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Comparison of spin anisotropy and exchange alternation

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Quasi-1-D magnetic systems with on the one hand an Ising-Heisenberg type spin anisotropy and on the other hand an alternating (dimerized) character have many interesting features in common and a few interesting differences in their phase behavior and general magnetic properties. This report reviews results rather scattered in the literature in addition to presenting new results. These rather complex quantum models present a theoretical challenge. It is also hoped that this work will be helpful to magnetochemists interested in identifying the underlying magnetic character of their systems, and to experimentalists in general.

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1. INTRODUCTION

Quasi-one-dimensional systems have the virtue that various types of magnetic behavior can be investigated rather thoroughly, both theoretically and experimentally. From time to time it has been noted that one-dimensional spin models with anisotropy of the Ising-Heisenberg type have qualitative features in common with one-dimensional models which one isotropic in spin-space, i.e. Heisenberg, but with exchange constants J_1 and J_2 alternating in magnitude. There seems at present no clear theoretical arguments to explain this similarity: the two systems do not, for example, belong in the same universality class. In fact, as we shall see below, the resemblance is strong, but not quite complete. Certain aspects of the phase behavior of the weakly interacting spin systems do show some interesting differences. Homologous series of compounds with a uniform character are currently under scrutiny by coordination chemists, who study the variation of J with bond length, bond angle and, perhaps, other factors. These empirical studies can then be used to check the reliability of current theories of superexchange. Very recently, families of alternating (also called dimerized) spin systems have been discovered, which may also be used for this purpose. The problem for magneto-chemists is which model to use; spin anisotropic or alternating. These considerations, and also current interest in the spin-Peierls phenomenon,[1] have motivated this study.

2. SPECTRAL EXCITATIONS

The Hamiltonians for the two types of system may be written (all systems discussed have spin S=1/2):

$$\underline{\text{Spin Anisotropy}}\ (\text{SA}):\quad H=2J\sum_{i=1}^{N}\{S_i^{\,z}S_{i+1}^{\,z}+\gamma(S_i^{\,x}S_{i+1}^{\,x}+S_i^{\,y}S_{i+1}^{\,y})\} \tag{1}$$

where the anisotropy parameter, γ, varies between 0 (Ising model) and 1 (Heisenberg model).

$$\underline{\text{Alternation}}\ (\text{Alt.}):\quad H=2J\sum_{i=1}^{N/2}\{\vec{S}_{2i-1}\cdot\vec{S}_{2i}+\alpha\vec{S}_{2i}\cdot\vec{S}_{2i+1}\}, \tag{2}$$

where the alternation parameter, α, varies between 0 (limit of isolated dimer spin pairs) and 1 (uniform model). We consider J>0, antiferromagnetic. Hamiltonian (2) may also be written in terms of exchange constants J_1 and J_2, where $J_1 \equiv J$ and $J_2 \equiv \alpha J$ ($J_2<J_1$). In connection with spin-Peierls theory it is often convenient to define a dimerization parameter, $\delta=(1-\alpha)/(1+\alpha) = (J_1-J_2)/(J_1+J_2)$.

An analytic solution is available for the lowest-lying excitations of Hamiltonian (1)[2], but at present no non-trivial exact analytic results are available for any property of Hamiltonian (2). It would therefore be valuable to begin by reviewing a related pair of Hamiltonians, for the Ising-XY linear chain and the alternating XY chain, both of which may be solved exactly via a standard transformation from spin to pseudo-fermion operators. The Hamiltonians are:

$$\text{SA:}\quad H = 2J\sum_{i=1}^{N}\{S_i^x S_{i+1}^x + \gamma S_i^y S_{i+1}^y\} \tag{3}$$

$$\text{Alt:}\quad H = 2J\sum_{i=1}^{N/2}\{S_{2i-1}^x S_{2i}^x + S_{2i-1}^y S_{2i}^y + \alpha(S_{2i}^x S_{2i+1}^x + S_{2i}^y S_{2i+1}^y)\}. \tag{4}$$

Both models are variants on the 1-D uniform XY model, first solved by Lieb et al. and Katsura[3].

A comparative discussion is facilitated by considering a more general Hamiltonian, containing (3) and (4) as particular cases, studied by Dubois and Carton and Perk and Capel.[4] The exact dispersion relations are:

$$\varepsilon_1(q) \sim \frac{2(1+\gamma\alpha)}{(1+\gamma)(1+\alpha)}\left[\cos^2 q+\left(\frac{1-\gamma\alpha}{1+\gamma\alpha}\right)^2\sin^2 q\right]^{\frac{1}{2}} \tag{5}$$

$$\varepsilon_2(q) \sim \frac{2(\gamma+\alpha)}{(1+\gamma)(1+\alpha)}\left[\cos^2 q+\left(\frac{\gamma-\alpha}{\gamma+\alpha}\right)^2\sin^2 q\right]^{\frac{1}{2}}. \tag{6}$$

Note first of all the complete equivalence of γ and α in (5) and (6). If either $\gamma = 1$ (isotropic case) or $\alpha = 1$ (uniform case), (5) and (6) become degenerate as, say

$$\varepsilon_{1,2}(q) \sim \left[\cos^2 q + \left(\frac{1-\gamma}{1+\gamma}\right)^2\sin^2 q\right]^{\frac{1}{2}}. \tag{7}$$

The excitations are gapless when $\alpha=\gamma=1$, otherwise the energy gap, $\Delta E \sim (1-\gamma)$ or $(1-\alpha)$. It is very interesting that there is another case when branch (6) of the excitations is gapless, namely when $\gamma=\alpha$. In some sense the anisotropy and alternation compensate so as to give quasi-uniform-Heisenberg behavior. This implies that an anisotropic XY spin-Peierls system should show unusual behavior, and possibly an Ising-Heisenberg spin-Peierls system also.

Let us now compare the Heisenberg-like systems [(1),(2)] with the XY-like systems [(3),(4)]. There is a qualitative similarity in that models (1) and (2) show a spectral excitation gap vanishing only in the limits $\gamma=1$ or $\alpha=1$,[5,6] respectively. However, both gaps now have very different functional forms. In Fig. 1 we show a sequence of exact finite chain anisotropy energy gaps for systems of up to 12 spins, together with an extrapolated, numerical, $N \to \infty$ estimate (indicated by crosses). An exact analytic result is available[2]. The gap rises

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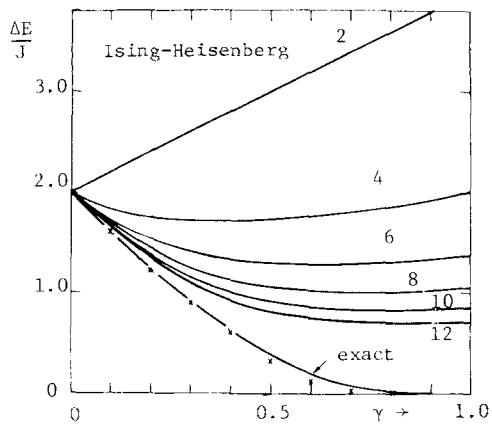

Fig. 1 Ising-Heisenberg energy gaps as function of γ, showing finite N results, the exact result, and extrapolations (crosses).

exponentially slowly away from the Heisenberg limit [as $\exp(-A[1-\gamma]^{-\frac{1}{2}})$].

The agreement with numerical extrapolations is really quite good[7,8] over the whole γ range. This is important in connection with Fig. 2, where we show alternation energy gaps. Since no analytic solution exists for this problem, we will rely on numerical extrapolations. Again, a sequence of exact finite chain alternation gaps for systems of up to 12 spins is shown, together with $N \to \infty$ extrapolations (dashed curve). The gap apparently vanishes only in the uniform (Heisenberg) limit, but the functional form is quite different from the spin anisotropy case. A theoretical approach by Cross and Fisher[9] based on the Luttinger-Luther-Peschel continuum lattice model predicts that $\Delta E \sim \delta^{2/3}$, consistent with a zero temperature RG approach[10] and also (qualitatively) with the extrapolations.

The specific heat and susceptibility of Ising-Heisenberg chains has been investigated both numerically[11] and analytically[7], and agreement is good. Both specific heat and parallel susceptibility have typical rounded maxima, and vanish exponentially as $T \to 0$ on account of the energy gap. For the alternating model, numerical calculations of Duffy and Barr[12] have been extended by considering longer chains (up to 12 spins) so that reliable extrapolations may be made closer to the uniform limit. Detailed results for the susceptibility for a wide range of α have been presented[13] and new results for the specific heat and zero-point magnetization in a field are available. Again, specific heat and susceptibility have rounded maxima, and vanish exponentially as $T \to 0$ on account of the energy gap.

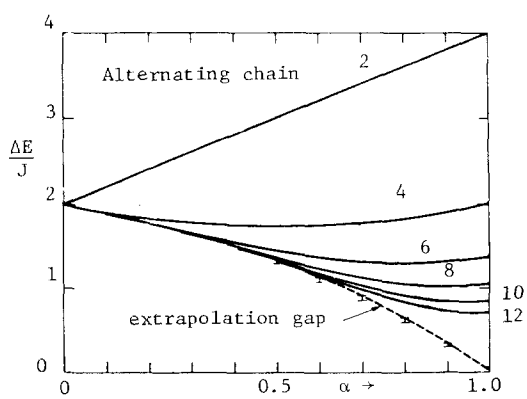

Fig. 2 Alternating energy gaps as function of α, showing finite N results, extrapolations and error bars.

The important difference between the two types of systems lies in the susceptibility. Since the alternating chain remains isotropic in spin space, there is no distinction between parallel and perpendicular susceptibility. The susceptibility for both powder and single crystals always goes to zero at T = 0. For the Ising-Heisenberg model, only the parallel susceptibility vanishes, the perpendicular susceptibility is finite and non-zero. Closely related is the low temperature magnetization as a function of field. For powder Ising-Heisenberg samples, the magnetization is always non-zero for $H > 0$, whereas for powder samples of alternating chains, the magnetization remains zero until a threshold field is reached, when it rises rather rapidly. This feature has been used to identify copper bromide imidazole as an alternating system, whereas chemically related sister compounds apparently behave like uniform chains.[14]

4. CRITICAL BEHAVIOR

The simple antiferromagnet (AFM) has a single critical field (at T = 0) above which AFM ordering is destroyed by the field. For both the spin anisotropic and alternating 1-D models there are <u>two</u> critical fields, lower and upper, H_{c1} and H_{c2}, respectively. For both models, H_{c2} is given exactly by simple spin-wave theory. Again, for both models, H_{c1} is a direct measure of ΔE, the energy gap, since H_{c1} is the field at which a (magnetic) component of the excited states above the gap crosses the non-magnetic ground state(s) on account of the Zeeman term. For the XY-like models, of course, both H_{c1} and H_{c2} are known exactly. For Heisenberg-like models we have:-

$$\text{SA:} \qquad H_{c2} = 2J(1+\gamma). \tag{8}$$

H_{c1} can be found from the graph of Fig. 1, where the expression plotted can be obtained from ref. 2, equations (161, 162), or Yang and Yang[15], equation (8).

$$\text{Alt:} \qquad H_{c2} = 2J_1(1+\alpha). \tag{9}$$

H_{c1} can be found approximately from the graph of Fig. 2. There is also a third-order perturbation calculation of Harris[16] which gives

$$H_{c1}/J_1 \sim \Delta E/J_1 \simeq 2-\alpha-\frac{3}{4}\alpha^2+\frac{1}{16}\alpha^3+\ldots$$

This expression converges well from the dimer limit out to $\alpha \simeq 0.5$ and agrees with the numerical extrapolations in this alternation range. Note the isomorphism between γ and α in (8) and (9). At T = 0, critical singularities occur in $\chi_{(T=0)}$, but space prevents a discussion here.

For both Ising-Heisenberg and alternating chains, the behavior of the thermodynamic properties, e.g. the specific heat, is very similar. For both models we have the same functional forms for $T \to 0$:

$$0 \leq H < H_{c1}: \qquad C_H \sim T^{-3/2} e^{-\Delta E/kT} \tag{10}$$

$$H = H_{c1} \text{ and } H = H_{c2}: \qquad C_H \sim A_{1,2} T^{1/2} \tag{11}$$

$$H_{c1} < H < H_{c2}: \qquad C_H \sim B(H)T. \tag{12}$$

Exact results for the Ising-Heisenberg model expanded in γ are: $A_1 \simeq \frac{0.114}{\sqrt{8\gamma}}$; $A_2 \simeq \frac{0.229}{\sqrt{2\gamma}}$. (13)

For the alternating model, no such exact results are available but spin-wave theory and detailed experiment[17] confirm the correctness of the functional forms (10,11, 12). Note that for both models, the behavior resembles that expected for a uniform AFM at T = 0 in the range $H_{c1} < H < H_{c2}$; whereas at $H = H_{c1,2}$, the models resemble a zero-field ferromagnet. In both models there is asymmetry i.e. $A_1 < A_2$.

A zero temperature quantum RG method has been formulated where the quantum chain is divided into exactly solvable blocks of N_s spins, and the inter-block coupling is written in terms of a truncated block vector basis[6,10]. For alternating chains with $N_s = 3$, the RG iteration process yields two fixed points, $\alpha^* = 1$

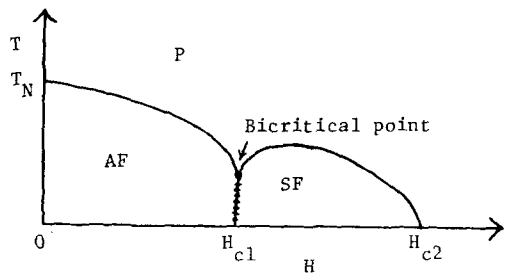

Fig. 3 Quasi-1-D spin-flop AFM phase diagram, showing AF ordered region, spin-flop region (SF) and bicritical point.

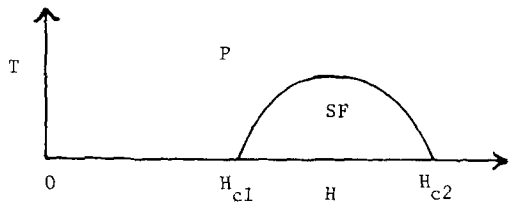

Fig. 4 Quasi-1-D alternating AFM phase diagram, showing spin-flop (SF) ordered region.

(unstable) and $\alpha^* = 0$ (∞) (stable). This result has the important physical implication that the system with non-zero alternation, i.e. $\alpha < 1$, will renormalize into a dimer system, characterized by a singlet-triplet energy gap. This implies that the excitation gap vanishes only in the uniform limit, $\alpha = 1$[6]. Repeating the calculations for a uniform Ising-Heisenberg system[19] strengthens this interpretation. Fixed points are found at $\gamma^* = 1$ (unstable) and $\gamma^* = 0,\infty$ (stable). This agrees with exact results[2]. If the RG calculations are repeated for the corresponding XY-type models, similar fixed point behavior appears, again in agreement with the exact results. It is interesting that the RG method gives equivalent recursion relations for both cases (3) and (4), apparently reflecting the equivalence of the two exact solutions noted above.

When the 1-D systems weakly interact, cooperative ordering occurs for $T > 0$. Since none of our systems is now exactly solvable, the following discussion relies on spin-wave theory, mean-field theory and experiment. The phase diagram for a quasi-1-D Ising-Heisenberg AFM, which is, of course, a spin-flop system is sketched in Fig. 3. The usual three phases appear, AFM, spin-flopped and paramagnetic. The corresponding phase-diagram for a quasi-1-D alternating AFM is sketched in Fig. 4. The surprising feature is the complete absence of the AFM phase. There is no phase transition of any type in zero field: cooperative ordering of a spin-flop type occurs only between H_{c1} and H_{c2}. There is likewise no trace of a first order anti/flop transition line: The phase boundary is second order. Such behavior typifies copper nitrate, $Cu(NO_3)_2 \cdot 2.5\ H_2O$, which has been very extensively studied, both experimentally and theoretically[17,18]. The presence of the AFM ordered phase in Fig. 3 is related to the existence of long-range-order (LRO) at $T = 0$ of the Ising-Heisenberg chain. The alternating chain has a non-degenerate singlet ground state; hence no LRO at $T = 0$, and therefore no transition will appear for $T > 0$ when the chains interact.

5. MAGNETIC COOLING

Quasi-1-D Ising-Heisenberg and alternating systems may show a striking difference in their phase behavior, but they show strong similarities in their cooling behavior, i.e. isentropes as a function of field and temperature. This is because magnetic cooling is intimately related to the entropy, on which the effects of a second order or continuous transition are rather minimal. Fig. 5 shows the results of an analytic calculation on an ideal Ising-Heisenberg chain with $\gamma = 0.2$.[20] Note

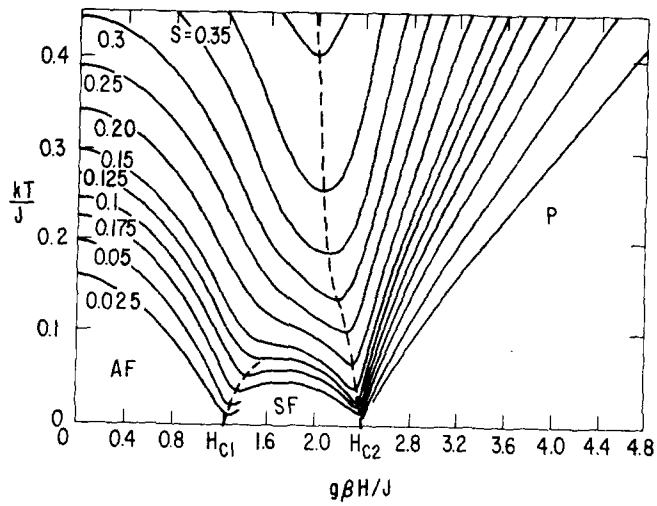

Fig. 5 Exact cooling isentropes for Ising-Heisenberg chain for $\gamma = 0.2$.

that four different types of cooling behavior, including both adiabatic magnetization and adiabatic demagnetization, are observed in this system. Entropy maxima and hence isentrope minima appear in the vicinity of H_{c1} and H_{c2}. For the alternating chain system copper nitrate, the cooling curves (theoretical and experimental) are remarkably similar to the Ising-Heisenberg case.[17]

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