Dilution-Induced Order in Quasi-One-Dimensional Quantum Antiferromagnets

Eugene F. Shender[a] and Steven A. Kivelson

Department of Physics, University of California at Los Angeles, Los Angeles, California 90024

(Received 9 July 1990)

We consider a quasi-one-dimensional spin S quantum antiferromagnet as a function of dilution x. We show that in some regimes, dilution suppresses quantum fluctuations. For small enough interchain coupling and integer S, the ground state is disordered for $x=0$, but antiferromagnetically ordered for $x>x_c$. We estimate that for large S, x_c is exponentially small. This is a novel dilution-induced ordering transition.

PACS numbers: 75.10.Jm

In a one-dimensional antiferromagnet, the quantum fluctuations are so strong that even at zero temperature there is no long-range antiferromagnetic order; for integer spin (S) chains the ground state has exponentially falling spin-spin correlation functions reflecting the existence of the Haldane gap Δ_H, while for half-integer S there is quasi-long-range order.[1,2] In the presence of weak interchain coupling, the quantum fluctuations are somewhat reduced: For the case of half-integer spin, in the presence of arbitrarily weak interchain coupling, there is a low-temperature phase with long-range antiferromagnetic order and a finite Néel temperature T_N. For integer spin, long-range order occurs only for interchain coupling strength greater than the Haldane gap. In this paper, we discuss the phase diagram and the nature of the order in a quasi-one-dimensional quantum antiferromagnet as a function of dilution x, where x is the fraction of spins that are removed randomly from the system. We show that for weak enough interchain coupling, dilution suppresses quantum fluctuations, as was originally suggested in Ref. 3. In particular, we show the following: (1) For integer S and small enough interchain coupling so that the ground state is disordered for $x=0$, for $x>x_c$ the system has an ordered ground state and a finite T_N. (x_c is exponentially small for large S.) It seems to us that this result is rather striking in that it implies that quenched disorder, in the form of dilution, can induce ordering, in the form of a broken symmetry phase. (2) For the case in which the interchain coupling is strong enough that the system has an ordered ground state with zero-temperature sublattice magnetization not too small compared to its classical value, the sublattice magnetization is a decreasing function of x for small x. (3) We make estimates of the magnitudes of the effects (1) and (2) as a function of the experimentally accessible parameters: the exchange coupling in the chain (J_0), the interchain exchange coupling (J_3), the dilution x, and S. Our results are summarized in the qualitative phase diagram shown in Fig. 1. (4) As a by-product, we obtain some new results for the system in the absence of dilution.

The model we consider is the anisotropic Heisenberg model:

$$H=\sum_{n,j} J_0\mathbf{S}_{n,j}\cdot\mathbf{S}_{n,j+1}+\sum_{|n,m|,j} J_3\mathbf{S}_{n,j}\cdot\mathbf{S}_{m,j}\,, \tag{1}$$

where $|n,m|$ runs over pairs of nearest-neighbor chains, j labels the atomic site along a chain, and $\mathbf{S}_{n,j}$ are spin S operators. Upon dilution, spins are removed from the system at random locations. We assume that the arrangement of chains is such that for $x=0$, the Néel state is unfrustrated; i.e., the system lives on a bipartite lattice. We will always assume that $J_3 \ll J_0$. It is useful to define the dimensionless parameter

$$y=(1/\pi S)\ln(J_0/J_3)\,. \tag{2}$$

Note that for large S it is possible to consider $y\sim 1$, even if $J_3 \ll J_0$.

A. Properties of the pure system, $x=0$.—For $x=0$,

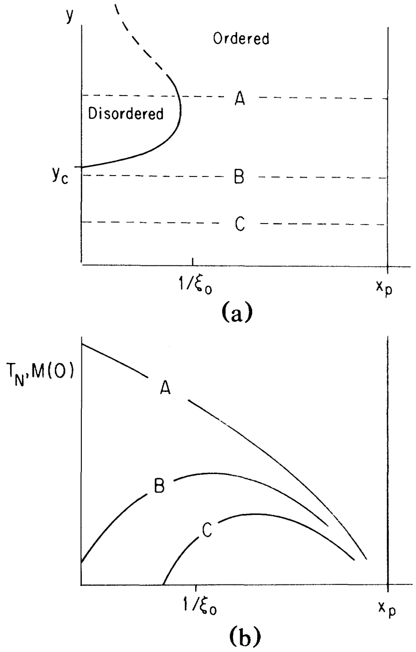

FIG. 1. (a) Schematic drawing of the zero-temperature phase diagram for integer S. The dashed portion of the phase boundary is drawn according to Eq. (9). (b) Schematic view of the phase diagram for fixed values of y [corresponding to the dotted lines in (a)]. The curves follow grossly from continuity and from the facts that T_N must be a strictly increasing function of J_3 for fixed x and must vanish at a critical concentration $x_c' \leq x_p$.

zero interchain coupling, and integer S, the ground state is disordered and unique and there is a gap Δ_H in the spectrum. As discussed in Ref. 4, this gap is related to the correlation length in an anisotropic two-dimensional classical Heisenberg model[5] with lattice constant a in the "space direction" and a/c_0 in the imaginary-time direction, where we identify J_0/kT in the classical model with $S/2$ in the quantum model, so

$$\Delta_H/J_0 \approx 2\pi A_1 S^2 \exp(-\pi S), \tag{3}$$

and A_1 is dimensionless. (A_1 is nonuniversal. If time were truly discrete, then we could use the results for the classical lattice model,[5] $A_1 \approx 100 \pm 30$.) For small S, $\Delta_H \sim J_0$. (For[6] $S=1$, $\Delta_H \approx 0.4 J_0$.) So long as $S^2 J_3$ is small compared to Δ_H, the effects of interchain coupling are strictly perturbative and the ground state is disordered. On the other hand, for J_3 large enough, the system is three dimensional and thus has an antiferromagnetically ordered ground state and a finite Néel temperature. For integer S, the critical value of J_3 can be estimated[6] as the value at which perturbation theory breaks down, i.e., when $S^2 J_3 \sim \Delta_H$, or equivalently when $y = y_c \sim 1$. The ground state is disordered for $y > y_c$ and ordered for $y < y_c$. Since y depends logarithmically on J_3/J_0, and linearly on $1/S$, we expect to find $y > y_c$ only in systems with rather small spin, no matter how anisotropic. If the transition is continuous, T_N rises from zero as y is increased above y_c. We estimate $T_N(y)$ in the usual fashion[6,7] in which purely one-dimensional fluctuations are treated exactly and the interchain coupling is treated in the mean-field approximation. Thus, we consider the staggered magnetization $M(h,T)$ of a single chain as a function of the staggered field h due to the neighboring chains, $h = zJ_3 M(h,T)$, where z is the number of nearest-neighbor chains and T is the temperature. We then solve self-consistently for the staggered field. T_N is the highest temperature at which this self-consistency condition can be satisfied for nonzero M. In the vicinity of T_N, h is small so the self-consistency equation can be linearized. Thus, T_N is obtained as the solution to the equation

$$1 = zJ_3 \chi_0(T_N), \tag{4}$$

where χ_0 is the staggered susceptibility of the one-dimensional chain. As with Δ_H, for large S, $\chi_0(T)$ can also be computed from the corresponding results for the classical two-dimensional Heisenberg model in a strip of width given by the thermal wavelength $\lambda_T = hc_0/kT$: For $kT \ll \Delta_H$, and in units in which $g\mu_B = 1$,

$$\chi_0(T) \sim A_2(\xi_0/\Delta_H)\{1 - O(e^{-\Delta H/kT})\}, \tag{5}$$

where $\xi_0 = hc_0/\Delta H$ is the zero-temperature correlation length and $c_0 = 2SJ_0/h$ is the spin-wave velocity. (For the classical lattice model,[5] $A_2 \approx 20 \pm 10$.) For $SJ_0 \gg kT \gg \Delta_H$, the staggered susceptibility can be computed as if the system were at its quantum critical point ($\xi_0 = \infty$), so we can use results from conformal field theory[8] to deduce that (up to possible logarithmic corrections)

$$\chi_0(T) \sim S/kT. \tag{6}$$

Thus, for $(y_c - y)/y_c \sim 1$, $kT_N \sim zSJ_3$. For $kT \gg SJ_0$, the susceptibility takes on its classical value,[9] $\chi_0(T) \approx \frac{2}{3} a^{-1} S^2 J_0/(kT)^2$.

For half-integer S, the one-dimensional model is gapless, so we expect Eq. (6) to be applicable at all temperatures $kT \ll SJ_0$.

B. Dilution-induced ordering, $x_p \gg x > 0$ and $y > y_c$.—Consider the case of $y \gg 1$ and integer S, i.e., deep in the quantum disordered regime, and study the effect of finite dilution $x > 0$, but still $x \ll x_p \approx 0.7$, where x_p is the site percolation threshold. In zeroth order, then, the system consists of a collection of isolated chain segments, "molecules," of average length $1/x$. It is straightforward to show[10] that all even-length chains have a unique, $S=0$ ground state while all odd-membered chains have a spin S ground state which is therefore $(2S+1)$-fold degenerate. The zeroth-order ground state of the diluted antiferromagnet is therefore highly degenerate; this degeneracy is lifted by even the weakest of interchain couplings.

Consider first the case of moderate doping concentration in which the typical chain segments (molecules) are shorter than ξ_0. Each molecule has a gap [i.e., the energy difference between the ground state(s) and the lowest excited states] which is at least of order Δ_H. So long as $J_3 \ll$ (the gap), the effect of interchain coupling can be studied using degenerate perturbation theory. The result is a new, effective Heisenberg model

$$H^{\mathrm{mol}} = \sum_{a,b} K_{ab} \mathbf{T}_a \cdot \mathbf{T}_b \tag{7a}$$

for the molecular spins $\mathbf{T}_a$, which live on a random, three-dimensional network, with sites a labeling the positions of the odd-membered molecules.

We now compute H^{mol} by perturbation theory in J_3. In particular, we will see that since the original model in Eq. (1) is defined on a bipartite atomic lattice and is thus unfrustrated, it follows that H^{mol} is unfrustrated as well. First, consider the interaction between two odd-membered chain segments that lie next to each other, i.e., nearest-neighbor molecular "sites" a and b. To determine the sign of K_{ab}, it suffices to consider the Ising piece K^z_{ab} of the interchain interaction. (Since the model is spin rotationally invariant, the xy piece of the interaction must equal the Ising piece, $K^z_{ab} = K^{xy}_{ab} = K_{ab}$.) We thus need simply to compute the piece of the interaction energy which couples the z component of the spins on molecules a and b. Since T_a determines the only preferred direction in spin space, the ground-state expectation value of the z component of the atomic spin on each atomic site i of molecule a, $m_i(a)$, must be proportional to the z component of the molecular spin, $m^a_i(T^z_a) = a^a_i$

$\times T_a^z$. Thus,

$$K_{ab} = J_3 \sum_{i \in a \cap b} \alpha_i^a \alpha_i^b \,, \tag{7b}$$

where the sum runs over the nearest-neighbor atomic sites on the two molecules. We can compute the sign of this interaction from a rather general knowledge of the sign of m_i. We speculate that in the highest-weight ground state (i.e., $T^z = S$), $m_i > 0$ for i on the more numerous sublattice and $m_i < 0$ for i on the other sublattice; in other words, the ground-state magnetization of a small odd-membered chain is staggered. It follows that the interchain interactions between molecular spins favor perfect ferromagnetic or antiferromagnetic alignment of the molecular spins depending on whether both chain segments have an excess of atomic sites belonging to the same or opposite sublattice; the interchain coupling favors alignment of the *molecular* spins consistent with Néel ordering of the *atomic* spins. If an odd-membered chain segment is completely surrounded by even-membered chain segments, then to first order in J_3, its molecular spin remains uncoupled to the rest of the system. However, there is a second-order interaction between second-neighbor molecular spins mediated by the intermediate even-membered chain. Again, without loss of generality, we compute only the Ising piece of the interactions. The spin on site i of the even-membered molecule sees an external field of strength $h_i = J_3[m_i^a(T_a^z) + m_i^b(T_b^z)]$ due to the spins on the neighboring odd-membered molecules a and b. Because the even-membered chain has a unique, spin-zero ground state, there is no change in the energy of the even-membered chain segment to first order in h. However, the energy is lowered to second order in h, since second-order perturbation theory always decreases the ground-state energy. Thus, to second order, the interaction energy between the molecular spins is optimal when $m_i^a(T_a^z)$ and $m_i^b(T_b^z)$ have the same sign; the effective coupling K_{ab} between second-neighbor molecular sites a and b is also compatible with perfect Néel order of the atomic spins. Of course, there is some probability that there will exist odd-membered molecules that have no first- or second-neighbor odd-membered molecules. The spin associated with such a molecule interacts only in higher order in J_3. They are, however, sufficiently rare that they can have no effect on the final order and we have not analyzed the nature of their interactions with the rest of the spins. The conclusion is that the interactions K_{ab} between molecular spins are compatible with perfect Néel ordering of the original atomic spins, and hence H^{mol} is unfrustrated.

We now estimate the strength of the effective interactions between molecular spins, so as to obtain an estimate of T_N. Recall that we are considering the case in which the length $L \sim 1/x$ of the typical molecule is shorter than the zero-temperature coherence length ξ_0. Therefore, we expect a power-law falloff of $|m_i|$ as a function of distance R_i from the chain end, $|m_i| \sim S/R_i$; the effective interactions between nearest-neighbor molecular spins then can be easily estimated according to Eq. (7) to be

$$K_{\mathrm{nn}} \sim J_3 S^2/L \sim J_3 S^2 x \,. \tag{8}$$

Thus, the effective molecular Heisenberg model is an unfrustrated random network with antiferromagnetic and ferromagnetic exchange couplings between molecular spins and a moderate distribution of coupling strengths with typical value $\sim J_3 S^2 x$. The lack of frustration insures that the classical ground state is ordered. Since the distribution of the magnitudes of the exchange couplings is not large, we expect that neither thermal nor quantum fluctuations will be enormously enhanced by the disorder and so the system will order at a Néel temperature, $k_B T_N \sim J_3 S^2 x$, for $x > 1/\xi_0$.

For $L > \xi_0$ $(x < 1/\xi_0)$, the situation is more subtle since $|m_i|$ is no longer approximately independent of i, nor is there a substantial gap in the molecular spectrum. Both exact results[11] for the Affleck-Kennedy-Leib-Tasaki model and numerical results on $S=1$ chains led to the conclusion that in this limit, the staggered magnetization is exponentially small in the center of the segment and reasonably large, $m \sim S/\xi_0$, only in a region of width ξ_0 near the ends of the segment. In this case, a spin $S/2$ must reside at the ends of the chains whether or not the chain is odd (since the chain end of a long chain cannot "know" whether it is the end of an even- or an odd-membered chain). In the limit $L/\xi_0 \to \infty$, the ground state would become $(S+1)^2$-fold degenerate since the coupling between the chain-end spins becomes exponentially small.

Thus, the degenerate perturbation theory used above breaks down; the spin at the right end of one molecule and the spin at the left end of the next molecule along the same chain of atoms will form a singlet due to second-order-induced interactions of magnitude $\mathcal{J}_0 \sim z\xi_0 (J_3)^2 \chi$. No matter how small J_3, for small enough x these interactions will be large compared to the typical first-order interactions between neighboring chains, $\sim J_3 \xi_0 \exp(-L/\xi_0)$, which would fall exponentially with $L/\xi_0 \sim 1/x\xi_0$. Indeed, equating these two energies, we obtain an estimate, valid for $\alpha \equiv 2\pi S(y - y_c) \gg 1$, for the critical value of x at which the crossover from essentially one-dimensional to essentially three-dimensional behavior occurs,

$$x_c \sim (1/\xi_0)\alpha^{-1} \,. \tag{9}$$

For $y \gg 1$ there exists a regime $1/\xi_0 \gg x \gg x_c$ in which the system is three dimensional but has a very broad distribution of exchange couplings. Here the ground state may be ordered or, conceivably, quantum fluctuations can lead to a novel disordered (random valence bond) ground state. In any case, in the dilute regime, $1/\xi_0 \gg x$, interesting local moment effects will be observable at temperatures $T > \mathcal{J}_0/k_B$, where the molecular spins are certainly disordered. For instance, due to the large dispersion in couplings between the spins on neighboring chains, the susceptibility will be roughly of the form $\chi(T) \sim x(S/2)^2/[T+\theta(T)]$, where

$$\theta(T) \sim xJ_3(\xi_0 S)^2\{1+O(J_3(\xi_0 S)^2/k_B T)\} .$$

C. Effect of dilution in the regime of weak quantum fluctuations, $x_p \gg x > 0$ and $y \ll y_c$.— For $y \ll y_c$ and $x \ll x_p$, the effect of quantum fluctuations is small, and the ground state is magnetically ordered with a sublattice magnetization slightly less than the classical value S. In this case, the first quantum corrections to the sublattice magnetization can be studied within spin-wave theory. In Ref. 3, Eqs. (11)-(14), a formal expression was obtained for the dynamical transverse susceptibility $\chi(q,\omega)$ for large S and for small x. From this, one can easily obtain a formal expression for the sublattice magnetization m as an integral over $\chi(q,\omega)$. We have evaluated this expression by a combination of analytic and numerical methods.[12] The result can be summarized as follows:

$$m/S = \{1 - \tfrac{1}{2}[y+O(1)] - (1/2\pi S)[A_4(x/\sqrt{u})+O(x)]+O(1/S^2)\} , \quad (10)$$

where $A_4 = 0.73 \pm 0.04$, $u = J_3/J_0 \ll 1$, and, of course, $y = -(1/\pi S)\ln u$. This result is the leading-order result for large S, and $x \ll x/\sqrt{u} \ll 1$. Note, if we estimate y_c by extrapolating the first-order expression with $x=0$ to the point $m=0$, the resulting y_c is the same as that obtained in Eqs. (4) and (5), $y_c = 2$. Also note that to leading order, m depends on x in the combination $x\sqrt{u}$, in agreement with Ref. 3. Thus, the effect of dilution is strongly enhanced by large anisotropy. The positive sign of A_4 implies that in this limit, dilution increases quantum fluctuations, although, still, quantum fluctuations all together remain small.

Along with the decrease in the $T=0$ staggered magnetization, we expect a corresponding linear decrease in T_N with $x(J_0/J_3)^{1/2}$.

D. Near the percolation threshold, $x \sim x_p$.— As x approaches x_p, T_N must vanish, and classically it does so continuously[13] as $T_N \sim (x-x_p)^{t-\nu}$, where t is the percolation-conductivity exponent and ν is the correlation-length exponent. This result could be affected by quantum fluctuations since at x_p the transition occurs at $T=0$. Previous calculation[14] reveal that no such effect occurs to first order in $1/S$.

E. Comments on other experimentally accessible quantities.— For $y > y_c$ and $x_c < x \ll x_p$, the Haldane gap should be observable spectroscopically or in the specific heat as a pseudogap, even though the ground state has long-range antiferromagnetic order and, correspondingly, gapless magnon excitations. For $y < y_c$, the very-low-energy excitations should be three-dimensional magnons, whereas for energies greater than $(J_0 J_3)^{1/2}$, they should be effectively one dimensional. A useful parameter to vary experimentally is the pressure, which should have a large effect on y. It would be particularly interesting to use this trick to explore the region of parameter space near $y = y_c$ and $x = x_c$, where novel quantum critical phenomena are possible.

We would like to acknowledge a number of extremely educational discussions with D. Arovas, M. Gelfand, A. B. Harris, and F. D. M. Haldane. S.K. was partially supported by NSF Grant No. DMR-87-17853 at UCLA. E.F.S. acknowledges the hospitality of the UCLA Physics Department where this work was performed.

Note added.— After the submission of this paper, we received a copy of a paper by Haiwara *et al.*[15] where similar ideas were discussed and, in particular, experimental evidence of the existence of spin-$\frac{1}{2}$ states at the end of a spin-1 chain were presented.

---

[a] Permanent address: Leningrad Nuclear Physics Institute, Leningrad, U.S.S.R.

[1] F. D. M. Haldane, Phys. Lett. **93A**, 464 (1983); Phys. Rev. Lett. **50**, 1153 (1983).

[2] For a review, see I. Affleck, J. Phys. Condens. Matter **1**, 3047 (1989).

[3] I. Ya. Korenblit and E. F. Shender (to be published).

[4] S. Chakravarty, B. I. Halperin, and D. R. Nelson, Phys. Rev. B **39**, 2344 (1989).

[5] S. H. Shenker and J. Tobochnik, Phys. Rev. B **22**, 4462 (1980).

[6] I. Affleck, Phys. Rev. Lett. **62**, 474 (1989).

[7] For a review, see, e.g., Yu. A. Firsov, V. N. Prigodin, and Ch. Seidel, Phys. Rep. **126**, 245 (1985).

[8] J. L. Cardy, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1987), Vol. 11, p. 55.

[9] M. E. Fisher, Am. J. Phys. **32**, 343 (1964).

[10] E. Leib and D. Mattis, J. Math. Phys. **3**, 749 (1962).

[11] T. Kennedy, J. Phys. Condens. Matter **2**, 5737 (1990).

[12] To evaluate the integrals over the component of the crystal momentum in the direction parallel to the chains, we have approximated the in-chain magnon dispersion relation by a linearized version, $\omega = J_0|k_z|$; this allows us to perform these integrals analytically. To evaluate the first correction due to finite x, we had to, in addition, perform the integrals over the perpendicular components of the crystal momentum and the frequency integral numerically. We did this by considering an array of 1000×1000 chains with periodic boundary conditions to turn the k integrals into sums; and we did the ω integral with a 1000-point mesh.

[13] E. F. Shender, Zh. Eksp. Teor. Fiz. **75**, 352 (1978) [Sov. Phys. JETP **48**, 175 (1978)].

[14] E. F. Shender (unpublished).

[15] M. Haiwara *et al.*, Phys. Rev. Lett. **65**, 3181 (1990).