Charge ordering and magneto-polarons in Na$_{0.82}$CoO$_2$

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Abstract

Using spectral ellipsometry, we have measured the dielectric function of a Na$_{0.82(2)}$CoO$_2$ crystal that exhibits bulk antiferromagnetism with $T_N = 19.8$ K. We identify two prominent transitions as a function of temperature. The first one at 280 K involves marked changes of the electronic and the lattice response that are indicative of charge ordering in the CoO$_2$ layers. The second transition coincides with $T_N = 19.8$ K and reveals a sizeable spin-charge coupling. The data are discussed in terms of charge ordering and formation of magneto-polarons due to a charge-induced spin-state transition of adjacent Co$^{3+}$ ions.
The recent discovery [1] of superconductivity at $T_c \simeq 5$ K in the hydrated cobaltate $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ has engendered many proposals for unusual electronic correlations. A particularly interesting perspective is a spin-triplet pairing state, which has been proposed on the basis of model calculations [2,3] and NMR experiments [4,5]. In this context, the unusual electromagnetic properties of the host material $\text{Na}_x\text{CoO}_2$ have also obtained renewed attention. Its layered crystal structure gives rise to strongly anisotropic electronic properties [6,7]. The essential structural element are metallic $\text{CoO}_2$ layers which consist of rhombohedrally distorted, edge sharing $\text{CoO}_6$ octahedra [8]. The triangular coordination of Co favors geometrically frustrated and thus unconventional magnetic and electronic ground states. The evidence includes an anomalous $T$-dependence of resistivity and Hall-effect [9] and an unusually large thermo-electric power in excess of $100 \mu\text{V/K}$ [6] that is strongly suppressed in a magnetic field [9]. Furthermore, angle resolved photo-emission spectroscopy (ARPES) reveals an extremely narrow ($\sim 70$ meV) and strongly $T$-dependent quasi-particle band [10] in contrast to the calculated band-width of about $1\ e\text{V}$ [7].

In an attempt to obtain additional information on the interplay of charge and spin degrees of freedom, we have performed broad-band (80-44000 cm$^{-1}$) ellipsometry measurements of the in-plane and out-of-plane dielectric function of a $\text{Na}_{0.82(2)}\text{CoO}_2$ single crystal that exhibits bulk antiferromagnetic (AF) order below $T_N=19.8\ K$ [11]. Our data complement recent reports for samples with lower Na content of $x=0.58$ [12] and 0.7 [13] where static magnetism is absent. We observe two prominent transitions as a function of $T$ that were previously not identified with optical experiments. The first transition occurs below 280 K and involves sizeable changes of the electronic and the lattice response that are suggestive of polaron formation and charge ordering within the $\text{CoO}_2$ layers. The second transition evident in the electronic response coincides with $T_N=19.8\ K$ and indicates a strong spin-charge coupling.

A $\text{Na}_{0.82(2)}\text{CoO}_2$ single crystal (3x4x0.3 mm$^3$) was grown in an optical floating zone furnace and characterized by x-ray, transport, magnetic susceptibility, specific heat, and muon-spin rotation ($\mu\text{SR}$) [11]. Susceptibility and $\mu\text{SR}$ experiments established that it
exhibits bulk AF order below $T_N=19.8$ K [11]. The ellipsometric measurements were performed for the range of 0.01-0.8 eV with a home-built ellipsometer in combination with a fast-Fourier-interferometer (FTIR) at the IR-beamline of the ANKA synchrotron at FZ Karlsruhe, Germany [14]. Another home-built ellipsometer [15] was used for the range of 0.5-5.6 eV.

Figure 1 displays the in-plane dielectric properties between 8 and 300 K in terms of the real parts of the optical conductivity, $\sigma_{1ab}=\frac{1}{4\pi \cdot \nu \cdot \varepsilon_{2ab}}$, and the dielectric function, $\varepsilon_{1ab}$. Figure 1a shows $\sigma_{1ab}$ for the entire range from 80 to 44,000 cm$^{-1}$ at 25 and 300 K. The solid arrows mark four bands corresponding to interband transition at 35850 cm$^{-1}$, 23850 cm$^{-1}$, 12200 cm$^{-1}$, 8800 cm$^{-1}$ (1eV $\cong$ 8066 cm$^{-1}$). Based on the band structure calculations [7] we assign the two lower bands to transitions between Co 3d derived bands and the stronger high frequency ones to charge transfer transitions between O-2p and Co-3d bands.

Figures 1b to 1e detail the frequency range below these interband transitions. First we concentrate on the spectra at $T > T_N=19.8$ K. At 300 K the spectral shape of $\sigma_{1ab}$ is characteristic of an incoherent transport mechanism. Whereas it is almost constant between 600 and 6000 cm$^{-1}$, it decreases below 600 cm$^{-1}$ and extrapolates well towards the dc value (black solid circle) [11]. Below 300 K the optical spectra undergo marked changes. With decreasing $T$ a partial gap, a so-called pseudogap (PG), develops which gives rise to a progressive decrease of $\sigma_{1ab}$ between 300 and 4500 cm$^{-1}$. Its onset is marked by an absorption band at higher energies, which most likely corresponds to charge excitations across the PG rather than to a conventional interband transition. At 300 K this band is still fairly weak and broad, whereas at lower T it rapidly sharpens, gains additional spectral weight (SW), and exhibits a sizeable blue-shift from about 3500 cm$^{-1}$ at 300 K to 4500 cm$^{-1}$ at 25 K. We argue below that the PG and the absorption band originate from a partially charge ordered state and the excitations thereof.

As detailed in Figs. 1c and 1d, the PG formation is also accompanied by the growth of two distinct low-frequency electronic modes. A band near 150 cm$^{-1}$ develops below 300 K. Its SW increases at low T, and the simultaneous appearance of anomalous phonon
modes (as discussed below) suggest that it involves small polarons [16]. In the presence of a charge ordered state (as suggested by the PG formation) it may also correspond to a pinned collective phase mode [17]. In addition we identify a very narrow Drude-peak at the origin which accounts for the metallic T-dependence of the dc conductivity [11]. While the narrow Drude-peak is not captured by the $\sigma_{1,ab}$ spectra at $\omega > 80 \text{ cm}^{-1}$, its presence is suggested by the dc conductivity which increases rapidly below 300 K to $\sigma_{dc} \approx 5000 \Omega^{-1}\text{cm}^{-1} >> \sigma(\omega = 80 \text{cm}^{-1}) \approx 600 \Omega^{-1}\text{cm}^{-1}$ at 25K. Moreover, the inductive free carrier response is apparent in $\varepsilon_{1ab}$ for $\omega > 80 \text{ cm}^{-1}$ where a decrease towards negative values at the origin is superimposed on the response of the polaronic mode at 150 cm$^{-1}$. Using a Drude-Lorentz-model we obtain at 25 K (dashed black line in Fig. 1d) $\omega_{pl} = 1300(1) \text{ cm}^{-1}$ and $\gamma_D = 30(10) \text{ cm}^{-1}$ for the plasma frequency and the scattering rate of the free carriers, respectively. The small plasma frequency corresponding to $\omega_{pl}^2 = \frac{2e^2 n}{\pi m^*}$, with $n$ the carrier density and $m^*$ their effective mass, is consistent with the very narrow and weakly dispersive quasi-particle band as seen in ARPES [10]. For the polaronic band we deduce an oscillator strength $S = 450(50)$, a center frequency $\omega = 150(1) \text{ cm}^{-1}$, and a full width at half maximum, $\gamma = 310(30) \text{ cm}^{-1}$.

Next we discuss the characteristic changes in the lattice response which underline that the PG and the polaron band are signatures of a charge ordering transition. Figures 1c, d and f highlight that additional phonon modes suddenly appear below 300 K. Some of these exhibit very asymmetric Fano line shapes that are indicative of a strong interaction with the electronic background, in particular, with the polaron band. At 300 K two phonon modes are resolved at 190 and 545 cm$^{-1}$ which are assigned to vibrations of Na against O and Co against O, respectively [18]. In addition there is a weaker mode at 515 cm$^{-1}$ which has not yet been assigned. Figure 1f details the T-dependence around the strongest mode near 550 cm$^{-1}$. Between 280 and 260 K this mode suddenly splits into a broader mode around 545 cm$^{-1}$ and a narrower one at 565 cm$^{-1}$. In addition the weaker mode around 515 cm$^{-1}$ seems to split into modes at 490 and 525 cm$^{-1}$. Simultaneously, several narrow modes appear below 280 K at 585, 430, 390, 335, 300, 275, and 250 cm$^{-1}$. These sudden changes in the lattice response highlight that a structural transition takes place between 260
and 280 K. Interestingly, this transition is not clearly resolved in the Raman-spectra nor in preliminary x-ray diffraction measurements on small pieces from this crystal, suggesting that the structural changes are fairly small. The sizeable oscillator strength of the additional IR-active phonons thus requires a charge density modulation which strongly couples to the lattice distortions and thereby enhances their dipolar moment. Overall, our optical data provide evidence that the charge carriers within the CoO$_2$ layers exhibit a charge ordering transition between 260 and 280 K. This conclusion is based on (i) the large splitting of the CoO stretching mode and the simultaneous formation of (ii) the PG, (iii) the polaron band, and (iv) the narrow Drude-like response. A freezing transition of the Na ions and subsequent small structural changes involving mainly the Na layer may influence the charge ordering pattern, but cannot account for the highly anomalous optical response. Notably, our conclusion is supported by recent NMR experiments for x=0.75 where a change in the NMR line shape and a sudden reduction in the Co-1/T$_1$ relaxation rate slightly below 300 K were also interpreted in terms of charge ordering in the CoO$_2$ planes [19].

Next we discuss the second transition of the electronic response which coincides with T$_N$=19.8 K. It is evident in Figs. 1c to 1d that the AF transition has a significant impact on the electronic excitations including the PG and the polaron mode at 150 cm$^{-1}$. Apparently, it leads to a partial reversal of the SW transfer that is associated with the charge ordering transition below 280 K. A significant amount of SW is removed from the band at 4500 cm$^{-1}$ and transferred to lower frequencies where it partially fills in the PG. The polaron band at 150 cm$^{-1}$ also exhibits a noticeable anomaly. A sizeable amount of SW is removed from its center at 150 cm$^{-1}$ and redistributed towards higher frequency. Concerning the Drude-peak we cannot draw a firm conclusion. A small upturn of the dc resistivity below T$_N$ [11] might indicate an anomalous SW loss of the Drude-peak, but it may also be explained in terms of an enhanced scattering from static magnetic defects. A reduction of the free carrier response is not evident in the low frequency part of $\varepsilon_1$. This unresolved issue notwithstanding, our optical data highlight a sizeable spin-charge coupling and suggest the presence of magneto-polarons.
This conclusion is underlined by the c-axis optical response as shown in Fig. 2 where the AF transition has an even stronger impact on the polaronic band. At 300 K the electronic c-axis response is rather weak and featureless. The spectra are dominated by two IR-active phonon modes at 300 and 585 cm$^{-1}$ which are assigned to out-of-plane vibrations of Na against O and Co against O, respectively [18]. In analogy to the in-plane response, the charge ordering transition below 280 K is accompanied by the formation of a polaronic band. In contrast to the in-plane response, however, there is no evidence for a PG formation. To the contrary, the inset of Fig. 2b shows that the SW nearly doubles between 300 and 25 K for the range below 3000 cm$^{-1}$. Accordingly, the electronic anisotropy between 80 and 4000 cm$^{-1}$ decreases from about 10 at 300 K to less than three at 25 K. The much larger anisotropy of $\sigma_{ab}^{dc}/\sigma_{c}^{dc}\sim200$ [6] is related to the absence of a Drude-response in the c-axis component. Here the dominant feature is the polaronic band centered around 400 cm$^{-1}$. Notably, it is subdivided by several deep and narrow minima near 265, 335, 565 and 665 cm$^{-1}$ which can be accounted for in terms of extremely asymmetric Fano-modes. These unusual anti-resonances may correspond to defect modes or to local vibrational modes whose response is out-of-phase with the one of the broad polaronic band. The second prominent feature in the c-axis spectra is the strong modification of the polaron band in the AF state. It becomes strongly suppressed below 500 cm$^{-1}$ whereas its SW increases at higher frequency up to 3000 cm$^{-1}$. This marked blue shift of the polaronic band signals an increased self-trapping energy of the magneto-polarons in the AF state where polaron hopping requires spin-flip excitations.

In an attempt to interpret the unusual optical response of Na$_{0.82}$CoO$_2$ we note that strong polaronic features are well known in the related compound La$_{1-y}$Sr$_y$CoO$_3$ [16,20]. Furthermore, it has been suggested that a charge induced spin-state transition of the Co$^{3+}$ ions takes place in La$_{1-y}$Sr$_y$CoO$_3$ which gives rise to a sizeable spin-charge coupling [21,22]. The underlying idea is that a localized positive charge (corresponding to a Co$^{4+}$ ion) lowers the crystal field symmetry of adjacent Co$^{3+}$ ions and thus significantly reduces the crystal field splitting, $\Delta (e_g - t_{2g})$, of the 3d levels favoring an intermediate-spin (IS) state with $S=1$.
over a low-spin (LS) state with S=0. The coupled spin-charge object can be viewed as a small magneto-polaron. The case of dilute magneto-polarons applies to Na$_x$CoO$_2$ (La$_{1-y}$Sr$_y$CoO$_3$) for large x (small y). With decreasing Na-content (increasing y) these magneto-polarons start to overlap and develop spatial correlations. In the absence of additional disorder, a perfect triangular Wigner-lattice of Co$^{4+}$ ions could be realized at quarter filling, i.e. for x=0.75 [23]. A sketch is shown as an inset in Fig. 1e. In this state, the Co$^{3+}$ sites are arranged on a Kagomé-lattice and their IS state can be stabilized due to the axial crystal field originating from the two neighboring Co$^{4+}$ ions. Following these arguments, our present Na$_{0.82}$CoO$_2$ crystal should exhibit a charge ordered state with a considerable number of defects. It is an interesting but yet open question whether these defects tend to segregate and form microscopic regions without charge order. Irrespective of the details, this scenario accounts for the PG in terms of an incomplete charge excitation gap. The large frequency scale of the PG of about 4500 cm$^{-1}$ is explained by the gain in Hund coupling, $J_H$, associated with the LS to IS transition. It also provides a strong spin-charge coupling and therefore naturally explains the large magneto-polaronic effects that occur in the AF state. The IS state of Co$^{3+}$ is Jahn-Teller active, which may explain the observed lattice anomalies. An interesting question concerns the role of the charge disordered regions which seem to give rise to the broad and incoherent electronic background that dominates above the charge ordering transition, i.e. above 280 K. At present we can not make an unambiguous assignment of the narrow Drude-peak and the polaronic band at 150 cm$^{-1}$. They either arise from mobile or weakly localized carriers within the charge disordered regions, or correspond to unpinned or pinned collective phase modes within the charge ordered regions. The latter possibility is favored based on recent IR-reflectivity data on samples with lower Na content where this kind of charge order should vanish. These data indicate indeed that the PG and the low-frequency polaronic band are weakened at x=0.7 [13] and finally absent at x=0.58 [12]. For these Na concentrations, the Drude-peak is significantly broader and less intense than the extremely narrow one in our Na$_{0.82}$CoO$_2$ crystal. Finally, another interesting issue concerns the role of the charge order induced S=1 spins of the Co$^{3+}$ ions in the AF state. As they
reside on a frustrated Kagomé-lattice, they may well remain in a quantum liquid state and not participate in the static magnetic order. Nevertheless, they will mediate an in-plane exchange coupling (likely ferromagnetic) between the S=1/2 moments of Co\(^{4+}\). The idea that the charge ordered state is a prerequisite for static magnetic order is indeed consistent with the finding that static magnetism occurs only for \(x \geq 0.75\) [24]. The expected spin and charge ordering scenario is also in good agreement with the observation of three different muon-spin-precession frequencies [11].

In summary, we have performed broad-band ellipsometric measurements of the in-plane and c-axis dielectric function of a Na\(_{0.82}\)CoO\(_2\) single crystal that exhibits bulk AF order below \(T_N=19.8\) K [11]. We identify two prominent transitions as a function of T. The first one below 280 K involves changes of the electronic and the lattice response which are suggestive of charge ordering in the CoO\(_2\) layers. The most prominent features are a pseudogap with an energy scale of about 4500 cm\(^{-1}\) and a low frequency band which is assigned to small polarons. The second transition coincides with \(T_N=19.8\) K. It strongly affects the polaronic band and the pseudogap and highlights a strong coupling between electronic and magnetic degrees of freedom that is discussed in terms of magneto-polarons, i.e. doped charges that stabilize an intermediate spin state on neighbouring Co\(^{3+}\) ions.

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Figure 1: The in-plane dielectric properties in terms of the real parts of the optical conductivity, $\sigma_{1ab}=1/4\pi\nu\cdot\varepsilon_{2ab}$, and the dielectric function, $\varepsilon_{1ab}$. The spectra of $\sigma_{1ab}$ (a) for the entire spectral range at 300 and 25 K (arrows mark interband transitions), (b) below 6000 cm$^{-1}$ and (c) below 650 cm$^{-1}$ (dc values from Ref. [11] are shown by solid circles, low-frequency extrapolations by dotted lines). Corresponding spectra of $\varepsilon_{1ab}$ are shown in (d) and (e). The black dotted line in (d) shows the Drude-Lorentz fit at 25 K as outlined in the text. The inset of (e) gives a sketch of the suggested charge ordering pattern at x=0.75. (f) Splitting of the strongest phonon mode. The dotted lines indicate the phonon splitting. Offsets have been added to the spectra for clarity.

Figure 2: The c-axis optical conductivity, $\sigma_{1c}$, for polarization perpendicular to the CoO$_2$ layers. (a) Detailed view of the low-frequency range below 650 cm$^{-1}$ and (b) the full measured range below 5000 cm$^{-1}$. The inset shows the integrated spectral weight $SW=\int_{80 \text{ cm}^{-1}}^{\omega'} \sigma_{1c}(\omega')d\omega'$ at different T.
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