

## Entropy driven dimerization in a one-dimensional spin-orbital model

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We study a version of the one-dimensional spin-orbital model with spins  $S=1$  relevant to cubic vanadates. At small Hund's coupling  $J_H$  we discover dimerization in a pure electronic system solely due to a dynamical spin-orbital coupling. Above a critical value  $J_H$ , a uniform ferromagnetic state is stabilized at zero temperature. More surprisingly, we observe a temperature driven dimerization of the ferrochain, which occurs due to a large entropy released by dimer states. This dynamical dimerization seems to be the mechanism driving the peculiar intermediate phase of  $YVO_3$ .

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In transition-metal oxides with perovskite structure the  $d$ -orbital level splits into a triplet of  $t_{2g}$  symmetry and an  $e_g$  doublet at higher energy. The sign and magnitude of the spin-spin interactions is determined by the orbital occupation resulting in a strong spin-orbital coupling. This leads to unusual magnetic properties of many vanadium, titanium, and manganese oxides.<sup>1</sup> The simplest spin-orbital model for spin- $\frac{1}{2}$  objects with twofold degenerated orbitals is the SU(4) symmetric model, where Hund's coupling, orbital anisotropy as well as the Jahn-Teller effect are ignored.<sup>2</sup> The one-dimensional (1D) version of this model has been solved by Bethe ansatz.<sup>3</sup> The ground state and the excitation spectrum consisting of three gapless mixed spin-orbital modes is obtained. The idea of mixed spin-orbital excitations was also crucial to understand anomalous magnetic properties of  $LaTiO_3$ ,<sup>4</sup> a system showing a coherent orbital-liquid ground state.<sup>5</sup> Thermodynamic properties of the SU(4) symmetric model in 1D have been investigated by the quantum Monte Carlo method.<sup>6</sup>

Recently vanadium oxides, where the  $t_{2g}$  orbitals are filled by two electrons, have attracted much attention, because of their unusual magnetic properties including temperature-induced magnetization reversals in  $YVO_3$ .<sup>7</sup>  $YVO_3$  shows a very puzzling intermediate phase at  $77 < T < 118$  K with  $C$ -type magnetic order (ferromagnetic chains along the  $c$  axis with antiferromagnetic coupling between the chains), which changes to a conventional  $G$ -type Néel structure at  $T=77$  K through a first-order transition.<sup>8</sup> A significance of  $t_{2g}$  orbital degrees of freedom for understanding the peculiar magnetic behavior of  $YVO_3$  has been emphasized.<sup>9-12</sup>

The relevant spin-orbital model to describe magnetism of vanadium oxides has to involve  $S=1$  spins because Hund's coupling  $J_H$  is large.<sup>13</sup> For the cubic vanadates  $LaVO_3$  and  $YVO_3$  a realistic superexchange model has been derived in Ref. 12 where two out of the three  $t_{2g}$  orbitals are active along a given cubic axis leading to a  $\tau=1/2$  orbital pseudospin. In the classical limit  $S \gg 1$  and neglecting Hund's coupling Shen *et al.*<sup>14</sup> have shown that the ground state in 1D is an orbital valence bond (OVb) solid formed by orbital singlets and parallel spins, where neighboring OVb's are noninteracting.

In this paper, we treat a realistic quantum spin-orbital model with  $S=1$  and a twofold orbital degeneracy in 1D where the effects due to Hund's coupling are included. Thermodynamics of two distinct phases, a four-site periodic quantum dimer phase, and a ferromagnetic state that occur at larger  $J_H$ , is studied numerically. A critical value of  $J_H$  separating the two phases is obtained. The most important observation is that strong dimer correlations develop *at finite temperature on the ferromagnetic side* of the transition, which are driven by large entropy of low-lying dimer states of the model. We discuss the relevance of these findings to the intermediate phase of  $YVO_3$ .

The Hamiltonian of the model is given by

$$H = J \sum_i \left[ \frac{1}{2} (\mathbf{S}_i \cdot \mathbf{S}_{i+1} + 1) \hat{J}_{i,i+1} + \hat{K}_{i,i+1} \right], \quad (1)$$

where  $\mathbf{S}$  being an  $S=1$  spin operator, and  $J=4t^2/U$  represents an overall superexchange energy scale. The operators  $\hat{J}_{i,j}$  and  $\hat{K}_{i,j}$  describe orbital exchange processes on the bond

$$\begin{aligned} \hat{J}_{i,j} &= (1+2R) \left( \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j + \frac{1}{4} \right) - r \left( \tau_i^z \tau_j^z + \frac{1}{4} \right) - R, \\ \hat{K}_{i,j} &= R \left( \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j + \frac{1}{4} \right) + r \left( \tau_i^z \tau_j^z + \frac{1}{4} \right), \end{aligned} \quad (2)$$

with  $\boldsymbol{\tau}$  acting in a  $\tau=1/2$  orbital pseudospin space. The coefficients  $R = \eta/(1-3\eta)$  and  $r = \eta/(1+2\eta)$  originate from the Hund's rule splitting of the excited  $t_{2g}$  multiplet by  $\eta = J_H/U$ . This is the Hamiltonian derived for cubic vanadates in Ref. 12 restricted here to one cubic axis. Physically, pseudospin  $\boldsymbol{\tau}$  describes 1D fluctuations of  $xz$  and  $yz$  orbitals along the  $c$  axis, while the third orbital  $xy$  is frozen below a structural transition at  $\sim 200$  K.<sup>9-11</sup>

To study the thermodynamic properties we apply the finite-temperature density-matrix renormalization group (DMRG), a numerical method which is particularly suited because the thermodynamic limit is performed exactly. By means of the Trotter formula the partition function is expressed as a product of local transfer matrices evolving along the spatial direction. For the calculations, we use the well-

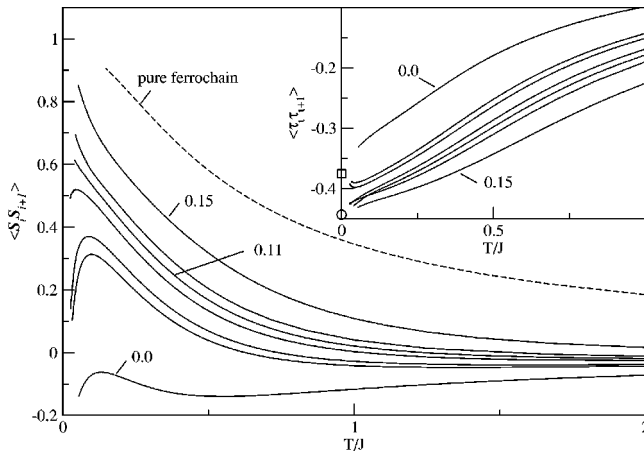


FIG. 1. The main figure (inset) show the temperature-dependence of nearest neighbor correlations  $\langle S_i \cdot S_{i+1} \rangle$  ( $\langle \tau_i \cdot \tau_{i+1} \rangle$ ) for  $\eta$  values 0.0, 0.07, 0.08, 0.1, 0.11, 0.12, 0.15. For comparison the spin only case is shown where  $J_{i,j}$  is fixed by its zero-temperature expectation value for  $\eta=0.15$ . The circle (square) at  $T=0$  in the inset denotes  $-\ln 2 + 1/4$  ( $-3/8$ ).

known decomposition of the Hamiltonian into even and odd parts leading to a classical model with checkerboard structure<sup>15</sup> as well as a different Trotter-Suzuki mapping leading to a classical model with alternating rows.<sup>16</sup> Within the alternative mapping correlation lengths (CL's) and corresponding wave vectors are determined unambiguously by the eigenvalues of the quantum transfer matrix (QTM). In the thermodynamic limit the free energy in both cases is given solely by the largest eigenvalue of the QTM, which is real and unique. The infinite DMRG algorithm is used to decrease the temperature where up to 120 states are kept in each renormalization step.

First, we consider the Hamiltonian for  $\eta=0$  (referred to as "isotropic" point below) where Eq. (1) simplifies to

$$H_0 = \frac{J}{2} \sum_i (S_i \cdot S_{i+1} + 1) \left( \tau_i \cdot \tau_{i+1} + \frac{1}{4} \right). \quad (3)$$

Note, that the model has a  $SU(2) \times SU(2)$  symmetry but not the higher  $SU(4)$  symmetry group as possible in the  $S=1/2$  case.<sup>2</sup> Regarding only a single bond, the lowest energy  $-J/2$  is obtained if the orbitals form a singlet with  $\langle \tau_i \cdot \tau_{i+1} \rangle = -3/4$  and the spins are ferromagnetically aligned. The first excited state is given by a spin singlet/orbital triplet and is separated by a gap of  $J/4$  only. Therefore, a strong orbital dimerization in the ground state is expected leading to alternating ferromagnetic-antiferromagnetic spin-exchange couplings, which would be given by  $-J/4$  and  $+J/8$  for perfect dimerization. Due to translational invariance the corresponding classical ground state would be fourfold degenerate. We also might expect mixed spin-orbital excitations playing an important role in thermodynamics.

In Fig. 1 the temperature dependence of the nearest-neighbor spin-spin correlation function  $\langle S_i \cdot S_{i+1} \rangle$  and orbital-orbital correlation function  $\langle \tau_i \cdot \tau_{i+1} \rangle$  for different  $\eta$  values is shown. First, we want to discuss in more detail the case  $\eta=0$  and turn to finite Hund's coupling later on. Note that in the zero-temperature limit the nearest-neighbor orbital

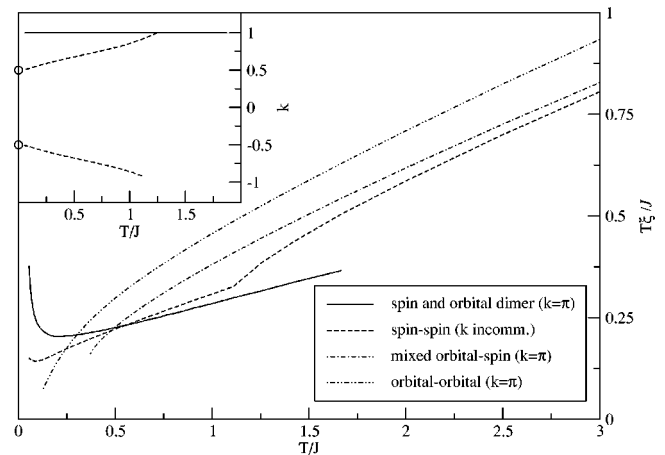


FIG. 2. The main figure shows the leading CL's times temperature in the isotropic case; the inset shows the corresponding wave vectors (in units of  $\pi$ ) with circles denoting  $k = \pm \pi/2$ .

correlation approaches  $-\frac{3}{8}$ , the value for perfect dimerization. In the high-temperature limit the orbitals are completely disordered and the spin-pair correlation is therefore negative. While lowering the temperature orbital singlets are formed and  $\langle S_i \cdot S_{i+1} \rangle$  increases due to the ferromagnetic spin interaction within an orbital singlet. The curve reaches a maximum at  $T/J \approx 0.13$  corresponding to the energy scale of the orbital gap (see below), and antiferromagnetic quantum fluctuations of spins in neighboring orbital singlets are strongly enhanced and dominate below. This emphasizes the differences between a quantum model with  $S=1$  and the classical limit  $S \gg 1$  investigated by Shen *et al.* (Ref. 14) where fluctuations in the antiferromagnetic bonds completely vanish.

An alternating ferromagnetic-antiferromagnetic spin exchange should also show up in the spin-spin correlation function  $\langle S_0^z S_r^z \rangle$  showing four-site periodicity (i.e.,  $\pi/2$  oscillations) and in a spin dimer correlation function  $\langle S_0^z S_1^z S_r^z S_{r+1}^z \rangle$  with long-range order and  $\pi$  oscillations.

In Fig. 2 numerical results for some leading CL's and the corresponding wave vectors are shown. Because it is known from conformal field theory that CL's  $\xi$  belonging to critical excitations diverge as  $\xi \sim 1/T$  in the low-temperature limit, CL times temperature versus temperature is plotted, thus separating correlation functions with long-range order at  $T=0$  from short-range correlations. A dimer CL showing  $k = \pi$  oscillations diverges as  $\xi \sim \exp(\Delta_D/T)/\sqrt{T}$  with  $\Delta_D \approx 0.08$  in the low-temperature limit indicating long-range dimer order at zero temperature. Second largest at low temperatures is a spin-spin CL showing incommensurate oscillations approaching  $\pi/2$  at zero temperature. Thus, the numerical results are consistent with the picture above. Note also that at high temperatures the orbitals have a short-range antiferromagnetic order and that a spin-orbital CL shows up, indicating the importance of mixed excitations.

For a dimerized orbital pseudospin- $\frac{1}{2}$  as well as for an  $S=1$  ferromagnetic-antiferromagnetic alternating Heisenberg chain a gap in the excitation spectrum is expected as visible in the susceptibility data shown in Fig. 3(a).

The quadratic dispersion of a gapped system leads in 1D to the low-temperature asymptotics  $\chi \sim \exp(-\Delta/T)/\sqrt{T}$ . Us-

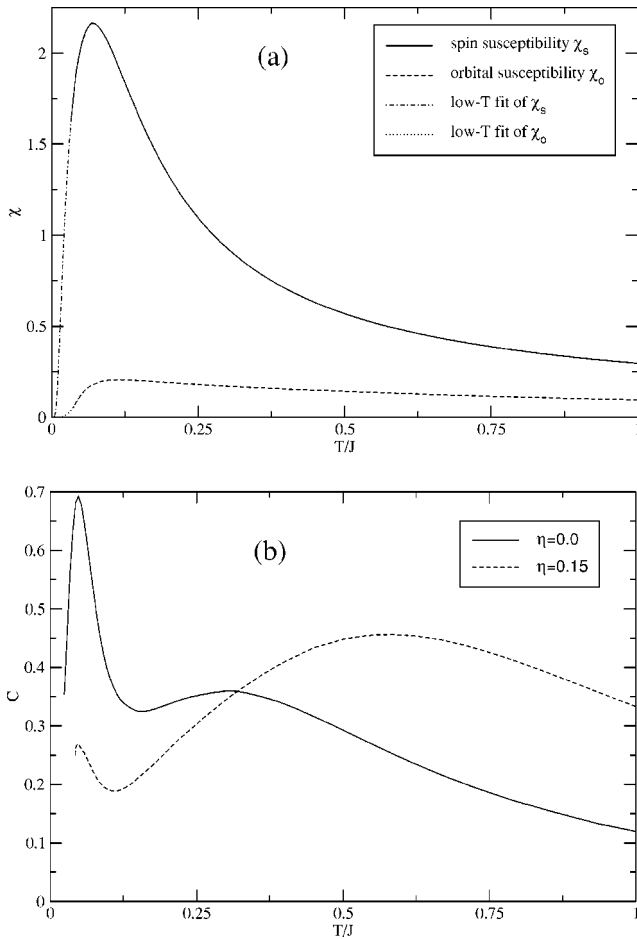


FIG. 3. (a) Spin and orbital susceptibility for  $\eta=0$  with low-temperature fits as specified in the text. (b) Specific heat for the isotropic and the finite Hund's coupling case.

ing this function for a fit, a spin gap  $\Delta_s = (0.041 \pm 0.002)J$  and an orbital gap  $\Delta_{orb} = (0.120 \pm 0.008)J$  is obtained. Note that the orbital gap is much smaller than the singlet-triplet splitting  $J$  of an isolated orbital dimer. The reason is that in the coupled spin-orbital system the spins form a singlet if the orbitals are excited to a triplet configuration and thus, the much smaller gap of the orbital triplet/spin singlet excitation appears in the orbital susceptibility data. More precisely, the thermal gap visible here is half of the spectral gap,<sup>20</sup> so that we obtain  $\Delta_{orb}^{spectr.} \sim 0.24J$ . This is very close to the value  $J/4$  for an isolated bond, showing that the orbitals are nearly perfect dimers in the ground state. Dynamical coupling of two sectors affects also the spin gap value. In a simple picture of spin-2 objects coupled antiferromagnetically with  $J/32$ ,<sup>14</sup> one would expect the  $S=2$  Haldane gap of about  $0.04(J/32) = J/800$ .<sup>17</sup> The observed spin gap is in fact much larger due to the coupling between spins and orbitals: A spin excitation introduces additional antiferromagnetic couplings between the orbital singlets, thus raising also the energy of the orbital sector without destroying the dimer state.

Now we want to discuss the effects of finite Hund's coupling. As easily understood from Eqs. (1) and (2) an additional, orbital free term  $R$  tends to stabilize a ferromagnetic spin order at large values of  $\eta$ . Numerical data for  $\eta=0.15$

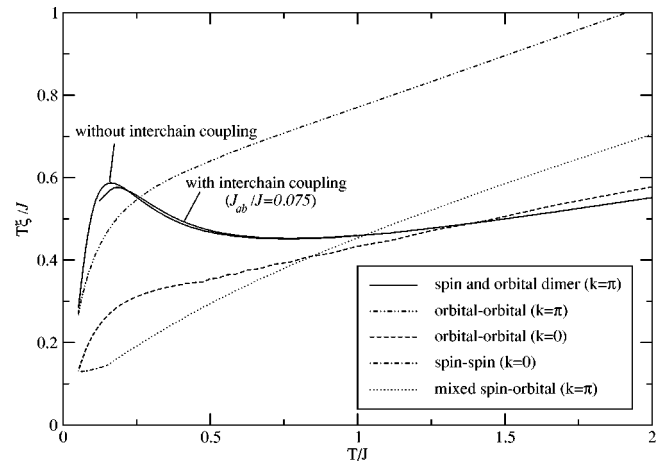


FIG. 4. The leading CL's times temperature for  $\eta=0.15$ . Note that all shown CL's have commensurate oscillations over the entire temperature range.

indeed show that  $\langle S_i \cdot S_{i+1} \rangle$  is monotonously increasing and reaches 1, the value expected for an uniform ferrochain, in the zero-temperature limit (Fig. 1). This leads to an exact cancellation of the orbital anisotropy terms in the ground state [see Eqs. (1) and (2)] and therefore to an isotropic antiferromagnetic coupling of the orbitals. From the Bethe ansatz result for the Heisenberg chain one expects  $\langle \tau_i \cdot \tau_{i+1} \rangle = -\ln 2 + 1/4$  consistent with the numerical result (see Fig. 1). Low-temperature asymptotics of the spin and orbital expectation values suggest a first-order phase transition between two possible ground states: Spin/orbital dimer phase and spin saturated ferrophase. A critical coupling  $\eta_c \sim 0.11$  separating them at zero temperature is just slightly below realistic values for vanadium oxides  $\sim 0.12$ .<sup>18</sup>

The specific heat [Fig. 3(b)] shows a two peak structure. The high-temperature hump is due to orbital and mixed spin-orbital excitations, whereas the low- $T$  peak is of spin origin. With increasing Hund's coupling, the hump is shifted to higher temperatures, whereas the low- $T$  peak is smaller and shifted to lower temperatures. It is striking that the high- $T$  hump contains such a large entropy weight. If it is due to orbital excitations only its entropy weight would be  $\ln 2$  but in fact it is  $\sim 1$ . This could be explained by a formation of an intermediate dimer state at finite temperature. In this case, the entropy weight of the hump is given by the total entropy  $\ln 6$  minus a spin entropy of  $S=2$  dimers given by  $1/2 \ln 5$  consistent with the numerical data. To support this scenario of a temperature driven dimerization further, we have calculated again the leading CL's (Fig. 4).

The dimer CL with  $\pi$  oscillations is indeed the largest CL in a certain temperature range and hence, dimerization is in this temperature range the leading instability towards the onset of long-range order in a 3D system. Note also, a large orbital CL with  $\pi$  oscillations indicating antiferromagnetic orbital order. At low temperatures there is a nonoscillating spin CL present as expected for an uniform ferrochain, however, this ferromagnetic CL is strongly suppressed at finite temperature due to a disorder effect of low-lying dimerized states. The competition between uniform and dimerized states is evident also from Fig. 1: In comparison to the spin

only case, where  $J_{i,j}$  is fixed by its zero-temperature expectation value for  $\eta=0.15$  and therefore all dimerization effects are omitted,  $\langle \mathbf{S}_i \cdot \mathbf{S}_{i+1} \rangle$  shows an unusual rapid decay of local spin correlations with temperature.

Finally, we address the relevance of these findings to the intermediate phase of  $\text{YVO}_3$ . Obviously, we have to take the coupling between different  $c$ -axis chains into account. The quasi-1D character of orbital physics is supported by the  $C$ -type spin structure leading to a weak interchain orbital coupling proportional to  $\eta$  only.<sup>12</sup> Interchain spin couplings can be explicitly included in the numerical calculations as a mean field,  $4J_{ab}\langle S^z \rangle$ . An estimation for  $J_{ab}$  can be obtained in the following way: Within linear response the susceptibility of the 3D system is given by  $\chi_{3D} = \chi_{1D}/(1 - 4J_{ab}\chi_{1D})$ . Taking  $T_{N1}/J \sim 0.25$  from experiment (a representative value of  $J \sim 40$  meV is used), demanding that  $\chi_{3D}$  diverges at this temperature and using the numerical data for  $\chi_{1D}$  calculated at  $\eta=0.15$ , we find  $J_{ab}/J \sim 0.075$  in good agreement with the experimentally observed value.<sup>19</sup> In Fig. 4 the dimer correlation length with this interchain molecular field included is displayed, showing that the results above are only weakly affected. The temperature range where dimerization is the leading instability approximately coincides with the  $C$  phase of  $\text{YVO}_3$ . We therefore believe that the model explains why in  $\text{YVO}_3$  a  $C$ -type magnetic order is stable as an intermediate phase. The gain of entropy due to the dimerization lowers the free energy  $F = \langle H \rangle - TS$  at finite temperature and stabilizes a formation of alternating weak and strong ferrobonds along one cubic axis (e.g.,  $c$  axis). In other words, a dimerization of

the *ferromagnetic* spin chain occurs due to the *orbital Peierls effect*, in which thermal spin fluctuations play a role of lattice degrees of freedom. The effect is dynamical in the present 1D case. However, as discussed before a weak but finite coupling between different  $c$  chains is present in  $\text{YVO}_3$ , which does not destroy the quasi-1D spin-orbital physics but leads to the onset of long-range dimer order. Doubling of the magnetic unit cell along the  $c$  axis is then expected. In fact, a modulation of ferrocouplings and related splitting of the magnon branches has recently been observed by Ulrich *et al.* (Ref. 19) in the  $C$  phase of  $\text{YVO}_3$ . As the dimerization is of electronic origin, concomitant lattice distortions are expected to be small because  $t_{2g}$  orbitals are not bond oriented and only weakly coupled to the lattice.

Summarizing, the one-dimensional spin-orbital model with  $S=1$  shows an intrinsic tendency towards dimerization. Large Hund's coupling can stabilize a uniform ferromagnetic ground state but strong dimer correlations develop again at finite temperature due to the orbital Peierls effect. Dimer states modulate spin and orbital bonds and release high entropy. The quasi-1D physics is not destroyed when realistic interchain couplings are taken into account on a mean-field level. The temperature driven dimerization in the 1D spin-orbital model could explain the stability of the intermediate  $C$ -type phase in  $\text{YVO}_3$ .

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<sup>20</sup>The origin of the factor 1/2 can be understood as follows: The elementary excitations are orbital "spinons" each with a gap  $\Delta$ , but they always appear in pairs so that  $\Delta_{orb}^{spectr} = 2\Delta$ . In the thermodynamic data the activated behavior is characterized by the energy  $\Delta$  of an elementary excitation irrespective of whether these excitations appear in pairs or not.