Effect of Na content and hydration on the excitation spectrum of the cobaltite Na$_x$CoO$_2$·yH$_2$O

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Abstract. We report on a Raman scattering study on the superconducting cobaltite Na$_x$CoO$_2$·yH$_2$O as function of Na content and hydration (x≈1/3, 3/4 and y≈0, 2/3, 4/3). The observed phonon scattering and scattering continua are analyzed in terms of lattice strain due to the structural misfit and disorder. Hydration, due to the intercalation of one or two H$_2$O layers, releases a part of this strain. Our Raman data suggest a connection between disorder on the partly occupied Na sites, the split off of the a$_{1g}$ level from the other t$_{2g}$ states of Co$^{4+}$ and superconductivity.

1. Properties of Na$_x$CoO$_2$·yH$_2$O

The transition metal compound Na$_x$CoO$_2$·yH$_2$O (x≈1/3, 3/4 and y≈0, 2/3, 4/3) has an appreciable, quasi-metallic conductivity and still shows aspects of strong electronic correlations. There is broader consensus that these correlations play an important role for the recently discovered superconductivity with T$_c$=4.6 K [1], the very large thermopower, and other anomalous transport properties [2–5, 6, 7].

The two-dimensional structure of Na$_x$CoO$_2$ is given by an incoherent coupling of CoO$_2$ layers with Na layers stacked along the c axis [8–11]. The resulting misfit and pronounced strain effects allow, similar to other misfit-layered oxides, for a considerable non-stoichiometry both on the cation and the oxygen sites and an inhomogeneity in charge distribution along the stacking direction of the compound [12, 13]. In Na$_x$CoO$_2$, with x≈0.7, two partly occupied Na sites on a honeycomb lattice alternate along the c axis with a CoO$_2$ layer of edge sharing CoO$_6$ octahedra [12]. Ionic conduction based on high Na mobility exists at room temperature. The octahedra in the CoO$_2$ layers are tilted and have only two oxygen coordinates per layer along the c axis. These oxygen sites

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Figure 1. a) and b) Two projections on a simplified structure of $NaCoO_2$ [9]. The Na sites in a) are only partially occupied. c) electronic level scheme of $Co^{3+/4+}$ with a sketch of two distorted CoO$_6$ octahedra [12]. The two sites Na1 and Na2 have an approximate occupation 1/4 and 1/2, respectively. The line gives the unit cell. The dashed line marks a distortion of the octahedron.

contain the single Co site. In the ab plane the Co sites form a planar triangular lattice, from geometrical point of view the perfect base for competing magnetic interactions. In Figure 1 a) and b) two projected views on the layered structure of $Na_xCoO_2$ are shown.

Samples of $Na_xCoO_2$ with a Na content $0.3<x<0.75$ have been reported. This stoichiometry range corresponds to an average Co valency between $Co^{3.7+}$ and $Co^{3.25+}$. The 3d$^5$ and 3d$^6$ configurations of $Co^{4+}$ and $Co^{3+}$ occupy $t_{2g}$ levels in a low spin state with $s=1/2$ and $s=0$, respectively. Therefore, the above mentioned triangular lattice of Co sites with $s=1/2$ is far from half-filled, i.e. the spins are considerably diluted with $s=0$ states. In Figure 1 c) the corresponding CEF level schemes are shown together with the local coordination of two distorted CoO$_6$ octahedra with the two Na sites, Na1 and Na2. Relevant states at the Fermi level are given by $a_{1g}$ states of 3d$^5$ in $Co^{4+}$ that are split off from the other $t_{2g}$ levels [14]. This split off is due to a combination of a trigonal distortion of the octahedra and kinetic effects [15].

The electronic state of $Na_xCoO_2$ shows some analogy to strongly doped high temperature superconductors with the additional very attractive aspect of frustration [16]. Such a triangular lattice is expected to stabilize a resonance valence bond state better than the well-studied CuO$_2$ square lattice. It also leads to three nesting vectors that could have important implications for the superconducting order parameter [17].
Single band Hubbard models have been proposed as a reasonable simplification taking the split off a $1g$ states as an underlying basis \cite{18, 19, 16}. From experimental point of view the role of electronic correlations and the minimal low-energy model is not clear \cite{17}, as the related Mott-Hubbard insulating phase of Na$_x$CoO$_2$ with 1/2 doping has never been prepared or observed and important electronic parameters could not be determined unambiguously.

The magnetic susceptibility $\chi(T)$ of Na$_x$CoO$_2$ shows a Curie-Weiss behavior with a negative Curie constant $\theta_{cw}$=-170 K for $x=0.75$, while $\chi(T)$ is less temperature dependent for smaller x, i.e. $\theta_{cw}$ is decreasing with increasing Co$^{4+}$/Co$^{3+}$. This composition dependence might be related either to spin frustration and/or additional ferromagnetic correlations. Only in samples with highest Na content ($x=0.75$) long-range magnetic ordering with ferrimagnetic or commensurate SDW ground state is observed with a $T_c$=22 K \cite{20, 21}. In systems with smaller x long-range ordering can only be induced by defects, as Cu substitution on the Co site \cite{22}. Interestingly, the flat magnetic susceptibility for $x=1/3$ has been compared with TiOCl, a two-dimensional quantum spin system with spin gap formation due to orbital ordering and strong spin-lattice coupled fluctuations \cite{23, 24, 25}.

Na$_x$CoO$_2$ has an enormous thermopower and excellent thermoelectric figure of merit \cite{3} that are comparable to the best broad-band semiconductors \cite{26, 27}. These effects origin from the CoO$_2$ layers as these layers are common structural elements for other known thermoelectric cobaltites, as Ca$_3$Co$_4$O$_9$ and Bi$_2$Sr$_2$Co$_2$O$_y$. The thermopower strongly depends on the ratio Co$^{4+}$/Co$^{3+}$. It increases with increasing x, i.e. for smaller Co$^{4+}$/Co$^{3+}$ and closer proximity to magnetic ordering \cite{5}. Applying a moderate longitudinal magnetic field in the ab plane it can be strongly depressed \cite{6}. The large magnetic field dependence rules out its origin in Fermi surface anomalies. Instead, the combination of a large spin/electronic degeneracy and hopping on a triangular, frustrated network has been suggested to be the origin of the large thermopower \cite{4, 6}. Furthermore, the linear temperature dependence of the Hall coefficient at high temperatures and the linear metallic-like conductivity conductivity at low temperatures are both proposed to be related to electronic correlations on such a triangular lattice \cite{7}.

If the Na content is strongly reduced to $x=0.33-0.35$ the resulting samples are extremely hygroscopic and loosely bind H$_2$O into two intercalated layers between the Na and the CoO$_2$ layers. The result is Na$_{0.35}$CoO$_2$·1.3H$_2$O with a nearly doubled c axis parameter \cite{1}. This systems shows superconductivity with $T_c$=4.6 K and considerable experimental and theoretical evidence for an unconventional superconducting order parameter exist \cite{17, 19}. Initial investigations show a complex defect chemistry that allows reversible changes of the hydration level even at room temperature \cite{28}. On the other side it can safely be assumed that strain related to incoherent coupling of CoO$_2$ layers to the partly occupied Na square planes is partly released by hydration. Therefore it might also have an effect on the electronic properties of Na$_{0.35}$CoO$_2$·1.3H$_2$O. At this point more explicit experimental information on the local site symmetries is highly
The existence range of the superconducting phase is very narrow \(0.25 < x < 0.33\) or has proposed to even be a single point of composition \((x=1/3, y=4/3)\). The former interval motivated theoretical investigations about possible competing charge ordered instabilities at the phase boundaries. These phases would correspond to a honeycomb and a Kagome lattice of \(s=1/2\), respectively. Until now no experimental evidence for such phases or the corresponding transitions exists. It should also be noted, that the electronic structure of \(\text{Na}_x\text{CoO}_2\) and the hydrated variant can be considered as Kagome-like even without charge ordering.

The superconducting properties of \(\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}\) resemble those of high temperature superconductors. The system is a type II superconductor with the critical fields \(H_{c1}=28\) Oe and \(H_{c2}=61\) T. The coherence lengths are \(\xi=2.3\) nm and \(\lambda=570\) nm with \(\kappa=250\). The large critical field \(H_{c2}=61\) T is exceptional if compared to the small transition temperature. The anisotropy in transport increases with hydration.
from $\rho_c/\rho_{ab}=200$ to 1000. The specific heat shows a maximum at the transition $\Delta C/T_c = 10.4$ mJ/molK$^2$ and an electronic term $\gamma = 12.2$ mJ/molK$^2$ leading to a reduced jump of $[\Delta C/T_c]/\gamma = 0.85$ considerably smaller than the BCS Value (1.43) \[31]. In another specific heat study a $T^2$ contribution to the specific heat is observed and attributed to line nodes of the superconducting order parameter [32]. Here, the other superconducting parameters differ considerably from above: $\Delta C/T_c = 7.13$ mJ/molK$^2$, $\gamma = 5.45$ mJ/molK$^2$ and $[\Delta C/T_c]/\gamma = 1.31$. In these data a larger non-superconducting volume fraction has been taken into account and $\gamma$ corrected accordingly.

Recent NMR/NQR data show a similar lack of consistency. In one study the Co-Knight is $T$-independent above $T_c$ and decreases moderately for smaller temperatures. Together with the coherence peak in NMR this would signal a singlet order parameter with a full superconducting gap [33]. Another experimental study highlights the negligible temperature dependence of the Knight-shift that is taken as evidence for spin-triplet state of superconductivity in Na$_{0.35}$CoO$_2$ · 1.3H$_2$O [34].

These and other experimental studies are strongly hampered by the easy degradation of the sample and disorder on the Na site. The resulting small superconducting volume fraction does not allow a sample assembly into a vacuum setup at RT. In the present Raman scattering study special care has been taken to avoid these problems using a setup that allows rapid cooling down in a helium contact gas or performing the experiments at Room temperature in a sample cell with humidified atmosphere. Thereby we searched for possible effects of charge ordering or other instabilities and used phonon scattering due to oxygen vibrations as a sensitive probe of the local electronic and structural configuration.

2. Experimental

We have performed Raman scattering experiments on powder and single crystal samples of Na$_x$CoO$_2$ · yH$_2$O as function of Na content $x$ and hydration $y$. (xx) light polarization has been investigated with the incident and scattered electric field vector $x$ in the ab plane of the crystallographic structure. Powder samples were prepared as described elsewhere [1] and cold pressed into tablets. Single crystals of Na$_{0.7}$CoO$_2$ were prepared using a travelling solvent floating zone optical furnace. In a following preparation step Na was deintercalated using a bromine or an electrochemical preparation step [35]. The final hydration and/or equilibration has been performed in humidified air [29].

3. Raman scattering results

3.1. Symmetry considerations and lattice shell model

A symmetry analysis taking into account the P6$_3$/mmc (194) point group for Na$_{0.7}$CoO$_2$ [12] and Na$_x$CoO$_2$ · yH$_2$O [11] leads to the following Raman-active modes

\[ \Gamma_{\text{Raman}} = A_{1g} + E_{1g} + 3E_{2g}. \]
Excitation spectrum of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$

**Figure 3.** Effect of sample environment on (xx) Raman spectra of $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$. a) freshly cleaved single crystal, b) after 2 days in humidified air, c) after 6 hours in helium exchange gas, d) after 3 hours and e) after 6 hours in vacuum. The spectra are normalized in intensity to the mode at 470 cm$^{-1}$.

and the infrared-active modes

$$\Gamma_{\text{IR}} = 4A_{2u} + 4E_{1u}.$$  

Each of the $E_{1g}, E_{2g}$ or $E_{1u}$ modes are doubly degenerate. In this analysis we skipped modes due to hydration of the samples, as no experimental evidence for such modes exist. In the following we will also not discuss anymore the $3E_{2g}$ modes related to Na and oxygen. These modes would be observable in (xz) polarization [36]. The two Na related modes are expected to be smeared out due to disorder and the small occupation of the Na sites.

For the considered modes at the $\Gamma$-point the displacement symmetries are $A_{1g}$ for a displacement in the $z$ direction and $E_{1g}$ for in-plane, diagonal $xy$ displacements. The $A_{1g}$ and $E_{1g}$ modes involve vibrations from only oxygen atoms. Due to full point-group symmetry the Co sites do not contribute to Raman scattering.

We have performed lattice shell model calculations of the phonon frequencies in $\text{Na}_{0.74}\text{CoO}_2$ [12]. To accommodate for the partial occupation of the two Na sites, Na1(0.24) and Na2(0.5), the phonon frequencies for either a fully occupied site Na1 (or a fully occupied Na2) site have been calculated. The frequency of the $E_{1g}$ and $A_{1g}$ modes are 458 cm$^{-1}$ (457 cm$^{-1}$) and 586 cm$^{-1}$ (574 cm$^{-1}$), respectively, i.e. the higher energy $A_{1g}$ mode strongly depends on the Na site occupancy. As mentioned above the
Excitation spectrum of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$

Figure 4. Comparison of single crystal spectra of superconducting and nonsuperconducting samples $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ in (xx) polarization at room temperature. The inset displays spectra on an enlarged scale together with fits. For $x,y=0.7/0.0$ three individual modes are resolved that overlap and form a broad band.

$E_{1g}$ mode is an in-plane oxygen mode with diagonal displacements while the $A_{1g}$ mode is an out-of-plane mode. This explains the strong sensitivity of this excitation to the Na content in the layers that divide the oxygen octahedra in c axis direction. In the following we will show that the pronounced frequency dependence of the $A_{1g}$ mode can be used as a very susceptible sensor of Na distribution/ordering.

3.2. Raman scattering on powder samples

Raman spectra of polycrystalline samples as given in Figure 2 show two sharp modes at 480 cm$^{-1}$ and 598 cm$^{-1}$. These modes correspond to the $E_{1g}$ and the $A_{1g}$ eigenmodes, respectively. The $E_{1g}$ mode hardens due to anharmonicity with decreasing temperature. The linewidth of the $A_{1g}$ mode is substantially broadened at higher temperature. This must be related to pronounced Na diffusion and disorder. At higher energies two very broad maxima exist at 800 and 1000 cm$^{-1}$. These signals are understood as two-phonon scattering. It is noteworthy, that the temperature dependence of this signal is most pronounced for samples that show superconductivity.

Reducing the hydration to zero, drastic effects happen at lower frequency. A broadened, quasi-elastic scattering is suppressed. This continuum might be related to quasi-diffusive excitations of $\text{H}_2\text{O}$ molecules. A second possibility are local paramagnetic fluctuations of the spin system. Such paramagnon scattering has been discussed for high
Excitation spectrum of Na$_x$CoO$_2$·yH$_2$O

temperature superconductors or other low-dimensional quantum spin systems. The continuum observed in Na$_x$CoO$_2$·yH$_2$O resembles to early observations in MnF$_3$ and would correspond to an exchange coupling constant of approximately 130 K. Its highest intensity is observed for y=0.7, i.e. in the sample with one H$_2$O layer. Other sharp modes that do not show a consistent stoichiometry dependence, e.g. at 240 and 700 cm$^{-1}$, are attributed to defect modes.

3.3. Raman scattering on single crystals

Raman scattering experiments on single crystal surfaces do in general provide a better and more consistent view on the excitation spectrum of a compound. In the case of Na$_x$CoO$_2$·yH$_2$O, however, due to the complex defect chemistry given by easy hydration loss, high mobility of Na and its hydroxide formation special precautions have to be taken.

To investigate such effects results of a helium gas and vacuum exposure study are shown in Figure 3. A similar study on Na$_{0.7}$CoO$_2$ can be found in Ref. [36]. The initial state of our Na$_{0.35}$CoO$_2$·1.3H$_2$O single crystal (curve a) has been prepared by a freshly cleaved surface. The sample has then been stored and investigated in humid air for two days (b) and then mounted into a cryostat with Helium contact gas. Consecutive spectra have been taken after a storage at RT in dry Helium gas (c) and later under vacuum (d and e). These steps were interrupted by a cooling down to 200 K or below with cooling rates of 2-4 K/min.

It is evident from these data that the intrinsic phonon linewidth of the fully hydrated, single crystalline Na$_x$CoO$_2$·yH$_2$O is very small. However, surface properties of the crystals show a degradation even under humidified air. Therefore, the linewidth of the c-axis A$_{1g}$ mode broadens. The following reduction of hydration in dry helium gas leads to a moderate decrease of the in-plane E$_{1g}$ mode by about 3 cm$^{-1}$. Most drastic is the effect of a vacuum treatment. The observed shift by 9 cm$^{-1}$ is exceptionally large and as the related mode is an in-plane oxygen vibration can not fully be accounted by the loss of hydration. Therefore we propose a loss of oxygen as the most probable origin of the phonon frequency shift in vacuum.

To figure out the effect of hydration on the "parent compound" (xx) polarized Raman spectra of single crystals at T=295 K are given in Figure 4. In addition to two-phonon scattering with a maximum at 1170 cm$^{-1}$ and modes in the anti-Stokes regime at -470 and -590 cm$^{-1}$ for x=0.3 and 0.7, respectively, there are remarkable changes of the phonon modes in the frequency regime from 450-650 cm$^{-1}$. Na$_{0.7}$CoO$_2$ shows a strongly broadened band-like scattering intensity that has a maximum at 588 cm$^{-1}$, very close to the frequency calculated in a lattice shell model with fully occupied Na1 site. In Na$_{0.3}$CoO$_2$·1.3H$_2$O, in stead, two modes are observed at 582 and 469 cm$^{-1}$. The inset shows a fit using Lorentzians to these intensities. Three modes with different frequencies can be fitted to the broad band of Na$_{0.7}$CoO$_2$.

We interpret the broad band of scattering in Na$_{0.7}$CoO$_2$ as due to a considerable
Excitation spectrum of Na$_x$CoO$_2$·yH$_2$O

strain and possible sublattice formation of the not fully occupied Na1 and Na2 sites. With decreasing temperature a part of this broadening is reduced, as e.g. also seen in the experiments on polycrystalline samples in Figure 2. Ordering processes have been evidenced from $^{23}$Na – NMR in the temperature regime 250-300 K and attributed to a charge disproportionation of the effective Co$^{3.4+}$ into Co$^{3+}$ Co$^{4+}$ [39]. The sensitivity of the c-axis A$_{1g}$ mode frequency on Na site occupation and the high mobility of Na at room temperatures, however, do not support this interpretation.

In the superconducting, hydrated system the phonon spectrum is not broadened although the Na sublattice is even more diluted. Therefore we conclude, that the intercalated and well-ordered H$_2$O layers shield the related disorder. As the observed phonon frequencies correspond to in-plane and out-of-plane eigenmodes of the CoO$_6$ octahedra and their trigonal distortion determines the above discussed Co a$_{1g}$ level energy, an effect of disorder on this level and the density of states at E$_F$ [14] is unquestionable. The observed broadenings and frequency shifts therefore suggest that the narrow superconducting phase space as function of x [29] and the reduced superconducting volume observed in specific heat measurements [31] are rather connected with Na disorder than with the proposed charge ordering instabilities that compete with superconductivity [19]. Further well-controlled studies as function of stoichiometry, disorder and temperature are underway.

4. Conclusions

Our Raman scattering investigations on the superconducting cobaltites Na$_x$CoO$_2$·yH$_2$O as function of Na content and hydration show pronounced effects related to partial occupation and disorder on the Na site. In contrast, no evidence for charge ordering has been found. The strong sensitivity of the transition temperature on local lattice distortions is proposed to origin from a local modulation of the a$_{1g}$ split off from the remaining Co t$_{2g}$ levels. These effects support models of superconductivity based on electronic correlations.

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