Magnetic ordering in a doped frustrated spin-Peierls system

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Based on a model of a quasi-one dimensional spin-Peierls system doped with non-magnetic impurities, an effective two-dimensional Hamiltonian of randomly distributed S=1/2 spins interacting via long-range pair-wise interaction is studied using a stochastic series expansion quantum Monte Carlo method. The susceptibility shows Curie-like behavior at the lowest temperatures reached although the staggered magnetisation is found to be finite for $T \to 0$. The doping dependence of the corresponding three-dimensional Néel temperature is also computed.

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Quasi one-dimensional (1D) quantum antiferromagnets exhibit fascinating magnetic properties at low temperatures. Some inorganic compounds, such as the germanate oxide CuGeO$_3$ and the vanadate oxide LiV$_2$O$_5$, are excellent realizations of weakly interacting frustrated spin-1/2 chains. A spin-Peierls (SP) transition to a gapped dimerised ground state (GS) has been seen experimentally in CuGeO$_3$, and theoretical calculations point toward a similar scenario in LiV$_2$O$_5$. Doping with non-magnetic dopants is realized experimentally in CuGeO$_3$ by substituting a small fraction of copper atoms by zinc (or magnesium) atoms. An intriguing low-temperature phase where antiferromagnetism coexists with the SP dimerisation was observed. Similar doping-induced antiferromagnetic (AF) ordering has also been observed in the interacting dimer compound TlCuCl$_3$. Theoretically, each dopant is expected to release a soliton which can be viewed as a single unpaired spin separating two dimer configurations, hence leading to a rapid suppression of the spin gap under doping. In an idealized spontaneously dimerised spin chain the soliton would not be bound to the dopant. The physical picture is in fact completely different: A static bulk dimerisation is enforced by, e.g., couplings to the three-dimensional (3D) lattice, thus generating an attractive potential between the soliton and the dopant.

The dopant-soliton confinement mechanism is responsible for the formation of local S=1/2 magnetic moment$^{5,6}$. Within a realistic model including an elastic coupling to a two-dimensional (2D) lattice$^6$, it was shown that these effective spins experience a non-frustrated interaction that could lead at $T=0$ to a finite staggered magnetization$^6$. Recently, similar conclusions were reached using a model with purely magnetic interactions including a four-spin exchange coupling$^7$. In this Letter, we analyze the formation of the dopant-induced AF order which coexists with the SP dimerisation. After using exact diagonalisation (ED) of small clusters (following Refs.$^{11,12}$) to construct an effective diluted S=1/2 model, we take advantage of the non-frustrated character of the resulting Hamiltonian to perform extensive state-of-the-art stochastic series expansion (SSE) quantum Monte Carlo (QMC) simulations on 2D lattices as large as $288 \times 288$ with up to $N_s=576$ (dopant) spins and down to temperature as low as $T=1/\beta=2^{-14}$ (or $2^{-18}$ for $N_s=256$). The uniform susceptibility is shown to exhibit a Curie-like behavior although the $T=0$ and infinite size extrapolated staggered magnetization is found to be finite down to the smallest dopant concentrations $x$ available. The Néel temperature (assuming a small 3D coupling) is also computed versus $x$ and compared to experiments.

We start with the microscopic Hamiltonian of a 2D array of coupled frustrated spin-$1/2$ chains and we summarize the procedure followed in refs.$^{11,12}$ to derive an effective Hamiltonian:

$$H = \sum_{i,a} [J(1 + \delta_{i,a}) \mathbf{S}_{i,a} \cdot \mathbf{S}_{i+1,a} + \alpha J \mathbf{S}_{i,a} \cdot \mathbf{S}_{i+2,a} + J_i h_{i,a} + \delta_{i,a} h_{i,a}^2],$$

(1)

where the $i$ and $a$ indices label the $L$ sites and $M$ chains respectively. The energy scale is set by the exchange coupling along the chain ($J=1$) and $\alpha$ is the relative magnitude of the next nearest neighbor frustrating magnetic coupling. Dopants are simply described as randomly located inert sites $(i,a)$ (see Fig.1) where $\mathbf{S}_{i,a}=0$ is set in Eq. (1). Small inter-chain couplings are included in a mean-field self-consistent treatment assuming,

$$h_{i,a} = J_1 (\langle \mathbf{S}_{i,a+1}^z \rangle + \langle \mathbf{S}_{i,a-1}^z \rangle),$$

(2)

$$\delta_{i,a} = \frac{J_2}{J} (\langle \mathbf{S}_{i,a+1} \cdot \mathbf{S}_{i+1,a+1} \rangle + \langle \mathbf{S}_{i,a-1} \cdot \mathbf{S}_{i+1,a-1} \rangle).$$

(3)

While the first term accounts for first-order effects in the inter-chain magnetic coupling $J_1$, the second term might have multiple origins: although a four-spin cyclic exchange mechanism provides the most straightforward derivation of $h_{i,a}$, at a qualitative level, $J_2$ can also mimic higher-order effects in $J_1$ or the coupling to a 2D (or 3D) lattice. In that case, due to a magneto-elastic coupling, the modulations $\delta_{i,a}$ result from small displacements of the ions. The elastic energy is the sum of a
local term \( \frac{1}{2}K_0 \sum_{i,a} \delta_{1,a}^2 \) and an inter-chain contribution \( K_1 \sum_{i,a} \delta_{1,a} \delta_{a+1} \) of electrostatic origin. In that case Eq. (3) is replaced by

\[
\frac{1}{2}K_0 \sum_{i,a} \delta_{1,a}^2 + K_1 (\delta_{1,a} + \delta_{a+1} + \delta_{a-1}) = J_1 \langle S_{i,a} \cdot S_{i+1,a} \rangle,
\]

giving very similar results so that we shall restrict to Eq. (3) here.

By breaking a dimer, each dopant releases a soliton carrying a spin 1/2. As shown previously, \( J_1 \) (or equivalently \( K_1 \)) in the alternative model leads to a confinement of the moment to the dopant with a localization length \( \sim J_1^{-1} \). At temperatures lower than the spin gap, these effective spins dominate the physics (see Fig. 1) and a low-temperature description of the doped system can be obtained using an effective model including only (long-range) pair-wise interaction between these local moments. The coupling \( J_{\text{eff}} \) between two effective spins at arbitrary relative distance is computed by ED as the energy difference between their singlet and triplet configurations. The sign of this interaction (i.e. its ferromagnetic or AF nature) depends on whether the two dopants lie on the same or opposite sublattices, so that an overall AF ordering is favored.

In order to derive an analytic expression for \( J_{\text{eff}} \) valid at long distances, we fit the numerical ED data (restricted to short and intermediate length scales). A long-range non-frustrated Heisenberg model of diluted effective spin-1/2 can then be defined,

\[
\mathcal{H}_{\text{eff}} = \sum_{r_1,r_2} \epsilon_{r_1} \epsilon_{r_2} J_{\text{eff}} (r_1 - r_2) S_{r_1} \cdot S_{r_2},
\]

with \( \epsilon_r = 1 \) with probability \( x \) and \( \epsilon_r = 0 \) with probability \( 1 - x \), where \( x \) is the dopant concentration. Such a model can be studied by QMC on \( L_x \times L_y \) clusters much larger than those accessible to ED and at all temperatures. Using five phenomenological parameters, two energy scales and three length scales, simple expressions fit the ED data for a wide range of (physical) parameters. Naturally, one has to distinguish four cases depending on whether the dopants are located on the same (\( \Delta a = 0 \)) or on different chains, and whether they are located on the same or on different sublattices. When \( \Delta a = 0 \) (same chain), \( J_{\text{eff}} \) approximately fulfills

\[
J_0(1 - \Delta i/\xi^0) \quad \text{for} \quad \Delta i < \xi^0 \quad \text{and otherwise} \quad J_{\text{eff}}(\Delta i, 0) = 0.
\]

FIG. 1: Schematic picture of a doped SP system. Thick bonds correspond to dimers, and non-magnetic dopants (released spin-\( \frac{1}{2} \)) are represented by open circles (arrows).

FIG. 2: Staggered magnetic structure factor per site vs inverse-temperature \( \beta \) computed using a \( \beta \)-doubling scheme and averaged over 1000 to 2000 samples. Results for \( N_s = 256 \) spins on \( 56 \times 56, 64 \times 64, 72 \times 72, 80 \times 80, 88 \times 88 \) and \( 96 \times 96 \) (from top to bottom) lattices correspond to the concentrations \( x \) indicated on the plot.
sites carrying a "dopant spin" contribute to this sum. It is convenient to normalized \( S \) with respect to the number of sites, i.e. to define a staggered structure factor per site: \( s(\pi, \pi) = S(\pi, \pi)/L_x L_y \). In an ordered AF state, \( s(\pi, \pi) \) should converge, with increasing size, to a non-zero value less than \( 1/4 \). The (finite size) sublattice magnetization \( m_{AF} \) can then be obtained by averaging \( s(\pi, \pi) \) over a large number of dopant distributions, i.e. \( (m_{AF})^2 = 3\langle s(\pi, \pi) \rangle_{\text{dis}} \), where the factor 3 comes from the spin-rotational invariance and \( \langle \ldots \rangle_{\text{dis}} \) stands for the disorder average. The staggered magnetization per dopant is then simply \( m_{\text{spin}} = m_{AF}/x \). We have checked that extrapolations to the thermodynamic limit using different aspect ratios \( L_y/L_x \) give similar results and, here, we only report data for \( L_y = L_x = L \).

Since, strictly speaking, in 2D the divergence of \( S(\pi, \pi) \) occurs only at \( T = 0 \) (\( \beta = \infty \)) it is appropriate to first extrapolate the finite size numerical data to \( T = 0 \). As shown in Fig. 3a the staggered structure factor saturates at sufficiently low temperature and the GS value of \( m_{AF} \) (averaged over disorder) can be safely obtained. Then, using a polynomial fit in \( 1/\sqrt{N_s} \) (order 2 is sufficient) an accurate extrapolation to the thermodynamic limit, \( N_s \rightarrow \infty \) (or \( L \rightarrow \infty \) at constant \( x \)), is performed as shown in Fig. 3a. The doping dependence of the extrapolated \( m_{AF} \) is given in Fig. 3b. Note that our results, although consistent with previous \( (T = 0) \) extrapolations attempted on small clusters, are far more accurate due to the use of much larger systems. We have tested various fits to the data. Assuming a power law \( \propto x^\mu \), the best fit (solid line in Fig. 3b)) gives an exponent \( \mu \approx 1.38 > 1 \). However, the alternative behavior \( a_1 x + a_2 x^2 \) would only be distinguishable at even smaller \( x \).

We have computed the uniform susceptibility \( \chi(T) \) for a wide range of temperatures. Results for the Curie constant \( C(T) = T\chi(T) \) are shown in Fig. 4. At the highest temperatures the effective dopant spins behave as free spins while at low temperature we observe a new Curie-like behavior with a reduced Curie constant \( \sim 1/12 \). Although the 2D system orders at \( T = 0 \) (as proven above) this behavior agrees with a qualitative argument by Sigrist and Furusaki based on the formation of large spin clusters. A detailed analysis of a low-temperature scaling regime similar to the one observed in random ferromagnetic-antiferromagnetic spin chains will be reported elsewhere.

We finish this investigation by calculating the Néel temperature, assuming a small (effective) 3D magnetic coupling \( \lambda_{3D} \) between the 2D planes. Using an RPA criterion, the critical temperature \( T_N \) is simply given by \( \chi_{\text{stag}}(T_N) = 1/|\lambda_{3D}| \) where the staggered spin susceptibility (normalized per site) is defined as usual by,

\[
\chi_{\text{stag}}(T) = \frac{1}{T^2} \sum_{i,j} (-1)^{r_i+r_j} \int_0^\beta d\tau \langle S^z_i(0) S^z_j(\tau) \rangle ,
\]

and averaged over several disorder configurations (typically 2000). Since \( \chi_{\text{stag}}(T_N) \) is expected to reach its thermodynamic limit for a finite linear size \( L \) as long as \( T_N \) remains finite, accurate values of \( T_N \) can be obtained using a finite size computation of \( \chi_{\text{stag}}(T) \) for not too small inter-chain couplings. Fig. 5a) shows that \( \chi_{\text{stag}}(T_N) \) diverges when \( T \rightarrow 0 \). \( T_N \) is determined by the intersection of the curve \( \chi_{\text{stag}}(T) \) with an horizontal line at coordinate \( 1/\lambda_{3D} \). Note that finite size corrections remain small, even in the worst case corresponding to very small \( \lambda_{3D} \) values and large dopant concentrations. The doping dependence of \( T_N \) is plotted in Fig. 5b) for a particularly small value \( \lambda_{3D} = 0.01 \) (in order to show the small size dependence observable in that case). It clearly reveals a rapid decrease of \( T_N \) when \( x \rightarrow 0 \), but, in agreement with experiments, does not suggest a non-zero critical concentration. In Fig. 5b), we show the behavior of \( T_N(x) \) down to \( x = 0.007 \). Note that from numerical fits of our data, we can not clearly distinguish between a power-law beh-
FIG. 5: (a) Staggered susceptibility of a 2D layer vs temperature (using log-log scales) for \( N_s = 256 \) (full symbols) and \( N_s = 576 \) (open symbols) spins. Concentrations \( x \) are shown on the plot (similar symbols as in Figs. 2 and 3). (b) Néel temperature vs dopant concentration \( x \) for a 3D RPA inter-plane coupling \( \lambda_{3D} = 0.01 \) and for \( N_s = 256 \) and \( N_s = 576 \) spins.

In summary, we have studied an effective low-energy Hamiltonian (valid for low temperature physics) describing the interaction of a finite concentration of spinless dopants randomly distributed in a generic low-dimensional (frustrated) SP system. The SSE method, which is applicable here because of the non-frustrated nature of the effective model, was used in combination with finite-size scaling to compute both GS and finite temperature properties. The uniform susceptibility exhibits a Curie-like behavior down to very low temperature. We also predict that the AF order develops continuously without any finite critical dopant concentration in agreement with experiment.

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