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Three-dimensional ordering of impure linear-chain systems

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The reduction of the three-dimensional ordering temperature T_c by random substitutional impurities in spin-1/2 Ising and classical Heisenberg quasi-one-dimensional systems is calculated within an approximation which treats interchain coupling in mean-field theory. The reduction can be substantial for highly one-dimensional systems even for impurity concentrations of 1-at.% or less. A qualitative analysis of impurity effects on ordering applicable both to magnetic and to nonmagnetic linear-chain systems is also given, with particular attention to the possible role of impurities in promoting incomplete three-dimensional ordering, such as that observed in the quasi-one-dimensional conductor $K_2Pt(CN)_4Br_{0.3}\cdot 3D_2O$(KCP).

I. INTRODUCTION

There are now known a substantial number of insulating crystals, including tetramethylammonium manganese trichloride (TMMC), $CsNiF_3$, $CsNiCl_3$ and other isomorphous salts, which exhibit quasi-one-dimensional magnetic behavior.[1] Although phase transitions are forbidden for isolated chains with short-range interactions, the weak but finite coupling between chains in these materials does result in three-dimensional (3D) magnetic ordering below a critical temperature T_c, substantially less than the characteristic intrachain interaction strengths. A useful picture[2,3] of the ordering process results from considering a group of spins within a correlation length of each other along a given chain as being oriented as a unit by an effective molecular field due to interactions with neighboring chains. The size of the unit grows with the correlation length as T decreases; in conjunction with the increasing mean-field susceptibility this monotonically increases the tendency to 3D order with decreasing T. The process is particularly sensitive to impurities and other defects because of the marked effect on correlation length these may have in one-dimensional structures. In particular, nonmagnetic impurities break communication along the chain and restrict the growth of the correlation length to the average impurity separation. We have considered a simple model for this situation in an earlier paper,[3] where the dramatic depression of T_c by nonmagnetic impurities was demonstrated. In the present paper we explore the effects of more general impurities on ordering in quasi-one-dimensional magnetic systems. We treat only the binary alloy, with a single type of substitutional impurity distributed randomly in the crystal, as expected for a quenched alloy (a more realistic model than the evenly spaced impurities chosen in Ref. 3 for simplicity of exposition). We will consider explicitly two models in which the isolated chain problem can be solved exactly: The $S=\frac{1}{2}$ Ising and the classical spin Heisenberg models with nearest-neighbor exchange interactions. The main approximation then involves the treatment of interchain interactions within mean-field theory to determine T_c. In Sec. II we present the necessary mathematical formulation for evaluating T_c in the above approximation. In Sec. III the results are discussed and plotted numerically for typical cases. This treatment holds only in the case where all the interactions in the system promote the same kind of ordering. An interesting situation occurs when the impurities divide the chains in such a way that the ordering of consecutive pure segments is not consistent with the interchain mean field. This can cause a "pinning" of the disorder by the impurities and is discussed in Sec. IV.

It should be noted that although we have specifically treated spin models, the spectacular influence of impurities is a general characteristic of many other quasi-one-dimensional systems. This is, in fact, perhaps one of the most important topological characterizations of one dimensionality. Thus, our results should be qualitatively relevant to other cases of experimental interest such as quasi-one-dimensional electronic systems, displacive transitions, etc. We believe that the results of Sec. IV may be relevant to explaining the apparent incomplete 3D ordering in the quasi-one-dimensional conductor

$K_2Pt(CN)_4Br_{0.3}\cdot 3D_2O$ (KCP).

II. FORMULATION FOR DETERMINING T_c

The method of calculation proceeds through nearly identical algebraic steps for the spin-$\frac{1}{2}$ Ising and classical Heisenberg models; although we use vector spin notation in what follows, with suitable interpretation, the results apply as well to the Ising problem. Consider a random alloy of "host" and "impurity" spins, with the latter present in a concentration ρ. We deal with the Hamiltonian

$$\begin{aligned}\mathcal{H} = &-2\sum J_{n,i;\,n,\,i+1}\hat{S}_{n,\,i}\cdot\hat{S}_{n,\,i+1}\\ &-\sum J'_{n,\,i;\,n+\Delta,\,i}\hat{S}_{n,\,i}\cdot\hat{S}_{n+\Delta,\,i}\\ &-\sum g_{n,\,i}\,\mu_B H_{n,\,i}S^z_{n,\,i}\quad ,\end{aligned}\tag{2.1}$$

where n is summed over all chains, Δ over vectors connecting nearest-neighbor chains, and i over sites in a chain. Thus J describes intrachain exchange; if we introduce the occupation number $P_{n,\,i}$ which is 1 if an impurity spin occupies the site n,i and 0 if host spin occupies that site, then

$$\begin{aligned}J_{n,\,i;\,n,\,i+1} = {}&P_{n,\,i}P_{n,i+1}\,J_{\mathrm{II}} + (P_{n,\,i} - P_{n,\,i+1})^2 J_{\mathrm{IH}}\\ &+ (1-P_{n,\,i})(1-P_{n,\,i+1})J_{\mathrm{HH}}\;,\end{aligned}\tag{2.2}$$

in an obvious notation where H denotes "host" and I "impurity." Similarly, there are three values J'_{II}, J'_{IH}, and J'_{HH} for the interchain exchange J', associated with impurity-impurity, impurity-host, and host-host pairs of coupled spins. In general, we can also take the g values g_{H} and g_{I} to be different. For the spin-$\frac{1}{2}$ Ising model $\hat{S}_{n,\,i}$ in Eq. (2.1) is to be interpreted as a unit vector in the z direction ($\hat{S}\to S^z = \pm 1$).

Magnetic quasi-one-dimensionality results from the relative weakness of interchain exchange interactions in the crystals under consideration: $J' \ll J$. Thus the spin correlations which, as the temperature is reduced, eventually lead to magnetic ordering at $T = T_c$, develop substantially along each chain at temperatures far above T_c (since they become important when $T\sim 2J$). It is therefore essential to include these intrachain correlation effects with some care; we take them to be those of single isolated chains, for which they can be found exactly in the models treated here. That approximation should be accurate until the onset of substantial three-dimensional cooperative behavior in the critical region just above T_c. (In principle, one should distinguish between two different temperature ranges around T_c: the region in which three-dimensional correlations start to be felt, and the one where critical fluctuations become important—the Ginzburg critical region. It turns out, however, that for the quasi-one-dimensional case, the two regions are of the same order of magnitude.) In contrast, the interchain spin correlations develop importantly only in the three-dimensional critical region. Thus we can expect to find a good estimate of T_c itself by treating these interchain interactions within a molecular-field approximation.[2-4] Even for the extreme case $J' = J$ in a pure Heisenberg square lattice Stanley and Kalplan[4] found only a 50% increase of T_c as estimated in this way over the high-temperature series-expansion results.

The approximation is certainly much better than that for $J' \ll J$, as it is used here; e.g., it is essentially exact in this limit for the 2D Ising model.[2] The results of such a calculation of T_c, described below in more detail, are shown in Fig. 1 for pure Ising spin $S=\frac{1}{2}$ and classical Heisenberg systems as functions of the ratio of interchain to intrachain exchange strengths, J'/J. Since T_c can be measured directly and J estimated from thermodynamic measurements, the plots indicate the range for the experimental quantity T_c/J over which a quasi-one-dimensional description is appropriate. It is clear that in a system where there is no supression of T_c due to competition for different types or order between various exchange interactions, $T_c/J \ll 1$ implies $J'/J \ll 1$, and quasi-one-dimensionality. What is perhaps not so immediately obvious is how sensitive the reduction in T_c/J with J'/J is to the form of the exchange (e.g., Ising versus Heisenberg), and in particular that in the Ising model, a decrease in J'/J of several orders of magnitude results in less than a factor of 2 decrease in T_c/J. We will see below that this is related to the extremely rapid (exponential) growth in the Ising model of the single chain correlation length with decreasing temperature. Leaving out these single chain correlation effects therefore gives drastically incorrect estimates of T_c. Thus Takeda *et al.*[5] used simple molecular-field theory and their measured values of J and $\chi(T)$ in $CoCl_2\cdot 2NC_5H_5$ to find an estimate of $z'|J'|/J \gtrsim 1$, in spite of the apparent highly one-dimensional behavior of the susceptibility and specific heat. Since $T_N/J \approx 1.2$, we see from Fig. 1 that this estimate of J'/J was too high by about two orders of magnitude.

Since we will treat the interchain interactions within a molecular-field approximation, we basically require the magnetic susceptibility of an isolated chain. In particular, we need the two-spin correlation functions $\langle S^z_0 S^z_l\rangle_{AB}$, where A, B take on the values I or H restricting the two spins to be either impurity or host atoms, respectively, and l labels position on a single chain (spins on different chains are uncorrelated in this approximation). The notation implies a configuration average over the occupation of all other spins than the two under consideration. We treat the "quenched" limit only, where the distribution of impurity spins is taken to be random. We make use of the techniques which were employed in Ref. 6 to calculate the thermodynamic properties of isolated impure classical Heisenberg chains.

For a given configuration the correlation functions are given by standard transfer matrix techniques:

$$\langle \hat{S}_0 \cdot \hat{S}_l \rangle = \begin{cases} \prod_{m=1}^{l} U_{m-1,m}, & l > 0 \\ 1 & l = 0, \end{cases} \tag{2.3}$$

where the characteristic function $U_{m-1,m}$ is given in terms of the exchange integrals as

$$U_{m-1,m} = \begin{cases} \coth(2\beta J_{m-1,m}) - (2\beta J_{m-1,m})^{-1} & \text{(classical Heisenberg)}, \\ \tanh(2\beta J_{m-1,m}) & (S = \tfrac{1}{2} \text{ Ising}), \end{cases} \tag{2.4}$$

and we note in the case of the classical model that $\langle S_0^z S_l^z \rangle = \frac{1}{3} \langle \hat{S}_0 \cdot \hat{S}_l \rangle$ by symmetry. In each case the function $U_{m-1,m}$ then has three possible values: U_{II}, U_{IH}, or U_{HH}. If we now take a configuration average, we find immediately a matrix recursion relation for these functions:

$$(\langle \hat{S}_0 \cdot \hat{S}_l \rangle_{AB}) = D(\langle \hat{S}_0 \cdot \hat{S}_{l-1} \rangle_{AB}), \tag{2.5}$$

$$D = \begin{pmatrix} \rho U_{\mathrm{II}} & (1-\rho) U_{\mathrm{IH}} \\ \rho U_{\mathrm{IH}} & (1-\rho) U_{\mathrm{HH}} \end{pmatrix}, \tag{2.6}$$

which gives, after iteration,

$$\begin{pmatrix} \langle \hat{S}_0 \cdot \hat{S}_l \rangle_{\mathrm{II}} & \langle \hat{S}_0 \cdot \hat{S}_l \rangle_{\mathrm{HI}} \\ \langle \hat{S}_0 \cdot \hat{S}_l \rangle_{\mathrm{IH}} & \langle \hat{S}_0 \cdot \hat{S}_l \rangle_{\mathrm{HH}} \end{pmatrix} = D^{l-1} \begin{pmatrix} U_{\mathrm{II}} & U_{\mathrm{IH}} \\ U_{\mathrm{IH}} & U_{\mathrm{HH}} \end{pmatrix} \quad (l \geq 1). \tag{2.7}$$

This is readily solved[6] explicitly in terms of the eigenvalues and the eigenvectors of D (see Appendix).

In the pure system $U_{m-1,m} = U$ independent of m, and $\langle \hat{S}_0 \cdot \hat{S}_l \rangle = U^l$. The characteristic distance of this exponential decay, the correlation length, is thus $\xi = -1/\ln U$. We are interested in low temperatures, $2\beta J \gg 1$, so $\xi \sim 2\beta J$ for the classical Heisenberg and $\xi \sim e^{4\beta J}$ for the $S = \frac{1}{2}$ Ising model. It is this relatively rapid (exponential) growth of ξ with β in the Ising case which we mentioned above as leading to the extraordinary sensitivity of the value of interchain to intrachain exchange ratio J'/J to T_c/J in the Ising system (see Fig. 1).

We turn now to the molecular-field calculation itself. We can treat straightforwardly only those cases where all exchange interactions favor the ultimate magnetic order. These include the fully ferromagnetic problem: all $J, J' \geq 0$; ferromagnetically coupled antiferromagnetic chains: all $J' \geq 0$, all $J \leq 0$; and if the array of chains can be separated into two sublattices with all nearest-neighbor chains on opposite sublattices: all $J' \leq 0$ and all J of the same sign. The case where the nature of the impurities is such that the exchange interactions favor competing ordering modes will be discussed in Sec. IV. We treat the fully ferromagnetic problem explicitly below, but the results can be immediately extended to these other cases. Each spin is surrounded by z' neighbors on nearest-neighbor chains. We take these z' spins to be statistically representative of the crystal as a whole, so that the molecular field on a host spin, e.g., is given as $2z'[(1-\rho) J'_{\mathrm{HH}} \sigma_{\mathrm{H}} + \rho J'_{\mathrm{IH}} \sigma_{\mathrm{I}}]$, where $\sigma_{\mathrm{I}} \equiv \langle S^z \rangle_{\mathrm{I}}$ and $\sigma_{\mathrm{H}} \equiv \langle S^z \rangle_{\mathrm{H}}$ represent averages over all environments of the given spin as well as thermal averages. The dominant correlations determining these averages are those associated with intrachain interactions; ignoring fluctuations due to differing neighboring configurations along a chain restricts validity of the approach to sufficiently low-impurity concentrations ρ. Since weakly coupled impurities—particularly nonmagnetic ones—also limit the intrachain correlation lengths approximately to the average impurity spacing, and since long intrachain correlation lengths are at the basis of the approximation for T_c, we must restrict consideration to sufficiently small ρ in any case. We therefore report results only for $\rho \leq 0.05$. Within this mean-field approximation the effective Hamiltonian for the nth chain can be written as $\mathcal{H}(n) = \mathcal{H}_0(n) + \mathcal{H}'(n)$, where $\mathcal{H}_0(n)$ contains only the intrachain interactions, and

$$\begin{aligned} \mathcal{H}'(n) \simeq -\sum \{ & P_{n,i} [g_{\mathrm{I}} \mu_B H_0 + 2\rho J'_{\mathrm{II}} z' \sigma_{\mathrm{I}} \\ & + 2(1-\rho) J'_{\mathrm{IH}} z' \sigma_{\mathrm{H}}] + (1 - P_{n,i}) [g_{\mathrm{H}} \mu_B H_0 \\ & + 2\rho J'_{\mathrm{IH}} z' \sigma_{\mathrm{I}} + 2(1-\rho) J'_{\mathrm{HH}} z' \sigma_{\mathrm{H}}] \} S_{n,i}^z , \end{aligned} \tag{2.8}$$

where the external uniform field strength is H_0.

Standard linear response theory gives

$$\langle S^z_{n,j}\rangle = -\beta\langle S^z_{n,j}\mathcal{H}'(n)\rangle \tag{2.9}$$

which results in two linear equations for σ_{H} and σ_{I}:

$$L(T)\begin{pmatrix}\sigma_{\text{I}}\\ \sigma_{\text{H}}\end{pmatrix} = H_0\begin{pmatrix}c_1\\ c_2\end{pmatrix}. \tag{2.10}$$

As we are interested only in $H_0 = 0$, we will have no further need of the constants c_1 and c_2. Explicit expressions for the matrix $L(T)$ are given in Ref. 6 for the classical Heisenberg case. It is clear from Eqs. (2.8) and (2.9) that the elements of $L(T)$ are linear in the sums over two-spin correlation functions,

$$\Omega_{AB} = \sum_{j\neq i}\langle \hat{S}_{n,i}\cdot\hat{S}_{n,j}\rangle_{AB}. \tag{2.11}$$

These functions are evaluated explicitly by the solution of Eq. (2.8), which has been carried out in detail in the Appendix. The critical temperature T_c is determined as the highest temperature T for which the homogeneous equation, (2.10) with $H_0 = 0$, has a nontrivial solution:

$$\begin{aligned}0 = \det L(T_c) = 1 &- 2\alpha\beta_c z'\{\rho(\rho\Omega_{\text{II}}+1)J'_{\text{II}}\\ &+2\rho(1-\rho)J'_{\text{IH}}\Omega_{\text{IH}}+(1-\rho)[(1-\rho)\Omega_{\text{HH}}+1]J'_{\text{HH}}\}\\ &+(2\alpha\beta_c z')^2[J'_{\text{II}}J'_{\text{HH}}-(J'_{\text{IH}})^2]\rho(1-\rho)\\ &\times[1+\rho\Omega_{\text{II}}+(1-\rho)\Omega_{\text{HH}}+\rho(1-\rho)(\Omega_{\text{II}}\Omega_{\text{HH}}-\Omega^2_{\text{IH}})],\end{aligned} \tag{2.12}$$

where α is the diagonal correlation function $\langle(S^z_{n,i})^2\rangle = 1$ (Ising) or $\frac{1}{3}$ (classical Heisenberg). We have solved this numerically for representative values of the parameters ρ, J_{AB} and J'_{AB}.

III. RESULTS AND DISCUSSION

A. Ising model

We consider first the Ising $S = \frac{1}{2}$ case. The most effective reduction of the single chain correlation range by substitutional impurities, and therefore the greatest reduction of the ordering temperature T_c, is accomplished if those impurities are nonmagnetic. This is clearly also a case of substantial experimental interest, with nonmagnetic ions readily identified and unambiguously characterized. The number of parameters characterizing the system is also reduced to a minimum. We treated this problem in Ref. (3) within a model, chosen for simplicity of exposition, in which the impurities were regularly spaced along the chains. The results can be immediately extended to the random distribution appropriate to a quenched alloy. The susceptibilities of the various magnetically isolated segments along a chain are weighted according to the statistical probabilities of finding segments of every possible length for a given impurity concentration, rather than taking the susceptibility of an average length segment as in the regularly spaced impurity model. The result for T_c is of course identical to that given by Eq. (2.12) with all impurity-associated exchange constants and correlation functions ($J'_{\text{IH}}, J'_{\text{II}}, \Omega_{\text{IH}}, \Omega_{\text{II}}$) set equal to zero:

$$2z'J'(1-\rho)\left(\frac{1+(1-\rho)\tanh 2\beta_c J}{1-(1-\rho)\tanh 2\beta_c J}\,\beta_c\right) = 1\ . \tag{3.1}$$

The factor in large brackets, which is $[(1-\rho)\Omega_{\text{HH}}+1]\beta_c$ in the notation appearing in Eq. (2.12), is readily identified as the spin susceptibility per magnetic ion of the isolated impure single chain.[7,8] The factor $2z'J'(1-\rho)$ is the average molecular field on that chain per unit magnetization. Thus Eq. (3.1) is the expected mean-field expression for the critical temperature. The factor of $(1-\rho)$ in the denominator of the susceptibility limits the growth of the coefficient of β_c; the single chain correlation range cannot increase beyond the average impurity spacing. Below the temperature where that is achieved the tanh factor saturates, and each highly correlated segment contributes a Curie law susceptibility $\sim\beta$. Then if J' is suffi-

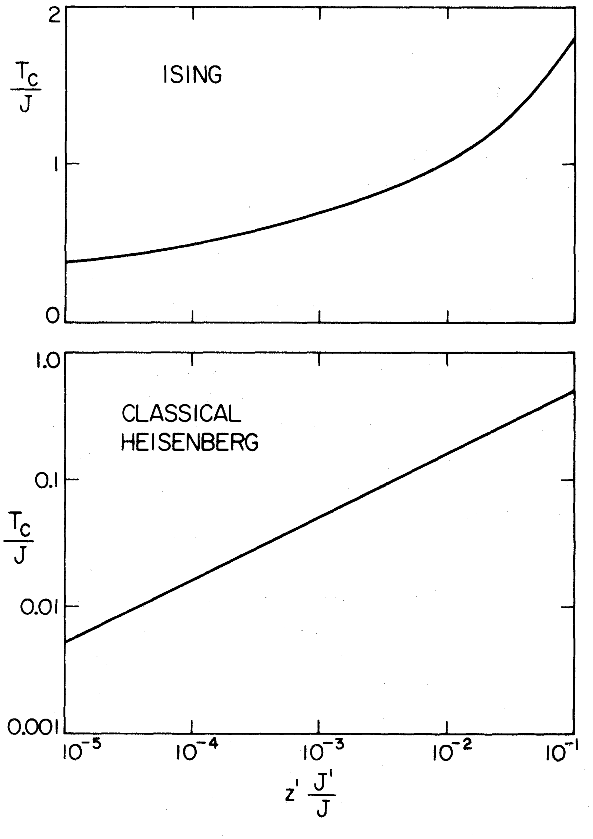

FIG. 1. 3D transition temperature T_c as a function of interchain molecular field $z'J'$, both in units of intrachain exchange J.

ciently small that ordering has not yet occurred at this temperature, the chain susceptibility grows with decreasing temperature at a slower rate than for the pure system and the critical condition (3.1) is correspondingly not achieved until a temperature lower than the pure T_c. This reduction in T_c is shown as a function of ρ in Fig. 2 for representative values of the interchain coupling. It can be very substantial even for impurity concentrations ρ of a few percent or less. Similar reductions should be expected from other defects which break spin communication along a chain. Considering the sensitivity of J'/J to small changes in T_c/J, it is clear that caution is warranted in estimating J' from measurements of T_c/J, and that care must be taken to eliminate nonmagnetic impurities and other defects or to know their concentration accurately. In fact, determination of J' might better be made with the deliberate, but well-controlled, introduction of nonmagnetic impurities.

For low critical temperatures $\beta_c J \gg 1$ and small concentrations ρ we can find asymptotic expressions for T_c useful for extending the results given in Fig. 2. If $e^{-4\beta_c^0 J} \ll \rho \ll 1$, then from Eq. (3.1) we have

$$T_c(\rho)/T_c(0) \approx (2/\rho) e^{-4\beta_c^0 J} . \tag{3.2}$$

We note the difference of a factor of 2 from the corresponding result [Eq. (8a) of Ref. 3] for equally spaced impurities with separation ρ^{-1}. The qualitative behavior is, of course, the same. For $\rho \ll e^{-4\beta_c^0 J}$ we obtain

$$T_c(\rho)/T_c(0) \approx 1 - [e^{4\beta_c^0 J}/2(1+4\beta_c^0 J)]\rho , \tag{3.3}$$

which is identical to the corresponding expression Eq. (8b) of Ref. 3.

We turn now to the behavior of magnetic impurities in these crystals. We have seen that impurities can substantially change the magnetic ordering temperature effectively by modifying the temperature-dependent correlation length ξ of individual chains. As long as the range of exchange coupling is restricted to nearest neighbors it is clear that strongly exchange coupled impurities can produce no significant changes in ξ, regardless of how strong their exchange with their neighbors may be. At best the impurity and its two neighbors will act as a completely coherent entity, simply increasing the effective length scale, or ξ, by a factor $(1+\rho)$. The critical temperature will increase essentially by this factor. Virtually the same argument holds even for strongly antiferromagnetic coupled impurities in the ferromagnet. Therefore the most interesting effects are associated with weakly coupled impurities ($J_{\mathrm{IH}}/J_{\mathrm{HH}} < 1$) and, in particular, the depression of T_c with decreasing exchange ratio $J_{\mathrm{IH}}/J_{\mathrm{HH}}$. In Fig. 3 we have plotted this behavior for a highly one-dimensional host crystal: $z'J'/J = 10^{-3}$, which from Fig. 1 corresponds to $T_c(\rho=0)/J_{\mathrm{HH}} \approx 0.685$. The solid lines give $T_c/T_c(\rho=0)$ as a function of $J_{\mathrm{IH}}/J_{\mathrm{HH}}$ for representative impurity concentrations of $\rho = 0.01$ and 0.05. We chose $J_{\mathrm{II}} = (J_{\mathrm{IH}} J_{\mathrm{HH}})^{1/2}$, but since this impurity-impurity exchange can enter only to order ρ^2, the results are very insensitive to the value chosen. There are two additional interchain exchange parameters, J'_{IH} and J'_{II}, which must also be specified, but as one would anticipate the results are also relatively insensitive to these values. They simply determine the strength of

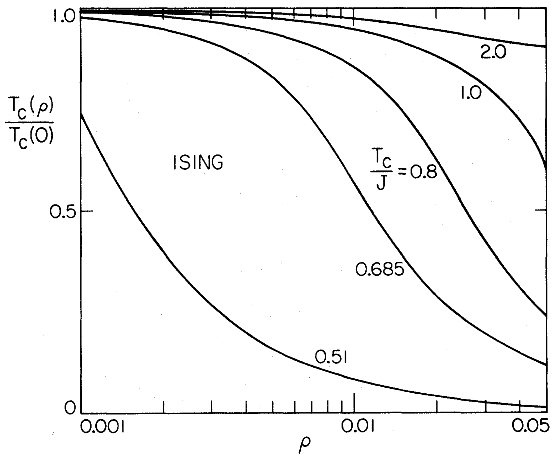

FIG. 2. Relative depression of T_c in the $S=\frac{1}{2}$ Ising system as a function of concentration ρ of nonmagnetic impurities (or equivalent defects). Different curves are labeled by T_c/J for the pure crystal; see Fig. 1 for the corresponding ratio of interchain to intrachain exchange ($z'J'/J \approx 0.2$, 10^{-2}, 2×10^{-3}, and 10^{-4}).

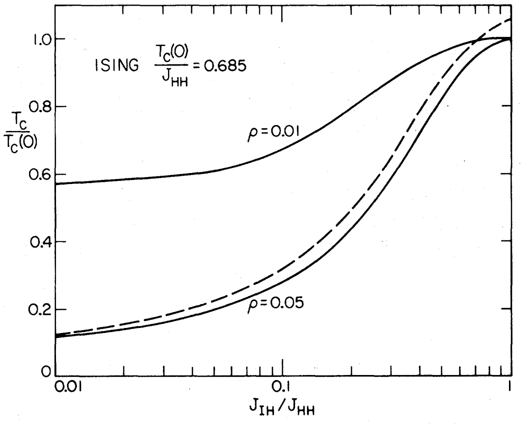

FIG. 3. Relative depression of T_c in the $S=\frac{1}{2}$ Ising system by weakly exchange coupled magnetic impurities as a function of the ratio of impurity-host to host-host exchange strengths, $J_{\mathrm{IH}}/J_{\mathrm{HH}}$. Host crystal is highly one dimensional: $T_c/J = 0.685 \rightarrow z'J'/J \approx 10^{-3}$.

the average effective molecular field, which is changed by terms of order ρ and ρ^2. To demonstrate this we have taken $J'_{\rm IH}=J'_{\rm II}=J'_{\rm HH}$ for the solid curves and $J'_{\rm IH}/J'_{\rm HH}=(J'_{\rm II}/J'_{\rm HH})^{1/2}=5$ for the dashed curve. Even for this unreasonably large value and for the relatively high concentration $\rho=0.05$ we see only a relatively small change in T_c. Fortunately it is then unnecessary to specify these additional parameters accurately in characterizing an experimental system. We point out that Fig. 3 implies substantial reductions in T_c for reasonable values of $J_{\rm IH}/J_{\rm HH}$—e.g., a few tenths or so—for concentrations of a few percent. The asymptotic value appropriate to nonmagnetic impurities is essentially reached for the systems under consideration by the time $J_{\rm IH}/J_{\rm HH}\approx 0.1$.

There are a few examples of quasi-one-dimensional systems that can be described at low temperature by a simple $S=\frac{1}{2}$ Ising model. They are the Co^{2+} salts, such as[5] $\mathrm{CoCl_2\cdot 2NC_5H_5}$ and $\mathrm{CsCoCl_3}$.[9] In the first case ferromagnetic chains are coupled to one another antiferromagnetically ($J>0$, $J'<0$, and $z'=4$), and in the second all exchange interactions are antiferromagnetic. Measurements of the transition temperatures of the above compounds doped with magnetic or nonmagnetic impurities would make an interesting test of our theoretical predictions.

B. Classical Heisenberg model

We can make a similar analysis of the classical Heisenberg system.[6,10] For nonmagnetic impurities we find directly from Eq. (2.12) as the condition determining T_c

$$2z'J'(1-\rho)\left[\frac{1+(1-\rho)U}{1-(1-\rho)U}\left(\frac{\beta_c}{3}\right)\right]=1\ , \qquad (3.4)$$

of the same form as Eq. (3.1) for the Ising model. The square bracket is to be interpreted, as before, as the single chain spin susceptibility per magnetic ion. It differs from the Ising result only in the factor of (1/3) associated with the isotropy of the exchange interactions and therefore of the spin correlation functions, and in form of the correlation function $U=\coth(2\beta_c J)-(2\beta_c J)^{-1}$ [see Eq. (2.4)]. For the large values of $2\beta_c J$ of interest to us $U\approx(1-2\beta_c J)^{-1}$. This gives from Eq. (3.4) the asymptotic expansions

$$\frac{T_c(\rho)}{T_c(0)}\approx\begin{cases}1-[J/T_c(0)]\rho, & \rho\ll T_c(0)/2J\ll 1\\ \frac{1}{2}[T_c(0)/J]\rho^{-1}, & T_c(0)/2J\ll\rho\ll 1\ .\end{cases} \qquad (3.5)$$

We have plotted the numerical results for $T_c(\rho)/T_c(0)$ as a function of ρ in Fig. 4 for values of $T_c(0)/J=0.2$, 0.05, and 0.015 (corresponding, respectively, to $z'J'/J\approx 10^{-2}$, 10^{-3}, and 10^{-4}, according to Fig. 1). As before, we see that there can be very substantial reductions of T_c for quite low concentrations of these nonmagnetic impurities or other defects which break magnetic communication along a chain, so that care must be taken to account for them in interpreting experimental results.

In Fig. 5 we have considered the reduction in T_c to be expected from magnetic impurities in a highly one-dimensional classical Heisenberg crystal: $T_c(0)/J_{\rm HH}=0.015$, or $z'J'/J\simeq 10^{-4}$, approximately the value appropriate to TMMC. We observe a more gradual approach to the nonmagnetic limit with decreasing $J_{\rm IH}/J_{\rm HH}$ than was seen in Fig. 3 for the Ising model. This is a consequence of the difference in dependence on J of the correlation lengths—exponential in the Ising model and algebraic for the Heisenberg—implying a higher sensitivity to the exchange parameters in the Ising case. As before, the solid curves are drawn for equal interchain exchange values $J'_{\rm IH}=J'_{\rm II}=J'_{\rm HH}$. The extreme choice of $J'_{\rm IH}/J'_{\rm HH}=(J'_{\rm II}/J'_{\rm HH})^{1/2}=5$ is given as a dashed curve to be compared with the corresponding solid line for $\rho=0.05$. In fact, these curves are very nearly proportional to one another. This can be seen analytically in the classical Heisenberg model; because of the simple algebraic expansion of $U\simeq 1-(2\beta J)^{-1}$ at large βJ we can find directly from Eq. (2.12)

$$\frac{T_c(\rho)}{T_c(0)}\approx 1-\left(\frac{J_{\rm HH}}{J_{\rm IH}}-\frac{J'_{\rm IH}}{J'_{\rm HH}}\right)\rho\quad (J'_{\rm IH}\neq 0)\ , \qquad (3.6)$$

when the second term is not too large (in particu-

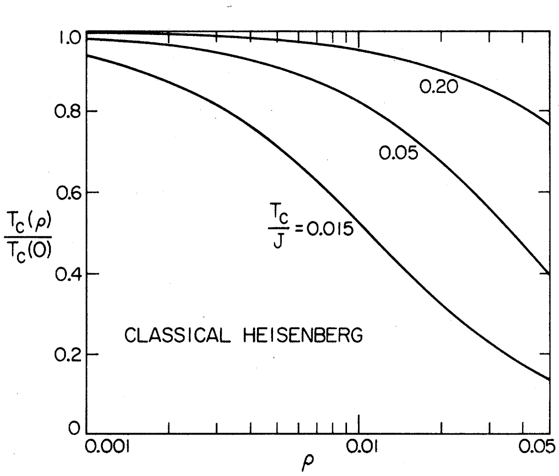

FIG. 4. Reduction of T_c in classical Heisenberg system with concentration ρ of nonmagnetic impurities. Values 0.2, 0.05, and 0.015 for T_c/J correspond (see Fig. 1) approximately to $z'J'/J=10^{-2}$, 10^{-3}, and 10^{-4}, respectively.

lar, the nonmagnetic case, $J_{IH}=0$, can never be expanded in this way).

There are several quasi-one-dimensional compounds whose magnetic properties have been successfully analyzed using the classical Heisenberg model. Among them TMMC (spin $S=\frac{5}{2}$) and $CsNiF_3$ (spin $S=1$), which are both highly one dimensional, may be particularly interesting candidates for experimental comparison with the theory.

IV. IMPURE SYSTEMS WITH "INCOMPLETE ORDERING"

The systems considered above have been characterized by interchain interactions between host spins which all promote the ultimate magnetic order. This order is of a conventional type, signaled by a divergence in the static susceptibility $\chi(q)$ at $T=T_c$, for some value of the wave vector q, with a nonvanishing order parameter $\langle S^z(q)\rangle$ below T_c. In this section we consider a class of impure systems which are not characterized by such an order parameter at low temperatures, because it is energetically unfavorable for the order parameter in consecutive pure segments along a chain to be consistent everywhere with the net interchain molecular field. As a simple example, let us compare the two situations shown in Fig. 6, both representing impure quasi-one-dimensional systems with ferromagnetic coupling between host spins. In Fig. 6(a) antiferromagnetic *site* impurities replace host spins located at positions labeled a_1 and a_2; in Fig. 6(b) antiferromagnetic *bond* impurities (e.g., substitution of ligand ions in a superexchange bond) are located at positions b_1 and b_2. In both cases we assume the "impurity-host" intrachain interaction strength, $|J_{IH}|$, to be of the same order of magnitude as the "host-host" value, J_{HH}. At low temperatures, $kT \ll |J_{IH}|$, J_{HH} the favored spin configurations (overwhelmingly determined by intrachain exchange) are shown schematically in the figure. In case a the spins on both sides of the impurity remain parallel, whereas in case b, the spins above and below the impurity are antiparallel. If we now consider the interchain configuration, neglecting the possibility that impurities on nearest-neighbor chains may face each other, we find that not all the interactions favor the assumed state. For example, all the spins below the impurity on the left-hand chain of Fig. 6(b) are conveniently parallel to the corresponding ones on the right-hand chain (this will not be the case once we get to the next impurity down either of the chains). However, the spins above b_1 and below b_2 are antiparallel, while those above both b_1 and b_2 are again parallel. It is clear that, on the average, there will be equal numbers of favorable and unfavorable interchain bonds in the assumed configuration.

While our formulation of Sec. II does not cover this interesting case, we believe the the physical understanding of the three-dimensional ordering process gained by our theory may tell us what should happen qualitatively. We tentatively expect the system to go, as $T\rightarrow 0$, to a state (which may well be one of a nearly degenerate manifold) in which each spin points in a well defined direction to optimize the exchange energy of the local impurity configuration discussed above; the con-

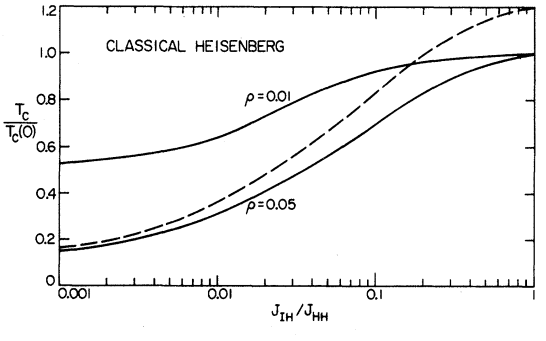

FIG. 5. Relative change in T_c for the classical Heisenberg system with impurity-host to host-host exchange ratio. Host crystal chosen has $T_c/J=0.015$, or $z'J'/J \approx 10^{-4}$.

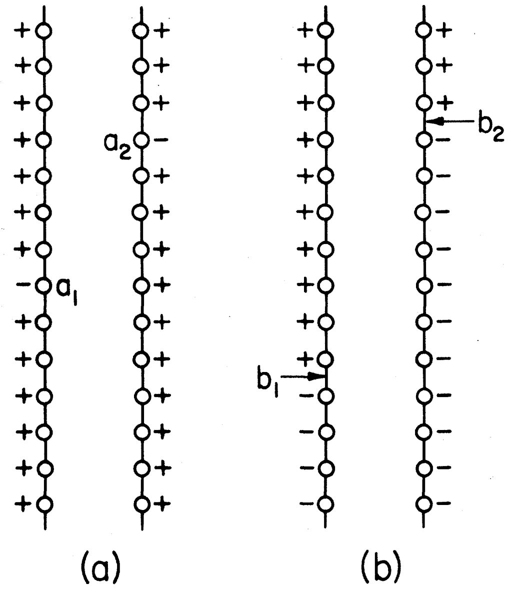

FIG. 6. Neighboring pairs of ferromagnetic chains ($J_{HH}>0$, $J'>0$) with (a) antiferromagnetic site impurities, $J_{IH}<0$, at positions a_1 and a_2; (b) antiferromagnetic bond impurities at positions b_1 and b_2. Labels + and − indicate the spin ordering imposed by intrachain interactions.

figuration of a given spin does not determine the average configuration of distant spins in an "ordered" (ferromagnetic, antiferromagnetic or any other type) fashion. Thus, there should be no magnetic Bragg scattering due to a long-range order. However, this sort of "spin glass" structure is almost static, except for extremely improbable jumps between nearly degenerate states. One would thus predict that neutron scattering from this structure should be essentially elastic. We can make a simple estimate of the characteristic temperature for this incomplete ordering. Recall that T_c in case a (all interactions favor the same ordering) was given in our approximation by $z'J'$ times the number of spins in a large length $L\sim\xi_{1\mathrm{D}}$. In fact, T_c is virtually unaffected by the impurities, even though they are antiferromagnetic, since for $|J_{\mathrm{IH}}|\sim J_{\mathrm{HH}}$ the correlation length in a single chain is substantially unchanged. Now consider case b. If $\xi_{1\mathrm{D}}$ is substantially less than the average interimpurity spacing $\rho^{-1}d$, we would expect L to remain of order $\xi_{1\mathrm{D}}$. However, in the opposite limit, $\xi_{1\mathrm{D}} >> \rho^{-1}d$, the reversal of all spins in a given correlated segment of length $\xi_{1\mathrm{D}}$ will raise the energy of some of its exchange bonds with neighboring chains and lower the energy of others. Since the impurity positions are random, the net change in energy will be of the order of $J'(z'\rho^{-1}\xi_{1\mathrm{D}}/d)^{1/2}$. Thus we estimate the characteristic temperature $T_{3\mathrm{D}}$, around which the 3D correlations build up, to be of the order

$$kT_{3\mathrm{D}}\sim\begin{cases} z'J'(\xi_{1\mathrm{D}}/d) & \text{for } \rho^{-1}d>>\xi_{1\mathrm{D}}\,, \\ J'(z'\rho^{-1}\xi_{1\mathrm{D}}/d)^{1/2} & \text{for } \rho^{-1}d<<\xi_{1\mathrm{D}}\,. \end{cases} \tag{4.1}$$

The same type of considerations should hold also for other quasi-one-dimensional systems. In particular, it is tempting to argue that the build up of incomplete three-dimensional ordering in the quasi-one-dimensional conductor KCP in the temperature region around 50–100 K is due to a similar mechanism. This incomplete ordering is now well documented by both x-ray and neutron scattering measurements.[11] The role of impurities in these one-dimensional conductors was emphasized by Sen and Varma,[12] while Sham and Patton[13] have recently proposed a model where the disorder along the chain, e.g., the bromine ions, smears the phase transition and leads to a central peak. Our considerations emphasize that defects and impurities, once their concentration is in the range of $\rho\sim d/\xi_{1\mathrm{D}}$ (which is less than 1% for[11] KCP at $T=T_c$) may be of decisive importance for the 3D ordering. An experimentally testable prediction of all the models in which the incomplete three-dimensional ordering is due to pinning by impurities is that the quasi-Bragg scattering characteristic of the 3D ordering, which has a finite width in $\mathbf{K}$ space, should be nearly elastic; i.e., centered around $\omega=0$ with a very small width as a function of the energy transfer $\hbar\omega$. This is due to the fact that the low-temperature structure, in spite of not having conventional long-range order, is essentially static, as discussed above. We reemphasize that although it is clear that the specifics of the impurities may determine even the nature of the low-temperature state, our conclusions in this section are rather tentative. Our main intention here is to call attention to the dramatic role of impurities, possibly even in concentrations of less than one percent, for chainlike systems. At the same time, the predictions of Secs. II and III remain quantitative. We hope that new experiments with small controlled impurity concentrations will further probe the quasi-one-dimensional structures.

APPENDIX: SOLUTION OF EQ. (2.7)

The calculation proceeds exactly as in Ref. (6). We diagonalize D by the similarity transformation

$$R^{-1}DR=\begin{pmatrix} d_+ & 0 \\ 0 & d_- \end{pmatrix},$$

where the secular equation $\det|D-d\underline{1}|=0$ gives immediately

$$d_\pm=\tfrac{1}{2}\left(\rho U_{\mathrm{II}}+(1-\rho)U_{\mathrm{HH}}\pm\{[\rho U_{\mathrm{II}}-(1-\rho)U_{\mathrm{HH}}]^2+4\rho(1-\rho)U_{\mathrm{IH}}^2\}^{1/2}\right), \tag{A1}$$

and R is formed from the eigenvectors of D:

$$R=[(1-\rho)U_{\mathrm{IH}}(d_+-d_-)]^{-1/2}\times\begin{pmatrix} (1-\rho)U_{\mathrm{IH}} & (1-\rho)U_{\mathrm{IH}} \\ d_+-\rho U_{\mathrm{II}} & d_--\rho U_{\mathrm{II}} \end{pmatrix}, \tag{A2}$$

which is indeterminate only in the case $J_{\mathrm{IH}}=0$ (so that $U_{\mathrm{IH}}=0$), when D is already diagonal and R is the unit matrix. Except for this case we can then write R^{-1} as

$$R^{-1}=[(1-\rho)U_{\mathrm{IH}}(d_+-d_-)]^{-1/2}\times\begin{pmatrix} \rho U_{\mathrm{II}}-d_- & (1-\rho)U_{\mathrm{IH}} \\ d_+-\rho U_{\mathrm{II}} & -(1-\rho)U_{\mathrm{IH}} \end{pmatrix}. \tag{A3}$$

For the solution of Eq. (2.7) we need

$$D^{l-1}=R\begin{pmatrix} d_+^{l-1} & 0 \\ 0 & d_-^{l-1} \end{pmatrix}R^{-1}\,.$$

Finally, summing over $l\neq0$ we have the result

$$\begin{pmatrix} \Omega_{\mathrm{II}} & \Omega_{\mathrm{HI}} \\ \Omega_{\mathrm{IH}} & \Omega_{\mathrm{HH}} \end{pmatrix} = 2R \begin{pmatrix} (1-d_+)^{-1} & 0 \\ 0 & (1-d_-)^{-1} \end{pmatrix} \times R^{-1} \begin{pmatrix} U_{\mathrm{II}} & U_{\mathrm{IH}} \\ U_{\mathrm{IH}} & U_{\mathrm{HH}} \end{pmatrix}, \qquad \text{(A4)}$$

where the $\mathbf{\Omega}_{AB}$ are defined in Eq. (2.11).

If one carries through these matrix multiplications, substituting the expressions (A1) for $d_\pm$, the expressions reduce to the relatively simple forms

$$\Omega_{\mathrm{II}} = 2\left[U_{\mathrm{II}} - (1-\rho)(U_{\mathrm{II}}U_{\mathrm{HH}} - U_{\mathrm{IH}}^2)\right]/B\,,$$
$$\Omega_{\mathrm{IH}} = 2U_{\mathrm{IH}}/B\,,$$
$$\Omega_{\mathrm{HH}} = 2\left[U_{\mathrm{HH}} - \rho(U_{\mathrm{II}}U_{\mathrm{HH}} - U_{\mathrm{IH}}^2)\right]/B\,, \qquad \text{(A5)}$$

where the denominator in each case is

$$B = 1 - \left[\rho U_{\mathrm{II}} + (1-\rho)U_{\mathrm{HH}}\right] + \rho(1-\rho)(U_{\mathrm{II}}U_{\mathrm{HH}} - U_{\mathrm{IH}}^2). \qquad \text{(A6)}$$

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