

Tetramerization of a Frustrated Spin-1/2 Chain

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We investigate a model of a frustrated spin-1/2 Heisenberg chain coupled to adiabatic phonons with a general form of magnetoelastic coupling. For large enough frustration and lattice coupling, a new tetramerized phase with three different bond lengths is found. We argue that the zigzag spin-1/2 chain LiV_2O_5 might be a good candidate to observe such a phase.

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Quasi-one-dimensional (1D) quantum antiferromagnets exhibit fascinating magnetic properties at low temperatures. Inorganic compounds such as CuGeO_3 (Ref. [1]) or LiV_2O_5 (Ref. [2]) are almost ideal prototypes of the spin-1/2 frustrated chain, the so-called antiferromagnetic (AF) Heisenberg $J_1 - J_2$ chain (see Fig. 1). The chemistry of these compounds enables the synthesis of single crystals much larger than their organic analogs and, consequently, the achievement of new experimental studies. Recently, the discovery of a spin-Peierls (SP) transition in CuGeO_3 (Ref. [3]) has drawn both experimental and theoretical interest.

At temperatures larger than the interchain couplings, the quasi-1D compounds CuGeO_3 or LiV_2O_5 are well described as independent AF Heisenberg chains including next-nearest neighbor (NNN) interactions responsible for frustration. The nearest neighbor (NN) J_1 and NNN J_2 exchange integrals can be estimated by a fit of the magnetic susceptibility, the high temperature behavior being governed by J_1 and the position of the maximum by the frustration ratio J_2/J_1 . Values such as $J_1 \approx 160$ K and $J_2/J_1 \approx 0.36$ have been proposed for CuGeO_3 (Ref. [4]). On the other hand, in LiV_2O_5 the spin-1/2 V^{4+} ions form double-chains similar to Fig. 1(b), well separated by inert double chains of V^{5+} ions. Quantum chemistry calculations suggest that J_2 could even be larger than J_1 in that case [5].

The SP transition is an instability due to magnetoelastic effects which is characterized (below a critical temperature T_{SP}) by the opening of a spin gap and the appearance of a lattice dimerization. It was first predicted to occur in the nonfrustrated $S = 1/2$ chain [6], but the properties of the $J_1 - J_2$ chain suggest that it is also a natural instability in that case, since the ground state of that model is spontaneously dimerized for $J_2/J_1 \geq 0.24$. This is particularly clear at the so-called Majumdar-Ghosh point [7] (MG) $J_2/J_1 = 0.5$, where the ground state (GS) is twofold degenerate, corresponding to two possible dimerization patterns formed by a succession of disconnected singlet dimers. However, when J_2/J_1 becomes very large, another instability could occur: The

J_2 chains are only weakly coupled, and they could undergo a SP transition of their own. The interplay between both instabilities has not been considered thus far.

In this Letter, we investigate on equal footings the role of the frustration and of the lattice coupling. Special emphasis is put on the search for new phases which would result from the combination of both effects. The competition between various orderings which could eventually appear simultaneously can be addressed only by going beyond perturbative approaches. Using exact diagonalization techniques, we report evidences for a new mixed phase with both dimerization and tetramerization amplitudes. Last, we discuss our results in the context of the quasi-1D antiferromagnets CuGeO_3 and LiV_2O_5 .

The Hamiltonian of a frustrated spin chain coupled to (adiabatic) lattice displacements is written as

$$\mathcal{H} = \frac{\mathcal{K}}{2} \sum_i \delta_i^2 + J_1 \sum_i (1 - A_1 \delta_i) \vec{S}_i \cdot \vec{S}_{i+1} + J_2 \sum_i [1 - A_2 (\delta_i + \delta_{i+1})] \vec{S}_i \cdot \vec{S}_{i+2}, \quad (1)$$

where δ_i is the distortion of the bond between site i and $i + 1$, \mathcal{K} is the spring constant, and the first term corresponds to the elastic energy loss. In general, this term might also contain cross terms such as $\delta_i \delta_{i+1}$ (depending on the underlying geometry of the structure). We have checked that they do not affect the basic physics of this model so that we omit them for simplicity. Unless specified otherwise, J_1 sets the energy scale. The spin-lattice

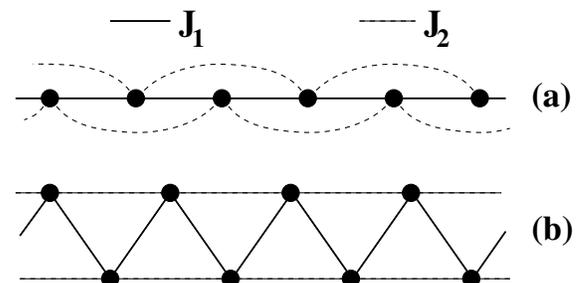


FIG. 1. (a) Linear $J_1 - J_2$ chain. (b) Zigzag $J_1 - J_2$ chain.

couplings A_a are assumed to be dimensionless so that the distortions δ_i are given in units of the lattice spacing. Note also that, as can be seen from a trivial redefinition of the δ_i , the coupling strengths can be redefined by the reduced variables $\tilde{A}_1 = A_1(J_1/\mathcal{K})^{1/2}$ and $\tilde{A}_2 = A_2(J_1/\mathcal{K})^{1/2}$ and used to investigate the phase diagram. However, the physical values for the modulations δ_i depend on A_1 , A_2 , and \mathcal{K} separately. Estimations of these parameters can be given on physical grounds as will be discussed later. Values such that $A_2 = A_1$ and $A_2 = 2A_1$ are relevant for the physical systems in which we are interested.

The phase diagram of the frustrated chain in the absence of lattice couplings ($A_1 = A_2 = 0$) is well known. The GS is uniform for small frustration (with power-law decay of the spin correlations) and becomes dimerized (with a finite spin gap) for J_2/J_1 larger than a critical value [8] j_c which has been determined with great accuracy by numerical methods, $j_c \simeq 0.241\,167$ (Ref. [9]). Interestingly enough, incommensurate spin correlations (away from the AF momentum $q = \pi$) appear for $J_2/J_1 > 0.5$ (Ref. [10]).

Before investigating the full Hamiltonian (1), it is instructive to first consider generalized dimer susceptibilities of the form

$$\tilde{S}(q, a) = \left\langle \frac{1}{L} \left| \sum_j \tilde{S}_j \cdot \tilde{S}_{j+a} \exp(iqr_j) \right|^2 \right\rangle, \quad (2)$$

where the expectation value is taken in the GS of the $J_1 - J_2$ chain in the absence of lattice coupling. Physically, any instability towards a modulated dimer phase involving dimers at distance a would be signaled by a sharp peak of $\tilde{S}(q, a)$ at a given q associated to the wave vector of the modulation. As seen in Fig. 2, sharp peaks are indeed seen in $\tilde{S}(q, 1)$ and $\tilde{S}(q, 2)$ at momentum $q = \pi$ and $q =$

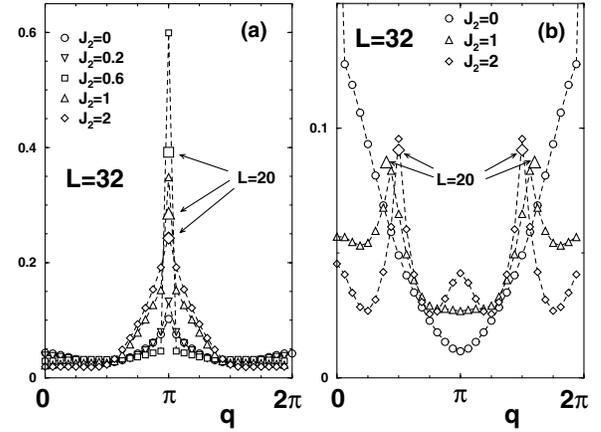


FIG. 2. Generalized dimer susceptibilities as a function of chain momentum q calculated by exact diagonalization on a 32 site ring. Some peak amplitudes for $L = 20$ are also shown as indicated on the plot. (a) NN dimer susceptibility ($a = 1$); (b) NNN dimer susceptibility ($a = 2$).

$\pi/2$, respectively, signaling proximity of instabilities toward the formation of dimerized ($q = \pi$) and tetramerized ($q = \pi/2$) phases involving NN and NNN dimers, respectively [11]. Note that NNN $q = \pi/2$ dimer correlations increase with increasing frustration J_2/J_1 while the maximum NN dimer susceptibility occurs around $J_2/J_1 \simeq 0.5$. Since the order parameter $\langle \frac{1}{L} \sum_j \tilde{S}_j \cdot \tilde{S}_{j+2} \exp(i\frac{\pi}{2} r_j) \rangle$ of the tetramerized phase is directly coupled to A_2 in Hamiltonian (1), the finite magnetoelastic A_2 coupling is then the key feature of the model.

In order to solve Hamiltonian (1) including the magnetoelastic coupling, we use Lanczos diagonalizations of small finite rings of size L with periodic boundary conditions. An iterative procedure is used to determine the displacements δ_i by solving a set of coupled nonlinear equations [12],

$$\mathcal{K} \delta_i - J_1 A_1 \langle \tilde{S}_i \cdot \tilde{S}_{i+1} \rangle - J_2 A_2 (\langle \tilde{S}_i \cdot \tilde{S}_{i+2} \rangle + \langle \tilde{S}_{i-1} \cdot \tilde{S}_{i+1} \rangle) = 0, \quad (3)$$

where $\langle \dots \rangle$ is the expectation value in the GS of Hamiltonian (1). Note that no translation symmetry is *a priori* assumed in order to search for lattice modulations of arbitrary periodicity (compatible with system size). A simple Fourier analysis of the equilibrium set of the δ_i shows that, generically, the GS lattice configuration is obtained for a single or a superposition of the following distortions: (i) a uniform (negative) component $\delta_i = \delta_0$ (which is due to the finite compressibility of the system [13]); (ii) a dimerization $\delta_i = \delta_D (-1)^i$; and (iii) a tetramerization $\delta_i = \delta_T \cos(\frac{\pi}{2} i + \phi_T)$. Although, the tetramerization could be either site centered (with $\phi_T = \pi/4$) or bond centered (with $\phi_T = 0$), only the second bond-centered type [i.e., a modulation of the bonds such as $\delta_T - 0 - (-\delta_T) - 0$] was found. This particular pattern can easily be understood in the large- J_2 limit which consists of two weakly coupled J_2 Heisenberg chains [see Fig. 1(b)]. In that limit, the magnetoelastic coupling A_2

tends to produce a dimerization of each chain so that $(\delta_{2p} + \delta_{2p+1}) \propto (-1)^p$, which can indeed be realized by a tetramerization of the chain with $\phi_T = 0$.

The domains of stability of the various phases are shown in Fig. 3 for two values of the parameter A_2/A_1 . Data are shown for cyclic rings of size $L = 12, 16$, and 20 , and a tentative phase diagram is obtained (see Fig. 4) from a finite size scaling analysis. Various regimes have to be distinguished for these extrapolations. First, when $J_2/J_1 < j_c$, the Heisenberg chain is critical and one expects that a dimerized GS would be stabilized for arbitrary magnetoelastic coupling [6]. Indeed, the finite critical value of the coupling \tilde{A}_1 exhibits a clear $1/\sqrt{L}$ power-law behavior with system size. In the range $j_c < J_2/J_1 < 0.5$, the system size dependence of the critical value of \tilde{A}_1 becomes exponential, signaling the fact that the infinite Heisenberg chain forms singlet dimers, even

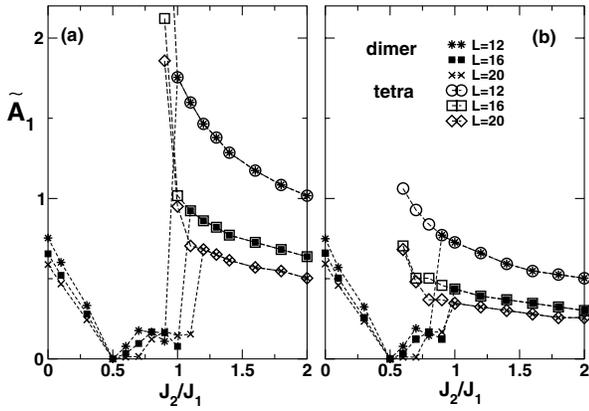


FIG. 3. Phase diagram in the \tilde{A}_1 -frustration plane for different system sizes L . The data points (and the dotted lines) correspond to the critical values of the (reduced) magnetoelastic coupling above which dimerization and/or tetramerization (as shown on the plot) appear. (a) $A_2/A_1 = 1$; (b) $A_2/A_1 = 2$. In that case, a very small region of uniform phase inside the dimerized phase area (omitted here for clarity) was found but shown to be a spurious finite size effect.

in the absence of the lattice. Note that at the special MG point $J_2/J_1 = 0.5$ the critical coupling for \tilde{A}_1 vanishes for all sizes. Special care is needed to analyze the data for $J_2/J_1 > 0.5$. In a narrow range of J_2/J_1 , $0.5 < J_2/J_1 < j_{\text{crit},1}$, which depends on the A_2/A_1 ratio, the system dimerizes only above a small critical value of the coupling A_1 . In a range $j_{\text{crit},1} < J_2/J_1 < j_{\text{crit},2}(L)$ (which extends with increasing system size), when \tilde{A}_1 exceeds a higher critical value, a tetramerization superposes to the existing dimerization. For $J_2/J_1 > j_{\text{crit},2}(L)$, dimerization and tetramerization occur both for the same critical value of the coupling constant. However, our data are consistent with the fact that $j_{\text{crit},2}(L) \rightarrow \infty$ when $L \rightarrow \infty$ so that this last regime seems irrelevant. For $0.5 < J_2/J_1 < j_{\text{crit},2}(L)$,

the critical coupling for dimerization rapidly vanishes with increasingly large system sizes (although some increase has been observed for small sizes). For $J_2/J_1 > j_{\text{crit},1}$ (e.g., $j_{\text{crit},1} \sim 0.85$ for $A_2 = A_1$), the finite size dependence of the critical coupling for tetramerization is consistent with a rapid exponential behavior converging to a finite value. An estimation of the infinite size phase diagram is then possible with reasonable accuracy as shown in Fig. 4. In summary, our calculations predict that the $J_1 - J_2$ chain is always dimerized once it is coupled to the adiabatic lattice. Tetramerization, however, occurs only for large enough frustration and when the lattice couplings \tilde{A}_1 and \tilde{A}_2 exceed some critical values which vanish when J_2/J_1 increases to infinity. Interestingly enough, our data also suggest that the nature of the $D \rightarrow T$ transition might change when frustration increases, from first order (with discontinuities in the dimerization and tetramerization amplitudes) to a continuous second-order-like line at large J_2 . Note that, even for large J_2/J_1 (limit of weakly coupled chains), one still expects finite critical lattice couplings since, in the absence of the lattice, an arbitrary small perturbation J_1 introduces an exponentially small gap and a finite spin correlation length. Note that our results might be further clarified and confirmed by density matrix renormalization group calculations taking advantage of the generic form of the modulation established here.

We finish by discussing some applications of the present study to real materials. The magnetoelastic couplings are generically due to strong dependence of the exchange integrals with respect to distance, typically $J_a(r) \propto r^{-\alpha_a}$, with an exponent α_a in the range 7–15. A small change of length $\delta\vec{r}$ of the bond connecting two sites at distance r_a along some direction \vec{u}_a ($\vec{r} = r_a\vec{u}_a$) leads to a linear change of the AF coupling,

$$J_a(\delta\vec{r}) = J_a \left(1 - \frac{\alpha_a}{r_a} \vec{u}_a \cdot \delta\vec{r} \right). \quad (4)$$

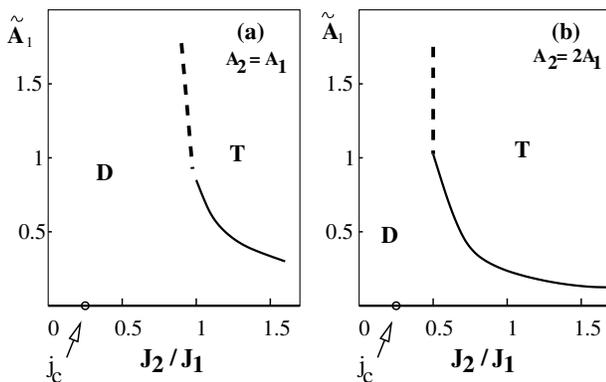


FIG. 4. Tentative phase diagrams in the \tilde{A}_1 -frustration plane obtained from a finite size scaling analysis of the data of Fig. 3. The dimerized and tetramerized phases are labeled by **D** and **T**, respectively. Thick dashed (full) lines correspond to first-order-like (second-order) transition lines. (a) $A_2/A_1 = 1$; (b) $A_2/A_1 = 2$.

In the case of the linear chain of Fig. 1(a) where the displacements occur along the chain direction, Eq. (4) predicts $A_2 = A_1/2$ assuming the same values of α_a for the two chemical bonds. In the case of CuGeO_3 , the superexchange path giving rise to J_2 involves more intermediate states (in particular germanium orbitals) so that one expects $\alpha_2 > \alpha_1$ and $A_2 \simeq A_1$ seems more physical in that case. According to the phase diagram of Fig. 4(a), conditions for a small tetramerization seem clearly not realized in CuGeO_3 . Indeed, for a frustration $J_2/J_1 \sim 0.4$ and a small physical value for the dimensionless coupling \tilde{A}_1 , the A_2 coupling becomes irrelevant (apart from producing a tiny overall contraction of the lattice) and we expect a simple dimerization $\delta_D \propto A_1 J_1 / \mathcal{K}$. Assuming $A_1 \sim 10$, $J_1 \sim 100$ K, and $\mathcal{K} \sim 10$ eV, a dimerization around 0.1%–0.3% of the lattice spacing is expected in agreement with x-ray diffraction experiments [14].

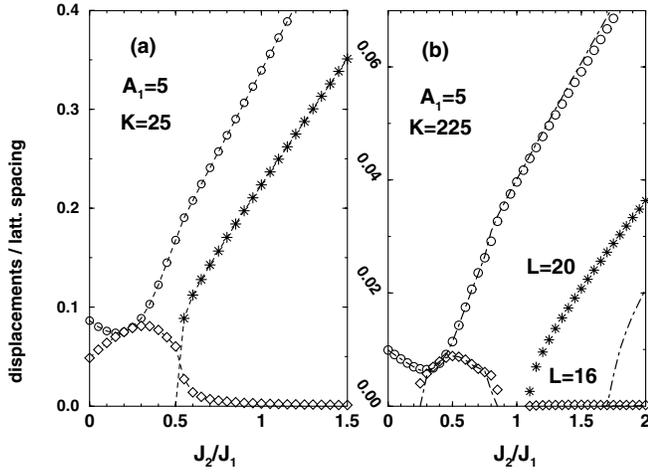


FIG. 5. Amplitudes of the relative bond length change $|\delta_0|$ (open circles), dimerization δ_D (diamonds), and tetramerization δ_T (stars) (in units of the lattice spacing) versus frustration calculated on $L = 20$ site rings for $A_1 = 5$ and $A_2 = 10$. Only nonzero amplitudes are shown; (a) $\tilde{A}_1 = 1$; (b) $\tilde{A}_1 = 1/3$: data for $L = 16$ (thick dot-dashed lines) are also shown in that case to indicate finite size effects.

We now turn to the case of the LiV_2O_5 compound. If one assumes that atomic displacements in Fig. 1(b) would occur along the zigzag chain direction and that the exponents α_a are identical for the two bonds, Eq. (4) implies that $A_2 = 2A_1$. As shown in Figs. 4(a) and 4(b), the stability of the tetramerized phase increases with increasing ratio A_2/A_1 . Hence, due to larger A_2/A_1 and J_2/J_1 ratios, LiV_2O_5 seems, contrary to CuGeO_3 , an interesting candidate for the new tetramerized phase. Typical exponents such as $\alpha_1 = \alpha_2 = 10$ give $A_1 = 5$ and $A_2 = 10$. Assuming a physical value $J_1 = 400$ K for the exchange constant and considering $\mathcal{K} = 10\,000$ K (~ 1 eV) and $\mathcal{K} = 90\,000$ K (~ 9 eV), we get $\tilde{A}_1 = 1$ and $\tilde{A}_1 = 1/3$, respectively. The magnitudes of the dimerization and tetramerization for these parameters are shown in Fig. 5 as a function of the frustration J_2/J_1 . For rather large magnetoelastic couplings such as the one used in Fig. 5(a) where finite size effects are negligible we observe, for increasing magnetic frustration, a transition from a purely dimerized phase to a new phase with a dominant tetramerization and a small dimerization component. For realistic couplings, i.e., $\mathcal{K}/J_1 > 200$, as seen in Fig. 5(b), finite size effects become large. Nevertheless we expect a behavior similar to that of Fig. 5(a) although with much smaller lattice displacements. Typically, while δ_T might be of the order of a percent of the lattice spacing, δ_D is expected to remain much smaller.

In conclusion, from numerical calculations, we have obtained the generic properties of the frustrated spin-1/2 chain coupled to adiabatic phonons. Our results are compared to experimental systems such as the (quasi)linear

CuGeO_3 chain and the zigzag LiV_2O_5 chain. While the observed small dimerization of the SP phase of CuGeO_3 can easily be accounted for within such a simple model, we argue that LiV_2O_5 is a good candidate to observe a novel tetramerized phase with a doubling of the zigzag chain periodicity (leading to new superstructure peaks in diffraction experiments) and two (slightly) nonequivalent V^{4+} sites, a feature which could be observed in NMR experiments. In that respect, we note that currently available data, including NMR data on single crystals of $\text{Li}_x\text{V}_2\text{O}_5$ with x in the range 0.96 to 1 (Ref. [15]), all point to dominant impurity effects at low temperatures. It is our hope that the present results will motivate further experimental efforts to synthesize very clean samples of LiV_2O_5 and to look for low temperature instabilities.

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