Static magnetic properties of $(CH_3)_4NMn_xCu_{1-x}Cl_3$, a quantum ferromagnetic chain with classical impurities: Experiment and theory

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The magnetic susceptibility of the mixed quasi-one-dimensional system $(CH_3)_4NMn_xCu_{1-x}Cl_3$ has been measured down to 0.32 K for x ranging between 0 and 1. At 4.2 K the susceptibility starts to increase with x up to $x \simeq 0.1$ and then decreases rapidly. The Néel temperature decreases from 1.24 K for $x \simeq 0$ to 0.35 K for $x = 0.22$. We present theoretical calculations developed for isotropic exchange interactions and we take into account the quantum and classical natures of the Cu^{2+} and Mn^{2+} spins, respectively. We show that to first order in x the problem of the disorder inside the chains can be reduced to the calculation of a transfer matrix. This matrix is calculated at high temperature as a function of a parameter v which can be determined by a more rigorous calculation made in the case of diamagnetic impurities and at lower temperatures. The experimental data at small values of x are well explained by this model.

I. INTRODUCTION

In the past few years, many experimental and theoretical studies have been devoted to one-dimensional (1D) magnetic systems.[1,2] A great number of quasi-1D materials with various spin numbers and ferro (F) or antiferromagnetic (AF) exchange interactions along the chains have been obtained. One of the best realizations of a 1D material is the insulating salt tetramethylammonium manganese chloride $(CH_3)_4NMnCl_3$ (TMMC), a linear Heisenberg antiferromagnet with $S = \frac{5}{2}$. The static and dynamic properties of this compound, pure and doped with magnetic and nonmagnetic impurities, have been extensively studied by many research teams and in particular in our laboratory.[3] In a quasi-1D compound, the introduction of impurities affects the growth of the correlation length along the chains at low temperatures, thus leading to drastic effects on the magnetic susceptibility, 3D ordering temperature, and dynamic properties. Theoretical calculations have been performed in the case of chains of classical spins with classical or quantum impurities at low concentrations; they describe satisfactorily the experimental results (see Sec. V).

Until recently, however, no physical example of an $S = \frac{1}{2}$ linear ferromagnet was known. It has been shown by Landee and Willett that tetramethylammonium copper trichloride $(CH_3)_4NCuCl_3$ (TMCuC), isomorphous of TMMC, is a good approximation of that case.[4] We have extended their measurements to lower temperatures and observed

the 3D ordering in TMCuC.[5]

In the present work, we have studied some static magnetic properties of the 1D mixed compounds $(CH_3)_4NMn_xCu_{1-x}Cl_3$. We have synthetized these compounds in the whole concentration range and obtained information on their crystalline structure. We have measured their magnetic susceptibility and the Néel temperature of the compounds with low Mn concentration. To our knowledge, at the beginning of our study, no theoretical calculations had been done on quantum chains of spins $\frac{1}{2}$ with classical impurities except in the rather peculiar case of Heisenberg chains with alternating spin quantum numbers.[6] In order to describe our experimental results we have developed a theoretical model for the magnetic susceptibility at low temperature, when the number $n(T)$ of correlated spins along the chains is of the order of 1. Another approach has been chosen for describing the variation of the 3D order temperature T_N in TMCuC:Mn, when $n(T) \gg 1$. This calculation gives, meanwhile, a complete justification to a method largely used before for determining T_N in doped 1D compounds. Finally, we obtained preliminary results on the spin-flop field in the 3D ordered state of some TMCuC:Mn compounds.

II. EXPERIMENTAL TECHNIQUES

A. Crystal growth and crystallography

The samples of $(CH_3)_4NMn_x Cu_{1-x}Cl_3$ have been grown by slowly evaporating at 50 °C saturated solu-

tions of $(CH_3)_4NCl$, $CuCl_2 \cdot 2H_2O$, and $MnCl_2 \cdot 4H_2O$ in boiling hydrochloric acid. We obtained monocrystalline samples in the case of high Mn concentrations $(x > 50$ wt. %), and powders for the alloys with high Cu concentrations. All the samples are more or less hygroscopic and alter rapidly when left under atmospheric conditions. The Mn and Cu concentrations were determined by chemical analysis (Microanalysis Laboratory of CNRS, Vernaison). Percentage of copper in the samples is higher than in the starting solutions and depends considerably on the evaporation temperature of the solution.

The crystal structure and cell parameters have been determined by x-ray diffraction at room temperature for several samples with Cu concentrations (x) lower than 0.5, by means of rotating crystal, Weissenberg, and powder diagrams. This study has been performed at the Université des Sciences et Techniques of Sfax (Tunisia). It shows that the compounds with moderate Cu concentrations belong at 300 K to the space group $P6_3/m$, like pure TMMC. Cell parameters were refined by a least-squares technique using the values obtained precisely on the powder diagrams. The parameters a and c of the hexagonal cell decrease regularly when the copper concentration increases from 0 to 0.5: in pure TMMC, $a = 9.151$ Å and $c = 6.494$ Å (Ref. 7); in $(CH_3)_4NMn_{0.5}Cu_{0.5}Cl_3$, $a = 9.075$ and $c = 6.435$ Å. The other part of the concentration diagram, leading to the $P2_1$ space group of TMCuC with helicoidal magnetic chains,[8] has not yet been explored. Detailed information on the crystallographic properties of these 1D manganese-copper alloys is to be published elsewhere.[9]

B. Magnetic measurements

We measured the ac magnetic susceptibilities of our samples by means of a mutual inductance bridge operating at low frequency (70 Hz) and in low applied ac field (about 5 Oe). In the temperature ranges 0.32–1.2 and 1.2–4.2 K, the sample was immersed in pumped liquid ^{3}He or ^{4}He. Between 4.2 and 77 K, the sample is put in a glass cryostat, with 1-torr gaseous ^{3}He ensuring a weak thermal link with the main ^{4}He bath. Temperature is stabilized electronically. In all cases, temperature is measured by carbon resistors calibrated against ^{3}He or ^{4}He vapor pressure and, in the 4.2–77-K range, with respect to the susceptibility of a chromium-potassium alum. At low temperature, dc magnetic fields up to 1300 Oe could be applied to the samples.

III. SUSCEPTIBILITY: EXPERIMENTAL RESULTS

A. Pure TMCuC

Landee and Willett measured the magnetization of a powdered TMCuC sample between 2 and 300 K.

They deduced the susceptibility from the low-field values of the magnetization.[4] On the other hand, we measured the ac susceptibility of TMCuC in zero dc applied field between 0.35 and 4.2 K.[5] Between 2 and 4.2 K, our values of X are higher than those of Landee and Willett. We thus measured the susceptibility of the sample between 4.2 and 77 K. Our values are always higher than those of the other two authors (Fig. 1). Several reasons can be found for this discrepancy: (a) the susceptibility of 1D compounds is very sensitive to the application of a dc magnetic field. (b) Three types of impurities can be found in TMCuC: isolated Cu ions, minute inclusions of the starting solution, or traces of $[(CH_3)_4N]_2CuCl_4$, all of which give a specific contribution to X lower than that of TMCuC (we measured the susceptibility of pure $[(CH_3)_4N]_2CuCl_4$, which is only 0.36×10^{-3} cgs emu/g at 4.2 K). For these two reasons, the present measurements are certainly more reliable than the pioneer ones.

For temperatures lower than 20 K, our measurements are well described by the series expansion given by Baker *et al.*[10] for the 1D Heisenberg FM with $S = \frac{1}{2}$, when taking $J_{Cu-Cu} = (45 \pm 1)$ K. This value is naturally higher than that (29 K) given by Landee and Willett. This is not surprising since our low-temperature data are at least 25% higher than those of these authors. It is not possible to describe the whole $X(T)$ curve between 2 and 77 K with a unique J value. This is due either to the lack of a sufficient number of terms in the series expansion, to a possible variation of J with T or, more probably, to the existence of some anisotropy terms in the Hamiltonian describing TMCuC.

Starting from the intrachain exchange value of 45 K and from the T_N value (1.24 K) we had previ-
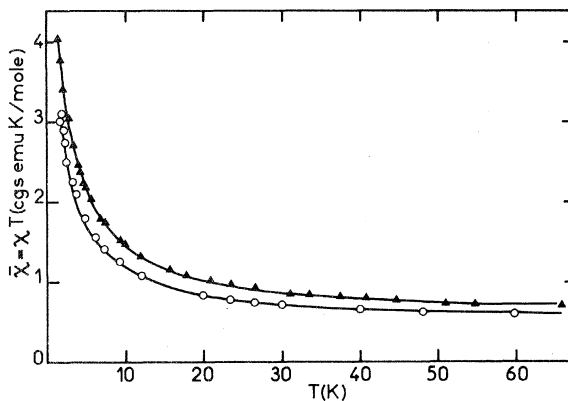

FIG. 1. Variation of XT vs T in pure TMCuC. ▲: this work; O: Landee and Willett (1979). The full lines are only guides to the eye; at low temperature ($T < 22$ K), our measurements are well described by a series expansion (Baker *et al.*, 1964) with $J = 45$ K.
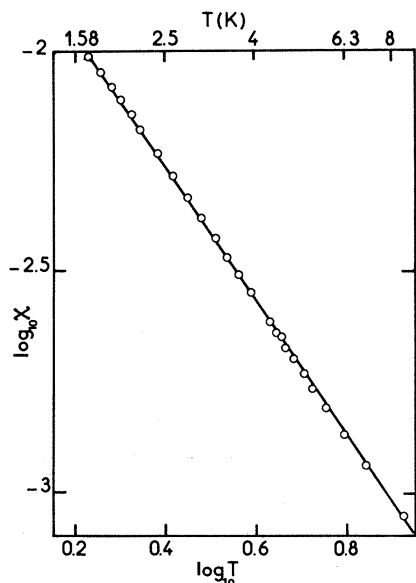
FIG. 2. Variation of $\log X$ vs $\log T$ at low temperature in TMCuC. The susceptibility diverges as $1/T^n$ with $n = 1.525 \pm 0.005$.

FIG. 3. Variation of X vs T in TMCuC:Mn. The manganese concentrations are, respectively, O: 0.02; ●: 0.08; ■: 0.22; ▲: 0.55.

ously measured in this salt we can recalculate the value of the interchain interaction J'. We find $|z'J'/zJ| = 0.9 \times 10^{-3}$, or $|z'J'| = 81$ mK (z and z' are the numbers of nearest neighbors along the chains and in the plane perpendicular to the chains). TMCuC is thus a good 1D Heisenberg FM.

The variations of $\log_{10} X$ vs $\log_{10} T$ are well described at low temperature by a straight line. At low T, $X \propto a/T^n$, with $n = 1.520 \pm 0.005$ (Fig. 2). This value of n is lower than in the expansion of Baker *et al.*,[10] (1.67) and than that determined by Bonner and Fisher[11] (1.8).

B. Mixed compounds $(CH_3)_4NMn_xCu_{1-x}Cl_3$

We measured the susceptibilities of such powdered compounds, for $x \lesssim 0.7$ and $1.2 < T < 77$ K. In all these samples, the magnetic susceptibility increases when decreasing temperature, as in ferromagnetic TMCuC (Fig. 3). A graph of X vs x at 4.2 K shows that when the concentration in manganese ions increases, the susceptibility exhibits a maximum value at about 10% and then decreases rapidly (Fig. 4). Notice that the value obtained by Richards[12] on TMMC: Cu 22 mol% fits well with the present results. A theoretical calculation of $X(x)$ at low x is reported in Sec. V, but we can give here some simple physical arguments explaining this behavior. When the Mn concentration is low, the probability of having in a copper chain Mn pairs or clusters is weak, and the Mn atoms are mainly isolated. These ions do
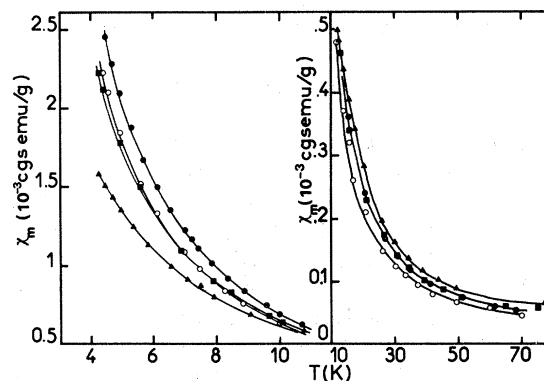
not modify drastically the susceptibility of the copper chain (we suppose here that the Mn-Cu exchange interaction is ferromagnetic like in TMMC-Cu) but give a paramagnetic contribution greater than that of the substituted Cu^{2+} ions. When x increases, pairs of Mn^{2+} ions form along the chain. The exchange interaction J_{Mn-Mn} being AF, the paramagnetic contribution of the pair is null: moreover, the Mn pair makes the two copper chain fragments antiparallel, thus reducing the susceptibility. For $x = 1$, we obtain the low susceptibility value of the antiferromagnetic chains in TMMC.

For all the samples, the susceptibility varies at low temperature like a/T^n, the exponent n depending on the Mn concentration x.
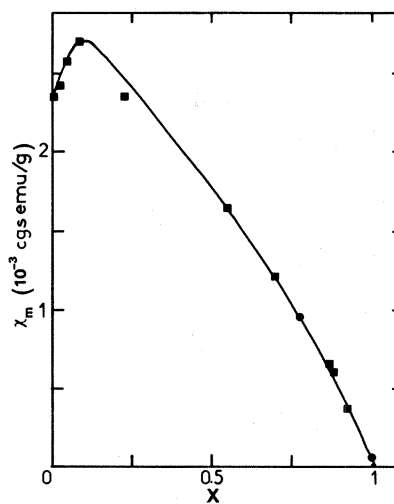

FIG. 4. Experimental values of the susceptibility X at 4.2 K vs manganese concentration x in $(CH_3)_4NMn_xCu_{1-x}Cl_3$: ■ our measurements; ● Richards (1976). The full line is a guide to the eye.

IV. THREE-DIMENSIONAL ORDERING IN TMCuC:Mn

A. Néel temperature

Dupas and Renard have shown that introducing Cu impurities in TMMC lowers the 3D ordering temperature T_N.[4] We present here measurements of the Néel temperature of TMCuC with a few percent of Mn^{2+} ions. We have studied the susceptibility below 1.2 K of four samples with, respectively, 2, 4, 8, and 22 mol% Mn impurities. The susceptibility exhibits a maximum at a certain temperature that we identified as T_N, this maximum being rounded by the introduction of Mn impurities and shifted to lower temperatures (Fig. 5). In fact, for antiferromagnets it is generally admitted that T_N is the temperature at which $d\chi/dT$ is maximum. In the present case, it is difficult to locate precisely this point except for pure TMCuC. However, it might be pointed out that (i) the temperature at which χ is maximum is generally close to T_N is many antiferromagnets; (ii) we are not interested here by the absolute value of T_N but rather by its relative variation with the impurity concentration $T_N(x)/T_N(0)$. It might be expected that this quantity does not strongly depend on the exact definition of T_N. For the compound with 22 mol% Mn, the maximum of $\chi(T)$ arises near 0.35 K, which is the lowest temperature in our experimental setup. The variations of $T_N(x)/T_N(0)$ vs x are shown in Fig. 6, where we have also reported the corresponding variations in TMMC:Cu. The lowering of T_N in TMCuC:Mn can be understood with simple considerations. The ratio of the impurity-host to host-
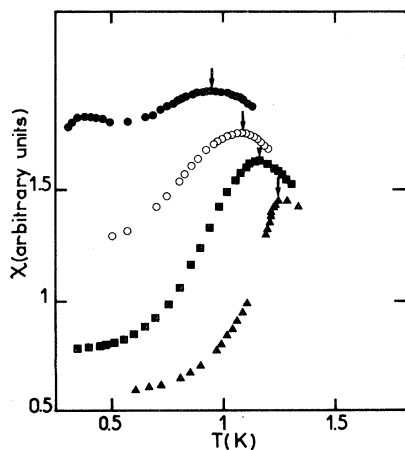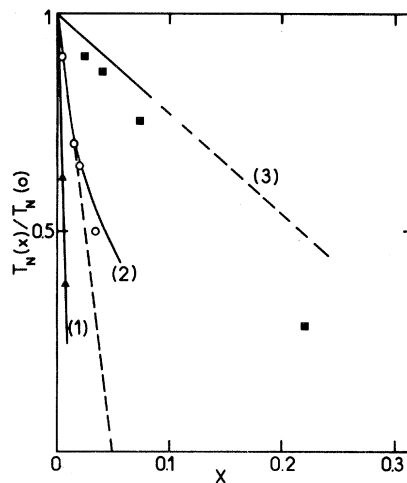

FIG. 6. Relative variation $T_N(x)/T_N(0)$ of the Néel temperature vs impurity concentration x in some quasi-1D systems. Symbols represent, respectively, ▲ TMMC:Cd; ○ TMMC:Cu; ■ TMCuC:Mn (this work). The curves (1), (2), and (3) are the results of the following theoretical calculations: (1) XY classical chain with diamagnetic impurities; (2) XY classical chain with $S = \frac{1}{2}$ impurities; (3) quantum Heisenberg chain with classical impurities (this work). The impurity-host interaction value is $J_{Cu-Mn} = 1.6$ K.

host energy interactions is

$$\frac{E_{Cu-Mn}}{E_{Cu-Cu}} = \frac{J_{Cu-Mn}SS'}{J_{Cu-Cu}S(S+1)} = \frac{1}{17} \; .$$

The Mn ions thus produce an effective breaking of the copper chains. This effect is more drastic in TMMC:Cu, where

$$E_{Cu-Mn}/E_{Mn-Mn} \simeq \frac{1}{30} \; .$$

Moreover, TMMC is a better 1D model than TMCuC. In TMMC and TMCuC, respectively, 5 mol% Cu and 15 mol% Mn are necessary to reduce the Néel temperature by a factor of 2.

B. Spin-flop transition

In order to confirm the existence of an antiferromagnetic long-range ordered state below the susceptibility maximum at low temperature, we have studied the effect of a dc magnetic field on the susceptibility of the preceding samples at temperatures lower than T_N. In pure TMCuC, the variation of the susceptibility versus magnetic field presents a maximum in the temperature range 0.95–1.25 K and two maxima at lower temperatures, one of them exhibiting hysteresis. The maxima are broad, due to the powdered nature of the sample. We attributed these
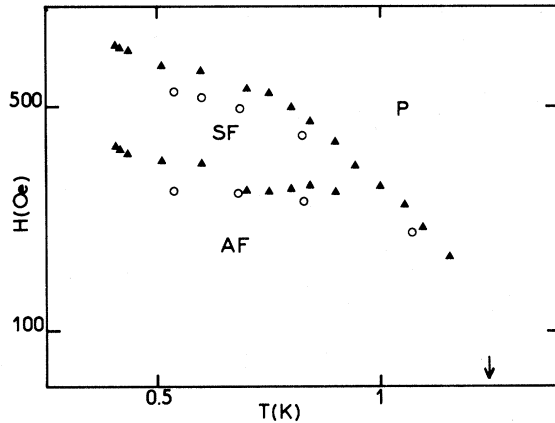

FIG. 5. Maximum of χ vs T at the Néel transition to the 3D AFM ordered state in some TMCuC:Mn compounds. Pure TMCuC ▲ $T_N = 1.24$ K; 2 mol% Mn doped compound ■ $T_N = 1.14$ K; 4 mol% Mn ○ $T_N = 1.10$ K; 8 mol% Mn ● $T_N = 0.96$ K.

FIG. 7. Magnetic phase diagram $H(T)$ in pure TMCuC ($\blacktriangle$) and in TMCuC:Mn 2 mol% ($\circ$). The regions corresponding to the antiferromagnetic (AF), spin-flop (SF), and paramagnetic (P) phases are shown. The arrow indicates the value of T_N in pure TMCuC.

two peaks to the antiferromagnetic $\rightarrow$ spin-flop (SF) and spin-flop $\rightarrow$ paramagnetic (P) transitions and could thus draw the magnetic phase diagram of this compound[5] (Fig. 7). From the value of the SF-P transition field ($H_{SF-P} \simeq 600$ Oe), we obtained a value of the interchain interaction J' in good agreement with that deduced from T_N/J.

We performed analogous measurements on the powdered TMCuC:Mn samples with 2, 4, and 7 mol% Mn. The compound with 2 mol% Mn exhibits a behavior similar to that of pure TMCuC, but the values of H_{AF-SF} and H_{SF-P} are lower than in TMCuC. The reduction of the spin-flop field when replacing some Cu^{2+} by Mn^{2+} ions can be understood: the Mn^{2+} ions are in an S state and their introduction lowers the anisotropy in the sample (moreover, the mean exchange field inside the chains is slightly reduced too by the introduction of Mn^{2+} impurities). In the more-Mn-doped samples, only a broad maximum of χ vs H can be seen at all temperatures below T_N (Fig. 7); the value of H at χ_{max} is lower than H_{SF-P} in the samples with 0 and 2 mol% Mn for the same temperature values. This broad maximum can be due to the overlapping of the AF-SF and SF-P maxima in these impure and powdered samples or even, perhaps, to the disappearance of the SF transition. Clearly, detailed experiments on monocrystalline samples would be necessary.

V. THEORY

A. Theoretical background

We turn now to the calculation of the susceptibility and Néel temperature in the compounds $(CH_3)_4NCu_{1-x}Mn_xCl_3$ for $x \ll 1$.

The problem of calculating the magnetic susceptibility of disordered magnetic chains has been considered by several authors. When only two distinct spin species exist in the crystal and can be treated as classical vectors ($\vartheta \gg 1$), and when all magnetic interactions are isotropic, the calculation can be performed using the Fisher's method[13] completed by the introduction of recurrence relations[14] between spin-correlation functions. This method has been extended to the case of $S = \frac{1}{2}$ impurities at low concentrations in a classical chain.[12] For anisotropic exchange interactions, a transfer-matrix formalism method can be used.[15]

Some attempts have been done too for antiferromagnetic chains of quantum spins $S = \frac{1}{2}$ with random isotropic exchange interactions. In that case, the formalism derives from the methods of the real-space renormalization group; the purpose is the study of the asymptotic properties at $T = 0$ of the thermodynamic functions. Some problems remain to be solved for the ferromagnetic random chains with $S = \frac{1}{2}$, all of which do not belong to the same universality class. Anyway, such methods would not be accurate enough in the temperature range of interest in our problem.[16]

We have to treat the case of a magnetic chain of spins $S = \frac{1}{2}$ with low atomic concentrations of classical spins $\vartheta \gg 1$. The starting Hamiltonian is

$$\mathcal{H} = \sum_p \mathcal{H}_p + \sum_p \mathcal{L}_p , \tag{1}$$

$$\mathcal{H}_p = -J \sum_{i_p} \vec{S}_{i_p} \vec{S}_{i_p+1} - g\mu_B H \sum_{i_p} S^z_{i_p} , \tag{2}$$

$$\mathcal{L}_p = -L \, \vec{\vartheta}_p(\vec{S}_{N_p} + \vec{S}_{1_{p+1}}) - g\mu_B H \vartheta^z_p . \tag{3}$$

In the following, we suppose $J \gg L > 0$. These conditions are satisfied in the compounds $(CH_3)_4NCu_xMn_{1-x}Cl_3$. Each spin interacts only with his two nearest neighbors. In TMCuC and TMCuC:Mn, the anisotropy is only approximately known but certainly weak, and will be neglected in our calculations. The classical spins $\theta_p (p = 1, \ldots, xN)$ cut randomly the chain of quantum spins. S_{i_p} is the ith spin in the pth fragment, which contains N_p spins [$\sum_p N_p = N(1-x)$]. The magnetic field is along Oz. To the first order in x, when $x \ll 1$, we suppose that two classical spins are never nearest neighbors (no cluster at low concentrations).

The static properties of the system are deduced from the free energy

$$F = -\frac{1}{\beta} \langle \ln Z \rangle_\gamma , \tag{4}$$

with

$$Z = \text{Tr} \exp(-\beta \mathcal{H}), \quad \beta = (k_B T)^{-1} .$$

The mean value $\langle \ln Z \rangle_\gamma$ is taken over all spatial configurations of $\vec{S}_{ip}$ and $\vec{\vartheta}_p$. A first approach consists in a series expansion of F vs β, but the calculations become rapidly intricate for $\beta^{-1} < J,L$. We will thus use some approximations, the validity domains of which are to be defined later.

The susceptibility $N \langle \chi \rangle_\gamma$ of the impure chain is given by the expression

$$N \langle \chi(x,T) \rangle_\gamma = \beta g \mu_B \left\langle \sum_{i,j} \langle S_i^z S_j^z \rangle + \sum_{i,\alpha} \langle S_i^z \vartheta_\alpha^z \rangle \right.$$
$$\left. + \sum_{\alpha,\delta} \langle \vartheta_\alpha^z \vartheta_\delta^z \rangle \right\rangle_\gamma \quad , \qquad (5)$$

where the interior angle brackets $\langle \ \rangle$ refer to the canonical mean values. There and in the following we shall omit for sake of clarity in the text the average $\langle \ \rangle_\gamma$ which are effected after the thermal average $\langle \ \rangle$. We suppose that if no anisotropy is present the susceptibility per spin χ_0 of the pure infinite ferromagnetic chain can be written as

$$\chi_0 = n(T)\beta g^2 \mu_B^2 \frac{S(S+1)}{3} \quad ,$$

$$n(T) \simeq 1 + 2 \sum_{l=1}^{\infty} \exp\left[\frac{-la}{\xi_0(T)}\right] \quad , \qquad (6)$$

where $n(T)$ is of the order of the number of spins S correlated to a given one. The correlation length $\xi_0(T)$ is thus of the order of $n(T)a$, a being the intrachain distance between adjacent spins. *We suppose* $n(T)x \ll 1$. The probability of finding in the impure chain two classical spins separated by less than $2an(T)$ is

$$x \sum_{l=0}^{2n}(1-x)^l \simeq 2n(T)x \ll 1 \quad .$$

The susceptibility difference $N(\langle \chi \rangle_\gamma - \chi_0)$ is due, to the first order in x, to the contribution of the spins located at a distance smaller than $n(T)a$ from a classical spin ϑ. Two such spin groups surrounding each impurity are not correlated. The correlations $\langle \vec{S}_i \vec{S}_j \rangle$ between two quantum spins can be assumed to be the same in the pure and impure chains if there is no classical spin between i and j and if their distances to the next ϑ_α and ϑ_β are greater than $n(T)a$. In the calculation, we thus take in account only those spatial configurations for which all the ϑ_α are separated by more than $2n(T)a$. In these cases, the susceptibility does not depend on the position of the classical spins and we can thus calculate χ for a regular configura-

tion in which all ϑ_α are equidistant.

The presence of the ϑ_α allows us to factorize $\exp(-\beta \mathcal{H})$:

$$\exp(-\beta \mathcal{H}) = \prod_p \exp -\beta[\mathcal{H}_p - L(\vec{\vartheta}_{p-1}\vec{S}_{1_p} + \vec{\vartheta}_p\vec{S}_{N_p})]$$

$$\times \exp \beta g \mu_B H \left(\frac{\vartheta_{p-1}^z + \vartheta_p^z}{2}\right) \quad , \qquad (7)$$

where $N_p = (1-x)/x$. Then, by calculating the trace over all quantum spins, we obtain

$$\mathop{\mathrm{Tr}}_{(S)} \exp(-\beta \mathcal{H}) = \prod_{p=1}^{xN} \langle \Omega_{p-1} | U | \Omega_p \rangle \quad . \qquad (8)$$

The vector $\vec{\vartheta}_p$ is given here by its spherical coordinates ϑ, Θ_p, $\phi_p = \vartheta$, Ω_p and U is independent of p — in fact, U is a symmetrical $(2\vartheta+1) \times (2\vartheta+1)$ matrix with real coefficients and real eigenvalues. If λ_0 is the greatest eigenvalue,

$$\mathrm{Tr}[\exp(-\beta \mathcal{H})] = Z \simeq (\Lambda_0)^{xN} \quad . \qquad (9)$$

The diagonalization of U, although analytically impossible, may be performed numerically.

B. High-temperature susceptibility

An approximate analytical solution can nevertheless be obtained by modifying the transfer matrix U using several approximations. If $|m_{ip}\rangle$ are the eigenstates of S_{ip}^z,

$$Z = \left(\frac{2\vartheta+1}{4\pi}\right)^{xN}$$

$$\times \sum_{m_{i_p}} \int \prod_p d\Omega_p \langle \cdots m_{i_p} \cdots \Omega_p \cdots |$$

$$\times \exp(-\beta \mathcal{H}) | \cdots m_{i_p} \cdots \Omega_p \cdots \rangle \quad . \qquad (10)$$

A first approximation consists in writing

$$\mathrm{Tr} \exp[-\beta(\mathcal{H}_p + \mathcal{L}_p)] \sim \mathrm{Tr}[\exp(-\beta \mathcal{H}_p)\exp(-\beta \mathcal{L}_p)] \quad . \qquad (11)$$

In fact, $\mathcal{H}_p$ and $\mathcal{L}_p$ do not commute with each other, and this approximation is only valid at high temperatures, i.e., $\beta L \vartheta S < 1$. We then define the matrices $\mathcal{H}_p$ and $\mathcal{J}_p$ as

$$\langle m_{1_p}, m_{N_p} | \mathcal{H}_p | m'_{1_p} m'_{N_p} \rangle = \sum_{m_{2_p} \cdots m_{(N_p-1)_p}} \langle m_{1_p} m_{2_p} \cdots m_{(N-1)_p} m_{N_p} | \exp(-\beta \mathcal{H}_p) | m'_{1_p} m_{2_p} \cdots m_{(N-1)_p} m'_{N_p} \rangle \quad , \quad (12)$$

$$\langle m_{N_p} m_{1_{p+1}} | \mathcal{J}_p | m'_{N_p}, m'_{1_{p+1}} \rangle = \frac{2\vartheta+1}{4\pi} \int d\Omega_p \langle m_{N_p}, \Omega_p, m_{1_{p+1}} | \exp(-\beta \mathcal{L}_p | m'_{N_p}, \Omega_p, m'_{1_{p+1}} \rangle \quad . \qquad (13)$$

The interactions being isotropic, the only elements in $\mathfrak{N}_p$ are the diagonal ones and those for which $m'_{1_p} \neq m_{1_p}$ and $m'_{N_p} \neq m_{N_p}$ simultaneously. When $n(T) \ll N_p$, these terms can be neglected. If we introduce now the matrix $\mathfrak{M}_p$ defined by

$$\mathfrak{M}_{m_1 m'_1} = \langle m_{1_p} m_{1_{p+1}} | \mathfrak{M}_p | m_{1_p} m_{1_{p+1}} \rangle = \sum_{m_{N_p}} \langle m_{1_p} m_{N_p} | \mathfrak{N}_p | m_{1_p} m_{N_p} \rangle \langle m_{N_p} m_{1_{p+1}} | \mathcal{J}_p | m_{N_p} m_{1_{p+1}} \rangle \ . \tag{14}$$

We have

$$Z \sim \mathrm{Tr}(\mathfrak{M})^{xN} = \mathrm{Tr}(\mathfrak{N}\mathcal{J})^{xN} \tag{15}$$

and $\mathfrak{M}$ constitutes an approximate form for U. If Λ is the greatest of the two eigenvalues of $\mathfrak{M}$,

$$\langle \ln Z \rangle_\gamma \sim xN \ln \Lambda \ . \tag{16}$$

The magnetic susceptibility is given by the expression

$$N \langle \chi \rangle_\gamma = \left[-\frac{1}{H} \frac{\partial F}{\partial H} \right]_{H=0} = \frac{1}{\beta} \left[\frac{1}{H} \left\langle \frac{\partial \ln Z}{\partial H} \right\rangle_\gamma \right]_{H=0} \ . \tag{17}$$

By developing Λ in powers of H to the second order we can calculate χ. We shall see later that $\mathfrak{M}$ has the form

$$\mathfrak{M} = \begin{pmatrix} m_{\uparrow\uparrow} + bH + cH^2 & m_{\uparrow\downarrow} + dH + cH^2 \\ m_{\downarrow\uparrow} - dH + eH^2 & m_{\downarrow\downarrow} - bH + cH^2 \end{pmatrix} \tag{18}$$

with $m_{\uparrow\uparrow} = m_{\downarrow\downarrow} = m$, $m_{\uparrow\downarrow} = m_{\downarrow\uparrow}$, $m_{\uparrow\uparrow} \simeq m_{\downarrow\downarrow}$ for

$n(T)x \ll 1$. We then find

$$\Lambda = 2m + \left(c + e + \frac{b^2 - d^2}{2m} \right) H^2 \ . \tag{19}$$

Coming back to the $\mathfrak{N}$ matrix, we can write

$$\mathfrak{N} = \begin{pmatrix} t_{\uparrow\uparrow} + \alpha H + \gamma_{\uparrow\uparrow} H^2 & t_{\uparrow\downarrow} + \gamma_{\uparrow\downarrow} H^2 \\ t_{\downarrow\uparrow} + \gamma_{\downarrow\uparrow} H^2 & t_{\downarrow\downarrow} - \alpha H + \gamma_{\downarrow\downarrow} H^2 \end{pmatrix} \ . \tag{20}$$

For isotropic couplings and $n(T)x \ll 1$, one finds

$$t_{\uparrow\uparrow} = t_{\downarrow\downarrow} = t, \quad t_{\uparrow\downarrow} = t_{\downarrow\uparrow} \simeq t \ ,$$

$$\gamma_{\uparrow\uparrow} = \gamma_{\downarrow\downarrow} = \gamma, \quad \gamma_{\uparrow\downarrow} = \gamma_{\downarrow\uparrow} \simeq \gamma \ .$$

If Q is the partition function of a chain fragment of N_p spins $S = \frac{1}{2}$, one has

$$Q = 4(t + \gamma H^2) = Q^0 + 4\gamma H^2 \ . \tag{21}$$

In order to estimate the α factor, we use the high-temperature approximation

$$\exp\left[\beta \left(J \sum_1^{N_p-1} \vec{S}_i \vec{S}_{i+1} + g\mu_B H \sum_1^{N_p} S_j^z \right) \right] \simeq \exp(\beta J \sum_i S_i S_{i+1}) \left(1 + \beta g \mu_B H \sum_j S_j^z + \cdots \right) \tag{22}$$

which we shall improve later. We find

$$\alpha_{m_1 m_{N_p}} \simeq \beta g \mu_B \sum_{m_2 \cdots m_{N_p-1}} \left\langle m_1 \cdots m_{N_p} \left| \left(\sum_j S_j^z \right) \exp\left(\beta J \sum_i S_i S_{i+1} \right) \right| m_1 \cdots m_{N_p} \right\rangle \ . \tag{23}$$

In (23), we first consider in the sum $\sum_j S_j^z$ the contribution of the spins S_i^z which are correlated to S_1^z. Using the identity

$$\langle m_1 | = \sum_{m'_1} \frac{\langle m_1 | S_1^z | m'_1 \rangle}{m_1} \langle m'_1 | \ ,$$

$$S_1^z | m_1 \rangle = m_1 | m_1 \rangle \tag{24}$$

this contribution to α is

$$\beta g \mu_B \frac{1}{m_1} \sum_{j=1}^{n(T)} \langle S_1^z S_j^z \rangle \ . \tag{25}$$

The same argument can be used for the other end

of the chain fragment and the spin $S_{N_p}^z$, and finally

$$\alpha_{m_1 m_{N_p}} \simeq \beta g \mu_B \left(\frac{1}{m_1} + \frac{1}{m_{N_p}} \right) \sum_{j=1}^{N_p} \langle S_1^z S_j^z \rangle t \ . \tag{26}$$

Consider the susceptibility χ_p defined by

$$N_p \chi_p = \beta g^2 \mu_B^2 \sum_{i=1}^{N_p} \sum_{j=1}^{N_p} \langle S_i^z S_j^z \rangle \ . \tag{27}$$

If we observe that $|m_1| = |m_{N_p}| = \frac{1}{2}$ and neglect the modification of the correlations at the end of the seg-

ment, we obtain

$$\alpha_{m_1 m_N} = \frac{(-1)^{m_1}}{g\mu_B} 2(\chi_\infty + \chi_p) t \delta_{m_1 m_N} \ , \tag{28}$$

where χ_∞ is the susceptibility per spin (6) for $n(T) = 1$. One finds easily that

$$N_p \chi_p = 2\gamma \frac{\beta^{-1}}{t} \ . \tag{29}$$

$\mathcal{J}$ may be expressed as follows:

$$\mathcal{J} = \begin{pmatrix} j_{\uparrow\uparrow} + \nu H + \epsilon H^2 & j_{\uparrow\downarrow} + \eta H^2 \\ j_{\uparrow\uparrow} + \eta H^2 & j_{\downarrow\downarrow} - \nu H + \epsilon H^2 \end{pmatrix} \ . \tag{30}$$

We put

$$\vec{S}_{N_p} + \vec{S}_{1_{p+1}} = \vec{\sigma}_p \ , \tag{31}$$

$$\exp\beta L\,\vec{\mathcal{S}}_p\,\vec{\sigma}_p = f(\vec{\mathcal{S}}_p, \vec{\sigma}_p) \ .$$

We introduce the representations $|\sigma, \sigma^z\rangle$ where $\vec{\sigma}$ is diagonal, and then $|\delta\rangle$ where the scalar product $\vec{\mathcal{S}}\cdot\vec{\sigma}$ is diagonal. Then

$$\langle m_{N_p} m_{1_{p+1}} | f(\vec{\mathcal{S}}, \vec{\sigma}) | m_{N_p}, m_{1_{p+1}} \rangle = \sum \langle m_{N_p} m_{1_{p+1}} | \sigma, \sigma^z\rangle \langle \sigma, \sigma^z | \delta\rangle f(\vec{\mathcal{S}}, \delta) \langle \delta | \sigma, \sigma'^z\rangle \langle \sigma, \sigma'^z | m_{N_p}, m_{1_{p+1}}\rangle \ , \tag{32}$$

where the summations are taken over the states $|\sigma, \sigma^z\rangle$, $|\sigma, \sigma'^z\rangle$, and $|\delta\rangle$ and where $f(\vartheta, \delta)$ $= \langle \delta | f(\vartheta, \sigma) | \delta\rangle$. The Clebsch-Gordan coefficients $\langle m_{N_p}, m_{1_{p+1}} | \sigma, \sigma^z\rangle$ are given by the equalities

$$\langle\uparrow\uparrow|1, 1\rangle = \langle\downarrow\downarrow|1, -1\rangle = 1 \ ,$$

$$\langle\uparrow\downarrow|1, 0\rangle = \langle\uparrow\downarrow|0, 0\rangle = 1/\sqrt{2} \ , \tag{33}$$

$$\langle\downarrow\uparrow|1, 0\rangle = \langle\downarrow\uparrow|0, 0\rangle = -1/\sqrt{2} \ .$$

In order to calculate $\langle \sigma, \sigma^z | \delta\rangle$, we first note that $\vec{\mathcal{S}}\cdot\vec{\sigma} = \vartheta\sigma_\vartheta$, where σ_ϑ is the projection of $\vec{\sigma}$ over the vector $\vec{\mathcal{S}}$ whose polar coordinates relatively to the magnetic field direction Oz are $\vartheta, \Theta, \varphi$. The eigenstates $|\delta\rangle$ of $\vec{\mathcal{S}}\cdot\vec{\sigma}$ can thus be deduced from $|\sigma, \sigma_z\rangle$

by the rotation bringing Oz over $\vec{\mathcal{S}}$; they will be labeled $|\delta\rangle = |\sigma, \tilde{\sigma}_z\rangle$. When $\sigma = 1$, the $\langle \sigma, \sigma^z | \sigma, \tilde{\sigma}_z\rangle$ are the matrix coefficients of Wigner's, irreducible representation $D^{(1)}$ of the rotation group, given by[17]

$$D^{(1)} = \begin{pmatrix} \dfrac{1+\cos\Theta}{2} e^{-i\phi} & -\dfrac{\sin\Theta}{\sqrt{2}} & \dfrac{1-\cos\Theta}{\sqrt{2}} e^{i\phi} \\[2mm] \dfrac{1}{\sqrt{2}} \sin\Theta e^{-i\phi} & \cos\Theta & \dfrac{1}{\sqrt{2}} \sin\Theta e^{i\phi} \\[2mm] \dfrac{1-\cos\Theta}{2} e^{-i\phi} & \dfrac{\sin\Theta}{\sqrt{2}} & \dfrac{1+\cos\Theta}{2} e^{i\phi} \end{pmatrix} \ . \tag{34}$$

The corresponding eigenvalues of $\vec{\mathcal{S}}\cdot\vec{\sigma}$ are ϑ, 0, and $-\vartheta$. Thus

$$\langle\uparrow\uparrow| f(\vec{\mathcal{S}}, \sigma) |\uparrow\uparrow\rangle = \frac{1+\cos\Theta}{2} e^{-i\phi} f(\vec{\mathcal{S}};1, \tilde{1}) \frac{1+\cos\Theta}{2} e^{i\phi} + \frac{\sin\Theta}{\sqrt{2}} f(\vec{\mathcal{S}};1, \tilde{0}) \frac{\sin\Theta}{\sqrt{2}}$$

$$+ \frac{1-\cos\Theta}{2} e^{i\phi} f(\vec{\mathcal{S}};1, -\tilde{1}) \frac{1-\cos\Theta}{2} e^{-i\phi} \ . \tag{35}$$

The preceding relation has been obtained by application of (32)−(34), with

$$f(\vec{\mathcal{S}};1, \pm\tilde{1}) = \exp(\pm\beta L\vartheta); \quad f(\vec{\mathcal{S}};1, \tilde{0}) = 1; \quad f(\vec{\mathcal{S}}, 0, \tilde{0}) = 1 \ . \tag{36}$$

Analogous calculations lead to the other matrix elements of the operator $f(\vec{\mathcal{S}}, \vec{\sigma})$. The next step is a summation over $d\Omega = \sin\Theta\, d\Theta\, d\phi$

$$\int d\Omega \langle\uparrow\uparrow| f(\vec{\mathcal{S}}, \vec{\sigma}) |\uparrow\uparrow\rangle = \int d\Omega \langle\downarrow\downarrow| f(\vec{\mathcal{S}}, \vec{\sigma}) |\downarrow\downarrow\rangle = \frac{4}{3}\pi(2\cosh\beta L\,\vartheta + 1) = \frac{4\pi}{2\vartheta+1} j_{\uparrow\uparrow} \ ,$$

$$\int d\Omega \langle\uparrow\downarrow| f(\vec{\mathcal{S}}, \vec{\sigma}) |\uparrow\downarrow\rangle = \int d\Omega \langle\downarrow\uparrow| f(\vec{\mathcal{S}}, \vec{\sigma}) |\downarrow\uparrow\rangle = \frac{4}{3}\pi(\cosh\beta L\,\vartheta + 2) = \frac{4\pi}{2\vartheta+1} j_{\uparrow\downarrow} \ . \tag{37}$$

But $j_{\uparrow\uparrow} = j_{\downarrow\downarrow}$, $j_{\uparrow\downarrow} = j_{\downarrow\uparrow}$. In order to obtain the terms in H and H^2 in J, one must write

$$\exp(-\beta\mathcal{L}) = \exp\beta L\,\vec{\mathcal{S}}\,\vec{\sigma}\left[1 + \beta g\mu_B H\vartheta\cos\Theta + \frac{\beta^2}{2!} g^2\mu_B^2 H^2\vartheta^2\cos^2\Theta + \cdots\right] \tag{38}$$

and the calculations are then identical to the preceding one for $j_{\uparrow\uparrow}$. Finally

$$\nu = \tfrac{1}{3}\vartheta(2\vartheta+1)\beta g\mu_B \sinh\beta L\,\vartheta \ ,$$

$$\epsilon = \vartheta^2(2\vartheta+1)\beta^2 g^2\mu_B^2(\tfrac{2}{15}\cosh\beta L\vartheta+\tfrac{1}{30}) \ , \tag{39}$$

$$\eta = \tfrac{1}{2}\vartheta^2(2\vartheta+1)\beta^2 g^2\mu_B^2(\tfrac{1}{15}\cosh\beta L\vartheta+\tfrac{4}{15}) \ .$$

In order to obtain Λ, one calculates the coefficients of $\mathfrak{M}=\mathfrak{M}\mathcal{J}$ (18). The final result is

$$\frac{\Lambda}{2\vartheta+1} = \tfrac{1}{2}Q^0(\cosh\beta L\vartheta+1) + \left[2\alpha\nu+2\gamma(\cosh\beta L\vartheta+1)+(\epsilon+\eta)\frac{Q^0}{2}+\frac{2\alpha^2}{Q}\frac{\cosh\beta L\vartheta-1}{3}\right]H^2 \ . \tag{40}$$

The total susceptibility of the impure chain is

$$N\bar{\chi}=xN\frac{1}{\beta}\left[\frac{1}{H}\frac{\partial\ln\Lambda}{\partial H}\right]_{H\to0} \simeq N(1-x)\chi_p+xN\left[\beta g^2\mu_B^2\frac{\vartheta^2}{3}+\frac{8}{3}\chi_T\vartheta\frac{\sinh\beta L\vartheta}{\cosh\beta L\vartheta+1}+\frac{8}{3}\frac{\chi_T^2}{g^2\mu_B^2}\frac{1}{\beta}\frac{\cosh\beta L\vartheta-1}{\cosh\beta L\vartheta+1}\right] \tag{41}$$

with $\chi_T \simeq \tfrac{1}{2}\chi_0$. But in order to improve this high-temperature calculation, we shall take $\chi_T=\tfrac{1}{2}\chi_0\nu$ where the parameter ν will be adjusted in the following: In the spirit of the preceding approximations, we admit that for $\beta L\vartheta \gg 1$, the correlation $\langle S_i^z \cdot S_j^z\rangle$ between two quantum spins located at each side of a classical spin ϑ_α is not greatly affected by ϑ_α when $2\xi(T) > r_{ij} > 2a$. Hence

$$N(1-x)\chi_p \simeq N(1-x)\chi_0 - \frac{8}{3}Nx\frac{\chi_T^2}{\beta g^2\mu_B^2} \tag{42}$$

and at last

$$N\langle\chi\rangle_\gamma \simeq N(1-x)\chi_0 + Nx\left[\beta g^2\mu_B^2\vartheta\frac{(\vartheta+1)}{3}+\frac{8}{3}\chi_T\vartheta\frac{\sinh\beta L\vartheta}{\cosh\beta L\vartheta+1}-\frac{16}{3}\frac{\chi_T^2}{\beta g^2\mu_B^2}\frac{1}{\cosh\beta L\vartheta+1}\right] \ . \tag{43}$$

C. Susceptibility at intermediate temperatures

At low temperature, when $n(T)\gg1$ and $\beta L\vartheta\gg1$, the decoupling relations (11) and (22) lead to poorly satisfying results. We go back to the general expression of the susceptibility $\langle\chi\rangle_\gamma$ (5). When $xn(T)\ll1$, the terms with $\alpha\neq\delta$ can be neglected. Let us consider the difference $\gamma(x,T)$ defined as follows:

$$N\gamma(x,T) = N[\langle\chi(x,T)\rangle_\gamma-\chi(0,T)]$$

$$= \beta g^2\mu_B^2\left[\sum_{i,j}[\langle S_i^z S_j^z(x)\rangle-\langle S_i^z S_j^z(0)\rangle]+\sum_{i,\alpha}[\langle S_i^z\vartheta_\alpha^z(x)\rangle-\langle S_i^z S_\alpha^z(0)\rangle]+\sum_\alpha\langle(\vartheta_\alpha^z)^2\rangle\right] \ . \tag{44}$$

The host and impurity spins S and ϑ are, respectively, labeled here by i, j, and α. The physical meaning of the terms to the right in (43) appears when comparing (44) and (43). The term in $\langle\vartheta_z\rangle^2$ (44) corresponds to that in ϑ^2 (43). The term $-\sum\langle S_i^z S_\alpha^z(0)\rangle$ (44) is equal to $-Nx\chi_0$ (43). The term $\sum\langle S_i^z\vartheta_\alpha^z(x)\rangle$ in (44) corresponds to the term proportional to χ_T in (43). Finally, the first term in (44) is in correspondence with the last one in (43).

We write this last term as

$$\sum_{ij}{}' \langle S_i^z S_j^z(x)\rangle - \langle S_i^z S_j^z(0)\rangle = \phi(x,T)-\phi(0,T)=\delta\phi \ . \tag{45}$$

The $\sum'$ summation has the following significance: As has been shown in Sec. V A, we need only to consider in $\phi(x,T)$ all the spins $\vec{S}_i$ and $\vec{S}_j$ whose distance to a same impurity spin ϑ_α does not exceed $\xi_0(T)$. An approximate value of $\delta\phi$ can be obtained by taking in account only the terms $\langle S_i^z S_j^z\rangle$ in which $r_{ij}<2\xi_0(T)$ and $\vec{S}_i$ and $\vec{S}_j$ are on each side of a $\vec{\vartheta}_\alpha$ spin. This approximation is valid when $n(T)\gg1$ and $\beta L\vartheta\geq1$. In order to estimate $\langle S_{i_1}^z S_{j_1}^z(x)\rangle$ (where $\vec{S}_{i_1}$ and $\vec{S}_{j_1}$ are the nearest neighbors of $\vec{\vartheta}_\alpha$) we suppose that their behavior is described by the coupling energy $\mathcal{L}_0=-L'\vec{\vartheta}_\alpha\cdot(\vec{S}_{i_1}+\vec{S}_{j_1})$. As $n(T)\gg1$ we suppose that S_{i_1} and S_{j_1} can only take

the values $\pm\frac{1}{2}$. We hope in this way to eliminate the quantum fluctuations of $\vec{S}_{i_1}$ and $\vec{S}_{j_1}$. With the Hamiltonian $\mathcal{L}_0$, such fluctuations appear for $\beta L\vartheta > 1$ and would oppose to the alignment assumed when writing $n(T) \gg 1$.

We put

$$P(m_i, m_j) = \int_0^\pi d\Theta \sin\Theta \exp[\beta L\vartheta\cos\Theta(m_i + m_j)] \quad .$$

$$(46)$$

For $\beta L\vartheta \gg 1$,

$$\langle S_{i_1}^z S_{j_1}^z(x) \rangle \simeq \rho(T)\frac{S(S+1)}{3} \quad ,$$

$$(47)$$

$$\rho(T) = \frac{P(m_i, m_i) - P(m_i, -m_i)}{P(m_i, m_i) + P(m_i, -m_i)} = \frac{\sinh\beta L\vartheta/\beta L\vartheta - 1}{\sinh\beta L\vartheta/\beta L\vartheta + 1} \quad .$$

When $r_{ij} \gg a$ and $n(T) \gg 1$, we have the approximation

$$\langle S_i^z S_j^z(x) \rangle \simeq \rho(T)\frac{S(S+1)}{3}\exp[-r_{ij}/\xi_0(T)] \quad (48)$$

and

$$\sum_{i,j}' \langle S_i^z S_j^z(x) \rangle \simeq \frac{2}{3}S(S+1)\rho(T)\sum_{l=1}^\infty l\exp[-la/\xi_0(T)]$$

$$= \frac{1}{6}S(S+1)\rho(T)Nn^2(T)x \quad , \quad (49)$$

where we have used the relation (6) between $n(T)$ and $\xi_0(T)$. It follows that

$$\delta\phi(x,T) = \frac{1}{6}S(S+1)Nn^2(T)x[\rho(T) - 1] \quad . \quad (50)$$

It is interesting to calculate the ratio of the two values of $\delta\phi(x,T)$ obtained in (50) and in (41).

$$V = \frac{n^2(T)[\rho(T) - 1][\frac{1}{6}S(S+1)]}{-\frac{4}{3}(\chi_0 v/\beta g^2 \mu_B^2)^2(\cosh\beta L\vartheta + 1)^{-1}} \quad . \quad (51)$$

Now, if we let $L \to 0$, we find

$$\lim_{L \to 0} V = \frac{3}{v^2} \quad (52)$$

so if we wish (43) to be valid also for diamagnetic impurities ($L \simeq 0$), we must require $v \simeq \sqrt{3}$. It can be shown that if $\beta L\vartheta > 1$,

$$\sum_i \langle (\vartheta_a^z S_i^z(x)) \rangle \leq \frac{n(T)}{2}\vartheta \quad (53)$$

and it follows that we must replace χ_T in the second

term between the brackets (43) by $\frac{1}{2}\chi_0 v'(T)$ with

$$\lim_{\beta L\vartheta \ll 1} v'(T) \simeq \sqrt{3} \quad ,$$

$$\lim_{\beta L\vartheta > 1} v'(T) \simeq 1.5 \quad . \quad (53')$$

At last, (43) takes the form

$$N\langle\chi\rangle = N(1-x)\chi_0$$
$$+ Nx\left[\beta g^2\mu_B^2\frac{\vartheta(\vartheta+1)}{3}\right.$$
$$+ \frac{4}{3}\chi_0 v'(T)\vartheta\frac{\sinh\beta L\vartheta}{\cosh\beta L\vartheta + 1}$$
$$\left. - \frac{4\chi_0^2}{\beta g^2\mu_B^2}\frac{1}{\cosh\beta L\vartheta + 1}\right] \quad (54)$$

valid for $\beta L\vartheta < 1$.

D. Néel temperature

The expression (54) just obtained gives the susceptibility of an isolated mixed chain, and can only be compared to experiment in the temperature range where the compounds studied exhibit a purely 1D behavior. At sufficiently low temperatures, the interchain interactions which cannot be neglected lead to a crossover to a 3D behavior and to the onset of a long-range-ordered state below a phase-transition temperature (see Sec. IV A). In the compounds $(CH_3)_4NMn_xCu_{1-x}Cl_3$, we have to explain why the Néel temperature $T_N(x)$ is reduced by increasing x at low Mn concentrations[18] while at the fixed temperature 4.2 K, the magnetic susceptibility $\chi(x,T)$ increases with x.

Many authors have calculated the Néel temperature of quasi-1D systems by treating the spins as classical vectors.[19] The effects of impurities and anisotropic couplings have also been considered.[20] The problems encountered are complex, and there exists no truly satisfying theoretical solution at this time. The solution we propose in the following is also approximate.

We restrict ourselves to the case of isotropic inter- and intrachain couplings. The interchain exchange interaction has the form $-J'\vec{S}_i \cdot \sum_q \vec{S}_q$, ($|J'| \ll |J|$) where we sum over the z nearest neighbors of a spin in the plane perpendicular to the chains.

The Néel temperature of ferromagnetic chains without impurities is given by

$$\frac{2z|J'|\chi_0(T_N)}{g^2\mu_B^2} \simeq 1 \quad (55)$$

with $\chi_0(T_N)$ extracted from (6). We wish to extend (55) to the case of impurity doped chains. We note

that in our compounds, at $T \simeq 1.2$ K:

$$N\gamma(x,T) \simeq \beta g^2 \mu_B^2 \sum_{i,j}' [\langle S_i^z S_j^z(x)\rangle - \langle S_i^z S_j^z(0)\rangle] \ .$$

(56)

More generally, there may exist a temperature range where (56) is valid: the right member of (56) is of the order of $n^2(T)$, while the other terms in (44) are of the order of $n(T)$.

In order to calculate $\gamma(x,T)$ at such temperatures, it is thus adequate to estimate the modification in the correlations between the spins $\bar{S}$ due to the presence of the $\vec{\mathcal{S}}_\alpha$. The effect of the classical impurity spins is thus only an indirect one. This result gives us the opportunity to use the relation (55) in order to estimate $T_N(x)$ by simply replacing $\chi_0(T_N)$ by $\langle\chi(x,T_N)\rangle_\gamma$ and J' by $J'(1-x)$ when $T_N(x)$ is in the validity range of (56). Indeed, relation (55) arose from a molecular-field approximation in which each spin $\bar{S}$ is supposed to have $zn(T)$ first neighbors on the adjacent chains. The value of the number $n(T)$ of spins S correlated on a given chain is given by $\chi_0(T_N)$. But as the $\vec{\mathcal{S}}_\alpha$ are eliminated from (44) because of (56), Eq. (44) gives also the number of correlated spins in the impure chain.

If $\delta T_N(x) = T_N(x) - T_N(0)$, we have, by using

(45) and (50),

$$\delta T_N(x)\frac{d\chi_0}{dT}(T_N) \simeq -[\langle\chi(T_N,x)\rangle_\gamma - \chi_0(T_N)]$$
$$-\chi_0\frac{\delta J'}{J'} \ .$$
(57)

If

$$\chi_0(T) \propto T^{-\alpha}, \quad \frac{d\chi_0}{dT}(T_N) = -\alpha\frac{\chi_0(T_N)}{T_N} \ ,$$

and finally, by using (54)

$$\frac{\delta T_N(x)}{T_N} \simeq -\frac{[n(T_N)-2][1-\rho(T_N)]+4}{2\alpha}x$$
(58)

in the validity range of (56) and for $\beta_N L\vartheta \gtrsim 1$.

VI. COMPARISON WITH EXPERIMENT

We have compared the experimental variation of the susceptibility in TMCuC:Mn versus maganese concentration x at the fixed temperature 4.2 K to the theoretical expression (54). We used for the Cu-Mn exchange interaction L the value 1.6 K deduced from susceptibility and T_N measurements in TMMC:Cu (Refs. 3 and 12) and for $V'(T)$ the value $V'(T) = 1.5$ (53'). As the agreement between theory and experiment seemed satisfactory, without any adjustable parameter, for the low values of x, we tried to extend the fit to higher values by estimating the terms in x^2:

$$N\langle\chi\rangle_\gamma \sim N(1-x)\chi_0 + Nx(1-2x)\left[\beta g^2\mu_B^2\frac{\vartheta(\vartheta+1)}{3} + \frac{4}{3}\chi_0 v'(T)\vartheta\frac{\sinh\beta L\vartheta}{\cosh\beta L\vartheta+1} - \frac{4}{3}\frac{\chi_0^2}{g^2\mu_B^2}\frac{1}{\beta}\frac{1}{\cosh\beta L\vartheta+1}\right]$$

$$+ Nx^2\left\{2\beta g^2\mu_B^2\frac{\vartheta(\vartheta+1)}{3} + 2\beta g^2\mu_B^2\left[\coth\beta J_1\vartheta^2 - \frac{1}{\beta J_1\vartheta^2}\right]\frac{\vartheta(\vartheta+1)}{3}\right.$$

$$\left. + \frac{8}{3}\chi_T\vartheta\frac{\sinh\beta L\vartheta}{\cosh\beta L\vartheta+1}\left[1 + \coth\beta j_1\vartheta^2 - \frac{1}{\beta J_1\vartheta^2}\right] + 8\chi_T^2\left[\left(\frac{\sinh\beta L\vartheta}{\cosh\beta L\vartheta+1}\right)^2\left(\coth\beta J_1\vartheta^2 - \frac{1}{\beta J_1\vartheta^2}\right)\right]\frac{1}{\beta g^2\mu_B^2}\right\}$$

with $\chi_T \simeq \frac{1}{2}\chi_0 v$. Here, we have assumed an isotropic exchange coupling $-J_1\vec{\mathcal{S}}_\alpha\vec{\mathcal{S}}_\gamma$ between two neighboring classical spins $\vec{\mathcal{S}}_\alpha$ and $\vec{\mathcal{S}}_\gamma$ and we take $J_1 = -6.7$ K which is the value of the intrachain coupling in TMMC.

The experimental values fit well with the theory (Fig. 8).

The expression giving $\delta T_N/T_N$ (58) also does not contain any adjustable parameter. The experimental value of the exponent $\alpha[\chi(T) \propto T^{-\alpha}]$ is $\alpha = 1.525$ (Sec. III A). With such a divergence law, the number $n(T_N)$ of correlated spins in the vicinity of T_N is of the order of 12 for pure TMCuC. An extrapolation of (58) would give a null value of T_N for $x = 37\%$. By comparison, the straight line tangential to the ex-

perimental curve for small x values intersects the $T_N = 0$ line for $x = 28\%$. This discrepancy could be ascribed to the value of L. It is not obvious why the Mn-Cu exchange interaction in TMCuC:Mn should be the same as in TMMC:Cu. In fact the value of this parameter depends drastically on the superexchange path Mn-Cl-Cu, which is different in TMMC and in TMCuC. Moreover, in this last salt, three different superexchange bridges with different angles are already observed at room temperature.[8] Nevertheless, the value $L = 1.6$ K gives a good fit for the susceptibilities at 4.2 K. The disagreement comes thus probably from the model. First, the approximations used in the course of our analytical calculations, which were detailed in Sec. V, lead to an overestimat-
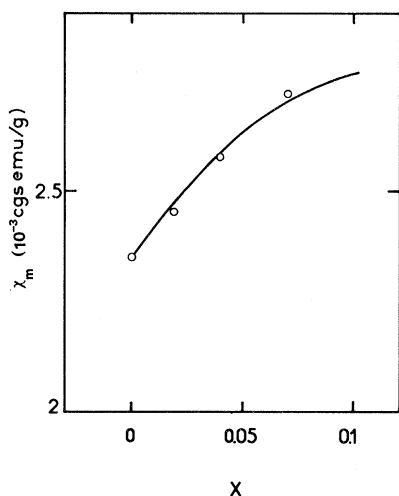
FIG. 8. Comparison between theory and experiment for the variation of X at 4.2 K vs Mn concentration x in TMCuC:Mn.

ed value of $\rho(T)$. But there is also a more fundamental cause, i.e., the starting Heisenberg Hamiltonian. In TMMC, the existence of an XY anisotropy at low temperature has been shown to lower considerably the theoretical values of $T_N(x)$ in the impure salt with respect to that obtained with a Heisenberg Hamiltonian.

In this paper, we have reported measurements of the magnetic susceptibility of powdered samples of $(CH_3)_4NMn_xCu_{1-x}Cl_3$ in a wide concentration range. The value of T_N has been obtained at low Mn concentration. An approach to the magnetic properties of quantum $S = \frac{1}{2}$ chains with classical impurities has been developed, which gives reasonable agreement with experiment for the susceptibility but only qualitative agreement for the T_N value. Measurements on monocrystalline samples would be highly desirable in order to determine the value of the anisotropy and the spin direction at low temperature in these compounds. Results on the dynamic properties of these systems obtained by means of EPR measurements are yet unpublished.

[1]L. J. de Jongh and A. R. Miedema, Adv. Phys. 23, 1 (1974).

[2]M. Steiner, J. Villain, and C. G. Windsor, Adv. Phys. 25, 87 (1976).

[3]C. Dupas, Ph. D. thesis (Orsay, 1978) (unpublished); S. Clément, Ph. D thesis (Orsay, 1977) (unpublished); C. Dupas and J. P. Renard, Phys. Rev. B 18, 401 (1978).

[4]C. P. Landee and R. D. Willett, Phys. Rev. Lett. 43, 463 (1979).

[5]C. Dupas and J. P. Renard, in *Proceedings of the 1980 Annual Conference of the Condensed Matter Division of the European Physical Society, Antwerpen (Belgium), 9–11 April 1980* (Plenum, New York, in press).

[6]H. W. J. Blöte, J. Appl. Phys. 50, 7401 (1979).

[7]B. Morosin and E. J. Graeber, Acta Crystallogr. 23, 766 (1967).

[8]J. W. Weenk and A. L. Spek, Cryst. Struct. Commun. 5, 805 (1976).

[9]A. Cheikh-Rouhou and A. Daoud (unpublished).

[10]G. A. Baker, G. S. Rushbrooke, and H. E. Gilbert, Phys. Rev. A 135, 1272 (1964).

[11]J. C. Bonner and M. E. Fisher, Phys. Rev. A 135, 640 (1964).

[12]P. M. Richards, Phys. Rev. B 14, 1239 (1976).

[13]M. E. Fisher, Am. J. Phys. 32, 343 (1964).

[14]H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University, New York, 1971); M. F. Thorpe, J. Phys. (Paris) 36, 1177 (1975); T. Tonegawa, H. Shiba, and P. Pincus, Phys. Rev. B 11, 4683 (1975).

[15]J. M. Loveluck, S. W. Lovesey, and S. Aubry, J. Phys. C 8, 3841 (1975).

[16]C. Dasgupta and S. K. Ma, Phys. Rev. B 22, 305 (1980); J. E. Hirsch and J. V. José, *ibid.* 22, 5339 (1980); J. E. Hirsch, *ibid.* 22, 5355 (1980).

[17]E. Wigner, *Group Theory* (Academic, New York, 1959).

[18]A. Cheikh-Rouhou, C. Dupas, and J. Seiden, C. R. Acad. Sci. Ser. B 291, 303 (1980).

[19]H. Sato, J. Phys. Chem. Solids 19, 54 (1961); H. E. Stanley and T. A. Kaplan, J. Appl. Phys. 38, 975 (1967); J. Villain and J. M. Loveluck, J. Phys. Lett. 38, L77 (1977); J. C. Schouten, F. Boersma, K. Kopinga, and W. J. M. de Jonge, Phys. Rev. B 21, 4084 (1980).

[20]Y. Imry, P. A. Montano, and D. Hone, Phys. Rev. B 12, 253 (1975); D. Hone, P. A. Montano, T. Tonegawa, and Y. Imry, Phys. Rev. B 12, 5141 (1975).