Research activity on Na$_x$CoO$_2$ single crystals: A brief review on optical conductivity and metamagnetic transition phenomenon

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Abstract

Na$_x$CoO$_2$ material is of great interest because of its rich electronic phase diagram, as well as for displaying superconductivity when intercalated with water. This paper briefly reviews our research activity on its optical properties and a metamagnetic transition phenomenon.

Keywords: Na$_x$CoO$_2$; Optical conductivity; Metamagnetic transition

1. Introduction

The discovery of superconductivity in hydrated Na$_x$CoO$_2$ [1] has stimulated much interest in this material, which has a layered structure with triangular lattice. A rich phase diagram has been revealed for Na$_x$CoO$_2$ with a change of Na content $x$ [2]. A spin ordered phase is found at high Na concentration $x>3/4$. With decreasing Na contents, the material becomes a 'Curie–Weiss metal' for $x$ near 2/3, then a charge-ordered insulator with $x$ near 2/3, and finally a paramagnetic metal with $x$ near 1/3. Superconductivity occurs when sufficient water is intercalated between the CoO$_2$ layers for $x$ near 1/3. The cobaltate provides a model system for studying the physics of correlated electrons in a 2D triangular lattice. It is also widely expected that the study of Na$_x$CoO$_2$ system may shed new light on high-temperature superconductivity in cuprates.

We have conducted active research on Na$_x$CoO$_2$ system [3–5]. This paper briefly reviews our research activity on Na$_x$CoO$_2$. We describe the optical properties and a metamagnetic transition phenomenon observed on Na$_x$CoO$_2$.

2. Optical conductivity

Optical spectroscopy yields rich information about electronic structure and charge dynamics. Fig. 1 shows the room temperature conductivity spectra for the three compositions. It indicates clearly that the spectral weight associated with the conducting carriers increases monotonously with decreasing Na contents [5]. In Na$_x$CoO$_2$ system, the $x=1$ endpoint member has a $t^0_{2g}e^0_g$ (low spin state of Co$^{3+}$) electron configuration and is expected to be a band insulator with completely filled $t_{2g}$ band and empty $e_g$ band; the $x=0$ end-point member with $t^5_{2g}e^0_g$ (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. Then, the metallic Na$_x$CoO$_2$ 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 support the picture of a doped band insulator.

Fig. 2(a) shows the optical conductivity spectra $\sigma_1(\omega)$ for metallic $x=0.7$ sample [3]. The main panel displays the low-$\omega$ spectra at different temperatures. The inset shows the room temperature spectrum over broad frequencies. Two broad interband transition peaks at 1.6 eV ($\alpha$) and 3.1 eV ($\beta$), and a weak midinfrared peak at 0.4 eV ($\gamma$) were observed. The former two peaks were explained as transitions between occupied $t_{2g}$ to empty $e_g$ bands by
invoking the effect of exchange splitting, while the \( \gamma \) peak was attributed either to the interband transition within the \( t_{2g} \) manifold or to the electronic correlation effect [3]. The intraband response is different from that of a simple Drude metal. The \( \sigma_1(\omega) \) exhibits a peak at finite frequency \(( \sim 200 \text{ cm}^{-1})\), which shifts slightly towards higher \( \omega \) with increasing \( T \). Usually, a drop of \( \sigma_1(\omega) \) at low \( \omega \) is considered as a signature of charge localization, however, the dc transport has a positive slope in the whole measured temperature range, and does not show any sign of the localization effect in \( \text{Na}_{0.7}\text{CoO}_2 \) compound. Therefore, the finite energy peak is not related to disorders or Anderson localization.

Although the \( \sigma_1(\omega) \) drops at very low \( \omega \), its low-\( \omega \) limit is found to agree well with the dc data at room \( T \). However, with decreasing \( T \), the dc conductivity data appear to have higher values. In particular, at 10 K, the dc conductivity is almost four times higher than the low-\( \omega \) optical data. This implies that the \( \sigma_1(\omega) \) would increase sharply below our low-\( \omega \) limit of measurement. Then, the conductivity drop tends to disappear due to the emergence of the new component at extremely low frequencies.

Correlation between the low-\( \omega \) optical response and the quasiparticle behavior seen from ARPES experiments was suggested [3]. For \( \text{Na}_x\text{CoO}_2 \) system, well-defined quasiparticle peaks were observed in ARPES only at low \( T \) where the \( c \)-axis transport becomes metallic [6,7]. The quasiparticle weight decreases to almost zero on raising \( T \) to above 100 K. It was suggested that the extremely sharp and narrow component developed below our measurement frequency at low \( T \) corresponds to the well-defined quasi-particle in ARPES, the low-\( \omega \) drop in \( \sigma_1(\omega) \) at high \( T \) corresponds to the incoherent electronic states in which the quasiparticle picture breaks down. Such unusual properties challenge greatly our understanding about the charge transport.

Different to \( x=0.7 \) composition, \( \text{Na}_{0.5}\text{CoO}_2 \) sample shows a charge ordering transition at \( T_{\text{co}} \approx 50 \text{ K} \). Fig. 2(b) shows the low-\( \omega \) \( \sigma_1(\omega) \) at different \( T \) [5]. In accord with nonmetallic dc resistivity behavior with a negative slope, we found that the low-\( \omega \) \( \sigma_1(\omega) \) decreases with decreasing \( T \). Upon entering the charge-ordered state \(( T<T_{\text{co}}), \) \( \sigma_1(\omega) \) below 250 cm\(^{-1}\) is severely suppressed, evidencing an opening of charge gap. The magnitude of the gap, \( 2\Delta \), defined as an onset energy of the steeply rising part of \( \sigma_1(\omega) \) is roughly 125 cm\(^{-1}\) at our lowest measurement \( T \), leading to the value of \( 2\Delta/k_B T_{\text{co}} \approx 3.5 \), which is in good agreement with the predicted value for a mean-field charge density wave (CDW) transition.

Besides the gap formation, a broad hump near 800 cm\(^{-1}\) develops at low \( T \). The feature is already evident at 100 K, much higher than \( T_{\text{co}} \), but becomes further enhanced at lower \( T \). Furthermore, dramatic change appears in phonon modes. In addition to the appearance of new phonon peaks below 100 K, very strong antiresonance feature or Fano lineshape has been found for phonons at the region where the electronic background is high, evidencing a strong electron–phonon coupling. The strong electron–phonon interaction may cause a formation of localized bounded states of charge carriers, or small polarons, which is also likely responsible for the observed hump feature.

In the paramagnetic metal region \(( x<0.5 \) of the phase diagram, peculiar charge dynamics is also observed. Fig. 3(a) shows the low-\( \omega \) \( \sigma_1(\omega) \) spectra of a \( \text{Na}_{0.18}\text{CoO}_2 \) crystal at different \( T \). The most striking observation here is that the \( \sigma_1(\omega) \) spectra show distinct suppressions at low \( T \) below about 2000 cm\(^{-1}\). Related to this, the low-\( T \) scattering rate spectra shown in Fig. 3(b), being obtained from extended Drude model, are also suppressed at low \( \omega \). A weak overshoot is present just above the suppression.
The feature significantly resembles those seen in high-Tc cuprates [8]. Our preliminary analysis indicates that the feature is caused by combination of a bosonic mode with which electrons couple strongly and a gap-like feature in the density of states.

3. Metamagnetic transition

The ground state of Na$_x$CoO$_2$ is found to be a paramagnetic metal at $x \sim 0.3$, and to be a ‘Curie–Weiss metal’ at $x \sim 0.70$ [2]. However, the ground state of Na$_x$CoO$_2$ for $x > 0.75$ is still not clear. A phase transition at around 20 K is observed in specific heat and susceptibility measurement for $x = 0.75$ [9,10]. Some works [11] show that Na$_x$CoO$_2$ with $x > 0.75$ undergoes a transition from a paramagnetic state to spin density wave state(SDW).

The authors claimed that the SDW occurs within the CoO$_2$ plane. However, the susceptibility, specific heat and $\mu$SR measurements [10] showed that Na$_{0.85}$CoO$_2$ exhibits a bulk antiferromagnetic (AF) long range order with a Neel temperature about 20 K, and the magnetic order encompasses nearly 100% of the crystal volume.

We studied magnetic susceptibility, specific heat and transport properties on a high quality Na$_{0.85}$CoO$_2$ single crystal in strong magnetic field. A field induced metamagnetic transition from an AF to a quasi-FM state is observed only for $H || c$. Our results suggest that the competition between the AF and FM correlations controls the physics of low-lying excitations in this material.

Fig. 4(a) shows the field dependence of magnetization $M$ on a high quality Na$_{0.85}$CoO$_2$ single crystal for $H || c$, and $H \perp c$, respectively. For $H || c$, a rapid superlinear rise in $M(H)$ is observed at $\sim 8.0 T$ for $T = 5 \text{ K}$. With increasing temperatures, this superlinear rise feature is weakened and disappears above 20 K. This can be more clearly seen from the $dM/dH$ plot (Fig. 4(b)). The appearance of the sharp peaks in $dM/dH$ is an indication of a phase transition. The peak position of $dM/dH$ increases from $\sim 8.0 T$ at $T = 5 \text{ K}$ to $\sim 9.0 T$ at $T = 15 \text{ K}$. For $H \perp c$, the magnetization shows a typical paramagnetic behavior, and $M$ increases linearly with $H$ up to 14 T. This anisotropic magnetic response of the system suggests that the magnetic moments of Co ions are along the $c$-axis.

Fig. 5. The specific heat $C$ of Na$_{0.85}$CoO$_2$ crystal for $H || c$ up to 14 T. (a) $C$ versus $T$ in the transition temperature regime at 0, 2, 4, 6, 8 and 10 T. (b) Same as for (a), but at 10, 12 and 14 T. (c) $C/T$ versus $T^2$ in zero field. (d) $C$ versus $H$ at 5 K.
The specific heat of Na$_{0.85}$CoO$_2$ shows a sharp peak at about 18.5 K at zero field. It corresponds to the magnetic ordering transition as observed in the susceptibility measurements. Fig. 5(a) and (b) show the specific heat $C$ from 16 to 20 K in eight different fields applied along the c-axis. The magnetic ordering transition temperature $T_m$ decreases with increasing $H$ below 10 T (Fig. 5(a)), but increases with $H$ above 10 T (Fig. 5(b)). Our specific heat results indicate that the magnetic ordering is AF-like in low fields, but FM-like in high fields. Fig. 5(d) shows the field dependence of $C$ at 5 K for $H || c$. In low fields, $C$ increases with increasing field, but drops down above 8 T. The critical field $H_m$ obtained from the specific heat is consistent with that obtained from magnetization measurements.

The above results suggest that there is a metamagnetic transition around 8 T in low temperatures. The results show unambiguously that the ground state of Na$_{0.85}$CoO$_2$ is AF ordered in low fields and FM ordered in high fields. Since the in-plane spin correlations revealed by the neutron scattering measurements are predominately FM [12], this suggests that the inter-layer spins are AF coupled but become ferromagnetic correlated after the spin flop transition in Na$_{0.85}$CoO$_2$. Thus the metamagnetic transition here corresponds to a spin flop transition from an AF to a FM state along the c-axis.

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