Competing orders in Na$_x$CoO$_2$ from strong correlations on a two-particle level

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Based on dynamical mean-field theory with a continuous-time quantum Monte-Carlo impurity solver, static as well as dynamic spin and charge susceptibilities for the phase diagram of the sodium cobaltate system Na$_x$CoO$_2$ are discussed. The approach includes important vertex contributions to the $q$-dependent two-particle response functions by means of a local approximation to the irreducible vertex function in the particle-hole channel. A single-band Hubbard model suffices to reveal several charge- and spin-instability tendencies in accordance with experiment, including the stabilization of an effective kagomé sublattice close to $x=0.67$, without invoking the doping-dependent Na-potential landscape. The in-plane antiferromagnetic-to-ferromagnetic crossover is additionally verified by means of the computed Korringa ratio. Moreover an intricate high-energy mode in the transverse spin susceptibility is revealed, pointing towards a strong energy dependence of the effective intersite exchange.

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The investigation of finite-temperature phase diagrams of realistic strongly correlated systems is a quite formidable task due to the often tight competition between various low-energy ordering instabilities. In this respect the quasi-two-dimensional (2D) sodium cobaltate system Na$_x$CoO$_2$ serves as a notably challenging case [1,2]. Here $x\in[0,1]$ nominally mediates between the Co$^{3+}(3d^6, S=1/2)$ and Co$^{3+}(3d^5, S=0)$ low-spin states. Thus the Na ions provide the electron doping for the nearly filled $t_{2g}$ states of the triangular CoO$_2$ layers up to the band-insulating limit $x=1$. Coulomb correlations with a Hubbard $U$ up to 5 eV for the $t_{2g}$ manifold of bandwidth $W\sim1.5$ eV [3] are revealed from photoemission [4]. Hence with $U/W\gg1$ the frustrated metallic system is definitely placed in the strongly correlated regime.

Various different electronic phases and regions for temperature $T$ vs. doping $x$ are displayed in the experimental sodium cobaltate phase diagram (see Fig. 1). For instance a superconducting dome ($T_c\sim4.5$K) stabilized by intercalation with water close to $x=0.3$ [5]. Pauli-like magnetic susceptibility is found in the range $x<0.5$ [1] with evidence for 2D antiferromagnetic (AFM) correlations [2,6]. For $x>0.5$ spin fluctuations and increased magnetic response show up for $0.6<x<0.67$, including the evolution to Curie-Weiss (CW) behavior [1] for $0.6<x<0.75$, and the eventual onset of in-plane ferromagnetic (FM) order. The ordered magnetic structure in the doping range $0.75<x<0.9$ with $T_N\sim19-27$K [7,10] is of A-type AFM for the FM CoO$_2$ layers. As the local spin-density approximation (LSDA) is not sufficient to account for the AFM-to-FM crossover with $x$ [9], explicit many-body approaches are needed [11,13].

Several theoretical works have dealt with the influence of the sodium arrangements on the electronic properties of Na$_x$CoO$_2$, both from the viewpoint of disordered sodium ions [12] as well as from orderings for certain dopings [13-16]. However, whether such sodium patterns are due to sole (effective) single-particle potentials or mainly originating from many-body effects within the CoO$_2$ planes is still a matter of debate [17,18].

In this letter, we report the fact that a large part of the electronic (spin and charge) phase diagram of sodium cobaltate may be well described within a Hubbard model using realistic dispersions, and without invoking the details of the sodium arrangement. Thereby most of the observed crossovers and instabilities are truly driven by strong correlation effects and cannot be described within weak-coupling scenarios. The theoretical study is elucidating the two-particle correlations in the particle-hole channel computed within dynamical mean-field theory (DMFT) including vertex contributions (for a review see e.g. [19,20]). So far the latter have been neglected in cobaltate susceptibilities based on LSDA [21,22] and the fluctuation-exchange approximation [22,23]. Our dynamical lattice susceptibilities allow to reveal details of the AFM-to-FM crossover with $T$ and of the intriguing charge-ordering tendencies, both in line with recent experimental data [2,24]. Moreover, insight in the $(x,q)$-dependent spin excitations at finite frequency is provided.

FIG. 1. (color online) Left: Sketched Na$_x$CoO$_2$ phase diagram, based on Ref.[2]. Right: $M^-$ (top) and $K^-$ (bottom) point ordering on the triangular lattice.
Since we are mainly interested in the $x>0.5$ part of the phase diagram, the low-energy band dispersion of sodium cobaltate is described within an $a_{1g}$-like single-band approach, justified from photoemission [24] and Compton scattering [26] experiments. We primarily focus on the in-plane processes on the effective triangular Co lattice with tight-binding parameters up to 3rd nearest-neighbor (NN) hopping, i.e., $(t, t', t'')=(-202, 35, 29)\text{meV}$ [27] for the 2D dispersion. Albeit intersite Coulomb interactions might play a role [13], the canonical modeling was restricted to an on-site Coulomb interaction $U=5\text{ eV}$. Our calculations show that already therefrom substantial nonlocal correlations originate. The resulting Hubbard model on the triangular lattice is solved within DMFT for the local one-particle Green’s function $G(\tau_{12})=-(T_{\tau}c(\tau_{1})c(\tau_{2}))$ with $\tau_{uv}=\tau_{u}-\tau_{v}$ and $T_{\tau}$ being the time-ordering operator. The DMFT problem is approached with the continuous-time quantum Monte Carlo methodology [28, 29] in its hybridization-expansion flavor [29] as implemented in the TRIQS package. [30] Additionally we implemented the computation of the impurity two-particle Green’s function $G^{(2)}(\tau_{12}, \tau_{34}, \tau_{14})=-(T_{\tau}c(\tau_{1})c(\tau_{2})c(\tau_{3})c(\tau_{4}))$ to address explicit electron-electron correlations. In the approximation of a purely local particle-hole irreducible vertex, $G^{(2)}$ allows to determine also lattice susceptibilities. [19] [20] [31] [32] These susceptibilities, e.g. for spin ($s$) and charge ($c$), written as

$$\chi_{s/c}(i\omega, q, T) = T^2 \sum_{\nu \nu'} \left( \bar{\chi}_{s/c, \nu \nu'}^{(0)}(i\omega, q, T) + v_{s/c, \nu \nu'}(i\omega, q, T) \right),$$

where $\omega$ ($\nu$) marks bosonic (fermionic) Matsubara frequencies, consist of two parts. Namely $\bar{\chi}_{s/c, \nu \nu'}^{(0)}$ denotes the conventional (Lindhard-like) term, build up from the (renormalized) bubble part, which is mainly capable of detecting Fermi-surface driven instabilities close to $T=0$. On the contrary, the second part $v_{s/c, \nu \nu'}$ (the vertex term) includes properly the energy dependence of the response behaviour due to strong local interactions in real space. It proves important for revealing, e.g. magnetic instabilities at finite $T$ due to the resolution of the two-particle correlations governed by an implicit intersite exchange $J$. Note that all numerics take advantage of the recently introduced Orthogonal Polynomial representation [33] of one- and two-particle Green’s functions to provide the needed high accuracy and to eliminate artifacts often stemming from truncating the Fourier-transformed $G^{(2)}$ in Matsubara space.

Within the first Brillouin zone (BZ) of the triangular coordination with lattice constant $a$ the coherent $\Gamma$-point instability signals FM order in the case of $\chi_s$ and phase separation for $\chi_c$. Additionally important are here the instabilities at the the $K$- and $M$-point. The associated ordering gives rise to distinct sublattice structures in real space (cf. Fig. 1). The $M$-point ordering leads to a triangular and a kagomé sublattice with lattice constant $a_{\text{eff}}=2a$, while the $K$-point ordering establishes a triangular and a honeycomb sublattice with $a_{\text{eff}}=\sqrt{3}a$, respectively.

We will first discuss the static ($\chi_{s/c}(\omega=0, q, T)$) response (read off from the zeroth bosonic Matsubara frequency), directly reflecting the system’s susceptibility to an order of the $(q$-resolved) type. The cobaltate intralayer charge-susceptibility $\chi_c(0, q, T)$ shows pronounced features in $q$ space with doping $x$ (see Fig 2). Close to $x=0.3$ our single-band modeling leads to increased intensity inside the BZ, pointing towards longer-range charge-modulation (e.g. $3\times3$, etc.) tendencies in real space. That Na$_{1/3}$CoO$_2$ is indeed prone to such 120°-like instabilities has been experimentally suggested by Qian et al. [33]. Towards $x=0.5$ the susceptibility for short-range charge modulation grows in $\chi_c$, displaying a diffuse high-intensity distribution at the BZ edge with a maximum at the $K$-point for $x=0.5$. No detailed conclusive result on the degree and type of charge ordering for the latter composition is known from experiment, however chain-like charge disproportionation that breaks the triangular symmetry is verified [34] [35]. The present single-site approach cannot stabilize such symmetry-breakings, but an pronounced $\chi_c$ at the $K$-point at least inherits some stripe-like separation of the two involved sublattices. Near $x=0.67$, the $\chi_c$ maximum has shifted to the $M$-point, in line with the detection of an effective kagomé lattice from nuclear magnetic resonance (NMR) experiments [24]. For even higher doping, this $q$-dependent structuring transmutes into a $G$-point maximum, pointing towards known phase-separating tendencies. [36] Figure 2 also exhibits the $x$-dependent intra-layer spin sus-
susceptibility, starting with strong AFM peaks at \( x=0.3 \) due to \( K \)-point correlations. With reduced intensity these shift to the \( M \)-point at \( x=0.5 \), consistent with different types of spin and charge orderings at this doping level \[35\]. For \( x>0.5 \), \( \chi_s(\mathbf{q}, T) \) first develops broad intensity over the full BZ, before forming a pronounced peak at the \( \Gamma \)-point above \( x \sim 0.6 \). Thus the experimentally observed in-plane AFM-to-FM crossover in the spin response is reproduced.

Lang et al. \[2\] revealed from the Na NMR that this crossover is \( T \)-dependent with \( x \), resulting in an energy scale \( T^* \) below which AFM correlations are favored (compare Fig. \[1\]). The slope \( \partial T^*/\partial x \) turns out negative, in line with the general argument that FM correlations are most often favored at elevated \( T \) because of the entropy gain via increased transverse spin fluctuations. In this respect, Fig. \[3\] shows the \( (x, T, \mathbf{q}) \) dependence of the computed \( \chi_s \). For \( x=0.55 \), 0.58 a maximum in the \( \Gamma \)-point susceptibility is revealed, which has been interpreted by Lang et al. \[2\] as the criterion for a change in the correlation characteristics, thereby defining the \( T^* \)-line. While the temperature scale exceeds the experimental value in the present mean-field formalism, the qualitatively correct doping behavior of the \( T^* \)-line is obtained.

Beyond the experimental findings our calculations allow to further investigate the nature of the magnetic crossover. Fig. \[3\] reveals that at lower \( T \) and \( x \) closer to \( x=0.5 \) the susceptibility at \( \Gamma \) is ousted by the one at \( M \), while \( \chi_s \) at \( K \) is mostly dispensable. The \( M \) susceptibility can be understood due to the proximity of the striped order at \( x=0.5 \). \[17\] \[37\], which is however not realized until much lower temperatures.

The inset of Fig. \[3\] follows the \( T \)-dependent \( \Gamma \)-point susceptibility through a vast doping range. Note the subtle resolution around \( x=0.5 \) as well as the large exaggeration especially for lower temperatures in the experimentally verified in-plane FM region. The main panel of Fig. \[3\] additionally shows for \( x=0.82 \) the spin susceptibility at the \( A \)-point (i.e., at \( k_z=(0,0,1/2) \) in the BZ), which denotes the \( A \)-type AFM order. While \( \Gamma \) and \( A \) show CW behavior, the extrapolated transition temperature however is \( \sim 7\% \) higher at \( A \) than at \( \Gamma \), verifying the experimental findings of \( A \)-type order \[7\] \[10\]. In the temperature scan we additionally introduced a nearest-layer inter-plane hopping \( t_1=13 \) meV \[9\] \[13\] \[38\], however the previous in-plane results are qualitatively not affected by this model extension. Due to known charge disproportionation the inclusion of long-range Coulomb interactions, e.g., via an inter-site \( V \) \[13\] \[18\], seems reasonable. This was abandoned in the present single-site DMFT approach, resulting generally in reduced charge response. Without \( V \), charge fluctuations are substantially suppressed for large \( U/W \), while the inter-site spin fluctuations are still strong due to superexchange. Aside from the static response, our method allows also access to the dynamic regime. Figure \[4\] shows the dynamical transverse spin susceptibility for selected \( x \). Note the broad \( \mathbf{q} \)-dependence and small excitation energy in the low-doping regime. In contrast, the FM correlations near \( x=0.82 \) are reflected by strong paramagnon-like gapless excitation at \( \Gamma \) combined with very little weight and rather high excitation energies at AFM wave-vectors. Interestingly, a comparably strong and sharp \( K \)-type high-energy excitation (\( \sim 1 \) eV) for larger \( x \) below the onset of in-plane FM order is revealed. Its amplitude is strongest at \( x=0.67 \) while its energy increases with \( x \) and its worthwhile to note that the mode is neither visible when ne-
FIG. 5. (color online) Korringa ratio versus doping for $T=580$ K. The experimental data, extracted from Ref. 40 and 2, was obtained for lower temperatures. The inset shows the evolution of the bubble-diagram contribution from the non-interacting ($U=0$) to the fully-interacting ($U=5$ eV) case.

can see that the bubble-only calculation yields a nearly flat Korringa ratio with doping, thus fails completely in explaining the experimental findings. In particular it does not reflect the strong FM correlations for high doping. This further proves the importance of strong correlations on the two-particle level, asking for substantial vertex contributions. [43] Note that the recently suggested lower-energy effective kagomé model [16] including the affect of charge ordering is not contradicting the present modeling. Since here the effective kagomé lattice naturally shows up and also the key properties of the spin degrees of freedom seem well described on the original triangular lattice.

In summary, the DMFT computation of two-particle observables including vertex contributions based on a realistic single-band Hubbard modeling for Na$_x$CoO$_2$ leads to a faithful phase-diagram examination at larger $x$, including the kagomé-like charge-ordering tendency for $x\sim0.67$ and the in-plane AFM-to-FM crossover associated with a temperature scale $T^*$. Thus it appears that many generic cobaltate features are already governed by a canonical correlated model, without invoking the details of the doping-dependent sodium-potential landscape or the inclusion of multi-orbital processes. Of course, future work has to concentrate on quantifying further details of the various competing instabilities (and their mutual couplings) within extended model considerations. Beyond equilibrium physics, we predict a strong energy dependence of the effective inter-site exchange resulting in an $K$-type high-energy mode around $x=0.67$, which could be probed in experimental studies.

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