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Effect of Na content and hydration on the excitation spectrum of the cobaltite $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$

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Abstract

We report on a Raman scattering study of the superconducting cobaltite $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ as function of Na content and hydration ($x \approx 1/3, 3/4$ and $y \approx 0, 2/3, 4/3$). The observed scattering intensity is analysed in terms of lattice strain, structural misfit and disorder. Hydration, due to the intercalation of one or two H_2O layers, releases a part of this strain. Our Raman data suggest a connection between disorder on the partly occupied Na sites and the narrow phase space of superconductivity.

(Some figures in this article are in colour only in the electronic version)

1. Properties of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$

The transition metal compound $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ ($x \approx 1/3, 3/4$ and $y \approx 0, 2/3, 4/3$) 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 in the recently discovered superconductivity with T_c up to 4.6 K [1], the very large thermopower and other anomalous transport properties [2–7].

The two-dimensional structure of Na_xCoO_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, 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_xCoO_2 , with $x \approx 0.7$, two partly occupied

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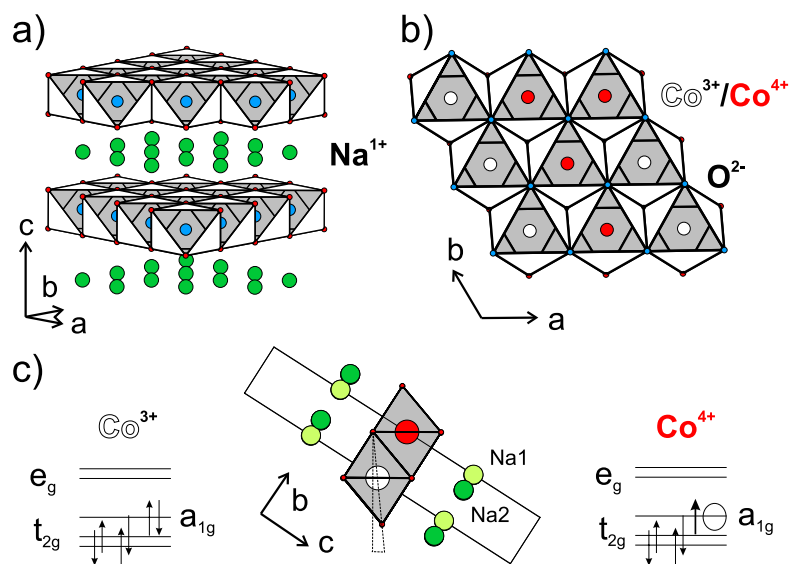


Figure 1. (a) and (b) Two projections on a simplified structure of NaCoO_2 [9]. The Na sites in (a) are only partially occupied. (c) Electronic level scheme of $\text{Co}^{3+/4+}$ with a sketch of two distorted CoO_6 octahedra [12]. The two sites Na1 and Na2 have an approximate occupation of 1/4 and 1/2 respectively. The line gives the unit cell. The dashed line marks a distortion of the octahedron.

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

Samples of Na_xCoO_2 with an Na content $0.3 < x < 0.75$ have been reported. This stoichiometry range corresponds to an average Co valency between $\text{Co}^{3.7+}$ and $\text{Co}^{3.25+}$. The electrons in 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 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 crystalline electric field (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]. It has recently been proposed that spin-orbit coupling shifts the a_{1g} state to lowest energy leaving the hole in two degenerate in-plane states [15]. This would imply orbital degeneracy for this system.

The electronic state of Na_xCoO_2 shows some analogy to strongly doped high-temperature superconductors (HTSC) with the additional very interesting aspect of frustration [16]. The triangular lattice is expected to be a better realization of the resonance valence bond state than the well-studied CuO_2 square lattice in HTSCs [17]. It also leads to three nesting vectors that could have important implications for the superconducting order parameter [18]. Single-band Hubbard models have been proposed as a reasonable simplification taking the split up t_{2g} levels an underlying basis [16, 17, 19–21]. From an experimental point of view the role of electronic correlations and the minimal low-energy model is not so clear [18], as the related

Mott–Hubbard insulating phase of Na_xCoO_2 with 1/2 doping has not been observed and important electronic parameters have not been determined unambiguously.

The magnetic susceptibility $\chi(T)$ of Na_xCoO_2 shows a Curie–Weiss behaviour with a negative Curie constant $\theta_{\text{CW}} = -170$ K for $x = 0.75$, while $\chi(T)$ is less temperature dependent for smaller x , i.e. θ_{CW} is decreasing with increasing $\text{Co}^{4+}/\text{Co}^{3+}$. This composition dependence might be related either to spin frustration and/or additional ferromagnetic correlations. Hopping on a diluted triangular lattice can induce ferromagnetic correlations [17]. Only in the samples with the highest Na content ($x = 0.75$) is long-range magnetic ordering observed at $T_c = 22$ K [22, 23]. Na_xCoO_2 has an enormous thermopower [3] comparable to broad-band semiconductors used for thermoelectric cooling [24, 25]. The thermopower increases with increasing x , i.e. for smaller $\text{Co}^{4+}/\text{Co}^{3+}$ and closer proximity to magnetic ordering [5], and can be strongly depressed in a magnetic field [6]. Therefore it is not related to Fermi surface anomalies but due to a combination of a large spin/electronic degeneracy and hopping on a triangular, frustrated network [4, 6]. If the Na content is strongly reduced to $x = 0.33$ – 0.35 the resulting samples are extremely hygroscopic and loosely bind H_2O into two intercalated layers between the Na and the CoO_2 layers. The result is $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ with a nearly doubled c -axis parameter and superconductivity at $T_c = 4.6$ K [1]. Although this critical temperature might appear small, it is comparable to systems like Sr_2RuO_4 [26] ($T_c = 1.5$ K) that shows triplet superconductivity with broken time-reversal symmetry [27, 28]. Also for $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ there exists experimental and theoretical evidence for an unconventional superconducting order parameter [18, 20, 21]. Initial investigations, however, are mainly related to its complex defect chemistry that allows reversible changes of the hydration level even at room temperature [29]. The effect of hydration and its interplay with the strain induced by partly occupied Na sites might be a key element in understanding this compound.

The range of existence of the superconducting phase is very narrow $0.25 < x < 0.33$ [30], and has even been proposed to be a single point of composition ($x = 1/3$, $y = 4/3$) [11]. The former interval motivated theoretical speculations about competing charge ordered states at the phase boundaries. These correspond to a honeycomb or a Kagome lattice of $s = 1/2$ respectively [20]. It should be noted that the electronic structure of Na_xCoO_2 and the hydrated variant can be considered as Kagome-like even without charge ordering [15].

$\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ is a type II superconductor with critical fields $H_{c1} = 28$ Oe and $H_{c2} = 61$ T [31]. Such a large H_{c2} can be taken as anomalous if compared with the small transition temperature. The specific heat shows a maximum at the transition with a reduced jump of $[\Delta C/T_c]/\gamma = 0.85$, much smaller than the BCS value (1.43) [32]. 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 [33]. Here, the superconducting parameters differ considerably from those given above, as a larger non-superconducting volume fraction was taken into account. This leads to $[\Delta C/T_c]/\gamma = 1.31$. Evidence for unconventional superconductivity is clearer in recent nuclear magnetic resonance (NMR)/nuclear quadrupole resonance (NQR) data. However, the data reported here by different groups vary considerably in this case as well. In one study the Co Knight shift decreases moderately at low temperatures [34]. Another experimental study highlights the negligible temperature dependence of the Knight shift that is taken as evidence for a spin-triplet state of superconductivity in $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ [35]. The latter scenario has been backed up by theoretical considerations and modelling [16, 18, 20]. Recent muon spin resonance (μSR) experiments also support a spin-triplet superconducting state. However, they rule out a breaking of time-reversal symmetry [36].

These and other experimental studies are strongly hampered by the easy degradation of the samples and the narrow range of existence of superconductivity. In the present Raman

scattering study special care has been taken to avoid these problems by using a set-up that allows rapid cooling down in a helium contact gas or by performing the experiments at room temperature in a sample cell with a 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 details

We have performed Raman scattering experiments on powder and single-crystal samples of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ 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 $\text{Na}_{0.7}\text{CoO}_2$ 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 [37]. The final hydration and/or equilibration was performed in humidified air [30].

3. Raman scattering results

3.1. Symmetry considerations and the lattice shell model

A symmetry analysis taking into account the $P6_3/mmc$ (194) point group for $\text{Na}_{0.7}\text{CoO}_2$ [12] and $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ [1] leads to the following Raman-active modes

$$\Gamma_{\text{Raman}} = A_{1g} + E_{1g} + 3E_{2g},$$

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 neglected modes due to hydration of the samples, as no experimental evidence for such modes exists. In the following we will also not discuss the $3E_{2g}$ modes related to Na and oxygen. These modes would be observable in (xz)-polarization [38]. 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 Γ -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 oxygen atoms only. 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 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 occupation of a layer that divides the oxygen octahedra in the 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 sensitive probe of Na distribution/ordering.

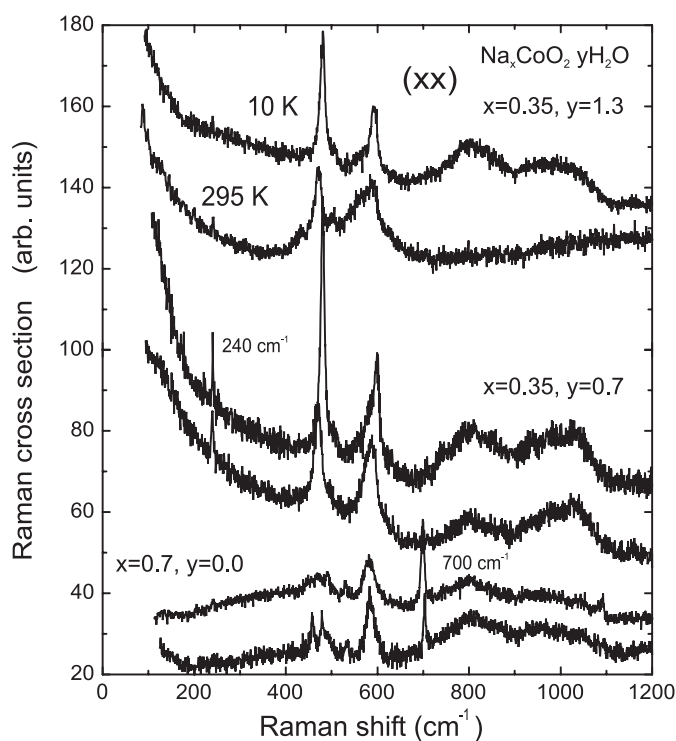


Figure 2. Raman scattering intensity divided by the Bose factor of polycrystalline $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ as a function of Na content x and hydration y at 10 and 295 K in the upper and lower curves respectively. The curves are shifted for clarity. The sharp lines at 240 and 700 cm^{-1} are attributed to second phases.

3.2. Raman scattering on powder samples

Raman spectra of polycrystalline samples as given in figure 2 show two sharp modes at 480 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.

Upon reducing the hydration to zero, drastic effects occur at lower frequency. A broadened, quasi-elastic scattering contribution is suppressed. This continuum might be related to quasi-diffusive excitations of H_2O molecules. A second possibility is local paramagnetic fluctuations of the spin system. Such paramagnon scattering has been discussed for high-temperature superconductors or other low-dimensional quantum spin systems [40]. The continuum observed in $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ resembles early observations in RbMnF_3 [41] 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_2O layer. However, its onset does not scale with Na content x . A final possibility would be unscreened electronic fluctuations. These are observable in Raman scattering if the Fermi surface is anisotropic or consists of two bands, as electronic fluctuations between light and heavy quasiparticles are not screened. Evidence for a two-band character at E_F has recently been extracted from

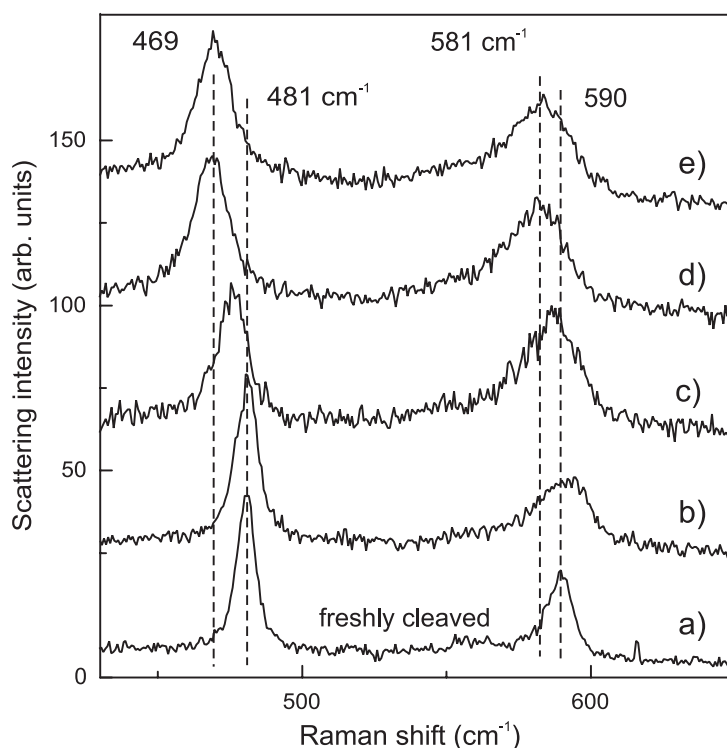


Figure 3. Effect of sample environment on (xx) Raman spectra of $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$. (a) Freshly cleaved single crystal, (b) after 2 days in humidified air, (c) after 6 h in helium exchange gas, (d) after 3 h and (e) after 6 h in vacuum. The spectra are normalized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

a combined transport/specific heat study [42]. Further investigations as a function of well-controlled stoichiometry and temperature aimed at a better understanding of this signal are under way.

3.3. Raman scattering on single crystals

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

To investigate such effects, the results of a helium gas and vacuum exposure study are shown in figure 3. A similar study on $\text{Na}_{0.7}\text{CoO}_2$ can be found in [38]. The initial state of our $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ single crystal (curve a) has been prepared by a freshly cleaved surface. The sample was then stored and investigated in humid air for 2 days (b) and then mounted into a cryostat with helium contact gas. Consecutive spectra have been taken after storage at room temperature in dry helium gas (c) and later under vacuum ((d) and (e)). These steps were separated by cooling down to 200 K or below at cooling rates of $2\text{--}4\text{ K min}^{-1}$.

It is evident from these data that the intrinsic phonon linewidth of the fully hydrated, single-crystalline $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ is very small. However, the 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

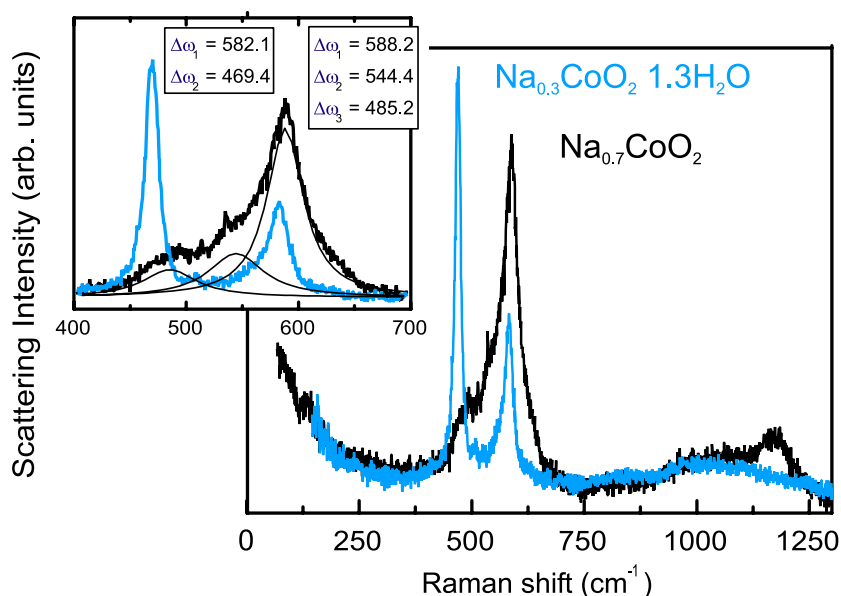


Figure 4. Comparison of single crystal spectra of superconducting and non-superconducting samples $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ in (xx) -polarization at room temperature. The inset displays spectra on an enlarged scale together with fits. For $x, y = 0.7/0.0$ three individual modes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

of the in-plane E_{1g} mode by about 3 cm^{-1} . Most drastic is the effect of a vacuum treatment. The observed shift of 9 cm^{-1} is exceptionally large and cannot be fully accounted by the loss of hydration because the related mode is an in-plane oxygen vibration. Therefore we propose a loss of oxygen connected with a charge transfer as the most probable origin of the phonon frequency shift in vacuum [39].

To figure out the effect of hydration on the ‘parent compound’ (xx) -polarized Raman spectra of single crystals at $T = 295 \text{ K}$ are given in figure 4. In addition to two-phonon scattering with a maximum at 1170 cm^{-1} there are remarkable changes of the phonon modes in the frequency regime from 450 to 650 cm^{-1} . $\text{Na}_{0.7}\text{CoO}_2$ 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 a fully occupied Na1 site. In $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$, instead, two modes are observed at 582 and 469 cm^{-1} . The inset shows a fit to these intensities using Lorentzians. Three modes with different frequencies can be fitted to the broad band of $\text{Na}_{0.7}\text{CoO}_2$.

We interpret the broad band of scattering in $\text{Na}_{0.7}\text{CoO}_2$ as due to a considerable strain and possible sublattice formation of the incompletely occupied Na1 and Na2 sites. With decreasing temperature part of this broadening is reduced, as is 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 $\text{Co}^{3.4+}$ into Co^{3+} and Co^{4+} [43]. The sensitivity of the c -axis A_{1g} mode frequency to the Na site occupation and the high mobility of Na at room temperature, 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. As a narrowing of the out-of-plane and full formation

of the in-plane CoO_6 eigenmodes are observed, we conclude that the intercalated and well-ordered H_2O layers [11] shield the related disorder. If trigonal distortions of the CoO_6 octahedra are important for the Co t_{2g} level splitting a sensitive interplay of stoichiometry and the local density of states at E_F [14] evolves. This strongly suggests a causality between the narrow superconducting phase space [30], the reduced superconducting volume [32] and disorder on the Na site.

Taking the evidence for spin-triplet superconductivity in the cobaltites from NMR and μSR seriously, there exists a very efficient mechanism to depress T_c with disorder and Na non-stoichiometry. This is the strong pair breaking that any defect or local variation of electronic parameters imposes on a system with an unconventional order parameter. In the well-established triplet superconductor Sr_2RuO_4 [44] disorder played a crucial role in determination of the non-s-wave gap symmetry [45]. To model the observed dome-shaped dependence of $T_c(x)$ centred at $(x = 1/3, y = 4/3)$ in the phase diagram, the Abrikosov–Gork'ov pair-breaking function may be mirrored about a single Na composition with minimum defect density. In this view the relevance of charge ordered phases at the boundary of superconductivity and the band filling scenario should be reconsidered.

4. Conclusions

Our Raman scattering investigations on the superconducting cobaltites $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ as a function of Na content x and hydration y 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 x and the related local lattice distortions may originate from a local modulation of the a_{1g} split-off together with strong pair breaking in a triplet superconductor.

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