Peierls Dimerization with Nonadiabatic Spin-Phonon Coupling

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We study the magnetic properties of a frustrated Heisenberg spin chain with a dynamic spin-phonon interaction. Using Lanczos diagonalization that preserves the full lattice dynamics, we explore the nonadiabatic regime with phonon frequencies comparable to the exchange coupling energy, which is, for example, the relevant limit for the spin-Peierls compound $CuGeO_3$. Compared to the static limit of an alternating spin chain, the magnetic properties are strongly renormalized due to the coupled dynamics of spin and lattice degrees of freedom. The dependence of the magnitude of the spin-triplet excitation gap changes from a strong to a weak dimerization with increasing phonon frequencies implying the necessity to include dynamic effects in a quantitative description of the spin-Peierls state in $CuGeO_3$. [S0031-9007(98)07570-X]

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Low dimensional quantum spin systems have attracted considerable attention of theorists over the past decades. Most of the remarkable features observed in these systems are pure quantum effects uniquely due to their low dimensionality. Among the current experimental and theoretical efforts for understanding the magnetic properties of linear chain and ladder materials, the recent discovery of a spin-Peierls (SP) transition at $T_{\rm SP} = 14.3$ K in the inorganic compound $CuGeO_3$ (CGO) [1] has received particular attention. In analogy to the Peierls instability towards dimerization in quasi-one-dimensional metals [2], the energy of spin chains is lowered by dimerizing into an alternating pattern of weak and strong bonds. The SP transition is therefore driven by the magnetic energy gain which overcompensates the lattice deformation energy [3]. In the SP phase of CGO, the copper moments form singlet dimers along the chains and there is an energy gap to spin triplet excitations. Experimentally, the SP nature of the transition and the spin gap have been firmly established by inelastic neutron scattering (INS), susceptibility, x-ray, and electron-diffraction experiments [4].

The Peierls transition also naturally involves the lattice degrees of freedom due to the alternating distortion of atomic positions. A rather common situation has been the clear separation of the electronic or magnetic energy scales from the frequencies of those phonons which couple most effectively to the SP lattice distortion. This adiabatic limit is, e.g., realized in transpolyacethylene [5] or organic SP materials [6]. In contrast, in CGO two weakly dispersive optical phonon modes involved in the SP transition have been identified with frequencies $\hbar\omega \approx J$ and $\hbar\omega \approx 2J$, where J is the superexchange coupling between neighboring Cu spins [7]. These hard phonons require a very strong spin-phonon coupling for a SP transition to occur [8]. A strong magnetoelastic coupling has indeed been observed in thermal expansion and magnetostriction experiments [9], and inferred from large uniaxial pressure (p_i) derivatives $\partial J/\partial p_i$ [10]. The SP physics in CGO is therefore in a *nonadiabatic* regime.

Despite this unusual situation, previous theoretical studies have commonly adopted an alternating and frustrated antiferromagnetic (AF) Heisenberg spin-chain model [11],

$$H = J \sum_i \{[1 + \delta(-1)^i]\mathbf{S}_i \cdot \mathbf{S}_{i+1} + \alpha \mathbf{S}_i \cdot \mathbf{S}_{i+2}\}, \quad (1)$$

with a static dimerization parameter δ, thus representing the extreme adiabatic limit of a SP chain. i denotes the sites of a chain with length N, and $\mathbf{S}_i$ are $S = 1/2$ spin operators. α determines the strength of a frustrating AF next-nearest-neighbor coupling. The model (1) contains two independent mechanisms for spin-gap formation. At $\delta = 0$ and for $\alpha < \alpha_c$, the ground state is a spin liquid and the elementary excitations are massless spinons [12]. $\alpha_c = 0.241$ was accurately determined by numerical studies [11,13]. For $\alpha > \alpha_c$ the ground state is spontaneously dimerized, the spectrum acquires a gap, and the elementary excitations are massive spinons [14,15]. On the other hand for any finite δ, the singlet ground state of (1) is also dimerized, but the elementary excitation is a massive magnon [12,16].

From fits to magnetic susceptibility data in the uniform high temperature phase [10,17] and from the requirement to reproduce the experimental triplet excitation gap [17,18], the parameter set $J = 160$ K, $\alpha = 0.36$, and $\delta = 0.014$ was estimated for CGO within the static model (1). However, the amplitude of the dimerization is substantially underestimated when compared to estimates from structural data in the SP phase [7,19]. In this Letter we show that, due to the nonadiabatic, phonon dynamics, a much larger dimerization is needed to achieve the same magnitude of the triplet gap and thus offer a possible route towards a quantitatively consistent description of both the structural distortion and the INS data.

The dimerization parameter δ in Eq. (1) may be viewed to result from a mean-field treatment of an interchain coupling which is generated by a purely elastic mechanism [20]. In fact, this coupling to neighboring dimerized chains provides an external potential, lifting the degeneracy between the two possible dimerized ground states [21]. Thereby, soliton and antisoliton excitations form spin triplet or spin-singlet bound states [22]; the former is the elementary massive magnon of the spin Hamiltonian (1) for $\delta > 0$.

In this Letter we choose a different starting point and use a Heisenberg chain model in which the spins are explicitly coupled to the lattice degrees of freedom maintaining their full quantum dynamics. Specifically, we study the magnetic properties of the Hamiltonian [21],

$$H_{\mathrm{SP}} = J \sum_i \{[1 + g(b_i^+ + b_i)]\mathbf{S}_i \cdot \mathbf{S}_{i+1} + \alpha \mathbf{S}_i \cdot \mathbf{S}_{i+2}\} + \hbar\omega \sum_i b_i^+ b_i \,, \tag{2}$$

with the local phonon creation and annihilation operators b_i^+ and b_i, respectively. For the optical phonon with frequency ω we thus choose a dispersionless Einstein mode—an appropriate choice for modeling those phonons in CGO which are most relevant to the Peierls distortion [7]. In the nonadiabatic ($\hbar\omega \sim J$) and intermediate coupling ($g \sim J$) regimes the spin and the phonon dynamics are intimately coupled, and integrating out the phonons in order to obtain an effective renormalized spin-only Hamiltonian is, in general, not possible [23].

This situation thus requires a numerical approach. We have performed exact diagonalizations on finite chains up to $N = 16$ sites with periodic boundary conditions. Since the Hilbert space associated with the phonons is infinite even for a finite system, we apply a controlled truncation procedure retaining only basis states with, at most M phonons [24]. M is fixed by requiring a relative error in the ground-state energy less than 10^{-7}. In our calculations all possible phonon modes are taken into account.

Figure 1 demonstrates, for a 12-site chain, how many phonons have to be included to achieve convergence for the ground-state energies of the singlet $S = 0$ and the triplet $S = 1$ sectors. Although the specific value of α is not crucial for our arguments, we keep the frustration parameter $\alpha = 0.36$ in all calculations fixed to its most likely value in CGO. Figure 1 contrasts the results obtained if phonons only with wave vector $q = \pi$ or $q = \pi$ *and* $q = 0$ are used to the case where all phonon modes are included. While it has been argued in Ref. [25] that keeping the $q = \pi$ mode only should already capture the dominant dimerization effect of the spin-phonon interaction, we find in Fig. 1, that e.g., the singlet-triplet excitation gap is strongly renormalized when phonons of *all* q are taken into account, implying that a spin-triplet excitation is accompanied by a *local* distortion in the lattice.

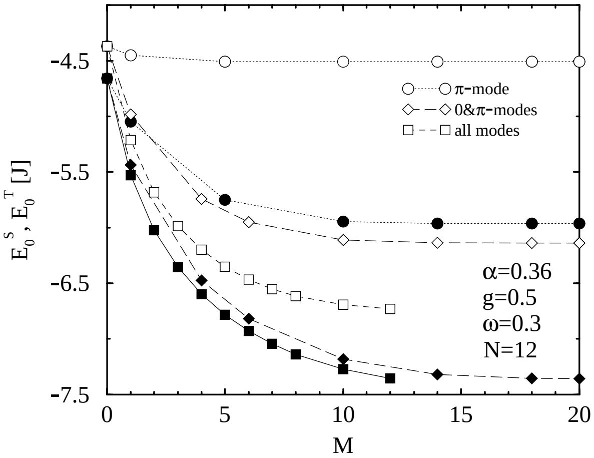

FIG. 1. Energies of the singlet ground state (solid symbols) and the lowest triplet excitation (open symbols) vs the number of phonons used in the numerical diagonalization. The different symbols indicate the results obtained by including phonons (i) only with $q = \pi$ (circles), (ii) with $q = 0$ and $q = \pi$ (diamonds), and (iii) at all wave vectors (squares). The singlet-triplet gap is given by $\Delta^{ST} = E_0^T - E_0^S$. As in all subsequent figures, energies are measured in units of J.

The renormalization of the singlet-triplet gap Δ^{ST} is shown in the scaling plot in Fig. 2. It is contrasted to the result with a restriction to the $q = \pi$ phonons only. In spite of the limited system sizes of up to 16 sites the data are well fitted by the scaling function [18,26]

$$\Delta^{ST}(N) = \Delta^{ST} + \frac{A}{N} e^{-N/N_0}. \tag{3}$$

It appears that the restriction to the π modes substantially overestimates the size of the gap for $N \to \infty$.

The triplet dispersion shown in Fig. 3 supports the expectation—as inferred from the neutron scattering studies of the phonons [7]—that the frequencies of the

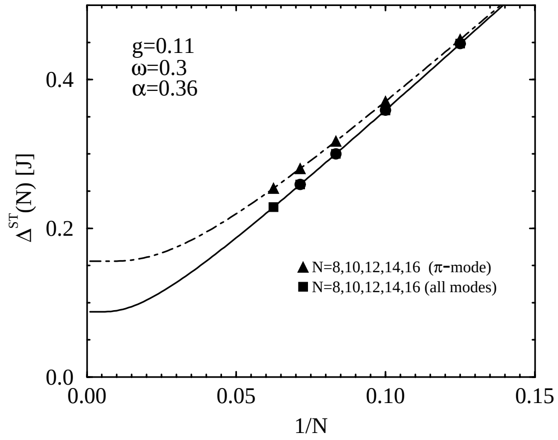

FIG. 2. Finite-size scaling behavior of the triplet excitation gap Δ^{ST} for $\alpha = 0.36$. The lines result from the fit to the scaling function (3). The (almost adiabatic) phonon parameters $g = 0.11$ and $\omega = 0.3$ were used in order to make contact with previous numerical studies [25].

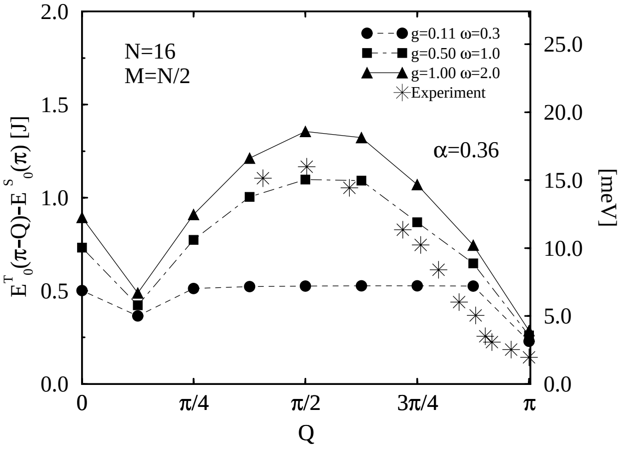

FIG. 3. Dispersion of the elementary triplet excitation (left scale) for a chain with $N = 16$ sites for different phonon frequencies and spin-phonon coupling constants. Experimental data ($*$, right scale) are also included from Ref. [29].

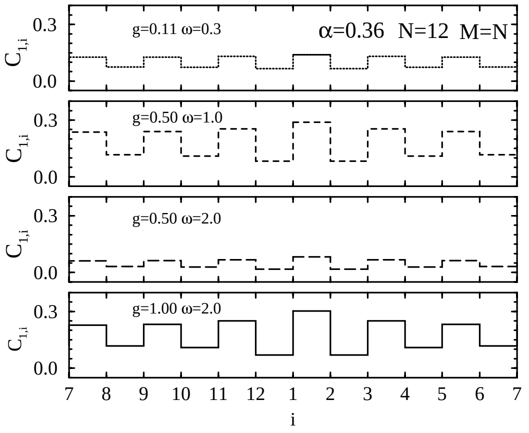

FIG. 4. Displacement correlation function $C_{1,i}$ as defined in the text for different phonon frequencies and spin lattice coupling constants for a chain with $N = 12$ sites.

relevant optical phonon modes in CGO are comparable to, or larger than, the exchange coupling J. Because $\hbar\omega < J$, the phononic character of the excitation dominates, leading to a flattening of the dispersion [27,28]. This, however, is incompatible with the magnetic INS data [29] which do not show any signature for a flat dispersion of the triplet excitation branch. We have included in Fig. 3 experimental data on CGO from Ref. [29] which, however, are not intended as a fit to the data—our results in Fig. 3 are for a fixed chain length with $N = 16$ site—but rather show the shape of the triplet dispersion. We stress that the upturn at $Q = 0$ is a finite-size effect which also occurs for the pure spin model and rapidly decreases with increasing N [30]; for $N \to \infty$, $E^T_0(\pi)$ and $E^T_0(0)$ become degenerate.

The Peierls ordering structure of the ground state has to be demonstrated in different ways for the static (1) and the dynamic model (2). For the Heisenberg spin-chain model (1) the *magnetic* order parameter,

$$D = \left\langle \frac{1}{N} \sum_i (-1)^i (\mathbf{S}_{i-1} \cdot \mathbf{S}_i - \mathbf{S}_i \cdot \mathbf{S}_{i+1}) \right\rangle . \quad (4)$$

is the proper choice to describe the formation of local singlets. For the translationally invariant quantum spin-phonon model (2), D vanishes [31] and the Peierls distortion of the lattice is reflected in the spatial structure of the displacement correlation function,

$$C_{1,i} = \langle (b_1 + b_1^+)(b_i + b_i^+) \rangle - \delta_{1,i} . \quad (5)$$

The alternating structure of the correlation function $C_{1,i}$ shown in Fig. 4 implies the Peierls formation of short and long bonds and thus alternating strong and weak AF exchange interactions, i.e., a dimerized ground state. Naturally the dimerization is enhanced (weakened) by increasing the spin-phonon coupling (phonon frequency). We note that for any finite phonon frequency there exists a critical coupling constant g_c [32]; in the infinite system quantum lattice fluctuations will destroy the Peierls dimerization for couplings $g < g_c$. For nonadiabatic phonon frequencies $\hbar\omega \sim J$ also the critical coupling g_c is comparable to J—a situation which matches the strong magnetoelastic coupling and the SP physics in CGO [19].

In order to quantify these results we obtain the magnitude of the Peierls dimerization order parameter δ from the static (lattice) structure factor at wave number $q = \pi$,

$$\delta^2 = \frac{g^2}{N^2} \sum_{i,j} \langle u_i u_j \rangle e^{i\pi(R_i - R_j)} , \quad (6)$$

where $u_i = b_i + b_i^+$. As in the ordinary Peierls phenomenon, a finite dimerization $\delta > 0$ necessarily leads to a gap Δ^{ST} in the magnetic excitation spectrum. For evaluating the relation between the dimerization and the resulting magnitude of the spin-triplet excitation gap, we keep the phonon frequency fixed, vary the coupling strength g, and calculate for each parameter set Δ^{ST} (see Fig. 5) and the dimerization δ from Eq. (6).

The results for the static (spin-only) and the dynamic spin-phonon model are compared in Fig. 5 for three different chain lengths. For vanishing lattice dimerization, i.e. in the absence of any spin-phonon coupling ($g = 0$), the results for the static and dynamic model naturally agree (note that for $\delta = 0$ there remains a spin excitation gap even for $N \to \infty$ due to the frustration driven singlet dimer ordering $D \neq 0$). The important message of Fig. 5 is that a substantial enhancement of the dimerization is needed to achieve a given triplet excitation gap, if the dynamic phonons have frequencies comparable to J. This partially resolves the quantitative problem encountered within the alternating and frustrated Heisenberg spin-chain model (1), because fixing parameters J and α, by fitting the high temperature susceptibility, and δ, by matching Δ^{ST} to the INS data in CGO, the dimerization parameter δ is underestimated by roughly a factor of 5

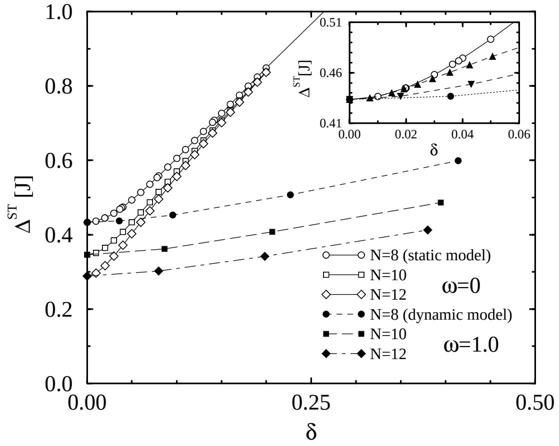

FIG. 5. Triplet excitation gap Δ^{ST} vs dimerization δ for the static spin-only ($\omega = 0; \diamond, \square, \circ$) and the dynamic spin-phonon model (solid symbols) with phonon frequency $\omega = 1$ for different chain lengths at $\alpha = 0.36$. The inset shows the results for the dynamic 8-site model [filled symbols: $\omega = 0.1$ (0.3) triangles up (down); $\omega = 1.0, (\bullet)$] in comparison to the static case ($\circ$).

[33]. From the uniaxial pressure derivatives of the exchange coupling J [10] and the structural distortion in the dimerized phase [7], it is possible to show that the dimerization of J is in fact significantly stronger than $\delta = 1.4\%$. The result of a straightforward data analysis leads to an estimate $\delta \approx 4\% - 5\%$ [19]. The inset in Fig. 5 shows the evolution of the Δ^{ST} vs δ results with increasing phonon frequency ω at a fixed chain length. With decreasing ω the data smoothly merge with the result for the static spin-only model.

In conclusion, we have numerically analyzed the Peierls dimerized ground state and the spin–triplet excitations in a Heisenberg chain model with dynamic spin-phonon coupling. The magnetic excitations inherently include a local lattice distortion requiring a multiphonon mode treatment of the lattice degrees of freedom. A spin-phonon coupling-induced flattening of the triplet dispersion is avoided for a strong spin-phonon coupling in the nonadiabatic regime. The nonadiabatic phonon dynamics strongly renormalizes the magnetic excitation spectrum and the dimerization dependence of the triplet excitation gap. These features are in accordance with experimental data on CGO, suggesting the necessity for a nonadiabatic spin-phonon approach to the SP physics in this material.

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