# Effect of impurities on the Néel temperature and the low-temperature magnetic susceptibility of the quasi-one-dimensional antiferromagnet TMMC

Claire Dupas and Jean-Pierre Renard
*Institut d'Electronique Fondamentale, Laboratoire Associé au Centre National de la Recherche Scientifique, Université Paris XI, Bâtiment 220, 91405 Orsay Cedex, France*
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Low-temperature magnetic susceptibility and Néel-temperature measurements of tetramethylammonium trichloromanganate (TMMC) doped by different impurities, Cd, Cu, Co, and Ni, are reported. For TMMC:Cd, an additional susceptibility proportional to $T^{-1}$ above $T_N$ and a drastic reduction of $T_N$ by a factor of 2 for Cd concentration as low as 0.5 at.% have been observed. These features are well explained by assuming complete breaking of the Mn antiferromagnetic chains. Both susceptibility and $T_N$ measurements in TMMC with magnetic impurities have demonstrated the existence of an impurity-Mn interaction $J_1$ and allowed its estimation: $J_{1\text{Cu-Mn}} = 1.4$ K and $|J_{1\text{ Ni-Mn}}| = 1.9$ K. We give experimental evidence of the $XY$ behavior of the one-dimensional correlations at low temperature.

## I. INTRODUCTION

Since the early work of Ising, many theoretical studies have been devoted to one-dimensional (1D) magnetic systems.[1] Indeed, exact calculations or good approximations are more likely developed in 1D models than in three-dimensional (3D) ones. An important characteristic of the 1D model with short-range interactions is the lack of long-range magnetic order at any temperature, the 1D correlation length diverging at $T = 0$. Recently, several real magnetic compounds which approximate 1D theoretical models have been discovered, the properties of most of them being reviewed by de Jongh *et al.*,[2] Hone *et al.*,[3] and Steiner *et al.*[4] In a simple quasi-1D magnetic compound, the magnetic ions are arranged in linear chains with a nearest-neighbor interchain interaction $J$ which is much greater than the interchain interaction $J'$. Due to this interchain interaction, 3D long-range magnetic ordering occurs below a critical temperature $T_c$ substantially less than the Curie-Weiss temperature $\Theta$ which characterizes the interchain interaction. In a molecular-field picture of interchain couplings, $T_c$ is proportional to $J'$ and to the 1D correlation length at $T = T_c$, $\xi(T_c)$. Thus, as pointed out by Imry *et al.*,[5] $T_c$ must be strongly depressed by impurities, especially nonmagnetic impurities which break the chains into independent finite segments. The theory of this effect for general impurities has been developed by Hone *et al.*[6] for spin-$\frac{1}{2}$ Ising and classical Heisenberg quasi-1D systems. The first experimental strong $T_c$ reduction was observed by the present authors in copper-doped tetramethylammonium trichloromanganate (TMMC).[7] In this paper, we report the effects of various magnetic impurities (Cu, Co, Ni, and a nonmagnetic impurity Cd) on the 3D ordering of TMMC and on its low-temperature susceptibility. TMMC is well suited for this study because it is one of the best quasi-1D antiferromagnets. Its 1D character has been demonstrated by neutron scattering,[8] susceptibility,[9] and specific-heat measurements[10] which allowed the determination of the nearest-neighbor interchain interaction $J/k_B = -6.7$ K. Three-dimensional antiferromagnetic ordering was observed by proton magnetic resonance[11] and chlorine quadrupolar resonance[12] at $T_N = 0.85$ K. This $T_N$ value which is consistent with other determinations (Table I) is much lower than $\Theta = 4|J|S(S+1)/3k_B = 78$ K and corresponds to an interchain interaction $J'$ which can be estimated to be about $10^{-4}J$. Close to $T_c$, the 1D correlation length includes at least 100 $Mn^{2+}$ spins[8] and thus drastic effects are expected in TMMC samples with impurity content of a few atomic percent.

## II. EXPERIMENTAL TECHNIQUE

Single crystals of TMMC were grown by slowly evaporating at 30 °C solutions of $MnCl_2 \cdot 4H_2O$

TABLE I. $T_N$ values of pure TMMC determined by different techniques.

| Experimental technique | $T_N$ (K) | Reference |
|---|---|---|
| Susceptibility | 0.84 | 9 |
| Magnetization at 250 Oe | ~0.9 | 15 |
| Proton magnetic resonance | 0.850 ± 0.005 | 11 |
| $^{35}Cl$ nuclear quadrupole resonance | 0.853 ± 0.002 | 12 |
| Neutron diffraction | 0.841 | 19 |
| Specific heat | 0.835 ± 0.010 | 20 |
| | 0.829 ± 0.002 | 21 |
| | 0.850 ± 0.005 | 22 |

 

(Merck) and $(CH_3)_4NCl$ (Eastman-Kodak) in $2N$ HCl. Impurity-doped crystals were obtained by adding to the solution the corresponding chloride. To avoid a macroscopic inhomogeneous distribution of impurity ions inside the crystal, we take care to start the crystallization of only one single crystal in a large solution bath (100–400 $cm^3$), and to limit the final crystal weight to about 0.5 g. The impurity concentration $x$ was determined by the Microanalysis Laboratory of CNRS, Thiais, France. In the case of $Cu^{2+}$ impurity, the impurity concentration $x$ of the crystal is about one-half that of the starting solution while for $Co^{2+}$ and $Ni^{2+}$, $x$ is about twenty times lower in the crystal than in the solution. On the other hand, for the crystal $(CH_3)_4NCd_xMn_{1-x}Cl_3$ (TMMC : Cd) $x$ is 50 times larger than the cadmium concentration of the starting solution. In this case, it is almost impossible to achieve a perfectly homogeneous impurity distribution in the crystal since the Cd concentration of the solution decreases rapidly during the crystal growth. In order to estimate the macroscopic dispersion of $x$ in the sample, chemical analysis was performed at the beginning and at the end of the crystallization. Many attempts to introduce in TMMC other nonmagnetic impurities such as Zn, Mg, and Ca were unsuccessful.

Magnetic susceptibility was measured by means of a mutual inductance bridge operating at 70 Hz. The amplitude of the oscillating field of the primary coil was about 3 Oe. The chlorine quadrupole resonance was observed by means of a frequency swept Robinson oscillator.

In the temperature range 1.2–4.2 K, the sample was directly immersed in a pumped liquid $^4He$ bath. In the range 0.32–1.2 K, the sample was cooled by liquid $^3He$ in a small glass cryostat. Experimental details concerning temperature measurements and bridge calibration have been reported in a previous paper.[13] Above 4.2 K, the same glass cryostat was used with 1 Torr gaseous $^3He$ insuring a weak thermal leak with the $^4He$ bath at 4.2 K. The crystal was held between two copper foils. A carbon resistor and a gold-silver alloy heater glued on one of these copper foils were part of a regulation system while a second carbon resistor glued on the other foil was used as a thermometer. Temperature calibration was obtained from the susceptibility of a chromium-potassium-alum crystal.

## III. SUSCEPTIBILITY ABOVE $T_N$

Neglecting the anisotropic dipolar interaction between the $Mn^{2+}$ spins and the interchain coupling, TMMC may be considered as a classical 1D Heisenberg antiferromagnet (AFM) since the $Mn^{2+}$ spin value $S=\frac{5}{2}$ is large. The susceptibility of pure TMMC is indeed correctly explained by the theory of Fisher[14] for the isotropic classical chain above 20 K.[9] Below 20 K, the effects of anisotropy become evident, the susceptibility parallel to the chain axis, $\chi_{O\parallel}$ being larger than $\chi_{O\perp}$.[15] Nevertheless, the orientation averaged susceptibility $\chi_O = \frac{1}{3}(\chi_{O\parallel} + 2\chi_{O\perp})$ remains close to the isotropic theoretical value. The susceptibility of the impure classical Heisenberg chain has been calculated by Tonegawa *et al.*[16] for random-site classical impurities and the calculation was extended by Richards[17] to the classical chain with spin-$\frac{1}{2}$ quantum impurities. The molar susceptibility of the 1D Heisenberg AFM with an atomic impurity concentration $x$ has the simple following expression to first order in $x$ when the impurity-host coupling $J_1$ is equal to zero

$$\chi = (1-x)\chi_O + \tfrac{1}{2}x\,\frac{Ng^2\mu_B^2 S(S+1)}{3k_BT} + x\,\frac{Ng'^2\mu_B^2 S'(S'+1)}{3k_BT}\,. \tag{1}$$

$g$, $S$ and $g'$, $S'$ are, respectively, associated with the host and impurity spins.

In addition to the pure chain contribution $(1-x)\chi_O$, there are two terms proportional to $T^{-1}$, the first one is the paramagnetic susceptibility of the $\frac{1}{2}Nx$ chain segments with an odd number of host spins and the second one is the susceptibility of the $Nx$ isolated impurities. Relation (1) holds with

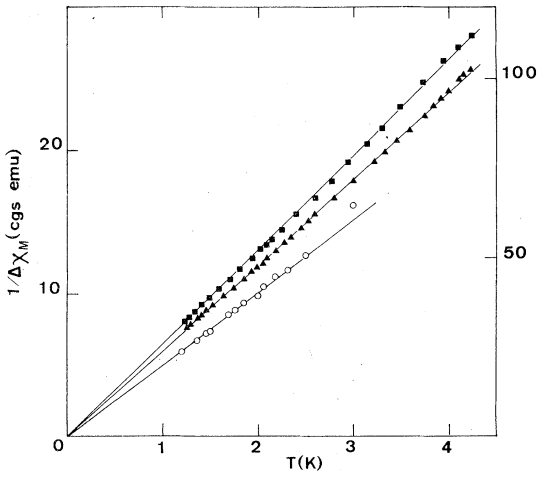


FIG. 1. Inverse additional molar susceptibility $(\Delta\chi_M)^{-1} = |\chi - (1-\chi)\chi_0|^{-1}$ of three TMMC:Cd powders vs temperature. The experimental data fit Curie laws. The slopes of the $\Delta\chi_M^{-1}(T)$ lines correspond to Cd concentrations $x = 0.023$ (circles, right scale), 0.076 and 0.08 (triangles and squares, left scale), which are in reasonable agreement with the respective values given by analysis: $x = 0.027$, $x$ : 0.068, and $x = 0.09$.

$S'=0$ in the case of diamagnetic impurities. It has been checked on three $(CH_3)_4NMn_{1-x}Cd_x$ (TMMC : Cd) powders with $x=0.027$, 0.07, and 0.09. As shown in Fig. 1, a good linear dependence of $|\chi-(1-x)\chi_0|^{-1}$ versus temperature has been observed in these samples.

In addition, the principal magnetic susceptibilities $\chi_{\parallel}$ and $\chi_{\perp}$ of a TMMC : Cd single crystal with a large Cd concentration ($x=0.20$) have been measured above 1.2 K. The experimental data between 1.2 and 4.2 K are shown in Fig. 2. In this temperature range, TMMC : Cd exhibits a net anisotropic behavior with $\chi_{\perp}>\chi_{\parallel}$ while for pure TMMC $\chi_{\parallel}>\chi_{\perp}$. A similar anisotropic behavior of impure chains has been previously observed by Richards[17] for TMMC : Cu. It is likely due to the Mn-Mn dipole coupling within the chain segments. Above 4.2 K, the effect of anisotropy becomes relatively small for TMMC : Cd and we have fitted $\chi_{\parallel}$ to the theory of Richards for the isotropic impure chain. Within the experimental errors, the fit between experiment and theory is fairly good without any adjustable parameter (Fig. 3). This result indicates that the host-host exchange is not significantly modified by the presence of cadmium impurities, probably because the crystal structure of $(CH_3)_4NCdCl_3$ (TMCC) is rather similar to that of TMMC.[18]

The behavior of TMMC doped with magnetic impurities is more complex. The principal magnetic susceptibilities of a single crystal of TMMC : Cu with $x\simeq 0.04$ have been measured in the temperature range 1.2–4.2 K and the orientation averaged susceptibility $\chi$ compared to relation (1). As shown in Fig. 4, $\chi-(1-x)\chi_0$ does not follow the Curie law in this sample but is more likely described by a Curie-Weiss law with a positive Curie-Weiss temperature. This indicates that the Mn-Cu superexchange interaction $J_1$ is ferromagnetic. The fit of the experimental points for TMMC : Cu to the theory of Richards is very good with $J_1/k_B=1.4$ K. This value is consistent with that of 1.6 K reported by Richards for TMMC : Cu with $x=0.026$. We lacked sufficiently doped

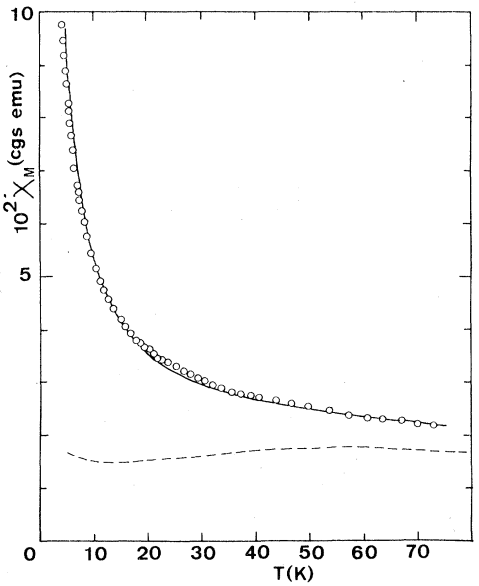


FIG. 3. Molar susceptibility $\chi_{\parallel}$ of a single crystal of $(CH_3)_4NMn_{0.8}Cd_{0.2}Cl_3$ vs temperature in the range 4.2–77 K compared to $\chi_{0\parallel}$ of pure TMMC (dashed curve). The solid curve is the result of the calculation for a $1D$ impure Heisenberg model with $J=-6.7$ K.

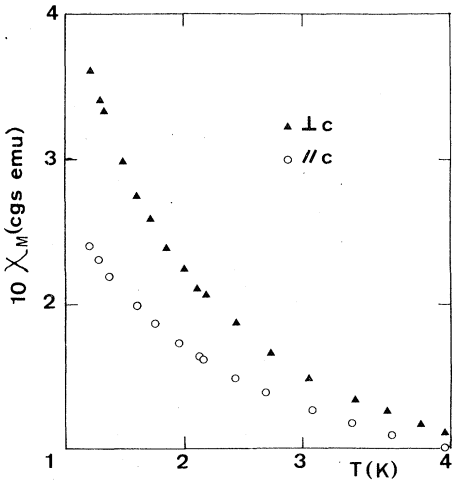


FIG. 2. Molar susceptibility parallel to the chain axis $c$, $\chi_{\parallel}$, and perpendicular to $c$, $\chi_{\perp}$, of a single crystal of $(CH_3)_4NMn_{0.8}Cd_{0.2}Cl_3$, vs temperature. A net anisotropic behavior is observed with $\chi_{\perp}>\chi_{\parallel}$ while for pure TMMC $\chi_{\perp}<\chi_{\parallel}$.

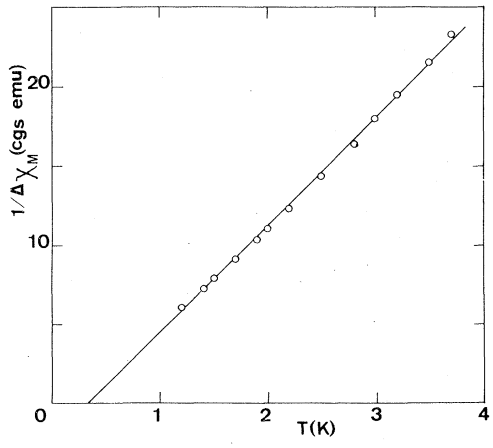


FIG. 4. Inverse additional molar susceptibility $\Delta\chi_M^{-1}=|\chi-(1-x)\chi_0|^{-1}$ for TMMC:Cu with $x=0.04$ vs temperature. The experimental data fit a Curie-Weiss law with a positive Curie-Weiss temperature.

TMMC : Ni and TMMC : Co samples for making significant comparisons between their susceptibility and that of pure TMMC [the maximum impurity concentrations in the crystals were $x_{max}(\mathrm{Ni}) = 1.75\%$ and $x_{max}(\mathrm{Co}) = 0.4\%$].

## IV. NÉEL TEMPERATURE

### A. Method of $T_N$ determination

The Néel temperature $T_N$ of pure TMMC, below which three-dimensional ordering occurs, has been measured by various experimental techniques. A satisfactory agreement between the $T_N$ values obtained by these different ways is observed as shown in Table I. Since the present work required $T_N$ measurement in many samples, we chose two simple techniques: susceptibility and nuclear-quadrupole-resonance (NQR) measurements. Furthermore, these techniques do not need an applied dc magnetic field. It is advantageous since $T_N$ is especially sensitive to magnetic field in TMMC.[23]

Due to a weak ferromagnetism previously observed by Walker *et al.*,[15] the parallel susceptibility of TMMC exhibits at $T_N$ a sharp intense peak; the half-amplitude width of this peak is as low as 3 mK with an amplitude of the measuring field of 0.3 Oe and compensation of the earth magnetic field. In impure TMMC samples, the susceptibility peak is always observed at lowest temperatures and is weaker and wider than in pure TMMC due to an inhomogeneous distribution of the impurities. $T_N$ is chosen as the temperature of the peak maximum. In order to improve this method of $T_N$ determination, $^{35}$Cl NQR has been studied in a few TMMC samples. At $T_N$, the remaining $^{35}$Cl pure quadrupole resonance (PQR) line (at 5.592 MHz in pure TMMC) vanishes and splits below $T_N$ into four NQR lines (two $\alpha$ and two weaker $\beta$ components). The Zeeman splitting is induced by the local average magnetic field arising from the long-range magnetic ordering. Thus, $T_N$ may be accurately determined from the frequency diagram of $^{35}$Cl NQR, or from the PQR line intensity versus temperature. The first method is well suited to samples with a narrow $T_N$ distribution and the second one to samples with a large $T_N$ distribution. Figure 5 shows the $^{35}$Cl NQR frequency diagrams of pure TMMC and TMMC : Ni with $x = 0.0052$ and the parallel susceptibility peaks of the same samples. The NQR and susceptibility determination of $T_N$ are close to each other: respectively, 0.853 and 0.846 K for pure TMMC, 0.810 and 0.806 K for TMMC : Ni. The decrease of $T_N$ due to the Ni impurities is clearly evidenced from both NQR and susceptibility measurements. In Fig. 6 the susceptibility peak and the amplitude of the $^{35}$Cl PQR in a TMMC : Cd single crystal with $x = 0.002$ are shown. The half-amplitude peak width is about 100 mK, indicating a relatively large $T_N$ dispersion. Nevertheless, the temperature of the peak maximum corresponds to a decrease of the $^{35}$Cl PQR signal by a factor of 2 and thus may be chosen as the mean $T_N$ value of this sample.

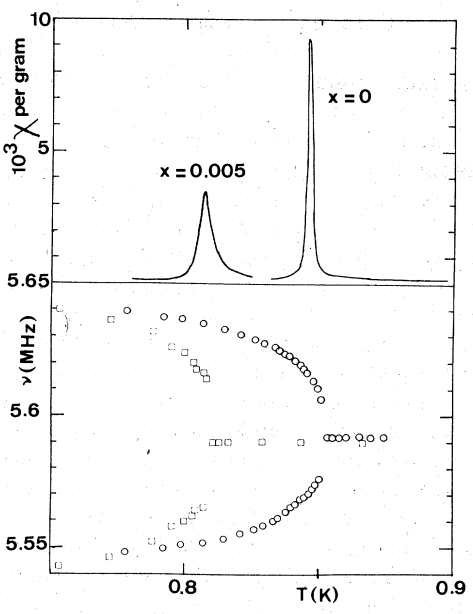


FIG. 5. Susceptibility peaks: upper curves, and $^{35}$Cl nuclear quadrupole resonance frequencies: lower curves in pure TMMC (circles) and TMMC: Ni with $x = 0.0052$ (squares). Only the frequencies of the two $\alpha$ lines of the $^{35}$Cl NQR diagram are shown for the two samples. The temperature of the peak maximum nearly coincides with that of the pure quadrupole resonance splitting. For pure TMMC, the observed discrepancy of 7 mK is probably due to the fact that NQR and susceptibility measurements were not done on the same crystal.

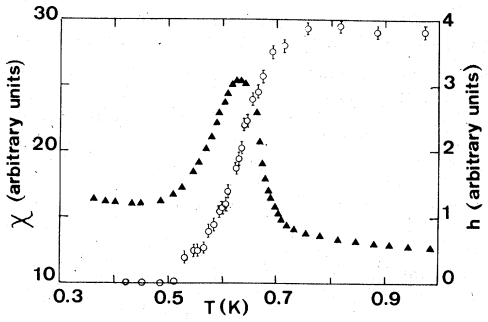


FIG. 6. Susceptibility peak (triangles) and pure $^{35}$Cl quadrupole resonance amplitide $h$ (circles) in TMMC:Cd with $x = 0.002$. The peak maximum temperature coincides with the temperature at which the PQR amplitude is reduced by a factor of 2. This temperature is chosen as the mean $T_N$ value of the sample.

### B. Experimental results and discussion

The experimental $T_N$ values of several single crystals of TMMC doped with Cd, Cu, Ni, and Co impurities are given in Table II and the $T_N$ relative decrease $T_N(x)/T_N(0)$ versus impurity concentration $x$ is shown in Fig. 7. In all cases, $T_N$ is strongly depressed by the presence of impurities. For a fixed impurity concentration, the largest $T_N$ decrease is observed for diamagnetic Cd which provides the best break of the Mn chains. From the relative position of the experimental points, we can conclude that the Mn-impurity exchange energy is approximately the same for Co and Cu, and slightly larger for Ni than for Cu.

A detailed comparison between theory and experiment is shown in Fig. 7(a) for TMMC : Cd. The experimental $T_N$ decrease is much larger than the theoretical one calculated by Hone *et al.*[6] for the quasi-1D Heisenberg model with diamagnetic impurities. This could be expected since the $XY$ anisotropy due to the dipolar interaction of Mn spins plays an important role below 20 K. This $XY$ anisotropy per Mn spin is of the order of magnitude of $k_B T_N$ for TMMC, but the effective anisotropy is the total anisotropy energy of the Mn spins within the correlation length, which is much larger than $k_B T_N$ at low temperature. Thus, the behavior of TMMC is more likely described by the $XY$ model than the Heisenberg one at temperatures near $T_N$. This assumption is supported by a recent calculation of Hone *et al.*[24] which shows that the 1D correlation length of TMMC gradually shifts from the Heisenberg one to the $XY$ one with decreasing temperature. The reduced correlation length $\xi$ of the 1D Heisenberg model with diamagnetic impurities is simply given, to first order in $x$, by the following relation[6,25]

$$1/\xi = 1/\xi_{0H} + x, \tag{2}$$

TABLE II. Measured reduced Néel temperatures $T_N(x)/T_N(0)$ for various impure TMMC crystals $(CH_3)_4$ N $Mn_{1-x}$ $I_x$ $Cl_3$ with $I$ = Cd, Cu, Ni, and Co.

| | | | | | | |
|---|---|---|---|---|---|---|
| Cd | $x$(at. %) | 0.1 | 0.2 | 0.36 | 0.43 | 0.70 |
| | $T_N(x)/T_N(0)$ | 0.86 | 0.73 | 0.61 | 0.43 | 0.38 |
| Cu | $x$(at. %) | 0.35 | 0.78 | 1.35 | 2 | 3.4 |
| | $T_N(x)/T_N(0)$ | 0.92 | 0.84 | 0.71 | 0.64 | 0.475 |
| Ni | $x$(at. %) | 0.52 | 1.75 | Co | | 0.42 |
| | $T_N(x)/T_N(0)$ | 0.945 | 0.85 | | | 0.925 |

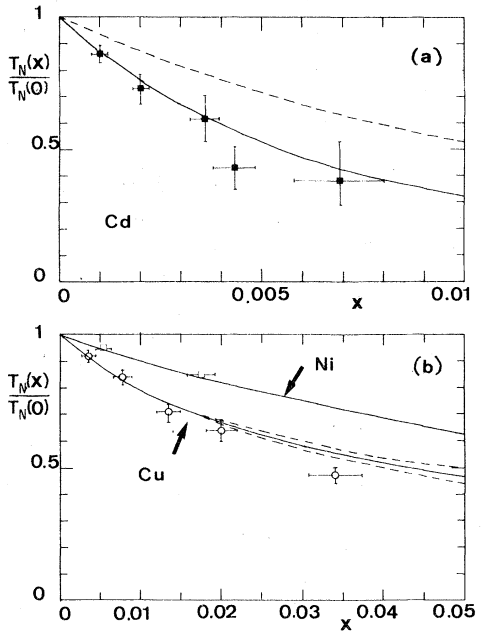


FIG. 7. Variation of the relative Néel temperature $T_N(x)/T_N(0)$ vs impurity concentration $x$ in impure TMMC. (a) Cd impurity: the dashed curve and the solid curve are the theoretical ones for, respectively, the 1$D$ Heisenberg and $XY$ models. The vertical errors represent the half-amplitude widths of the susceptibility peaks. (b) Cu and Ni impurities: the upper solid curve which fits the TMMC:Ni measurements is the theoretical one for Ni-Mn interaction $|J_1| = 1.9$ K and Ni-Ni interaction $J_2 = 0$. The lower solid curve is the theoretical one for Cu-Mn interaction $J_1 = 1.4$ K and $J_2 = 0$. The dashed curves slightly above and below correspond, respectively, to Cu-Cu interactions $J_{2\,cl} = -10$ and $+10$ K and to the same $J_1 = 1.4$ K. Obviously the effect of impurity-impurity interaction is negligible for $x < 0.05$.

where $\xi_{0H}$ is the correlation length of the pure 1D Heisenberg model. This relation is physically meaningful since at high temperatures $\xi$ coincides with $\xi_{0H}$ and at 0 K $\xi$ tends to $1/x$ which is the mean distance between impurities. We assume that relation (2) is still valid for the $XY$ model by replacing $\xi_{0H}$ by $\xi_{0XY}$. At low temperature, $\xi_{0XY}$ is given by

$$\xi_{0XY} = 2\xi_{0H} = 4|J|S(S+1)/k_B T. \tag{3}$$

$T_N(x)$ is then obtained from the relation

$$k_B T_N(x) = zJ'\xi(x, T_N), \tag{4}$$

where $z$ is the number of neighboring chains and $J'$ the interchain interaction determined for $x = 0$ by using relation (3). The resolution of (4) leads to the theoretical curve $T_N(x)$ of the impure quasi-1D $XY$ model (Fig. 7) which is in very good agreement with the experimental data for TMMC : Cd.

As may be noticed, the $T_N$ decrease due to diamagnetic impurities is about two times greater for

the $XY$ model than for the Heisenberg model, for the following reasons: (a) for pure TMMC and for given values of $J$ and $T_N(0)$, $J'$ is two times smaller for the $XY$ than for the Heisenberg model [following (3) and (4) for $x=0$]; and (b) in impure TMMC, the correlation length at low temperature is essentially given by the mean distances between impurities, i.e., $\xi_{XY} \simeq \xi_H \simeq 1/x$. It thus appears clearly from (4) that $T_{N\,XY}(x) \simeq \frac{1}{2} T_{N\,H}(x)$.

The effect of magnetic impurities is rather different. Indeed, the magnetic impurities do not achieve complete breaking of the Mn chains, owing to the Mn-impurity exchange interaction $J_1$, and the correlation length may still diverge at $T=0$. An explicit expression of $1/\xi$ for the 1D Heisenberg model with classical magnetic impurities has been given by Thorpe.[25] To first order in $x$, $1/\xi$ is given in the low-temperature limit by the following simple relation

$$1/\xi(x,T) = \frac{k_B T}{2|J|S(S+1)}\,(1 - 2x + 2x/|\rho|)\,, \qquad (5)$$

where $\rho$ is the ratio of the classical impurity-Mn interaction $J_{1c1}$ to the classical Mn-Mn interaction $J_{c1} = JS(S+1)$. Relation (5) is valid in the temperature range $k_B T \ll |J_{1c1}|$, $|J_{c1}|$. For an impurity of spin $S'$, we assume that $J_{1c1} = J_1 SS'$ and thus $\rho = J_1 S'/J(S+1)$. From relations (4) and (5), $T_N(x)$ is expressed as follows

$$T_N(x)/T_N(0) = (1 - 2x + 2x/|\rho|)^{-1/2}\,. \qquad (6)$$

An interesting feature is that the same relation (6) is obtained for the $XY$ model. Indeed $T_N(x)/T_N(0)$ depends only on the ratio $\xi(x)/\xi(0)$ which is the same for the $XY$ and Heisenberg models in the low-temperature limit since $\xi_{XY} = 2\xi_H$. When taking into account the second order in $x$, $\xi$ diverges at $T=0$ if the impurity-impurity interaction $J_2$ has the same sign as $J$, but does not diverge if $J_2$ and $J$ have opposite signs.[25] In the latter case $1/\xi$ tends to $x^2$ at $T=0$. We have calculated $T_N(x)/T_N(0)$ for TMMC : Cu in three different cases: $J_2 = 0$, ferro- and antiferromagnetic $J_2$ with $|J_{2c1}| = |J_2|S'(S'+1) \gg k_B T$. The $J_1$ value which has been determined in Sec. III, from susceptibility measurements, corresponds to $\rho = -0.03$. The theoretical curves associated with the different $J_2$ values [Fig. 7(b)] are close to each other since the impurity-impurity interaction appears only to second order in $x$. A satisfactory agreement with experiment is observed except for the experimental point at $x = 0.035$ which is below the theoretical curves.

For TMMC : Ni, a good agreement with theory is obtained for $|\rho| = 0.081$ [Fig. 7(b)] which corresponds to the Mn-Ni exchange interaction value: $|J_1| = 1.9$ K.

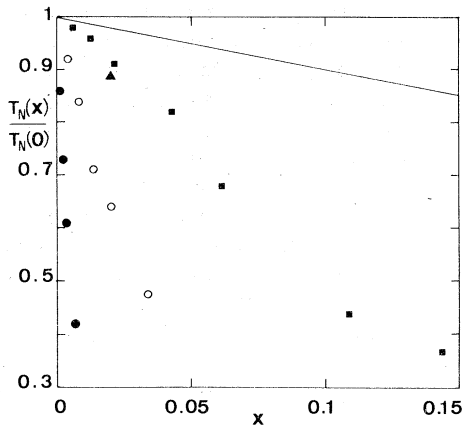


FIG. 8. Comparison between experimental reduction of $3D$ ordering temperature for three quasi-$1D$ magnetic insulators: black circles: TMMC:Cd, open circles: TMMC:Cu, triangle: $CsNiF_3$:Mg and squares: $(CH_3)_3NHCoCl_3 \cdot 2H_2O$:Mn. The interchain to intrachain ratio $J'/J$ is respectively of about $10^{-4}$, $10^{-3}$, and $10^{-2}$ for these quasi-$1D$ magnets. The solid line is the theoretical one for the $3D$ Heisenberg model.

Finally, our $T_N$ measurements on impure TMMC have been compared in Fig. 8 with $T_N$ measurements on other impure 1D magnetic insulators: Mg-doped $CsNiF_3$,[26] which is a ferromagnet with a large planar single-ion anisotropy, and Mn-doped $(CH_3)_3NHCoCl_3 \cdot 2H_2O$ considered as an Ising ferromagnet.[27] The respective values of interchain to interchain ratio $J'/J$ are of about $10^{-3}$ for $CsNiF_3$ and $10^{-2}$ for $(CH_3)_3NHCoCl_3 \cdot 2H_2O$. Figure 8 shows clearly that the $T_N$ decrease is more important for TMMC than for these two quasi-1D magnetic insulators, because it is a much better 1D model ($J'/J \simeq 10^{-4}$). It is surprising that the observed $T_N$ decrease in $CsNi_{0.98}Mg_{0.02}F_3$ is consistent with the Heisenberg prediction, $CsNiF_3$ conforming more closely to and $XY$ model owing to its large planar anisotropy.

## V. CONCLUSION

The present experimental study has demonstrated that the low-temperature magnetic properties of TMMC are drastically sensitive to impurities, as expected for a very good one-dimensional magnetic insulator. Mn chains breaking into independent segments is fairly well achieved by diamagnetic Cd. This leads to an additional susceptibility proportional to $T^{-1}$, in contrast with the more complex behavior exhibited by TCNQ salts.[28] The rather large $T_N$ decrease is consistent with the predicted $XY$ character of the 1D correlations at low temperature. It may be pointed out that this $XY$ behavior also causes the large $T_N$ increase recently observed in an applied magnetic field.[29]

The susceptibility and $T_N$ measurements on TMMC doped with magnetic impurities reflect the existence of an impurity-Mn interaction $J_1$ and allow its estimation. An unique feature of 1D magnetic insulators is that $J_1$ can be determined from low temperature macroscopic measurements. The high-temperature dynamical behavior is also sensitive to impurities as proved by EPR measurements on TMMC : Cu,[30] and nuclear relaxation studies.[31] These measurements can give information about $J_1$ but their interpretation is much more complex.

It would be interesting to extend the present study at very low temperatures to TMMC samples with large impurity contents, in connection with the theory of anisotropic percolation[32] for nonmagnetic impurities, and to evidence the interaction between magnetic impurities. Direct correlation measurements by neutron scattering will be also useful. Further work is in progress.

ACKNOWLEDGMENTS

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