Creation and destruction of a spin gap in weakly coupled quarter-filled ladders

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We investigate weakly coupled quarter-filled ladders with model parameters relevant for NaV_2O_5 using density-matrix renormalization group calculations on an extended Hubbard model coupled to the lattice. NaV_2O_5 exhibits super-antiferroelectric charge order with a zigzag pattern on each ladder. We show that this order, with a periodicity of four ladders, causes a spin dimerization along the ladder and a corresponding spin gap of the same magnitude as that observed experimentally. The spin gap is destroyed again at large charge order due to a restructuring of the spins. An analysis of an effective spin model predicts a re-creation of the gap by inter-ladder singlets when the charge order increases further.

PACS numbers: 71.10.Fd, 71.38.-k, 63.22.+m

The discovery of a phase transition at $T_C \approx 34K$ [1] in NaV_2O_5, below which charge order and a spin gap appear [2], has precipitated intensive theoretical investigation. NaV_2O_5 consists of well-separated planes which contain weakly coupled quarter-filled vanadium ladders [3] (Fig. 1). They can be described by an extended Hubbard model (EHM) [2]. A zigzag charge order as observed in NaV_2O_5 [4] is already created in this model by the nearest-neighbor Coulomb repulsion V for an isolated ladder, but only at overly large values of V [5, 6, 7, 8, 9, 10]. In a recent DMRG study [8], we showed that the inclusion of a strong effective Holstein coupling to the lattice, which was found in LDA calculations [11], reduces the required Coulomb repulsion to a realistic value. The DMRG calculations then yielded good agreement between theoretical and experimental results for the amount of charge order, the extent of lattice distortion in the c-direction, the effective spin coupling $J_{\rm eff}$ in the b-direction, and the charge gap.

However, on an isolated ladder [7, 8] the spin gap vanishes in the thermodynamic limit. The occurrence of the spin gap in NaV_2O_5 appears to be intimately connected to the coupling of ladders, as indicated, e.g., by the splitting of magnon branches [4, 12, 13]. An intriguing scenario has been put forward by Mostovoy and Khomskii [14]. It is based on the fact that the experimentally observed unit cell of NaV_2O_5 in the ordered phase is $2a \times 2b \times 4c$ [15, 16]. The charge order then has a periodicity of *four* parallel ladders in the a-direction, and is thus super-antiferroelectric (SAF) [17]. The corresponding polarization of the electrons on the rungs is illustrated by wide-narrow ellipses in Fig. 1(b) (top). Each ladder exhibits antiferroelectric charge order along the ladder (generally called zigzag charge order) as well as an antiferroelectric order to the next nearest ladder. The ladders correspond to effective antiferromagnetic spin-1/2 chains in the b-direction. For each ladder, the two closest sites on the neighboring in-plane ladders alternate between low charge occupation [indicated by dashed loops in Fig. 1(b)] and large occupation. Large charge occupation should effectively weaken the electron hopping along the ladder, both through purely electronic interactions as well as by pushing away the neighboring oxygen atoms and thus reduce the spin coupling. With SAF charge order, the effective spin chains are therefore dimerized, which was proposed to lead to the formation of spin singlets [Fig. 1(b), bottom] and to the observed spin gap. This scenario is difficult to evaluate quantitatively. It has been investigated using exact diagonalization [4, 9, 18] on small clusters and by means of an approximate xy-model together with a mean-field approximation [17]. It has also

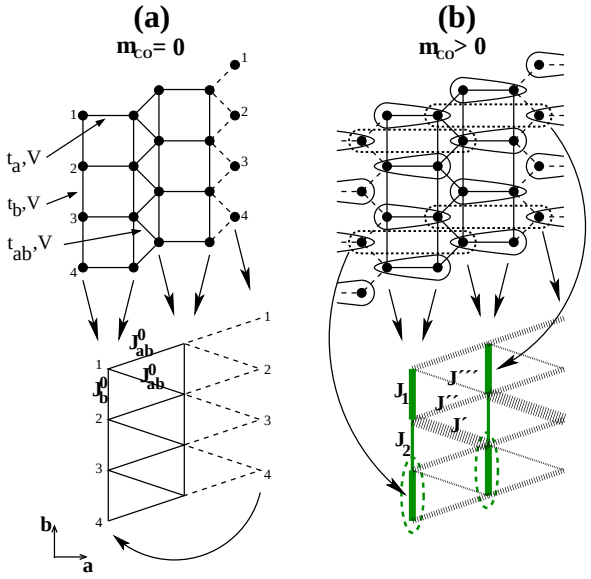

FIG. 1: Quarter-filled coupled ladders in NaV_2O_5. The mapping of a rung (top) onto an effective spin site (bottom) is illustrated for (a) a charge-disordered and (b) a SAF-ordered regime. The shifted periodic boundary conditions in the a-direction are indicated by numbers which identify identical sites. The proposed singlet formation for NaV_2O_5 is depicted by dashed ellipses in the effective spin model (b, bottom).

been argued that the mechanism proposed by Mostovoy and Khomskii cannot work for NaV_2O_5 [19].

In the present paper, we use the Density Matrix Renormalization Group (DMRG) to study the extended Hubbard model with coupling to the lattice [8] for large systems of coupled ladders up to length 20, with periodicity of four ladders in the a-direction. We show that the scenario proposed by Mostovoy and Khomskii indeed works. In the thermodynamic limit, it produces a dimerization and a spin gap of similar size to that seen in the experiment. The spin gap appears concurrently with charge ordering and is found *only* in the case of the 4-ladder SAF order; it does not appear for charge ordering with 2-ladder periodicity. Surprisingly, the spin gap closes again at large Coulomb repulsion V. We explain this behavior by considering an effective spin model for which DMRG calculations on larger systems with lengths of up to 120 rungs are possible.

Model. We use the extended Hubbard model with coupling to the lattice as introduced in Ref. 10, $H = H_{\rm EHM} + H_{\rm l} + H_{\rm e\text{-}l}$, where

$$H_{\rm EHM} = -\sum_{\langle ij\rangle,\sigma} t_{ij}\left(c^\dagger_{i\sigma}c_{j\sigma} + {\rm h.c.}\right) + U\sum_i n_{i\uparrow}n_{i\downarrow} + \sum_{\langle ij\rangle} V_{ij}n_i n_j \ , \qquad (1)$$

with hopping matrix elements from first-principles calculations [3, 11, 20], $t_{\rm a} = 0.35\,eV$, $t_{\rm b} = 0.5\,t_{\rm a}$, $t_{\rm ab} = 0.17\,t_{\rm a}$ and $0.33\,t_{\rm a}$, and a uniform on-site repulsion $U = 8.0\,t_{\rm a}$. The lattice and the corresponding model parameters are illustrated in Fig. 1(a). Since the nearest-neighbor Coulomb repulsion V is difficult to estimate, we investigate the functional dependence on this parameter. Recent LDA calculations [11] have shown that there is a very large Holstein-like coupling to out-of-plane movements of oxygen atoms, which can be modeled by including the terms $H_{\rm l} = \kappa\sum_i \frac{z_i^2}{2}$ and $H_{\rm e\text{-}l} = -C\sum_i z_i n_i$, with $\kappa = 0.125\,t_{\rm a}$ and $C = 0.35\,t_{\rm a}$, and z_i in units of 0.05 Å, in the Hamiltonian. We treat these movements adiabatically like in Refs. 10 and 8. The optimal configuration for the distortions z_i is then a zigzag-pattern [8] with amplitude $z_{\rm opt}$, for which we take the results from an isolated ladder [8]. This simplification is reasonable since we showed in Ref. 8 that distortions remain unchanged in the case of two coupled ladders with periodic boundary conditions (*pbc*) in the a-direction. Then, $H_{\rm l}$ becomes an irrelevant constant and $H_{\rm e\text{-}l}$ reduces to a zigzag alternation of the local chemical potentials.

In order to investigate the proposal by Mostovoy and Khomskii, a system with a periodicity of four ladders is necessary. Within the DMRG, calculations on an extended Hubbard model of four coupled ladders would be, however, too restricted in length. We therefore employ a system of only two coupled ladders of length up to 20, but with *shifted periodic boundary conditions*, as illustrated in Fig. 1. They ensure the proper periodicity and the same SAF structure of neighboring charges in the ordered phase as in a four-ladder system. We apply open boundary conditions (*obc*) in the b-direction.

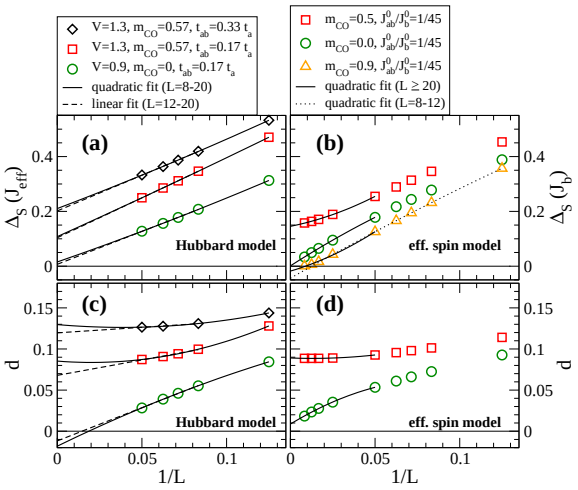

FIG. 2: Examples of finite-size extrapolations for (a,b) the spin gap $\Delta_{\rm S}$ and (c,d) the dimerization d of (a,c) the Hubbard model and of (b,d) the effective spin model. Linear and quadratic fits in $\frac{1}{L}$ are illustrated for charge-disordered states ($m_{\rm CO} = 0$, circles) and SAF-ordered states ($m_{\rm CO} > 0$).

Results. We calculate the spin gap using [7]

$$\Delta_{\rm S}(L) \ = \ E_0(L, N, S_z = 1) - E_0(L, N, S_z = 0)\,,$$

where E_0 is the ground state energy, L is the length of each ladder, $N = L/2$ is the number of electrons, and S^z is the total spin in z-direction. The results are extrapolated using linear and quadratic fits in $1/L$, including $L = (8), 12, 14, 16, 20$, as illustrated in Fig. 2(a). Due to broken translational invariance in the b-direction (*obc*), we can define a spin dimerization d as

$$d = \frac{1}{2}\frac{1}{4}\sum_{l={\rm I,II}}\sum_i (-1)^i \langle \hat{S}^z_{i,l}\,(\hat{S}^z_{i+1,l} - \hat{S}^z_{i-1,l})\rangle \ ,$$

where i counts the rungs in the b-direction. We restrict $\sum_i$ to four rungs in the middle of each ladder ($l = {\rm I, II}$). Here $S^z_{i,l}$ is the sum of the S^z-spin at the i-th rung. The dimerization d is an indicator for bond alternation and spin singlets along the ladder, as illustrated in Fig. 1(b) (bottom). Translational invariance in the b-direction is additionally broken by the lattice distortions, and we then find the contributions to d to be positive on both ladders. A state consisting of consecutive singlets in the a-direction [Fig. 1(b), bottom] would give the maximum value for d, i.e., $|d_{\rm max}| = 1/4$. The charge order parameter $m_{\rm CO}$ is given by [10]

$$m^2_{CO} = \frac{1}{N^2\langle n\rangle^2}\sum_{ij} e^{i\mathbf{Q}(\mathbf{R}_i - \mathbf{R}_j)}\left(\langle n_i n_j\rangle - \langle n\rangle^2\right) \ ,$$

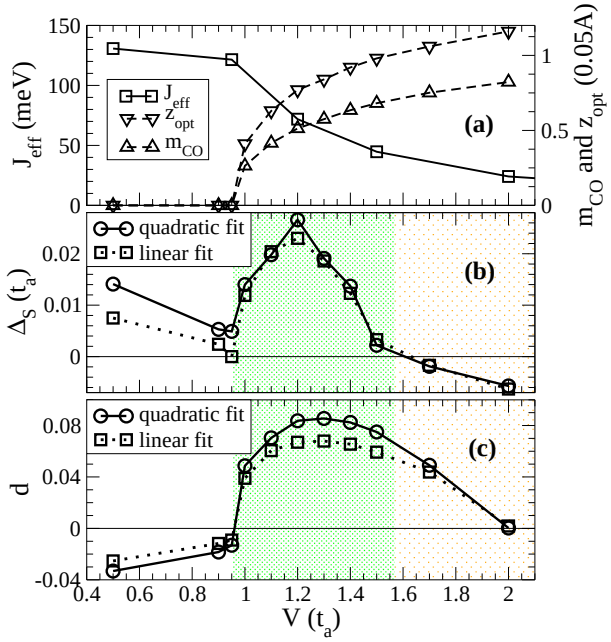

FIG. 3: Results for the EHM with coupling to the lattice, as a function of V. Extrapolated values of (a) the charge order parameter $m_{\rm CO}$, (b) the spin gap $\Delta_{\rm S}$, and (c) the dimerization d are illustrated for two coupled ladders ($t_{\rm ab} = 0.17\,t_{\rm a}$). The effective magnetic exchange constant $J_{\rm eff}$ [8] and the distortion $z_{\rm opt}$ [8] of an isolated ladder are also shown in (a). The three regimes discussed in the text are highlighted.

where $\mathbf{Q} = (\pi, \pi)$ and N is the total number of sites on the ladder. We calculate m_{CO}^2 for each ladder separately and then average.

In the thermodynamic limit, we obtain the results shown in Fig. 3 for the charge order parameter $m_{\rm CO}$, the spin gap $\Delta_{\rm S}$, and the dimerization d, as a function of V. For comparison, we also show the lattice distortion $z_{\rm opt}$ and the effective spin coupling $J_{\rm eff}$, which were determined for an isolated ladder in Ref. 8. Here $m_{\rm CO}$ corresponds to charge occupations $(1 \pm m_{\rm CO})/2$ of two inequivalent sites and becomes finite concurrently with $z_{\rm opt}$. We can identify three different regimes:
(i) For small nearest-neighbor Coulomb repulsion $V \leq 0.95\,t_{\rm a}$, the lattice distortion and the charge order are both zero. The estimation of the spin gap Δ_S is difficult, as illustrated by the relatively large disagreement between the linear and the quadratic extrapolations in that regime. From calculations on a system with pure *pbc* in the a-direction [8] and from considerations of an effective spin model (see below), we expect a vanishing gap in the 2d thermodynamic limit as long as $m_{\rm CO} = 0$. The dimerization d, which is expected to be zero in this regime, shows slightly negative values, probably due to finite-size effects.
(ii) At a critical $V_{\rm C} \approx 0.95\,t_{\rm a}$ [8], the lattice distortions become finite and cause charge ordering in a SAF pattern for our choice of boundary conditions. Linear and quadratic extrapolations to $L = \infty$ match quite well and we find that the spin gap $\Delta_{\rm S}$ and the intra-ladder dimerization d are finite. This is in contrast to the non-SAF charge-ordered system of two coupled ladders with purely periodic boundary conditions studied in Ref. 8, which shows *neither* a finite spin gap *nor* finite dimerization in the thermodynamic limit. The concurrent appearance of intra-ladder dimerization and a spin gap only when SAF charge ordering occurs strongly indicates that here charge ordering indeed causes singlet formation along the ladder.
(iii) At larger $V \approx 1.6\,t_{\rm a}$, the spin gap vanishes again, to our initial surprise. Concurrently, the dimerization becomes smaller, but does not completely disappear. This behavior and the negative extrapolations for the spin gap are consistent with the effective spin system (see below).

Regime (*ii*) can be associated with NaV_2O_5 because it provides a description for the concurrent appearance of lattice distortions, zigzag charge order, and the opening of a spin gap in the low temperature phase. At the effective $V = 1.3\,t_{\rm a}$ previously determined [8], the spin gap is of the same magnitude as in NaV_2O_5 ($\Delta_{\rm S}^{\rm exp} \approx 10\,meV = 0.029\,t_{\rm a}$ [2]). Calculations for different inter-ladder hopping strengths $t_{\rm ab}$ show that the maximal size of the gap increases with $t_{\rm ab}$ ($t_{\rm ab} = 0/0.17/0.33\,t_{\rm a} \Rightarrow \Delta_{\rm S,max} \approx 0/0.025/0.05\,t_{\rm a}$), but that concurrently the transition from regime (*ii*) to (*iii*) appears at smaller V (for $t_{\rm ab} = 0.33\,t_{\rm a}$ at $V \approx 1.4\,t_{\rm a}$), corresponding to smaller $m_{\rm CO}$. In summary, finite SAF charge ordering and inter-ladder hopping $t_{\rm ab}$ are both necessary to produce dimerization and a spin gap, while very large charge order destroys the spin gap again.

Effective spin model. In order to better understand the behavior of the spin gap in the EHM, we consider an effective spin model for NaV_2O_5 which was introduced in Ref. 13. This model allows us to investigate much larger systems – up to length $L = 120$ – and thus to extrapolate results to the thermodynamic limit more accurately. By replacing the quarter-filled rungs (one electron on each rung) by a single effective spin site, we obtain the the Heisenberg spin model whose lattice structure is depicted in Fig. 1(a) (bottom) with two different magnetic exchange constants, $J_{\rm b}^0$ along the effective chains, and $J_{\rm ab}^0$, inter-chain. The chains in this effective spin model correspond to the ladders of the original system. In the SAF charge-ordered state with weakly coupled effective chains [Fig. 1(b)], the magnetic exchange $J_{\rm ab}^0$ differentiates to three different values depending on the positions of the electrons on the interacting rungs [13]: large $J' = J_{\rm ab}^0\,(1 + m_{\rm CO})^2$, medium $J'' = J_{\rm ab}^0\,(1 - m_{\rm CO}^2)$, and small $J''' = J_{\rm ab}^0\,(1 - m_{\rm CO})^2$, as illustrated in Fig. 1(b). The bond alternation along the b-direction is taken to be $J_{1/2} = J_{\rm b}\,(1 \pm \delta)$, where $J_{\rm b} = J_{\rm b}^0\,(1 - m_{\rm CO}^2)$, and we set $\delta(m_{\rm CO} = 0) = 0$ and $\delta(m_{\rm CO} \approx 0.44) \approx 0.034$ [13]. Assuming a linear dependence yields $\delta(m_{\rm CO}) \approx 0.076\,m_{\rm CO}$. Together with $J_{\rm ab}^0/J_{\rm b}^0 = 1/45$ [13] (or $J_{\rm ab}^0/J_{\rm b}^0 = 1/25$),

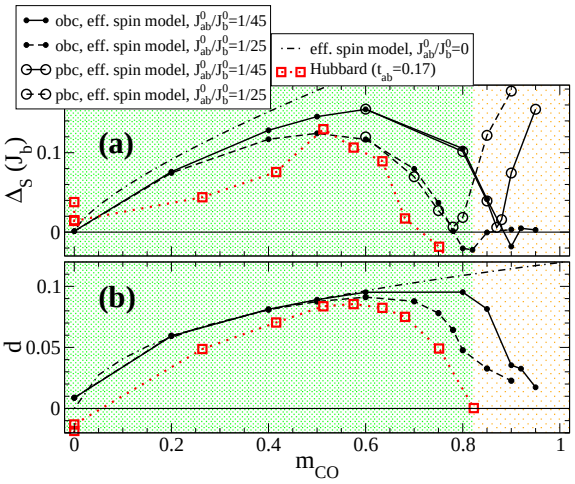

FIG. 4: Effective spin model. Quadratically extrapolated values ($L = \infty$) for (a) the spin gap Δ_S and (b) the dimerization d, as a function of the charge order parameter m_{CO}. Calculations with *obc* (black dots) and *pbc* (open circles) in the b-direction are shown. For comparison the spin gap Δ_S for the EHM is shown, in units of J_{eff} [Fig. 3(a)].

where J^0_{ab} and J^0_b are the exchange constants at $m_{CO} = 0$, the parameters of the effective spin model are completely determined and the behavior can be investigated as a function of the strength of the charge order parameter, m_{CO}.

Like in the Hubbard system, we apply the DMRG to two coupled spin chains (corresponding to two Hubbard ladders) with shifted *pbc* in the a-direction and *obc* as well as *pbc* in the b-direction. Due to the small inter-chain couplings, the finite-size effects in the a-direction are small [21], justifying calculations on only two coupled effective chains. A quadratic extrapolation [Fig. 2(b),(d)] of the finite system sizes ($L = 20-120$ for *obc*, $L = 20-60$ for *pbc*) to the thermodynamic limit provides the m_{CO}-dependence of dimerization d and spin gap Δ_S. The dimerization and the spin gap increase with m_{CO} up to a maximum (Fig. 4); then, both decrease even though the bond alternation still increases. This behavior matches well with the results from the EHM. In contrast, uncoupled chains (1D spin-1/2-Heisenberg chains) show a continuing increase of dimerization and spin gap.

The destruction of the spin gap is likely due to a restructuring of the singlets, which now occur with a larger probability on the J'-bonds. For small charge ordering, all inter-chain exchanges are of comparable size and are small in units of J_b. The singlet formation along the b-direction is then only marginally influenced. On the other hand, a large value of m_{CO} drastically changes the inter-chain exchanges, e.g., for $m_{CO} = 0.9$ and $J^0_{ab}/J^0_b = 1/45$, they become $J'/J_b \approx 0.4$, $J''/J_b \approx 0.02$, and $J'''/J_b \approx 0.001$. The large inter-chain exchange J' destroys the spin gap and causes a restructuring of the singlets. For *pbc* along the ladder [open circles in Fig. 4(a)] a re-creation of the spin gap is observed after passing a critical charge ordering m^*_{CO}. In contrast, *obc*-calculations (black dots) show a vanishing gap for all $m_{CO} \geq m^*_{CO}$, although both calculations match excellently for $m_{CO} < m^*_{CO}$ [Fig. 4(a)]. This strongly suggests a singlet formation on the J'-bonds [5] with increasing J'. In the case of *obc*, unpaired spins are then present at the ends of the ladders [Fig. 1(b)], preventing a spin gap. This explanation is supported by a considerable increase of inter-chain spin correlations on the J'-bonds for $m_{CO} > m^*_{CO}$.

For *obc*, after passing the critical charge order m^*_{CO}, the spin gap extrapolates to values that are slightly negative [Fig. 4(a)]. If the extrapolation is restricted to smaller system sizes [dotted line in Fig. 2(b)], the values become more negative. This is in agreement with the negative extrapolations for Δ_S in the Hubbard model in the large m_{CO}-regime [Fig. 3(b)]. The magnitude of these negative values gives a minimal estimate of the error in the extrapolation.

Conclusions. We have studied coupled quarter-filled ladders in an extended Hubbard model with lattice coupling and with model parameters appropriate for NaV_2O_5. In a super-antiferroelectric charge-ordered regime, we find spin dimerization along the ladder which generates a spin gap that matches the experimental result. This provides strong support for the mechanism of Mostovoy and Khomskii [14]. The spin gap will likely be further enhanced by in-plane atomic movements due to the super-antiferroelectric order [14, 19, 22, 23, 24]. The super-antiferroelectric charge-ordered state provides a possibility to understand the concurrent appearance of charge order, lattice distortions, and spin gap in NaV_2O_5. It is in agreement with experimental observations [15] and explains the puzzling properties of the low-temperature phase. Our calculations match the effective spin model proposed by Gros and Valenti [13] and show a vanishing spin gap at very large charge ordering which is caused by an increased inter-ladder magnetic exchange and the corresponding restructuring of the spins.

This work was supported by the Austrian science fund FWF, project P15520. We thank M. Aichhorn, C. Gros, T.C. Lang, and F. Michel for useful conversations.

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