Impurities in quasi-one-dimensional Heisenberg systems: The effect of anisotropy

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The effect of small concentrations of impurities on the magnetic behavior of quasi-one-dimensional Heisenberg systems with a small orthorhombic anisotropy has been studied both theoretically and experimentally. The predicted reduction of the ordering temperature T_N as a function of impurity concentration x is compared with experimental data on $(CH_3)_2NH_2Mn_{1-x}Cd_xCl_3$ (DMMC:Cd), $(CH_3)_2NH_2Mn_{1-x}Cu_xCl_3$ (DMMC:Cu), and $CsMn_{1-x}Cu_xCl_3 \cdot 2H_2O$ (CMC:Cu). We also measured the magnetic phase diagram of DMMC:Cd $(x = 0.77\%)$ along each of the three principal directions. The observed behavior can be qualitatively explained by the theory presented in this paper.

I. INTRODUCTION

In the last few years, many experimental and theoretical studies have been devoted to the influence of impurities on the behavior of magnetic systems. Especially in quasi-one-dimensional antiferromagnetic systems, the substitution of weakly or nonmagnetic impurities at magnetic sites has been found to have rather drastic effects.[1-7] One of the most pronounced features is the strong reduction of the three-dimensional ordering temperature T_N. This reduction is generally explained[8,9] as follows. Because of the large intrachain interaction J, the magnetic correlations along the individual chains are very well developed in the paramagnetic region, especially at lower temperatures. Therefore, the presence of even a very small interchain coupling J' may already trigger three-dimensional long-range order. As a first approximation, it is assumed that the substitution of impurities gives rise to a decrease of the intrachain correlations, which strongly reduces the "net effect" of the interchain interactions and hence the three-dimensional ordering temperature.

Generally, the problem is treated theoretically by considering the interchain coupling within a mean-field approach, whereas the properties of the individual chains are calculated within the classical spin formalism.[8-11] Using this approach, Hone *et al.*[9] have evaluated the reduction of T_N for quasi-one-dimensional systems in which the magnetic interactions are fully isotropic.

Recently it has been found[7] that the experimental reduction of T_N in Cd- or Cu-doped $(CH_3)_4NHMnCl_3$ (TMMC) is significantly larger than this theoretical prediction. It was assumed that the discrepancy results from the anisotropy of dipolar interactions between the Mn^{++} spins, which has been shown[12,13] to give rise to an XY rather than Heisenberg-like behavior of the correlation length ξ at lower tempera-

tures in this compound. The large effect of even a small amount of anisotropy on the properties of quasi-one-dimensional magnetic systems seems to be a quite common feature, as is also evident from the peculiar behavior of their magnetic phase diagrams.[14,15] Therefore we thought it worthwhile to investigate in more detail the reduction of T_N as a function of the concentration of nonmagnetic impurities in the presence of orthorhombic anisotropy.

The organization of this paper will be as follows. In the next section we will extend the calculations on the linear chain classical spin model including orthorhombic anisotropy[15] to the randomly diluted system. In Sec. III the results will be confronted with experimental data on $(CH_3)_2NH_2Cd_xMn_{1-x}Cl_3$ (DMMC:Cd). Some attention will be given to the effect of substitution of Cu instead of Cd and the behavior of $CsMnCl_3 \cdot 2H_2O$ (CMC). The effect of dilution on the magnetic phase diagram will also be considered.

II. THEORY

Given the fact that the characteristics of quasi-one-dimensional systems are believed to arise largely from the properties of the individual chains, we will follow the usual approach, in which the magnetic behavior of the isolated chains is calculated as accurately as possible, whereas the interchain interactions are treated within the mean-field approximation. If the intrachain interaction is antiferromagnetic, the ordering temperature T_N of such a system is given by[16]

$$2zJ'\chi_{st}^{1D}(T_N) = 1 , \tag{1}$$

where χ_{st}^{1D} denotes the staggered susceptibility of an isolated chain and $2zJ'$ represents the interchain coupling.

Let us consider the following classical Hamiltonian

of orthorhombic symmetry describing an individual chain:

$$\mathcal{H}_{chain} = \sum_{i=1}^{N} \mathcal{H}(\vec{s}_i, \vec{s}_{i+1})$$

$$= -\sum_{i=1}^{N} \{\tfrac{1}{2} g\mu_B HS(s_i^z + s_{i+1}^z) + 2JS(S+1)[\vec{s}_i \cdot \vec{s}_{i+1} + e_z(s_i^z s_{i+1}^z - \tfrac{1}{2} s_i^x s_{i+1}^x - \tfrac{1}{2} s_i^y s_{i+1}^y) + \tfrac{1}{2} e_{xy}(s_i^x s_{i+1}^x - s_i^y s_{i+1}^y)]\} \quad . \tag{2}$$

In this equation

$$\vec{s}_i = (s_i^x, s_i^y, s_i^z) = (\cos\phi_i \sin\theta_i, \sin\phi_i \sin\theta_i, \cos\theta_i) \quad ,$$

H denotes the external magnetic field ($\||z$), and J corresponds to the isotropic part of the nearest-neighbor interaction. $e_z = (J^{zz} - J)/J$ and $e_{xy} = (J^{xx} - J^{yy})/J$ denote the axial and nonaxial part of the anisotropy with respect to z, respectively. Generally a Hamiltonian of this type is solved by means of the transfer-matrix formalism.[17-19] The transfer matrix is given by

$$A(\vec{s}_i, \vec{s}_{i+1}) = \exp[-\beta\mathcal{H}(\vec{s}_i, \vec{s}_{i+1})] \tag{3}$$

$$(\beta = 1/kT) \quad .$$

Its eigenfunctions $\psi_{lm}(\vec{s})$ and eigenvalues λ_{lm} are defined by the integral equation:

$$\int A(\vec{s}_i, \vec{s}_{i+1})\psi_{lm}(\vec{s}_{i+1}) \, d\vec{s}_{i+1} = \lambda_{lm}\psi_{lm}(\vec{s}_i) \quad , \tag{4}$$

in which i can be chosen arbitrarily. In the present case, this equation can be written as:

$$\int_0^\pi d\theta_2 \int_0^{2\pi} d\phi_2 \sin\theta_2 \exp[-\beta\mathcal{H}(\vec{s}_1, \vec{s}_2)]\psi_{lm}(\theta_2, \phi_2)$$

$$= \lambda_{lm}\psi_{lm}(\theta_1, \phi_1) \quad . \tag{5}$$

In the thermodynamic limit ($N \to \infty$) all static properties of the chain can be expressed in the eigenvalues and eigenfunctions defined by this equation; in particular the correlation function of the spin components along the z direction is given by

$$\langle s_i^z s_{i+q}^z \rangle = \sum_{l=0}^{\infty} \left(\frac{\lambda_{l0}}{\lambda_{00}}\right)^q \left| \int \psi_{l0}^*(\vec{s}) s^z \psi_{00}(\vec{s}) \, d\vec{s} \right|^2$$

$$\equiv \sum_{l=0}^{\infty} \left(\frac{\lambda_{l0}}{\lambda_{00}}\right)^q c_l^2 \quad , \tag{6}$$

whereas the expectation value $\langle s_q^z \rangle^2$ can be written as

$$\langle s_q^z \rangle^2 = \left| \int \psi_{00}^*(\vec{s}) s^z \psi_{00}(\vec{s}) \, d\vec{s} \right|^2 \equiv c_0^2 \quad . \tag{7}$$

Similar expressions can be derived for $\langle s_i^x s_{i+q}^x \rangle$, $\langle s_i^y s_{i+q}^y \rangle$, $\langle s_q^x \rangle^2$, and $\langle s_q^y \rangle^2$. In Eqs. (6) and (7) $\psi_{00}(\vec{s})$ denotes the eigenfunction corresponding to the largest eigenvalue λ_{00}. The calculation of the eigenvalues λ_{lm} and the eigenfunctions ψ_{lm} from Eq.

(5) has been briefly outlined in Ref. 15. A more detailed treatment of the various numerical procedures will be published elsewhere.[20] The values of c_l^2 and λ_{l0} depend on J/kT, e_z/kT, e_{xy}/kT, and the magnitude of the applied magnetic field.

As was already mentioned in the Introduction, the intrachain correlations largely dominate the behavior of a quasi-one-dimensional system upon dilution. In order to obtain a qualitative picture of the effect of anisotropy, we have calculated the inverse correlation length κ, which for an antiferromagnetic chain can be defined by[17,18]:

$$\kappa_\alpha^2 = \frac{2\sum_q[(-1)^q(\langle s_0^\alpha s_q^\alpha \rangle - \langle s_0^\alpha \rangle^2)]}{\sum_q[(-1)^q q^2(\langle s_0^\alpha s_q^\alpha \rangle - \langle s_0^\alpha \rangle^2)]}, \quad \alpha = x,y,z \quad . \tag{8}$$

In Fig. 1 the inverse correlation length κ of the spin components along the "preferred" direction is plotted as a function of the reduced temperature T^* $= kT/2|J|S(S+1)$ for several values of the anisotropy. The dashed curves denote the limiting cases: isotropic (Heisenberg), XY ($J_{zz} = 0, J_{xx} = J_{yy} = J$), and Ising. The drawn curves reflect the results for CMC and DMMC, using the values for the anisotropy reported in the literature.[15,22] Inspection of this figure shows that a small orthorhombic anisotropy, which will be present in all real systems, except when forbidden by symmetry, causes a drastic increase of the correlation length at lower temperatures. Hence the substitution of nonmagnetic impurities will have a more pronounced effect on the intrachain correlations than in the isotropic case, and one may anticipate a larger reduction of the reduced three-dimensional ordering temperature (T_N^*). A quantitative description of this effect is most readily given in terms of the staggered susceptibility [cf. Eq. (1)].

The wave-vector-dependent susceptibility per spin along the z axis of an isolated chain of infinite length is given by

$$\chi^{zz}(k) = \frac{g^2\mu_B^2 S(S+1)}{kT}$$

$$\times \sum_{q=-\infty}^{\infty} \cos(qak)(\langle s_0^z s_q^z \rangle - \langle s_q^z \rangle^2) \quad ; \tag{9}$$

a denotes the spacing between adjacent magnetic ions. A similar expression can be derived for $\chi^{xx}(k)$
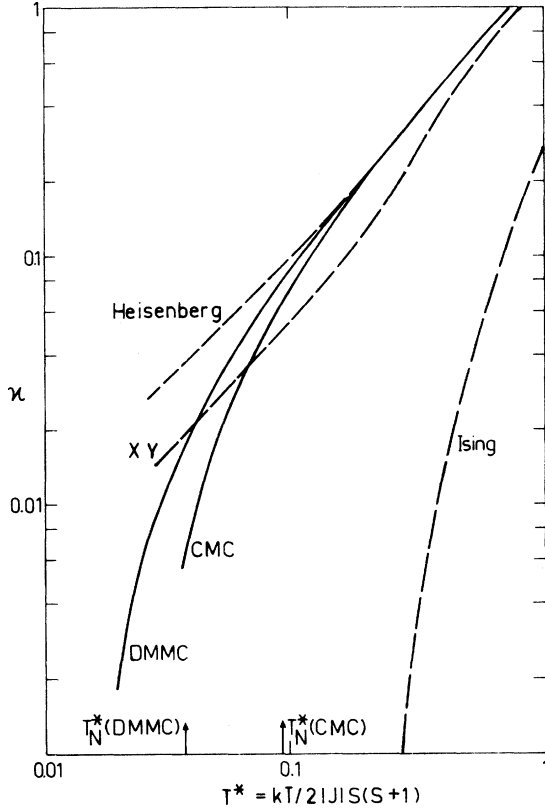
FIG. 1. Temperature dependence of the inverse correlation length κ of the spin components along the "preferred" direction for some one-dimensional magnetic systems having different degrees of anisotropy. The drawn lines denote the behavior of the individual chains in DMMC and CMC.

and $\chi^{yy}(k)$. Substitution of Eqs. (6) and (7) in Eq. (9) yields

$$\chi^{zz}(k) = \frac{g^2\mu_B^2 S(S+1)}{kT} \sum_{q=-\infty}^{\infty} \cos(qak) \sum_{l=1}^{\infty} \left[\frac{\lambda_{l0}}{\lambda_{00}}\right]^q c_l^2 .$$

(10)

For $k = 0$ and π/a the summation over q consists of two geometric series, and can be performed analytically. Formally Eqs. (6) and (7) are only correct in the thermodynamic limit, in which case the largest eigenvalue is sufficient to describe the partition function $Z = \sum_n (\lambda_n)^N$. For a randomly diluted system, these equations are only correct if the average length of the chain segments is very large, i.e., for small impurity concentrations x. Numerical calculations for a set of parameters appropriate to DMMC indicate that at an impurity concentration of 1%, the actual partition function differs only a few percent from λ_{00}^N. Secondly, we wish to note that for a finite anisotropic chain $\langle s_i^z s_{i+q}^z \rangle$ is dependent of both i and the length N of the chain. Therefore the staggered susceptibility will not be the same for all magnetic

ions, a complication which does not occur for isotropic or Ising systems in zero magnetic field. In principle, the resulting modifications for the isolated chain may be calculated.[19] However, in our opinion the rather tedious numerical procedures involved with such an approach would only be justified if the interchain interactions were described in much more detail than the present mean-field approximation. Therefore, we will assume that for $x \ll 1$, Eqs. (6) and (7) describe the overall behavior of the various chain segments fairly accurately, an assumption that is certainly correct in the limit $x \rightarrow 0$.

As the correlation function $\langle s_0^z s_q^z \rangle$ falls off with distance as a sum of exponentials instead of a single exponent as in the isotropic or Ising case, we will not apply the recursion relation formalism given by Thorpe[11] and Hone et al.,[9] but proceed in a slightly different way. We assume that the impurities are randomly distributed (quenched limit). In principle, Eq. (9) is still valid for an infinite diluted chain with the following obvious modifications. If the site labeled 0 contains an impurity, both $\langle s_0^z s_0^z \rangle$ and $\langle s_0^z \rangle^2$ are equal to zero; $\langle s_q^z \rangle^2 = 0$ if the site q is occupied by an impurity. If we have a random distribution of impurities, a configuration average over an infinite system yields

$$\langle\langle s_0^z s_0^z \rangle\rangle = (1-x) \sum_{l=0}^{\infty} c_l^2 ,$$

$$\langle\langle s_0^z \rangle^2\rangle = \langle\langle s_q^z \rangle^2\rangle = (1-x)c_0^2 ,$$

(11)

in which we used Eqs. (6) and (7). The configuration average $\langle\langle s_0^z s_q^z \rangle\rangle$ can be obtained as follows. Let s_0 be a magnetic ion belonging to an arbitrary chain segment. The probability that s_1 is also a magnetic ion is equal to $(1-x)$ and hence the probability that a chain of magnetic ions $s_0, s_1, \ldots, s_q$ is present is equal to $(1-x)^q$. For such a chain we have assumed that $\langle s_0^z s_q^z \rangle$ may be approximated by Eq. (6); if an impurity would be present within the chain, $\langle s_0^z s_q^z \rangle$ would be equal to zero. If we take a configuration average over all sites s_0 (both magnetic and nonmagnetic), we obtain

$$\langle\langle s_0^z s_q^z \rangle\rangle = (1-x)(1-x)^q \sum_{l=0}^{\infty} \left[\frac{\lambda_{l0}}{\lambda_{00}}\right]^q c_l^2 . \quad (12)$$

Substitution of Eqs. (11) and (12) in Eq. (9) yields the average wave-vector-dependent susceptibility per site for a diluted system:

$$\chi^{zz}(k,x) = (1-x)\frac{g^2\mu_B^2 S(S+1)}{kT}$$

$$\times \sum_{q=-\infty}^{\infty} \cos(qak) \sum_{l=1}^{\infty} \left[\frac{\lambda_{l0}}{\lambda_{00}}(1-x)\right]^q c_l^2 . \quad (13)$$

The calculation of the eigenfunctions and eigenvalues of the transfer matrix remains unaffected, the only

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modification is the multiplication of $\lambda_{l0}/\lambda_{00}$ by $(1-x)$. For the isotropic case, the procedure outlined above yields a result identical to that given by Thorpe.[11] The average staggered susceptibility $\chi_{st}^{zz}(x)$ may be obtained from Eq. (13) by setting $k = \pi/a$.

As already mentioned above, the three-dimensional ordering temperature of an infinite ensemble of loosely coupled chains is implicitly given by Eq. (1). In a diluted system, however, the effective interchain coupling zJ' is reduced by a factor $(1-x)$, at least for impurity concentrations $x \ll 1$. Therefore this equation should be modified to

$$2zJ'(1-x)\chi_{st}^{1D}(x,T_N) = 1 \quad . \tag{14}$$

If the intrachain interaction and the magnetic anisotropy are known, the behavior of $T_N(x)$ may be found by plotting $(1-x)\chi_{st}^{1D}(x,T)$ as a function of temperature for different values of x. In Fig. 2 a graphical method is shown to obtain $T_N(x)$. The mean-field interaction $2zJ'$ between the chains may be eliminated by inserting the experimentally observed ordering temperature $T_N(x=0)$. Some typical results of this procedure are shown in Fig. 3 for an isotropic and anisotropic system. The value of $T_N^* = kT_N/2|J|S(S+1)$ indicates the degree of one dimensionality. Inspection of this figure shows that the effect of anisotropy drastically increases with increasing degree of one dimensionality (low values of T_N^*), as might have been anticipated already from the behavior of the correlation length, presented in Fig. 1. For the isotropic case, our results show a slightly larger decrease of T_N than the prediction given by Hone et al.[9] This is caused by the fact that Hone et al. described the response of the diluted chains to a staggered field by the staggered susceptibility per *magnetic ion* instead of the staggered susceptibility per *site*. The behavior of $T_N(x)$ derived above will be confronted with experimental results in the next section.
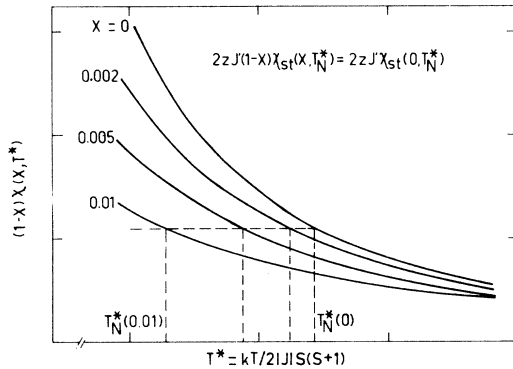

FIG. 2. Temperature dependence of the staggered susceptibility per site for a diluted classical Heisenberg chain. The curves are characterized by the impurity concentration x. The construction to obtain $T_N(x)$ using Eq. (14) is also shown.
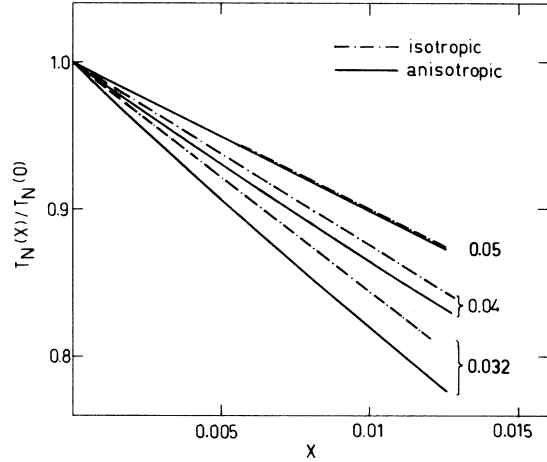

FIG. 3. Reduction of the three-dimensional ordering temperature as a function of impurity concentration x for several quasi-one-dimensional magnetic systems having different degrees of one dimensionality. The results are characterized by the value of the reduced ordering temperature for $x=0$: $T_N^*(0) = kT_N(0)/2|J|S(S+1)$. Dashed lines denote the isotropic case; drawn curves denote the results obtained using the anisotropy parameters for DMMC; i.e., $e_z = -5.75 \times 10^{-3}$, $e_{xy} = +1.15 \times 10^{-3}$.

III. RESULTS AND DISCUSSION

Single crystals of DMMC were obtained by cooling a saturated solution of equimolar quantities of $MnCl_2$ and $(CH_3)_2NH_2Cl$ in absolute ethanol from 60 to 20 °C. Specimens diluted with Cd and Cu were obtained by adding the corresponding chlorides to the solution. To prevent an inhomogeneous impurity distribution within the single crystals only small crystals were used, which were grown from a large amount of the appropriate solution. The impurity concentration x was determined by chemical analysis. The impurity content in the crystals was roughly 1.5 times larger than the corresponding concentration in the solution for DMMC:Cd and 0.4 times for DMMC:Cu. Single crystals of CMC were grown by evaporation of a saturated aqueous solution of $MnCl_2 \cdot 4H_2O$ and CsCl. The Cu doped crystals were obtained by adding $CuCl_2$ to the solution. The Cu concentration in the crystals was found to be 3 times smaller than the concentration in the solution.

The three-dimensional-ordering temperature was obtained from heat-capacity measurements on single crystals of about 0.2 g, and was identified by the maximum of the λ anomaly. The error in T_N due to uncertainties in the calibration of the thermometer and the "rounding" of the specific-heat anomaly did amount to 10–40 mK. As the magnitude of the λ anomaly drastically decreases with increasing impurity

content, our measurements were limited to the region $x < 0.02$ for DMMC and $x < 0.04$ for CMC.

First, we will discuss the results on impurity-doped DMMC. The data are presented in Fig. 4. The theoretical reduction of T_N predicted by Hone *et.al.*,[9] which is represented by a dashed-dotted line, is about 40% smaller than the reduction following from the experimental data on DMMC:Cd if we use an intrachain interaction $J/k = -5.8$ K. This value has been obtained from an analysis of the heat capacity of DMMC in the paramagnetic region.[21] The agreement with the experimental data is significantly improved by the introduction of an appropriate amount of anisotropy. The easy-plane anisotropy may be found experimentally from the magnitude of the spin-flop field. The anisotropy perpendicular to the easy plane may be estimated from a dipole calculation based upon the inferred magnetic space group $P2'_1/c$.[22] Although it is not fully established that the anisotropy in DMMC is completely dipolar in origin, the calculated magnitude correctly explains the observed magnetic phase diagram.[15] In order to obtain a satisfactory agreement with the experimental data on $T_N(x)$, using the anisotropy parameters given in Ref. 15, we have to assume an intrachain exchange interaction $J/k = -6.5$ K. This value is just within the limits of uncertainty $J/k = -5.8 \pm 0.7$ K given in Ref.
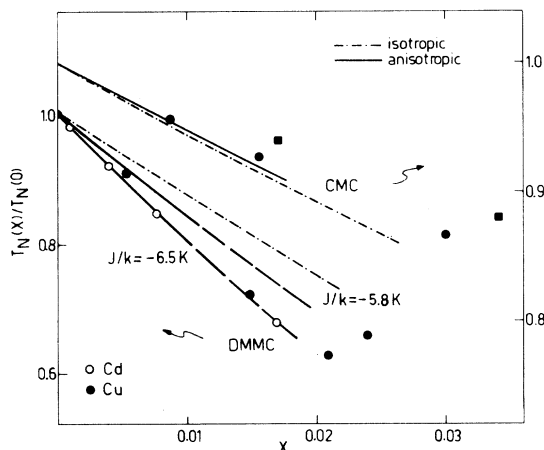

FIG. 4. Behavior of $T_N(x)$ for DMMC:Cd, DMMC:Cu, and CMC:Cu. Experimental data on DMMC:Cd are denoted by open circles, data on DMMC:Cu and CMC:Cu are denoted by black dots. The black squares represent data on CMC:Cu obtained by Velu *et al.* (Ref. 23) from susceptibility measurements, and are plotted for comparison. The predictions assuming an isotropic intrachain interaction ($J/k = -3.0$ K for CMC, $J/k = -5.8$ K for DMMC) are represented by a dashed-dotted line. The drawn curves reflect the effect of an appropriate amount of anisotropy. The dashed part of these curves indicates the region where the actual partition function differs more than 2% from the theoretical approximation. For DMMC $T_N(x)$ is calculated for $J/k = -5.8$ and -6.5 K.

21, but seems somewhat high. Probably this may be caused by the theoretical approximations mentioned in the preceding section, although the quantitative effect of these approximations is very hard to estimate. Just for comparison, we like to note that the theory given by Hone *et al.*[9] yields the observed reduction of T_N for $J/k = -8.2$ K, which is far too high.

In Fig. 4 we have also plotted the results on DMMC:Cu. The experimental decrease of $T_N(x)$ is found to be almost equal to that for DMMC:Cd, indicating a rather small host-impurity interaction J_{IH}. A rough estimate, based upon the theory developed by Hone *et al.*[9] for the isotropic case, yields an upper limit of $|J_{IH}|/k = 0.4$ K. This situation is quite different from TMMC, where substitution of Cu has a much smaller effect on T_N than substitution of Cd, from which an impurity-host interaction $J_{IH}/k = 1.4$ K was inferred.[7] This difference is rather surprising, given the fact that the $Mn-Cl_3-Mn-Cl_3$ chains in DMMC and TMMC are largely similar.[22,24] One might suspect that the relatively small effect of substitution of Cu on the ordering temperature of TMMC is due to clustering of the Cu ions, but this is somewhat unlikely, since also susceptibility measurements give comparable results; $J_{IH}/k = 1.6$ K.[4] Microscopic determination of J_{IH} seems necessary to clarify this question.

The results on CMC:Cu are also plotted in Fig. 4. Both the theoretical predictions for the isotropic and the anisotropic case yield a reduction of T_N which is larger than that shown by the experimental data. The effect of anisotropy is not very pronounced, as might have been anticipated (Fig. 1) from the rather high value of the reduced three-dimensional ordering temperature of CMC ($T_N^* = 0.093$) compared to DMMC ($T_N^* = 0.036$). The calculated reduction of $T_N(x)$ for the anisotropic case is somewhat smaller than that for the isotropic case, which seems rather unphysical. This small discrepancy may result from the fact that the theory outlined above is only strictly valid for $x \to 0$, but may also be attributed to the approximative nature of Eq. (1). Inspection of Fig. 4 shows that in CMC:Cu the host-impurity interaction is not negligible. Since in CMC the anisotropy has only a minor effect, J_{IH} was estimated from the theory outlined in Ref. 9. The result is $|J_{Cu-Mn}|/k = 1.0$ K. A direct comparison of this value with the results on DMMC:Cu and TMMC:Cu is not very meaningful, since the magnetic chains and the intrachain interaction in CMC are quite different from those in DMMC and TMMC.

Next, we will consider the effect of an applied magnetic field H. It is obvious, that the presence of impurities reduces the intrachain correlations. On the other hand, it has been found that these correlations are enhanced by an applied magnetic field.[13-15,18] As the theory presented in Sec. II is in
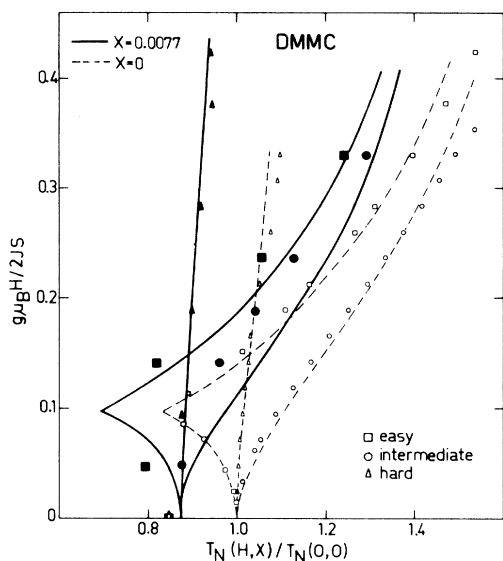
FIG. 5. Magnetic phase diagram of DMMC:Cd for each of the three principal directions. Data for $x = 0.77\%$ and 0 are denoted by black and open symbols, respectively. The theoretical curves are calculated using an intrachain interaction $J/k = -5.7$ K.

principle also valid for $H \neq 0$, we thought it worthwhile to investigate the magnetic phase diagram of DMMC:Cd in order to study the competitive effect of H and dilution both theoretically and experimentally. In Fig. 5 the magnetic phase diagram of DMMC:Cd ($x = 0.77\%$) is plotted for each of the three principal directions for $0 < H < 90$ kOe. The open symbols denote the data for $x = 0$, which are plotted for comparison. For all three principal direc-

tions, the phase boundaries of the diluted system display a more or less constant shift towards lower temperatures with respect to pure DMMC, except for the highest fields. The theoretical curves show the same tendency. A detailed quantitative agreement between theory and experiment could not be obtained. Partly this may be due to the various approximations mentioned in the preceding section, but one should note that the phase boundaries were calculated using an intrachain interaction $J/k = -5.7$ K, according to Ref. 15, instead of the value $J/k = -6.5$ K giving the best description of $T_N(x)$. The qualitative effect of dilution on the magnetic phase diagram, however, is explained correctly by the present theory.

The fact that the data on DMMC:Cd show a more or less constant shift towards lower temperatures upon dilution is in remarkable contrast to the behavior reported for TMMC:Cu,[25] where the shape of the phase boundary observed with H perpendicular to the chain direction changes drastically with increasing impurity content. It is not clear whether this discrepancy is caused by the impurity-host interaction J_{Cu-Mn} in TMMC or by a change of anisotropy induced by the Cu ions. Additional measurements are necessary to clarify this question. A more detailed study of the behavior of the spin-flop transition in DMMC upon dilution is in progress.

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