Phase diagram of disordered spin-Peierls systems

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We study the competition between the spin-Peierls and the antiferromagnetic ordering in disordered quasi-one-dimensional spin systems. We obtain the temperature versus disorder-strength phase diagram, which qualitatively agrees with recent experiments on doped CuGeO$_3$. [S0163-1829(98)07737-6]

The discovery of the first inorganic spin-Peierls (SP) material CuGeO$_3$ opened the possibility to study the influence of doping on the SP transition.[1] The recently obtained phase diagram of doped CuGeO$_3$ has several surprising features.[2-5] It turns out that doping, while suppressing the SP state, at the same time induces long-range antiferromagnetic (AF) order, with the Néel temperature initially increasing with the doping concentration. Furthermore, a doping range is found where SP and AF order coexist.

At first glance, it seems very strange that disorder (doping) may lead to the enhancement of some order parameter (in this case the AF one). Also, the coexistence of the dimerized SP state, in which spins are bound into singlets, with a spontaneous sublattice magnetization that requires the presence of free spins, is rather puzzling. In this paper we address both these issues and obtain a phase diagram that is very similar to the experimental one. We also find a reentrance transition from the dimerized SP state back into the undimerized state with decreasing temperature.

Theoretically, the possibility of long-range magnetic order in doped SP systems was discussed in Refs. 7–9, where the lattice was treated classically and it was assumed that impurities "cut" the spin chains into finite segments. It was argued that the lattice relaxation in these segments results in the appearance of regions with a suppressed dimerization (close to impurities in the model of Ref. 7, or centered at kinks in the lattice dimerization in Refs. 8,9). The AF correlations that develop in these regions may, in principle, stabilize an inhomogeneous state in which the SP and AF orders coexist. The enhancement of the magnetic susceptibility by disorder-induced kinks was also discussed in Ref. 10. Although these considerations provide a qualitative understanding of the magnetic ordering in doped SP materials, the description of the thermodynamics of the mixed SP+AF state within the same approach is complicated and so far has not been given.

In this paper we consider a model that allows for a detailed study of the competition between the SP and AF phases in the presence of disorder. Instead of considering disorder that randomly cuts chains into finite segments, we assume that doping results in small fluctuations of the spin-exchange constants on many bonds. Furthermore, we treat the lattice and the interchain spin exchange in the "chain mean field" approximation.[11,12] Then, the effective single-chain Hamiltonian reads

$$H_s = \sum_n \left[J_{n,n+1}\mathbf{S}_n \cdot \mathbf{S}_{n+1} - h(-)^n S_n^z + \frac{h^2}{2zJ_\perp} + \frac{(J_0\delta)^2}{2K\alpha_s^2} \right],$$
(1)

where the exchange constants have the form

$$J_{n,n+1} = J_0[1 + (-)^n\delta] + \tilde{J}_{n,n+1}.$$
(2)

Here, δ is the average value of the alternating part of $J_{n,n+1}$ and $\tilde{J}_{n,n+1}$ is the random contribution due to doping. The antiferromagnetic order parameter h in Eq. (1) is the amplitude of the alternating magnetic field created by z neighboring chains and $J_\perp$ is the exchange constant for nearest spins from neighboring chains. The last term in Eq. (1) is the lattice energy, K is the spring constant, and α_s is the spin-lattice coupling. The minimization of the chain free energy with respect to δ and h gives the self-consistency equations for these two order parameters.

We use the procedure developed in Ref. 13: by means of the Jordan-Wigner transformation the spin Hamiltonian Eq. (1) is mapped on a Hamiltonian of spinless fermions and the interaction between the fermions is treated in the Hartree-Fock approximation. The values for the energy, specific heat, and magnetic susceptibility of an AF spin-$\frac{1}{2}$ chain obtained by this simple method are rather close to exact results.[13] Furthermore, this method is known to provide a good semi-quantitative description of a wide range of phenomena related to the SP transition.[14] Finally, although the Hartree-Fock approximation does not maintain the rotational invariance of the spin-exchange interaction, it should also be well suited to describe disordered spin systems: the low-temperature response of disordered chains to uniform and alternating magnetic fields is universal, i.e., independent of the anisotropy of the spin exchange.[15-17]

In the weak-coupling and weak-disorder limit, i.e., for $\delta J_0, h, \tilde{J} \ll J_0$, we now introduce a continuum description of the chain (cf. Ref. 18). The Hamiltonian then becomes

$$H = \int dx \left\{ \psi^\dagger(x) \left[\sigma_3 \frac{v_F}{i}\frac{d}{dx} + \sigma_1[\Delta + \eta(x)] + \sigma_2 h \right] \psi(x) + \frac{1}{2\pi v_F}\left(\frac{\Delta^2}{\lambda_\Delta} + \frac{h^2}{\lambda_h} \right) \right\},$$
(3)

where σ_i ($i=1,2,3$) are the Pauli matrices. The first term in the Hamiltonian H describes the free motion of the fermions with the Fermi velocity $v_F = paJ_0$, where a denotes the lattice constant in the chain direction and p is a renormalization factor that for $T \ll J_0$ equals $1 + 2/\pi$.[13] The second and the third terms describe the backward scattering caused by the

dimerization $\Delta = p\,\delta J_0$, the disorder, and the staggered magnetic field. The disorder $\eta(x)$ is related to the disorder in the spin-exchange constants by

$$\eta(2na) = \frac{p}{2}(\tilde{J}_{2n-1,2n} - \tilde{J}_{2n,2n+1}). \qquad (4)$$

We will assume white noise disorder with a correlator

$$\langle \eta(x)\eta(y) \rangle = A\,\delta(x-y), \qquad (5)$$

which corresponds to the statistical independence of the variations of the exchange couplings on different bonds in the discrete model Eq. (1). Finally, the constants $\lambda_\Delta = p\,\alpha_s^2/\pi K J_0$ and $\lambda_h = z J_\perp/\pi p J_0$ characterize the strength of, respectively, the spin-lattice and the interchain spin exchange interactions.

In the absence of a magnetic field ($h=0$), the disorder-averaged density of single-fermion states $\rho(\varepsilon)$ of the Hamiltonian Eq. (3) was found analytically in Ref. 19. The density $\rho(\varepsilon)$ is a symmetric function of the energy ε. Its form depends crucially on the parameter $g = A/(v_F\Delta)$. For $g<2$ the density of states has a pseudogap (a Peierls gap filled by disorder-induced states), while for $g>2$ (strong disorder) the pseudogap disappears and $\rho(\varepsilon)$ diverges at $\varepsilon=0$ [$\rho(\varepsilon) \propto |\varepsilon|^{2/g-1}$ at $|\varepsilon| \ll \Delta$].

A nonzero alternating magnetic field mixes the $h=0$ eigenstates with opposite energies and transforms the pair of eigenstates with energies $\pm\varepsilon$ into a pair of eigenstates with energies $\pm\sqrt{\varepsilon^2+h^2}$. Therefore, the disorder-averaged Ω potential ($\Omega_f = -T\langle \ln\Xi_f \rangle$, Ξ_f being the partition function of the grand-canonical ensemble of fermions with zero chemical potential) is given by

$$\Omega_f = -\frac{2}{\beta}\int_0^W d\varepsilon\,\rho(\varepsilon)\ln\left[2\cosh\left(\frac{\beta\sqrt{\varepsilon^2+h^2}}{2}\right)\right], \qquad (6)$$

where W is the energy cutoff. The two order parameters Δ and h satisfy the self-consistency equations

$$\Delta = -\pi v_F \lambda_\Delta \langle\langle \sigma_1 \rangle\rangle = -\pi v_F \lambda_\Delta \frac{\partial\Omega_f}{\partial\Delta}, \qquad (7)$$

$$h = -\pi v_F \lambda_h \langle\langle \sigma_2 \rangle\rangle = -\pi v_F \lambda_h \frac{\partial\Omega_f}{\partial h}, \qquad (8)$$

where $\langle\langle \cdots \rangle\rangle$ denotes the thermal and disorder average.

In the absence of disorder, Ω_f depends on Δ and h only through the combination $\sqrt{\Delta^2+h^2}$. As a result, the two self-consistency equations acquire the same (BCS) form; as, however, they have different coupling constants, they cannot be satisfied simultaneously, unless $\lambda_\Delta = \lambda_h$. Thus, in agreement with previous studies,[20] we find that in the absence of disorder the AF and SP phases cannot coexist and the phase with the larger coupling constant is realized. A competition between these two phases always exists in spin chain materials and some special conditions, such as a strong spin-phonon coupling[14] or a significant next-nearest-neighbor interaction,[21] are necessary for the SP state to win. This explains why the number of SP materials is small.

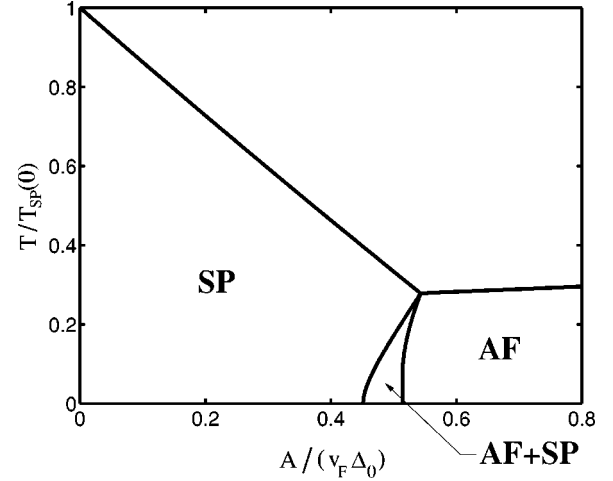Disorder in the spin-exchange constants suppresses the dimerized state by filling the SP gap with single-fermion

FIG. 1. The phase diagram of the disordered SP system described by Eqs. (3), (7), and (8) for $\lambda_\Delta > \lambda_h$. The dimensionless disorder strength $A/(v_F\Delta_0)$ is proportional to the concentration of dopands x (see discussion in the text). The temperature is measured in the units of the SP transition temperature at zero disorder.

states and thus reducing the energy gain due to dimerization. At the same time, these disorder-induced states enhance the antiferromagnetic susceptibility of the chains: The effect of an alternating magnetic field is strongest for the fermionic states with $|\varepsilon| \lesssim h$, as the occupied state with energy $-|\varepsilon|$ is pushed down to $-\sqrt{\varepsilon^2+h^2}$. The higher the density of states near $\varepsilon=0$, the more energy is gained when AF order appears. Within the mean field approximation, this enhancement of the chain magnetic susceptibility due to disorder results in an increase of the Néel temperature.

From the above we conclude that for $\lambda_h > \lambda_\Delta$ the SP state is less favorable than the AF state at all values of the disorder strength A. If, on the other hand, $\lambda_\Delta > \lambda_h$, a much richer phase diagram arises, as is observed in Fig. 1. This diagram was obtained by numerically solving Eqs. (7) and (8) for $\lambda_\Delta \approx 0.37$ and $\lambda_h \approx 0.25$, so that $T_N^0(0)/T_{SP}^0(0)=1/4$, where $T_{SP}^0(A)$ is the SP transition temperature at $h=0$ and $T_N^0(A)$ is the Néel temperature at $\Delta=0$.[22] Four phases appear: SP, AF, mixed SP+AF, and disordered, separated by second order transition lines. At low temperature and weak disorder the system is in the SP state. The SP temperature $T_{SP}(A)$ decreases almost linearly with the disorder strength. In particular, it can be shown that at small A

$$T_{SP}(A) = T_{SP}(0)\left(1 - C\frac{A}{v_F\Delta_0}\right), \quad C = \frac{\pi^2}{4\gamma} \approx 1.39, \quad (9)$$

where Δ_0 is the value of Δ for $T, A=0$, and $\gamma = 1.78\ldots$, is the exponential of Euler's constant.

Above some critical disorder strength A_N, the system undergoes at $T_N(A) < T_{SP}(A)$ a second (Néel) transition into the mixed state, in which the SP and AF orders coexist. This coexistence region becomes narrower when λ_h approaches λ_Δ. T_N rapidly increases with the disorder strength until at some $A = A_*$ it becomes equal to the SP transition temperature $T_{SP}(A_*) = T_N(A_*) = T_*$. Above A_* only AF long-range order exists and the Néel temperature continues to grow slowly with the disorder strength.
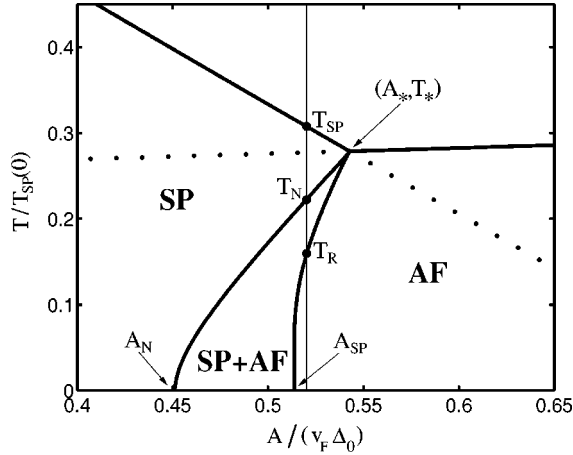
FIG. 2. Detail of the phase diagram Fig. 1. The vertical line $A/(v_F\Delta_0)=0.52$ passes through three phase-transition points: the SP transition temperature T_{SP}, the Néel temperature T_N, and the temperature of reentrance into the undimerized state T_R. Dotted lines show T_{SP}^0 for $A>A_*$ (the SP transition temperature calculated at $h=0$) and T_N^0 for $A<A_*$ (the Néel temperature calculated at $\Delta=0$).

The surprising feature of our phase diagram is the fact that the disorder strength A_{SP} at which the dimerization disappears at zero temperature, is smaller than A_*. This implies that for $A_{SP}<A<A_*$ the system experiences three consecutive transitions as the temperature goes down (see Fig. 2): first the SP transition, next the Néel transition, and then the ''anti-spin-Peierls'' transition, at which the SP order disappears. The reentrance into the undimerized state occurs because the rapid growth of the AF order parameter below the Néel temperature suppresses the SP state.

The reentrance transition can be discussed quite generally (without reference to a particular model) using the Landau expansion of $\Omega=\Omega_f+(1/\pi v_F)(\Delta^2/2\lambda_\Delta+h^2/2\lambda_h)$ near the multicritical point (T_*,A_*):

$$\Omega=\alpha_\Delta[T-T_{SP}^0(A)]\Delta^2+\frac{b_\Delta}{2}\Delta^4$$

$$+\alpha_h[T-T_N^0(A)]h^2+\frac{b_h}{2}h^4+c\Delta^2h^2. \quad (10)$$

In Eq. (10) the coefficients $\alpha_\Delta,\alpha_h>0$. Furthermore, the stability of the system described by Eq. (10), requires b_Δ, b_h, and $D\equiv b_\Delta b_h-c^2$ to be positive.

In the presence of a dimerization (at $A<A_*$) the Néel temperature becomes

$$T_N(A)=T_N^0(A)-\frac{c}{\alpha_h}\Delta^2. \quad (11)$$

As the dimerization suppresses the AF state, $c>0$. Similarly, one can find a temperature $T_R(A)$, at which Δ becomes zero at nonzero h:

$$T_R(A)=T_{SP}^0(A)-\frac{c}{\alpha_\Delta}h^2, \quad (12)$$

which is the temperature of the reentrance into the undimerized state.

To obtain the dependence of $T_N(A)$ and $T_R(A)$ on the disorder strength, we find Δ and h that minimize Ω and substitute them into Eqs. (11) and (12). The result is

$$T_N(A)\approx T_*+(A-A_*)$$

$$\times\left[\frac{c\alpha_\Delta(dT_{SP}^0/dA)-b_\Delta\alpha_h(dT_N^0/dA)}{c\alpha_\Delta-b_\Delta\alpha_h}\right]_{A=A_*},$$

$$(13)$$

$$T_R(A)\approx T_*+(A-A_*)$$

$$\times\left[\frac{c\alpha_h(dT_N^0/dA)-b_h\alpha_\Delta(dT_{SP}^0/dA)}{c\alpha_h-b_h\alpha_\Delta}\right]_{A=A_*}.$$

From Eq. (13) and the fact that $T_N^0(A)$ increases with A, while $T_{SP}^0(A)$ decreases, it is easy to find that for

$$c>b_h\frac{\alpha_\Delta}{\alpha_h} \quad (14)$$

both $T_N(A)$ and $T_R(A)$ increase linearly with disorder at $A<A_*$ and $T_R(A)<T_N(A)$. Therefore, inequality (14) is the condition for the existence of the reentrance transition. In our model, its validity can be checked analytically for $\lambda_h\to\lambda_\Delta$, in which case $A_*\to0$, $\alpha_h\to\alpha_\Delta$, and $c\to2b_h$. Our numerical calculations suggest that condition (14) is satisfied for all $\lambda_h<\lambda_\Delta$.

Next we compare our phase diagram to experimental data. At small dopand concentrations x, the observed SP transition temperature in $Cu_{1-x}Zn_xGeO_3$ is described by

$$T_{SP}(x)=T_{SP}(0)(1-\alpha x), \quad (15)$$

where $\alpha\sim14$.[2] To compare this to our result Eq. (9), we have to relate the disorder strength A to the dopand concentration x. This can be done by assuming that the substitution of Cu by Zn changes the spin exchange constant by an amount $\sim J_0$. From Eqs. (4) and (5) we then obtain $A\sim a(pJ_0)^2x$. Equation (9) then reduces to Eq. (15) with $\alpha\sim C(pJ_0/\Delta_0)\sim15$ in good agreement with experiment (we use $J_0=150$ K and $\Delta_0=2.1$ meV). Also the even stronger suppression ($\alpha\sim50$) of the SP phase in Si doped $CuGeO_3$ (Refs. 3–6) may be understood: Si, substituting Ge, is located between two CuO_2 chains and thus influences two chains simultaneously.[8]

While the suppression of the SP transition temperature by doping is nicely described by our theory, the critical doping concentration x_c at which AF order appears in our model, is too large as compared with experiment.[6] The large value of x_c is an artifact of our continuum treatment of disorder and may be understood from the following considerations: Disorder enhances the AF susceptibility of spin chains by filling the SP gap with low-energy spin excitations. As was shown in Ref. 23, with highest probability the excited states with energy $\varepsilon\leqslant\Delta$ occur for disorder fluctuations $\eta(x)$ that have the form of a kink-antikink pair. For such a fluctuation, the order parameter $\Delta(x)=\Delta+\eta(x)$ has reversed sign in a domain of length $R=(v_F/\Delta)\ln(2\Delta/\varepsilon)$ between the kink and the antikink. The kink and antikink, being fractionally charged objects,[24] each carry spin $\frac{1}{2}$, which together form a weakly bound singlet. A low-energy excited state is then obtained by

exciting this singlet into a triplet. These weakly bound spins do not contribute to the dimerization, but they can give rise to AF ordering. However, for weak disorder (small x), the density of kink-antikink fluctuations is exponentially small in our model, implying that a critical dopand concentration x_c is necessary for AF order to appear. If one assumes that doping, instead of resulting in small disorder in all spin-exchange constants, strongly decreases the exchange on some randomly chosen bonds, the kink density is proportional to x at small doping, which then implies $T_N \propto x$.[8,9]

To summarize, we obtained the phase diagram of a disordered SP system, described by a mean-field model. We showed that disorder results in a strong suppression of the SP state and gives rise to AF long-range order, which in a certain range of the disorder strength coexists with the dimerization. These results are in agreement with the experimental data on doped $CuGeO_3$. Finally, our results suggest the possibility of a reentrance transition from the dimerized SP state back into the undimerized state.

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