Impurity effects on the three-dimensional ordering of magnetic chain systems

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We demonstrate the drastic reduction of the magnetic-ordering temperature T_c by nonmagnetic impurities in quasi-one-dimensional magnetic systems. Single-chain spin correlations are treated exactly for the classical Heisenberg and $S = 1/2$ Ising systems, with interchain correlations included in a mean-field approximation.

One-dimensional (1D) magnetic systems are of interest both because of their relative theoretical simplicity and because many real crystals show quasi-one-dimensional behavior.[1] One of the basic topological characteristics of a pure 1D system is its sensitivity to impurities and imperfections. Since there exists no "way around" a missing bond in a chain, a single missing bond will cut the chain into two independent segments. The introduction, e.g., of nonmagnetic impurities into a single magnetic chain with nearest-neighbor interactions will effectively divide it into a number of smaller noninteracting units. On the other hand, in a real linear magnetic system, weak interchain couplings exist, which, in fact, lead to three-dimensional (3D) ordering of these systems below a sufficiently low temperature T_c. Those 3D interactions should reduce the above-mentioned 1D impurity effect. In this paper, we study the effect of nonmagnetic impurities on the 3D ordering temperature. We find that this effect is quite drastic, and that it is much more important for the chain systems than for isotropic 3D systems. We cite examples where this effect appears to have been observed and give predictions for cases where impurity concentrations in the range of tenths of a percent may lead to easily observable reductions in T_c.

The impurities separate each chain into segments of average length n spins. We assume $n \gg 1$, the dilute-impurity limit. Rather than average over a random distribution of lengths (which can be done straightforwardly), we will here treat the length of the segments as uniform, for simplicity. Because of the large values of n considered here, the numerical results are only slightly modified by this simplification.

The estimate of T_c is made using an approximation[2,3] which treats the 1D correlations exactly and approximates the interchain interactions by a mean field. The breakdown of mean-field theory in predicting ordinary 3D transitions is associated with the neglect of the long-wavelength fluctuations of the order parameter which are so important near a second-order phase transition. These fluctuations are associated with the rapid growth of short-range order. But in the quasi-one-dimensional systems, while the correlation length is growing dramatically along the chains (so that the individual chains must be treated carefully, including fluctuation effects), it remains on the order of a lattice spacing perpendicular to the chains nearly down to the critical temperature. One therefore expects mean-field theory to be a very good approximation for the weak interchain interactions. We shall confine our attention to the Ising[4,5] and classical spin[6,7] models, where the 1D problem can be solved exactly. The Hamiltonian describing the Ising model is

$$\mathcal{H}_{\text{Ising}} = -2J\sum_{i,\vec{s}} \sigma_{i+1,\vec{s}}\sigma_{i,\vec{s}} - J'\sum_{i,\vec{s},\vec{\delta}} \sigma_{i,\vec{s}}\sigma_{i,\vec{s}+\vec{\delta}} , \qquad (1)$$

where J is the intrachain interaction, J' is the interchain interaction, and $\sigma_i = \pm\frac{1}{2}$. The index i runs along the chain, $\vec{s}$ designates the chain, and $\vec{\delta}$ is a nearest-neighbor interchain vector. For the classical spin model[6]

$$\mathcal{H}_{\text{cl}} = -2J_{\text{cl}}\sum \vec{S}_{i+1,\vec{s}}\cdot\vec{S}_{i,\vec{s}} - J'_{\text{cl}}\sum \vec{S}_{i,\vec{s}}\cdot\vec{S}_{i,\vec{s}+\vec{\delta}} , \qquad (2)$$

where the $\vec{S}_i$ are classical unit vectors. J_{cl} is the intrachain exchange interaction multiplied by $S(S+1)$, where S is the spin value and J'_{cl} is the interchain interaction. $\mathcal{H}_{\text{cl}}$ should be a reasonable approximation for Heisenberg models with $S \geq 1$. We note that the signs of J and J' are not restricted. For these classical models, the staggered susceptibility of the antiferromagnetic model is the same as the uniform susceptibility of a ferromagnetic model with the same value of $|J|/T$. Thus with proper identification of the quantities introduced, our treatment is applicable to both cases.

In the approximation[2,3] where the weak interchain interaction is treated in a mean-field approximation, the 3D ordering temperature T_c is given by

$$2zJ'\chi_{1\text{D}}(T_c) = 1 , \qquad (3)$$

where z is the number of nearest-neighbor chains (in the dilute impurity case which we consider, the modifications of the effective value of z due to the impurities are negligible), and $\chi_{1\text{D}}(T_c)$ is the susceptibility per spin of the system of isolated inde-

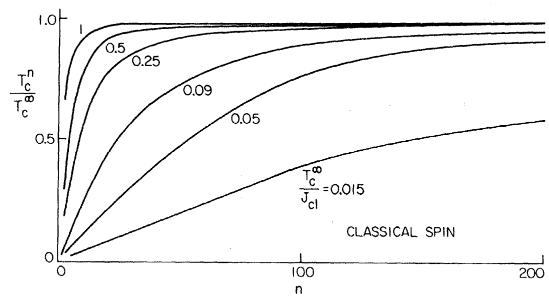

FIG. 1. T_c^n/T_c^∞ as a function of n for several values of T_c^∞/J_{c1} ($k_B=1$) for the classical spin model.

pendent linear chains. For $J' \ll J$, the long 1D correlation lengths at T_c make χ_{1D} large, and T_c becomes of the order of $J'\xi_{1D}$, where $\xi_{1D} \gg 1$ is the 1D correlation length in units of the lattice constant at T_c. The principal effect of the impurities will be to decrease χ_{1D} by reducing the effective chain length which may limit the correlation length and thus lead to a decrease of T_c. For the classical spin model, the susceptibility per spin of an open chain of n spins is given[6,8] by

$$\chi_n = \frac{S(S+1)}{3k_BTn}\left(n\frac{1+u}{1-u} - 2u\frac{1-u^n}{(1-u)^2}\right), \tag{4}$$

where

$$u = \coth(2J_{c1}/k_BT) - k_BT/2J_{c1} ;$$

for $k_BT \ll J_{c1}$, $u \simeq 1 - k_BT/2J_{c1}$. The 1D correlation length at a temperature T is given by $\xi_{1D} \simeq 2J_{c1}/k_BT$. The susceptibility per spin for $n \to \infty$ is given by $\chi_\infty \simeq 4J_{c1}/3(k_BT)^2$. Equation (4) yields the two following asymptotic limits: (a) The short-chain or "size-limited" case $n \ll \xi_{1D}$, where $\chi_n \cong \chi_\infty(n/2\xi_{1D})$; (b) the long-chain or "almost-infinite" limit $n \gg \xi_{1D}$, where $\chi_n \simeq \chi_\infty(1 - 2J_{c1}/k_BTn)$, i.e., an $O(1/n)$ "surface-to-volume" correction in 1D. We can now obtain from Eq. (3) the effect of finite n on T_c for the above cases:

$$\text{(a)}\ T_c^n/T_c^\infty \simeq (k_BT_c^\infty/4J_{c1})n\ ,\quad n \ll 2J_{c1}/k_BT_c^\infty\ ; \tag{5a}$$

$$\text{(b)}\ T_c^n/T_c^\infty \simeq 1 - J_{c1}/k_BT_c^\infty n\ ,\quad n \gg 2J_{c1}/k_BT_c^\infty\ . \tag{5b}$$

We have plotted T_c^n/T_c^∞ as a function of n, Fig. 1, for several values of $k_BT_c^\infty/J_{c1} \leq 1$, a convenient measure of the ratio of interchain to intrachain exchange coupling J'/J. It is seen that for decreasing values of $k_BT_c^\infty/J_{c1}$, the range of n over which T_c is substantially reduced becomes larger. For $k_BT_c^\infty/J_{c1} \ll 1$, T_c^n/T_c^∞ becomes a function of the single variable $(k_BT_c^\infty/2J_{c1})n$, which can be used to extend the range of parameters displayed in Fig. 1. We remark that for $k_BT_c^\infty/J_{c1} \sim 0.015$, a value appropriate to tetramethylammonium manganese chloride (TMMC),[1,9] the impurity effects should lead to significant decreases of T_c for impurity concentrations in the range of 10^3 ppm. An experimental indication of these effects is found in $CsNiCl_3$, where $T_c/J_{c1} \simeq 0.15$, and 4-at.% Fe substituted for the Ni appears to reduce T_c by (30–50)%.[10]

The impurity effect is much more spectacular for the Ising case, due to the exponential growth of ξ_{1D} as $T \to 0$, $\xi_{1D} \simeq e^{J/k_BT}$. This is also the source of the relatively high values of T_c/J, even for small J'/J.[1-3] We obtain,[4,5] for a chain of n spins with free ends,

$$\chi_n = (8nk_BT)^{-1}[2ne^{J/kT} + 1 - e^{2J/kT} + (1 - e^{J/kT})^2 \tanh^{n-1}(J/2kT)]\ . \tag{6}$$

The asymptotic behavior of Eq. (6) for $n \ll \xi_{1D}$ and $n \gg \xi_{1D}$ is given by

$$\chi_n \simeq \chi_\infty n\, e^{-J/k_BT}\ ,\quad n \ll e^{J/k_BT_c} \tag{7a}$$

$$\chi_n \simeq \chi_\infty(1 - e^{J/k_BT}/n)\ ,\quad n \gg e^{J/k_BT_c} \tag{7b}$$

which lead, using Eq. (3), to the following reductions of T_c:

$$T_c^n/T_c^\infty = n\, e^{-J/k_BT_c^\infty}\ ,\quad n \ll e^{J/k_BT_c^\infty} \tag{8a}$$

$$\frac{T_c^n}{T_c^\infty} = 1 - \frac{e^{J/k_BT_c^\infty}}{2(1 + J/k_BT_c^\infty)n}\ ,\quad n \gg e^{J/k_BT_c^\infty}\ . \tag{8b}$$

The results for T_c^n/T_c^∞ as a function of n for several values of $k_BT_c^\infty/J$ are plotted in Fig. 2. We have also studied the effect of boundary conditions by considering the case of a periodic boundary (see broken curve in Fig. 2 for $k_BT_c^\infty/J = 0.3$). The result is similar to (8a) for $n \ll e^{J/k_BT_c^\infty}$ and tends exponentially to unity for $n \gg e^{J/k_BT_c}$. Thus the $O(1/n)$ term in (8b) is a boundary or 1D "surface-to-volume" term. We emphasize that Ising-like chain magnets should be extremely sensitive to impurities. Thus $CoCl_2 \cdot 2NC_5H_5$ ($kT_c/J \simeq 0.3$) and $CsCoCl_3$ ($kT_c/J \simeq 0.15$), which appear to behave like Ising systems,[1,11] should be sensitive to impurities in the range of 10^3 ppm.

The large difference between the isotropic and Ising cases suggests that it would be interesting to study anisotropy effects. Also, results qualitatively

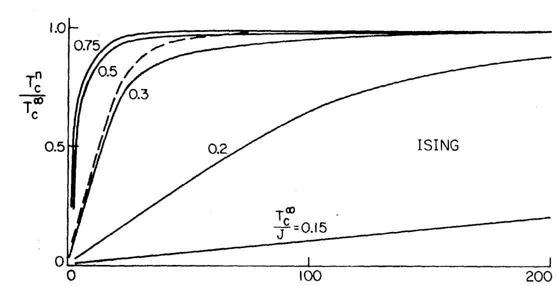

FIG. 2. Same as Fig. 1, for the Ising model. Solid curves: open chains; broken curve: rings (periodic chains) for $T_c/J = 0.3$.

similar to those of the classical spin model may be expected for $S=\frac{1}{2}$ Heisenberg models, where numerical results are available only for $n \leq 10$. Systematic experiments to check our results on quasi-1D materials as a function of impurity concentration would be valuable. We are currently studying the effects of magnetic impurities, using exact results[12,13] for disordered chains. In the limit where the host-impurity interaction is much weaker than the host-host interactions, the simple results of this work are recovered.

We finally reemphasize that the extreme importance of impurities in 1D magnetic systems is not peculiar to such systems but is rather a general topological characteristic of 1D geometry,[7] as has previously been noted[14] in discussions of the percolation problem.

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