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P Lemmens
*Max-Planck-Institute For Solid State Research*

K. Y. Choi
*Tohoku University*

E Sherman
*University of Toronto*

Dapeng Chen
*Max-Planck-Institute For Solid State Research*, dapeng@uow.edu.au

C T Lin
*Max-Planck-Institute For Solid State Research*

*See next page for additional authors*

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## Abstract

Raman scattering experiments on NaxCoO2·yH2O single crystals show a broad electronic continuum with a pronounced peak around 100 cm-1 and a cutoff at approximately 560 cm-1 over a wide range of doping levels. The electronic Raman spectra in superconducting and nonsuperconducting samples are similar at room temperature, but evolve in markedly different ways with decreasing temperature. For superconducting samples, the low-energy spectral weight is depleted upon cooling below T*∼150 K, indicating the opening of a pseudogap that is not present in nonsuperconducting materials. Weak additional phonon modes observed below T* suggest that the pseudogap is associated with charge ordering.



## Keywords

scattering, raman, electronic, anomalous, yh2o, naxcoo2


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## Authors

P Lemmens, K. Y. Choi, E Sherman, Dapeng Chen, C T Lin, F. C. Chou, and B Keimer

# Anomalous Electronic Raman Scattering in $Na_xCoO_2 \cdot yH_2O$

P. Lemmens,[1,2] K. Y. Choi,[3,4] V. Gnezdilov,[5] E. Ya. Sherman,[6] D. P. Chen,[1] C. T. Lin,[1] F. C. Chou,[7] and B. Keimer[1]

[1]*Max Planck Institute for Solid State Research, D-70569 Stuttgart, Germany*
[2]*Institute for Condensed Matter Physics, TU Braunschweig, D-38106 Braunschweig, Germany*
[3]*2. Physikalisches Institute, RWTH Aachen, D-52056 Aachen, Germany*
[4]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[5]*B. I. Verkin Institute for Low Temperature Physics, NASU, 61164 Kharkov, Ukraine*
[6]*Department of Physics, University of Toronto, Toronto, Ontario M5S 1A7, Canada*
[7]*Center for Materials Science and Engineering, MIT, Cambridge, Massachusetts 02139, USA*

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Raman scattering experiments on $Na_xCoO_2 \cdot yH_2O$ single crystals show a broad electronic continuum with a pronounced peak around 100 $cm^{-1}$ and a cutoff at approximately 560 $cm^{-1}$ over a wide range of doping levels. The electronic Raman spectra in superconducting and nonsuperconducting samples are similar at room temperature, but evolve in markedly different ways with decreasing temperature. For superconducting samples, the low-energy spectral weight is depleted upon cooling below $T^* \sim 150$ K, indicating the opening of a pseudogap that is not present in nonsuperconducting materials. Weak additional phonon modes observed below $T^*$ suggest that the pseudogap is associated with charge ordering.

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The hydrated cobaltate $Na_xCoO_2 \cdot yH_2O$ has recently been in the focus of research on correlated electron systems, because it enables investigations of the relationship between superconductivity (SC) [1] and magnetic ordering on a triangular lattice [2,3]. Electronic correlations can be tuned either by changing the Na content, leading to long-range antiferromagnetic order for $0.75 \leq x \leq 0.85$ ($T_N = 20$ K) [4,5] and an insulating, charge-ordered ground state at $x = 1/2$ [6,7], or by hydration leading to superconductivity [1,8] in Na-poor samples with $x \sim 1/3$ and $y \sim 4/3$.

For Na-rich cobaltates, angle-resolved photoemission experiments [9,10] show a large holelike, hexagonal Fermi surface dominated by Co $t_{2g}$ states of $a_g$ symmetry [11–13]. Several anomalies are observed in this doping range and for temperatures below approximately 150 K. Among them are a break in a weakly dispersing quasiparticle band at an energy of ~70 meV ≡ 560 $cm^{-1}$, which was attributed to a bosonic mode of electronic or lattice origin [9,10]; a $T$-linear resistivity; a colossal thermopower [14]; an anomalous linear frequency/energy dependency of the electronic scattering rates [15]; and a polaronic mode [16]. With increasing temperature the low-energy quasiparticle peaks broaden substantially and become incoherent [9,10]. Charge ordering on the cobalt sites for $x = 1/2$ with a metal-insulator transition at $T_{MIT} = 53$ K [17,18] is related to the nested Fermi surface with a flat-band feature. Furthermore, SC states with unconventional/anisotropic order parameters may be expected [13,19–21]. However, in Na-poor but still nonhydrated cobaltates ($x \approx 0.3$), charge is more delocalized and the Fermi liquid character of the quasiparticles appears to be recovered with noticeable mass enhancement [9].

Very little spectroscopic information has thus far been reported on hydrated, SC cobaltates. Here we report the observation of pronounced electronic Raman scattering (RS) over a wide range of doping levels comprising the SC regime of the phase diagram. This feature indicates strong carrier scattering by bosonic modes, similar to that observed in underdoped superconducting cuprates. The electronic RS continua in SC and non-SC samples are similar at room temperature, but evolve in a markedly different way as the temperature is lowered. Specifically, a pseudogap opens up below $T \leq T^* \sim 150$ K in SC, but not in non-SC samples. Weak additional phonon modes observed below $T^*$ indicate that the pseudogap may be associated with charge ordering.

Raman scattering experiments with an excitation wavelength $\lambda = 514$ nm, power $P = 6$ mW, and focus diameter $\varnothing = 100$ $\mu$m of parallel, in-plane light polarization were performed in quasibackscattering geometry. This scattering configuration allows both the $A_{1g}$ and the $E_{1g}$ symmetry component. To our knowledge, this is the first systematic RS study of freshly cleaved $ab$ surfaces of single crystals from optical traveling-solvent floating-zone furnaces [22–24]. After cleavage, the samples were instantaneously cooled down in He contact gas in order to prevent dehydration [28] or Na ordering at elevated temperatures [6,29]. We present RS data on four well characterized samples: three non-SC samples with $y = 0$ and $x = 0.5$, 0.83, and ≤1, and one SC sample with $x = 0.34$ and $y = 1.3$.

Figure 1 shows the low-temperature RS response Im$\chi$ (the measured RS cross section corrected for the Bose thermal population factor) of three non-SC samples with Na content $x = 0.5$, 0.83, and ~1. All spectra show two strong phonon modes around 580 and 480 $cm^{-1}$, which can be attributed to Raman-active out-of-plane $A_{1g}$ and in-plane $E_{1g}$ vibrations, respectively, of oxygen in the $CoO_6$

 

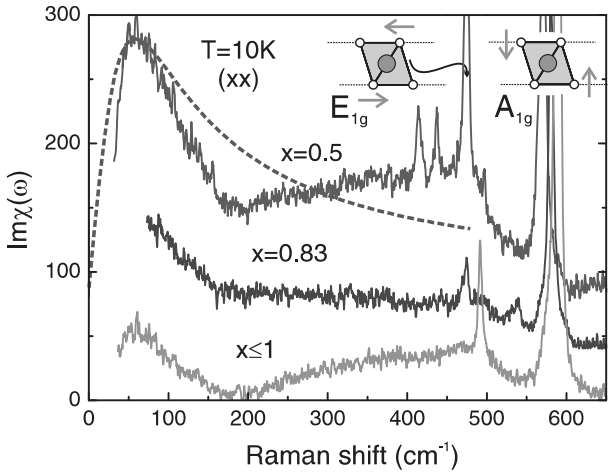


FIG. 1 (color online). Raman cross section at $T = 10$ K for $x = 0.5$, 0.83, and 1.0 with in-plane ($xx$) light polarization. The insets give oxygen displacements of the main phonon modes using small (large) circles for oxygen (cobalt) ions. The curves are shifted for clarity, and the dashed lines give an estimate of the background scattering. The curved dashed line corresponds to an electronic RS process with a single, frequency-independent scattering rate, $\Gamma = 58$ cm$^{-1}$.

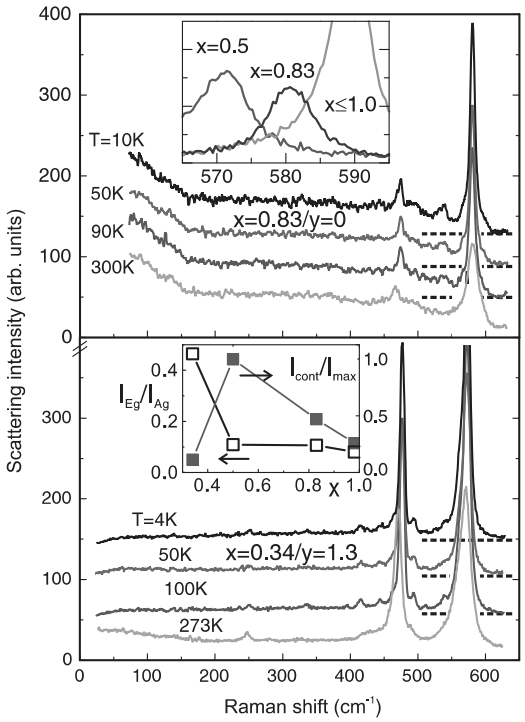


FIG. 2 (color online). RS intensity of $Na_{0.83}CoO_2$ (upper panel) and $Na_{0.34}CoO_2 \cdot 1.3D_2O$ (lower panel) in $xx$ light polarization with $x$ in the $ab$ plane of the crystal. Upper inset: zoomed view on the out-of-plane $A_{1g}$ mode ($T = 10$ K). Lower inset: intensity of the in-plane phonon (normalized by the out-of-plane phonon) and the normalized integrated intensity of the continuum in the frequency range 78 cm$^{-1} \leq \Delta\omega \leq 550$ cm$^{-1}$.

octahedra [25,26]. The eigenvectors are shown as insets in Fig. 1. The sharpness of the higher-frequency mode, whose frequency softens systematically with decreasing $x$ (inset of Fig. 2), testifies to the homogeneity of the samples. The sample with $x = 0.5$, for which Na ordering and a metal-insulator transition have been reported [6,7], shows additional modes at 413, 437, and 497 cm$^{-1}$, close to the energy of the in-plane phonon. This demonstrates the sensitivity of this phonon to structural and electronic ordering processes. In contrast, the sample with $x = 0.83$ exhibits weak modes around 485 and 540 cm$^{-1}$ that might be due to an admixture of interplane polarizations, attributable to an $E_{2g}$ mode involving both Na and O motions [25–27]. No anomalous behavior of the phonon modes is observed in frequency and temperature beyond lattice anharmonicities.

The most striking aspect of the spectra shown in Fig. 1 is a continuum with a pronounced, broad peak around $\sim$100 cm$^{-1}$. Above the peak, the intensity levels off, and a plateau extends up to about 550 cm$^{-1}$. Since the crystals are of high quality and show sharp phonon spectra, phonon density-of-states effects can be ruled out as the origin of the continuum. The upper cutoff of the continuum remains at roughly the same energy of 550 cm$^{-1}$ irrespective of Na contents. This is in excellent correspondence with the width of the quasiparticle band determined by photoemission spectroscopy [9,10] as well as with the knee in the reflectance seen by optical spectroscopy [7]. We hence attribute our observations to electronic RS. Noticeably, the continuum intensity increases nearly monotonically with increasing hole doping, corresponding to decreasing Na content (lower inset of Fig. 2). This effect corresponds to the increase of the Fermi surface with hole doping that satisfies the Luttinger theorem [10]. Deviations seen in the SC sample will be discussed below.

The upper panel of Fig. 2 shows the temperature evolution of the RS intensity of antiferromagnetic $Na_{0.83}CoO_2$ ($T_N = 19.8$ K). The data are intentionally presented as raw, non-Bose corrected RS intensity. The weak temperature dependence of the spectra demonstrates that the temperature dependence of the RS scattering cross section approximately compensates the Bose thermal population factor. The lower panel displays electronic Raman scattering in the superconducting sample of composition $Na_{0.34}CoO_2 \cdot 1.3D_2O$ and superconducting transition temperature $T_{sc} = 4.6$ K. The overall shapes of the continua are similar at room temperature, but the intensity is significantly weaker in the hydrated compound.

Similar flat and only weakly frequency- and temperature-dependent continua have been observed in RS on high-temperature superconductors and were interpreted in terms of a marginal Fermi liquid state. A scattering rate $\Gamma(T, \omega)$ that is linearly dependent on temperature and energy leads to such a plateau in a collision-limited RS process with $\mathrm{Im}\chi(q, \omega) \propto (\omega\Gamma)/(\omega^2 + \Gamma^2)$ [30,31]. The

plateau observed in the cobaltates could be the consequence of strong electronic correlations as in the high-$T_c$ cuprates. A linear temperature dependence of the scattering rate has also been observed in IR and photoemission experiments on cobaltates [9,15]. We notice that the plateau is restricted to a low-frequency region below 550 $cm^{-1}$ ($\approx$0.07 eV). Photoemission and IR spectroscopy measurements give indirect evidence for a bosonic mode of electronic, lattice, or magnetic origin in the same energy range [7,9,10]. Whatever its origin, interaction of charged quasiparticles with this mode may also be responsible for the sharp high-frequency cutoff of the RS continuum.

The enhanced intensity seen below $\sim$150 $cm^{-1}$ can also be discussed within the framework of collision-dominated RS, where a single, frequency-independent scattering rate $\Gamma \sim 60$ $cm^{-1}$ produces a broad peak in the RS response. Notably, this rate corresponds to the temperature scale at which the quasiparticle dynamics observed by photoemission becomes incoherent. However, the description of the data in terms of this simple model is not quantitatively accurate (dashed curve in Fig. 1 for $x = 0.5$), indicating that the situation realized in the cobaltates is more complex. It is also interesting to compare the low-energy data to RS spectra of ferromagnetic semiconductors such as $(Eu_{1-x}, Gd_x)O$, which evolve continuously from a high-temperature, collision-dominated regime to a low-temperature regime with Gaussian-shaped inelastic peaks attributable to magnetic polarons [32]. Our data most closely resemble those of $(Eu_{1-x}, Gd_x)O$ in an intermediate-temperature crossover regime, where ferromagnetic clusters are believed to coexist with a paramagnetic metallic state. This may reflect a similar situation in the cobaltates. Indeed, infrared spectra of $Na_{0.82}CoO_2$, where a similar peak was observed (albeit at a somewhat larger frequency of $\sim$150 $cm^{-1}$), as well as inelastic magnetic neutron scattering data [33] were interpreted in terms of a polaron picture [16].

The spectra of SC and non-SC samples show a very different evolution as the temperature is lowered. This is highlighted in Fig. 3, where the low-energy Im$\chi$ is presented for samples with $x = 0.34$ and $x = 0.83$. At high temperatures both spectra show similar kinks at 185 and 170 $cm^{-1}$, respectively. While the kink position is temperature independent in the non-SC sample [Fig. 2(a)], the SC sample shows a spectral-weight removal that gradually shifts from lower to higher energies with decreasing temperature. For $T < 150$ K, the low-energy spectral weight is sharply suppressed, opening up a "pseudogap" that is not present in samples with $x \geq 0.5$. At 4 K, the spectral depletion is most pronounced at energies below $\sim$70 $cm^{-1}$, but extends up to 230 $cm^{-1}$, only a factor of 2 smaller than the high-energy cutoff of the continuum. This implies that the pseudogap energy is not only large compared to the SC transition temperature, but also that it

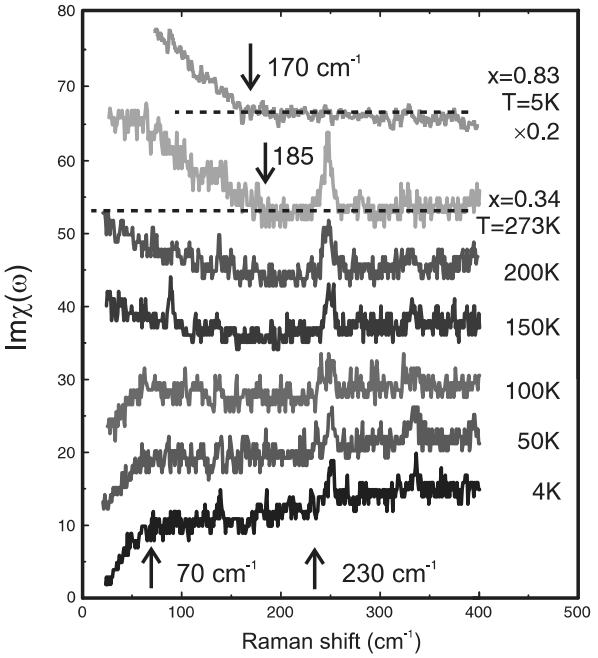


FIG. 3 (color online). Low-energy RS cross section Im$\chi$ as function of temperature for $Na_{0.34}CoO_2 \cdot 1.3D_2O$. The top curve gives one data set for $x = 0.83$ at $T = 4$ K scaled by a factor of 0.2. The arrows mark typical energy scales.

constitutes a significant fraction of the energy scales characterizing the electronic structure.

The experiments presented here are among the first to address electronic excitations in SC cobaltates. The reduced intensity of the RS continuum in SC compared to non-SC samples is in general agreement with prior photoemission experiments indicating a crossover from strongly to weakly renormalized quasiparticles with decreasing Na content. Our observation of a pseudogap is also consistent with a recent high-resolution photoemission experiment that has revealed hints of a partial spectral-weight depletion in $Na_xCoO_2 \cdot yH_2O$ in a similar temperature range as that covered by our experiment [34].

The phonon spectrum close to the in-plane $E_{1g}$ phonon gives a clue to the microscopic origin of the pseudogap (Fig. 4). Compared to the nonhydrated samples, this mode has gained considerable spectral weight in the hydrated, superconducting sample (lower inset of Fig. 2). Below $T^*$, weak sidebands develop in a manner similar to the charge-ordered state in $Na_{0.5}CoO_2$ (Fig. 1). In contrast, the out-of-plane mode does not couple strongly to the electronic states in the plane. In analogy to the sample with $x = 0.5$ (Fig. 1), this effect indicates the formation of a superlattice due to charge ordering. The weak intensity of these modes in the SC sample and their gradual onset point to a very small order parameter in the presence of strong fluctuations [35].

Evidence of charge ordering has thus far not been reported in SC samples. However, based on model calculations charge ordering has been proposed to be an instability

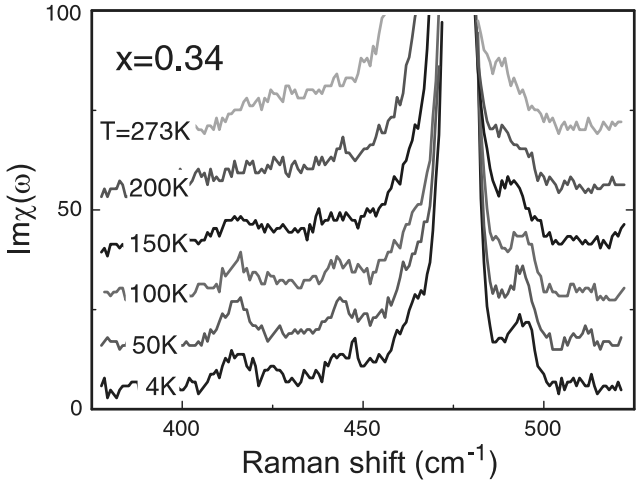


FIG. 4 (color online). Raman intensity in the vicinity of the $E_{1g}$ phonon with superlattice modes for $T < T^*$.

competing with SC [8,20,22]. In the charge-ordered state, the low-energy electronic fluctuations related to the Co $t_{2g}$ states at the Fermi energy are expected to be partially suppressed, consistent with our observation [12].

In conclusion, our observation of a low-energy spectral-weight depletion of the electronic RS continuum in SC cobaltates provides evidence for the formation of a pseudogap at temperatures below $T^* \sim 150$ K. Weak phonon anomalies point to the formation of a charge-ordered state below $T^*$. It is interesting to note that a pseudogap has recently also been observed in $La_{1.2}Sr_{1.8}Mn_2O_7$ and attributed to polaron dynamics [36]. With respect to the cobaltates, further experiments are required to assess whether charge order coexists microscopically with SC, or whether the material phase-segregates into SC and charge-ordered states.

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