Mean-field theory of the spin-Peierls state under magnetic field: Application to $CuGeO_3$

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A mean-field theory of the spin-Peierls ordered state in a magnetic field is proposed for the two-dimensional Heisenberg model coupled to phonons. We show that fermionic excitations dominate the thermodynamics of this kind of system leading to a robust spin-Peierls order parameter or energy gap over a wide range of magnetic field in the low-temperature limit. This picture is shown to be consistent with recent observations made in the $CuGeO_3$ material.

The recent discovery of a spin-Peierls (SP) transition in the inorganic compound $CuGeO_3$ prompts renewed interest for this kind of structural instability.[1,2] Evidence for such a nonmagnetic transition has been exemplified in several ways. The lattice distortion has been well established by x-ray and elastic neutron experiments.[3–5] The magnetic susceptibility decreases exponentially in the ordered state showing a gap in the spin excitations.[1,6] This is also confirmed by heat-capacity measurements which present a thermally activated component below the SP critical temperature.[7] An essential ingredient which enters in the theoretical description of thermodynamic properties of the SP ordered state is the spectrum of elementary excitations. Recent acoustic experiments[8] performed under magnetic field revealed that despite the expected reduction of the SP transition temperature under the application of a uniform magnetic field, the lattice distortion and in turn the gap remain unaffected by the field in the low-temperature domain of the ordered state. This rigidity of the SP order parameter was found to persist up to a field of 13 T or so. It clearly indicates that at variance with EPR and neutron-scattering experiments[6,9] the full triplet splitting does not show up for thermodynamic properties. This salient feature, though implicit in previous one-dimensional calculations[10,11] proved to be a natural consequence of Fermi statistics for elementary excitations of the spin-Peierls state. From the Bethe ansatz solution of the Heisenberg model, fermionic excitations are well known to already characterize the properties of the undistorted antiferromagnetic spin chain. This is also depicted by the Jordan-Wigner (JW) fermion representation of spins which tells us that a band picture of excitations in terms of particles and holes excited across a gap prevails in the one-dimensional dimerized case.[10] In this work, we present a mean-field theory of the spin-Peierls ordered state in two dimensions which establishes the fermionic nature of spin excitations in the thermodyanmic properties of $CuGeO_3$. The temperature profile of the energy gap as well as its field dependence are given and compared to experiments. Finally, the zero-temperature energy gap is calculated as a function of the dimerization by varying the spin-phonon coupling constant.

We start the analysis with the two-dimensional (2D) Heisenberg model

$$H=J\sum_{i,j}\mathbf{S}_{2i,j}\cdot\mathbf{S}_{2i+1,j}+J'\sum_{i,j}\mathbf{S}_{2i+1,j}\cdot\mathbf{S}_{2i+2,j}$$

$$+J_\perp\sum_{i,j}\mathbf{S}_{i,j}\cdot\mathbf{S}_{i,j+1}+\frac{1}{2}\frac{NK}{\gamma^2}\delta^2, \tag{1}$$

where $J^{(\prime)}=J_0(1\pm\delta)$ are the intrachain antiferromagnetic exchange couplings modulated by the lattice displacement $u=\delta/\gamma$ with γ being a constant. $J_\perp$ is the interchain antiferromagnetic coupling and K is the elastic constant for the lattice displacement which is taken in the static adiabatic limit.[14] The spin part of the Hamiltonian can be transformed by means of the generalized Jordan-Wigner (JW) transformation[15]

$$S^-_{i,j}=c_{i,j}e^{i\pi(\Sigma_{\ell=0}^{i-1}\Sigma_{f=0}^{\infty}n_{\ell,f}+\Sigma_{f=0}^{j-1}n_{i,f})}, \tag{2}$$

$$S^z_{i,j}=c^\dagger_{i,j}c_{i,j}-\tfrac{1}{2},$$

where $n_{i,j}=c^\dagger_{i,j}c_{i,j}$. Making use of the bipartite character of the lattice, the Hamiltonian can be written in the form

$$H=\sum_{i,j}\left\{\frac{J}{2}c^{A\dagger}_{2i,j}c^{B}_{2i+1,j}e^{i\Phi}+\frac{J'}{2}c^{B\dagger}_{2i+1,j}c^{A}_{2i+2,j}e^{i\Phi'}\right\}+\sum_{i,j}J_\perp\{c^{A\dagger}_{i,j}c^{B}_{i,j+1}+c^{B\dagger}_{i,j}c^{A}_{i,j+1}\}+\sum_{i,j}Jc^{A\dagger}_{2i,j}c^{A}_{2i,j}c^{B\dagger}_{2i+1,j}c^{B}_{2i+1,j}$$

$$+\sum_{i,j}J'c^{B\dagger}_{2i+1,j}c^{B}_{2i+1,j}c^{A\dagger}_{2i+2,j}c^{A}_{2i+2,j}+\sum_{i,j,n=\pm1}J_\perp c^{A\dagger}_{i,j}c^{A}_{i,j}c^{B\dagger}_{i,j+n}c^{B}_{i,j+n}+\frac{1}{2}\frac{NK}{\gamma^2}\delta^2 \tag{3}$$

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where A and B label the two sublattices and the phases Φ and Φ' of the XY part are chosen so that the flux per plaquette is π.[16] For the spin-Peierls problem at hand, the four fermion operator terms are decoupled in a Hartree-Fock approximation by introducing an alternating bond order parameter $Q=\langle c_{2i,j}c^{\dagger}_{2i+1,j}\rangle$ and $Q'=\langle c_{2i+1,j}c^{\dagger}_{2i+2,j}\rangle$ in the longitudinal direction, and a uniform one, $P=\langle c_{i,2j}c^{\dagger}_{i,2j+1}\rangle$ for the transverse direction. The choice of an alternated longitudinal order parameter is motivated by the alternation of the exchange interaction J and J'. Following the example of the XY part, the phases of the order parameters Q, Q', and P are fixed to π and 0 on adjacent longitudinal bonds whereas in the perpendicular direction the bonds are phaseless. In Fourier space the mean-field Hamiltonian becomes

$$H=\frac{1}{2}\sum_{\mathbf{k}}\{e(\mathbf{k})c^{A\dagger}_{\mathbf{k}}c^{B}_{\mathbf{k}}+e^{*}(\mathbf{k})c^{B\dagger}_{\mathbf{k}}c^{A}_{\mathbf{k}}\}+\frac{1}{2}\frac{NK}{\gamma^2}\delta^2+J_{\perp}N|P|^2 + JN|Q^2|/2+J'N|Q'|^2/2, \tag{4}$$

where $e(\mathbf{k})=J_1e^{ik_x}-J_2e^{-ik_x}+2J_{\perp 1}\cos k_y$ with $J_1=J(1+2|Q|)$, $J_2=J'(1+2|Q'|)$, and $J_{\perp 1}=J_{\perp}(1+2|P|)$. The Hamiltonian (4) is diagonalized using the following canonical transformation:

$$c^{A}_{\mathbf{k}}=u_kf_{\mathbf{k}}+v_kd_{\mathbf{k}},\qquad c^{B}_{\mathbf{k}}=v^{*}_kf_{\mathbf{k}}-u^{*}_kd_{\mathbf{k}}, \tag{5}$$

where $u_k=v_k=e^{i\alpha_k/2}/\sqrt{2}$. α_k is given by

$$\tan\alpha_k=\frac{(J_1+J_2)\sin k_x}{(J_1-J_2)\cos k_x+2J_{\perp 1}\cos k_y}.$$

The Hamiltonian then becomes

$$H=\sum_{\mathbf{k}}[E_{-}(\mathbf{k})d^{\dagger}_{\mathbf{k}}d_{\mathbf{k}}+E_{+}(\mathbf{k})f^{\dagger}_{\mathbf{k}}f_{\mathbf{k}}]+NK\delta^2/2\gamma^2+J_{\perp}N|P^2| + JN|Q|^2/2+J'N|Q'|^2/2, \tag{6}$$

N being the number of sites. As for the dispersion relation, it takes the form

$$E_{\pm}(\mathbf{k})=\pm\tfrac{1}{2}|e(\mathbf{k})|, \tag{7}$$

where $(\pm)$ refers to upper and lower band.

The equilibrium values of the order parameters are obtained from the minimization of the free energy per site

$$F=-\frac{1}{2\beta}\int\frac{d^2k}{(2\pi)^2}\sum_{p=\pm}\ln[n(E_p(\mathbf{k}))]+\frac{J|Q|^2}{2}+\frac{J'|Q'|^2}{2} + J_{\perp}|P|^2+\frac{J_0\delta^2}{2\lambda} \tag{8}$$

with respect to both spin and lattice order parameters and where $n(x)=(1+e^{\beta x})^{-1}$ is the Fermi distribution factor. This leads to a set of coupled mean-field equations which can be solved numerically.

The ground-state wave function corresponds to the case where the lower band is filled:

$$|\Phi_{\mathrm{GS}}\rangle=\prod_{\mathbf{k}}d^{\dagger}_{\mathbf{k}}|0\rangle. \tag{9}$$

It is formed by the pairs of fermions $(c^{A\dagger}_{\mathbf{k}},c^{B\dagger}_{\mathbf{k}})$ with the weights v_k and $-u^{*}_k$, respectively, which correspond from (2) to pairs of spins denoted $(\uparrow,\downarrow)_{\mathbf{k}}$ in reciprocal space. The ground state is a singlet since $\langle\Phi_{\mathrm{GS}}|S^z|\Phi_{\mathrm{GS}}\rangle=\langle\Phi_{\mathrm{GS}}|(\mathbf{S}_{\mathrm{tot}})^2|\Phi_{\mathrm{GS}}\rangle=0$, while excited states with a wave vector $\mathbf{k}'$, relevant to magnetic susceptibility, specific heat, etc., consist in creating *particle-hole* excitations, namely

$$|\Phi_{\mathrm{EX}}\rangle=f^{\dagger}_{\mathbf{k}'}d_{\mathbf{k}'}|\Phi_{\mathrm{GS}}\rangle=\prod_{\mathbf{k}}f^{\dagger}_{\mathbf{k}'}d_{\mathbf{k}'}d^{\dagger}_{\mathbf{k}}|0\rangle. \tag{10}$$

In terms of original spins, the particle and the hole, albeit delocalized as band excitations, will correspond to a kink in the spin configuration. Since $S^z=\pm 1$ for the particle and the hole, such excitations refer to the $S^z=0$ component of the $S=1$ triplet state. Generally speaking, this is consistent with the fact that the SP order parameter has only one component. It is worthwhile to note here that allowing for lattice fluctuations beyond mean field, namely statistical variation of δ with wave vectors different than $q=\pi$, the kink is present in both spin and lattice configurations. The dispersion relation for each member of the particle-hole pair is given by

$$\tfrac{1}{2}\langle\Phi_{\mathrm{EX}}|H|\Phi_{\mathrm{EX}}\rangle-\tfrac{1}{2}\langle\Phi_{\mathrm{GS}}|H|\Phi_{\mathrm{GS}}\rangle=E_{+}(\mathbf{k})=-E_{-}(\mathbf{k})$$

and corresponds to an energy gap

$$E_g=\tfrac{1}{2}|J_1-J_2| \tag{11}$$

at $\mathbf{k}_0=(0,\pi/2)$.

The temperature profiles for the gap $[E_g(T)]$ and the lattice distortion $[\delta(T)]$ are given in Fig. 1. Both quantities show the characteristic mean-field behavior in $(T_{\mathrm{SP}}-T)^{1/2}$ near T_{SP}. By way of an application to real material, the use of the estimated values[3,7] $J_0\approx 117$ K $\approx 14J_{\perp}$ for the longitudinal and transverse exchanges interactions in $CuGeO_3$ allows to adjust the spin-phonon coupling constant $\lambda=J_0\gamma^2/K\approx 0.069$ in order to get the experimental value $T_{\mathrm{SP}}\approx 0.124J_0\approx 14.5$ K. With such parameters, one gets $E_g\approx 27$ K for the zero-temperature gap which is close to observation. It corresponds to the ratio $E_g(0)/T_{\mathrm{SP}}\simeq 1.86$ showing a slight deviation from the BCS value.

The effect of a uniform magnetic field h is of interest here. Indeed, h will couple to both particles and holes through the Zeeman term $H_h=-g\mu_B\Sigma_iS^z_ih$ which becomes $-g\mu_Bh\Sigma_{\mathbf{k}}(d^{\dagger}_{\mathbf{k}}d_{\mathbf{k}}+f^{\dagger}_{\mathbf{k}}f_{\mathbf{k}})$ in the JW representation. This simply adds to H in (6) as a chemical potential. The mean-field solution for finite h leads as expected to a reduction of T_{SP}.[10,12] At very low temperature, the gap and in turn the lattice distortion order paramater are found to be *field-independent*. As shown in Fig. 1, this result is consistent with recent acoustic data for $\delta(T,h)$ in $CuGeO_3$,[8] confirming the band or fermionic nature of excitations. Physically, the number of thermally excited particle-hole pairs decreases exponentially as the temperature is lowered leading to a vanishingly small effect of h on each member of the pairs. The energy of the ordered phase and the order parameter are thus unaffected by the field as $T\to 0$. The rigidity of $E_g(0)$ with respect to h, depicted in Fig. 1, will then lead to a ratio

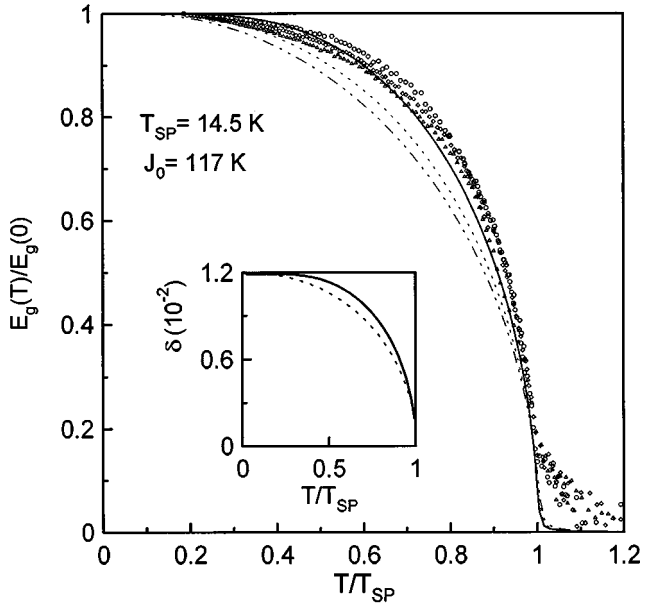

FIG. 1. The temperature profile for the gap is drawn for several values of the magnetic field h: $h=0$, 8, and 10 T corresponding to the full, dotted, and dashed-dotted lines, respectively. The experimental data of Ref. 8 are reported for comparison for $h=0$ (circles), 8 (squares), and 10 T (triangles). In the inset, the dimerization parameter δ as a function of T for $h=0$ (full line) and $h=10$ T (dashed line).

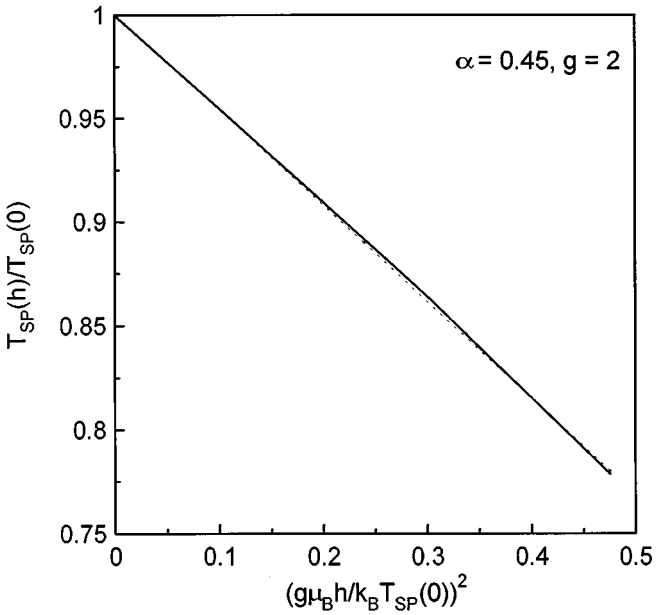

FIG. 2. The spin-Peierls critical temperature is displayed as a function of the square of the magnetic field using the parameters $T_{SP}(h=0)=14.5$ K and $J=117$ K for $CuGeO_3$. The dotted line is a fit using Eq. (12) with the value $\alpha\simeq 0.45$.

$E_g(0)/T_{SP}(h)$ that grows away from the BCS value. It is worthwhile to note that similar effects have been recently observed for the Peierls state under field, that is a system for which a band picture of electronic excitations is well known to prevail.[13] The situation is clearly different near T_{SP} where the number of thermally excited particles and holes is much larger yielding to a sizable effect of h on the energy and in turn on T_{SP}. In low field, the latter is found to follow the usual quadratic decrease with h (Refs. 10 and 12) as shown in Fig. 2:

$$T_{SP}(h)\approx T_{SP}(0)[1-\alpha(g\mu_B h/k_B T_{SP}(0))^2]. \qquad (12)$$

Using the above set of parameters, we find $\alpha\simeq 0.45$ ($g\approx 2$) which is compatible with the experimental estimation.[17]

As for a thermodynamic quantity like the longitudinal magnetic susceptibility $\chi(T,h)=1/2g\mu_B(d\langle N\rangle/dh)_h$, its evaluation is actually equivalent to the one of compressibility of JW fermions which becomes

$$\chi(T,h)=-\frac{1}{4}g^2\mu_B^2\sum_{\mathbf{k},p=\pm}\frac{\partial n[E_p(\mathbf{k})-g\mu_B h]}{\partial E_p(\mathbf{k})}$$

$$\sim\frac{1}{2}g^2\mu_B^2\mathscr{D}(E_g)\beta e^{-\beta E_g}\quad(\beta E_g\gg 1) \qquad (13)$$

at low temperature. Here $\mathscr{D}(E_g)$ is the density of states at the energy gap. Therefore the lowest energy gap to be observed in experiments (e.g., in $CuGeO_3$) like magnetic susceptibility[1] of the condensed SP state is characterized by the above particle-hole character. A similar field-independent thermal activation will be found for the hole and particle contributions to specific heat, in contrast with the analysis of the data under field made in Ref. 7.

The low-temperature energy gap profile at higher magnetic field is also of interest here. As reported in Fig. 3, the $T\to 0$ gap is essentially field independent up to $h_c\approx 13$ T where a rapid drop is found. This critical field signals an instability of the mean-field solution with a gap that goes down to zero.[11] Actually h_c proves to be close to the experimental value of 13 T found in Ref. 8 and at which a sharp drop of the gap amplitude is observed. The result for a lower temperature $T=0.35$ K (curve 3) shows a sharp drop only around $h_c=14$ T whereas the gap remains unchanged below

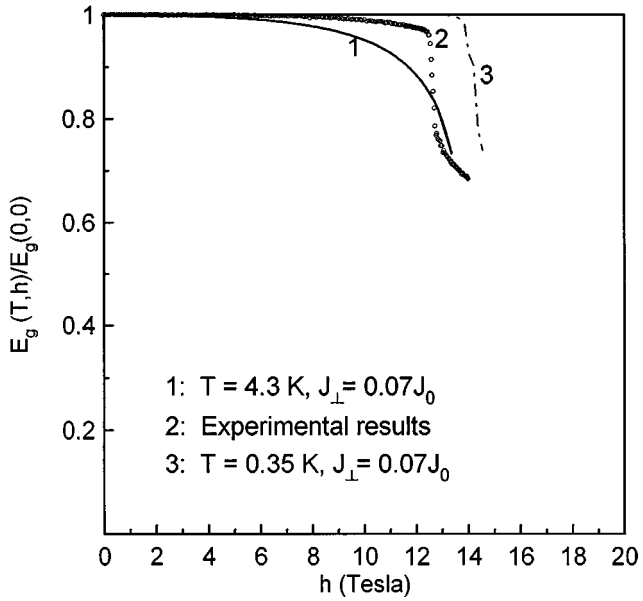

FIG. 3. The energy gap is plotted as a function of the magnetic field. Curves 1 and 2 correspond to the present 2D calculations and experimental data of Ref. 8 for $T=4.3$ K, respectively. Curve 3 is the mean-field prediction for a lower-temperature $T=0.35$ K.

14 T. The instability of the mean-field solution at large field indicates that the modulation wave vector is no longer pinned at the commensurate value (π,π) and must be adjusted to an incommensurate value in order to compensate the effect of the Zeeman energy.

The last point we would like to address concerns the dependence of the energy gap on the amplitude of the dimerization parameter δ. At finite $J_\perp$, it is of the form

$$E_g(\delta)=E_0+c(2\delta/(1+\delta))^\nu \quad (J_\perp \ll J_0, \delta>0). \quad (14)$$

The present two-dimensional bond mean-field theory thus gives a finite value E_0 of the gap as $\delta\rightarrow 0^+$. A similar discontinuity for the gap at $\delta=0$ has been found recently using a bond mean-field theory in one dimension.[18] Using the above set of parameters relevant to $CuGeO_3$, namely $J_\perp=0.07$, one gets, for example, $E_0\simeq 0.18, c\simeq 0.83$, and the exponent $\nu\simeq 0.68$. As for the influence of the transverse exchange in the present SP theory, antiparallel spin alignment promoted by $J_\perp$ tends to reduce the amplitude of the SP gap, albeit keeping the value of the exponent ν essentially unchanged. Incidentally, the value of ν obtained here is close to other mean-field results.[19] As for the critical temperature T_{SP}, it is found to vary linearly with the spin-phonon coupling constant λ in the weak-coupling domain. If $J_\perp$ becomes sufficiently large, however $(J_\perp > J_{\perp c}\approx 0.13 J_0)$, the frustration is strong enough to necessitate a finite spin-phonon coupling constant λ_c for the stabilization of a SP ordered state.

In summary, we have proposed a bond mean-field theory of the two-dimensional Heisenberg model for the description of the ordered SP state in a magnetic field. We have shown that the apparent rigidity for the zero-temperature gap of $CuGeO_3$ over a wide range of magnetic field is a signature of particle-hole fermion statistics for the thermodynamic properties of this kind of system. Finally, transverse spin exchange is found to compete with the SP ordered state which can even be suppressed at sufficiently small exchange anisotropy.

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