Wong Education Foundation, and the Knowledge Innovation Project of the Chinese Academy of Sciences. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract no. DE-AC05-00OR22725.

-
- [1] K. Takada *et al.*, Nature (London) **422**, 53 (2003).
 - [2] I. Terasaki *et al.*, Phys. Rev. B **56**, 12685 (1997).
 - [3] I. Terasaki, Physica B (Amsterdam) **328**, 63 (2003).
 - [4] D. J. Singh, Phys. Rev. B **61**, 13397 (2000).
 - [5] T. Valla *et al.*, Nature (London) **417**, 627 (2002).
 - [6] M. Z. Hasan *et al.*, Phys. Rev. Lett. **92**, 246402 (2004).
 - [7] H. B. Yang *et al.*, Phys. Rev. Lett. **92**, 246403 (2004).
 - [8] D. J. Singh, Phys. Rev. B **68**, 020503(R) (2003).
 - [9] J. Kunes, K. W. Lee, and W. E. Pickett, Phys. Rev. B **70**, 045104 (2004).
 - [10] H. Sakurai *et al.*, Phys. Rev. B **68**, 132507 (2003).
 - [11] B. Lorenz *et al.*, Phys. Rev. B **68**, 132504 (2003).
 - [12] R. Jin *et al.*, Phys. Rev. Lett. **91**, 217001 (2003).
 - [13] Y. Wang *et al.*, Nature (London) **423**, 425 (2003).
 - [14] M. L. Foo *et al.*, Phys. Rev. Lett. **92**, 247001 (2004).
 - [15] C. C. Homes *et al.*, Appl. Opt. **32**, 2973 (1993).
 - [16] A. V. Puchkov *et al.*, J. Phys. Condens. Matter **8**, 10049 (1996).
 - [17] S. Lupi *et al.*, Phys. Rev. B **69**, 180506R (2004).
 - [18] A. T. Boothroyd *et al.*, Phys. Rev. Lett. **92**, 197201 (2004).
 - [19] E. J. Singley *et al.*, Phys. Rev. B **60**, 4126 (1999).
 - [20] I. I. Mazin and D. J. Singh, Phys. Rev. B **59**, 411 (1999).
 - [21] B. Liu *et al.*, Phys. Rev. B **69**, 224506 (2004).
 - [22] J. D. Jorgensen *et al.*, Phys. Rev. B **68**, 214517 (2003).
 - [23] Z. Li, J. Yang, J. G. Hou and Q. Zhu, Phys. Rev. B **70**, 144518 (2004).
 - [24] C. Bernhard *et al.*, Phys. Rev. Lett. **93**, 167003 (2004).
 - [25] J. K. Freericks *et al.*, Phys. Rev. B **67**, 155102 (2003).
 - [26] N. L. Wang *et al.*, Phys. Rev. B **67**, 134526 (2003); K. Takenaka *et al.*, Phys. Rev. B **68**, 134501 (2003), and references therein.
 - [27] L. Degiorgi, Rev. Mod. Phys. **71**, 687 (1999).