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Recent progress in experimental one-dimensional magnetism

J P RENARD*, S CLEMENT and M VERDAGUER[1]

Institut d'Electronique Fondamentale, CNRS UA022 Bâtiment 220, Université Paris-Sud, 91405 – Orsay, France

[1] Laboratoire de Spectrochimie des Eléments de Transition, CNRS UA 420 Université Paris-Sud, 91405 – Orsay, France

[1] Permanent address: ENS, Le Parc, 92211, Saint-Cloud, France

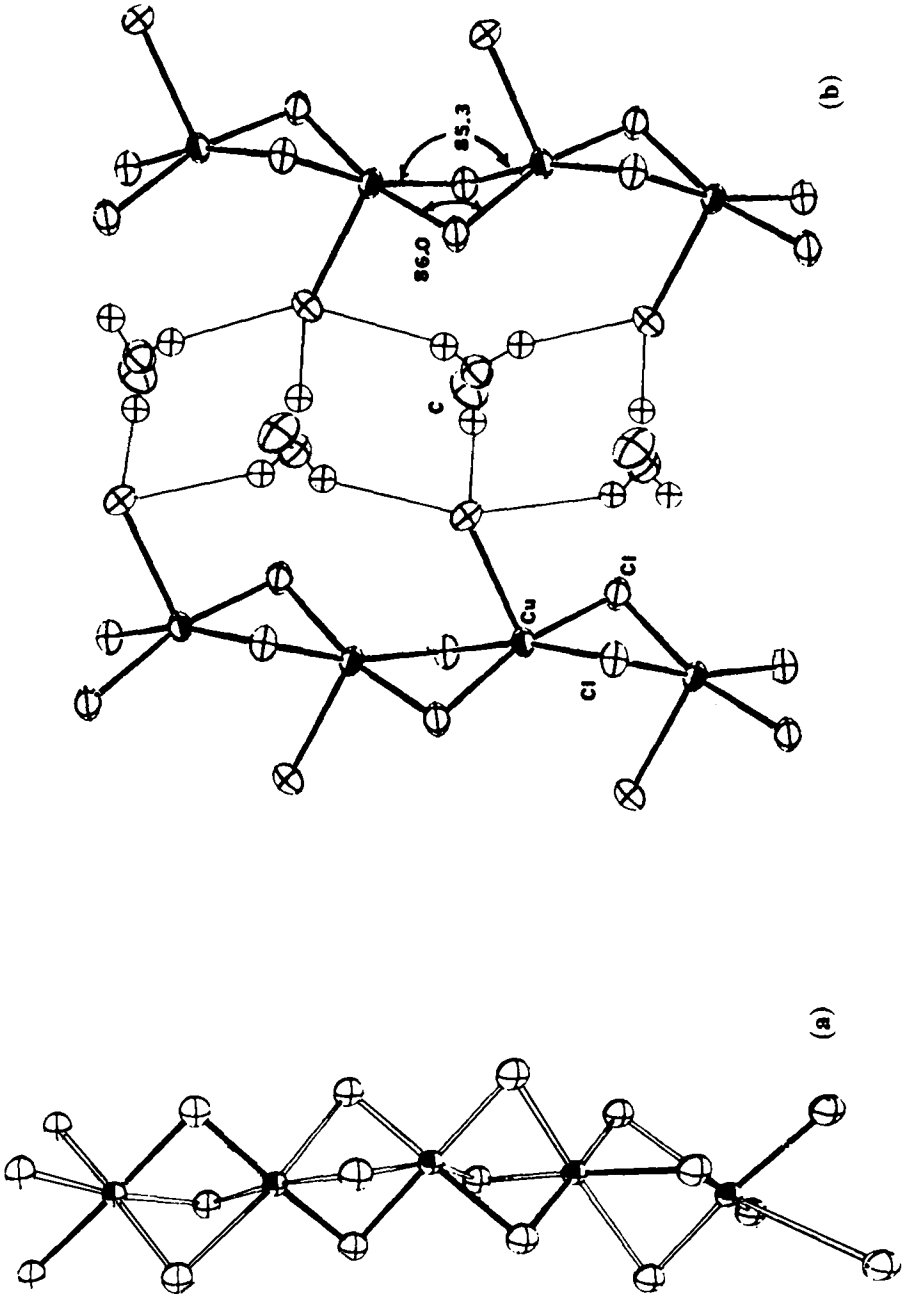
Abstract. New phenomena characteristic of one-dimensional magnetism have been studied in model systems: quantum effects in one-dimensional Heisenberg ferromagnets (1*D*-HF) with $S = 1/2$ and in one-dimensional Heisenberg antiferromagnets (1*D*-HAF) with $S = 1$; peculiar anisotropic behaviour of electron spin resonance (ESR) at low frequency and high temperature. The magnetic susceptibility in $(CH_3)_4NCuCl_3$ and $(C_6H_{11}NH_3)CuBr_3$, close to the $S = 1/2$, sD-HF show the expected deviation from the classical behaviour while the recently predicted quantum energy gap for the 1*D*-HAF is observed in $Ni(C_2H_8N_2)_2NO_2ClO_4$. Low frequency ESR in $(CH_3)_4NMnCl_3$, the archetype of 1*D* classical AF, is highly sensitive to the polarization of the oscillating field. In particular, for field direction along the chain axis, the signal is strongly enhanced while it remains at its expected value for perpendicular orientation. This behaviour is related to the axial symmetry of the system.

Keywords. One-dimensional magnetism; Heisenberg ferromagnets; Heisenberg antiferromagnets; quantum energy gap; electron paramagnetic resonance.

1. Introduction

Since the early work of Ising (1925), a lot of theoretical studies have been devoted to one-dimensional (1*D*) magnetism. In contrast with what happens in three dimensions, exact solutions and accurate approximations have been developed for several 1*D* magnetic models (Bonner 1985). In the last two decades the interest in 1*D* magnetism has been strongly renewed with the synthesis of many magnetic compounds which exhibit a quasi-1*D* magnetic behaviour. Besides the opportunity for checking the numerous theoretical predictions, this opened a new research area in magnetism, owing to the peculiarities of 1*D* magnetic systems. One of these peculiarities is the absence of a long range magnetic ordered phase at any finite temperature for the ideal 1*D* system with short range interactions. However, a short range order (SRO) arises as T decreases below $|J|S(S+1)/k$ (where J is the intrachain exchange interaction and S the spin). This SRO is characterized by a correlation length $\xi(T)$ which diverges as T tends to zero. For isotropic interactions described by the Heisenberg-Dirac hamiltonian $\mathcal{H} = -J \sum_i \mathbf{S}_i \mathbf{S}_{i+1}$, the high temperature spin dynamics are also very different from that of 3*D* systems. Since the total spin component $\sum_i \mathbf{S}_i^\alpha (\alpha = x, y, z)$ commutes with $\mathcal{H}$, the time correlation functions $\langle S_i^\alpha(0) S_j^\alpha(t) \rangle$ decay slowly as $t^{-1/2}$ at long times. This slow diffusive behaviour partly inhibits the usual exchange narrowing process and leads to drastic

*To whom all correspondence should be addressed.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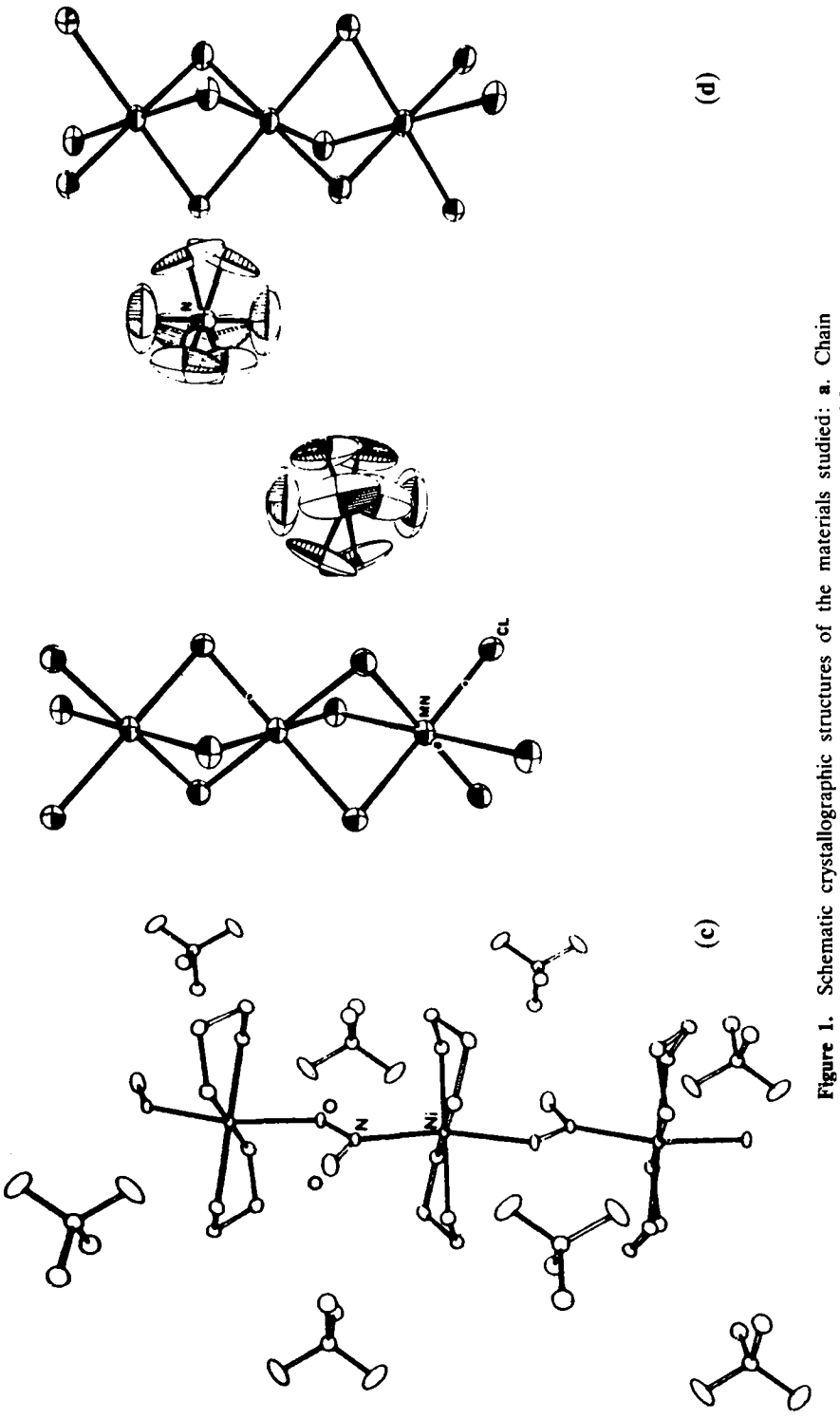

Figure 1. Schematic crystallographic structures of the materials studied: **a**. Chain structure of TMCuC (Willett *et al* 1983); **b**. Projection of the crystal structure of CHAC on to the *bc* plane; CHAB is isostructural with CHAC (Willett *et al* 1983); **c**. Perspective view of NENP; Chains are parallel to **b** axis (Meyer *et al* 1982); **d**. Crystal structure of TMMC; the $MnCl_3^-$ chains are parallel to **c** axis (Willett *et al* 1983).

variations of the EPR line-width and NMR relaxation times with the applied magnetic fields. At low temperatures, where SRO takes place, the spin dynamics is governed by $1D$ spin waves and in some cases by nonlinear excitations, known as magnetic solitons.

The peculiar behaviour of the static and dynamic magnetic properties at $D = 1$ has been well-evidenced by experiments performed on so-called model systems in which the interchain interactions are much smaller than the intrachain one. The results are reported in several review papers (De Jongh and Miedema 1974; Steiner *et al* 1976; De Jongh 1981; Renard 1985). We restrict there to a few new phenomena not yet reviewed, which are characteristic of $1D$ magnetism:
(i) the quantum effects exhibited at low temperature by the one-dimensional Heisenberg antiferromagnet ($1D$-HAF) with spin $S = 1$ and by the one-dimensional Heisenberg ferromagnet ($1D$-HF) with spin $S = 1/2$;
(ii) the *anomalous* behaviour of the ESR lines at low frequencies and high temperatures in the nearly ideal $1D$-HAF, $(CH_3)_4NMnCl_3$ (TMMC). Figure 1 displays the crystallographic structures of the compounds studied.

2. Quantum effects in 1D–magnetic systems

2.1 *Theoretical survey*

It is well-established from the renormalization group theory (Wilson 1971) that the value of the spin is not a relevant parameter for the critical behaviour of $3D$ magnetic systems. Indeed, the values of the critical exponents do not depend on S, as shown by the series expansion calculations as well by the experiments on magnetic compounds (Kadanoff *et al* 1967). Furthermore as T tends to zero, the functional shape of the spontaneous magnetization M_s is also independent of S: $M_s(T) \simeq M_s(0) - aT^{3/2}$ for Heisenberg ferromagnets (HF), $M_s(T) \simeq M_s(0) - bT^2$ for Heisenberg antiferromagnets (HAF). The kinematic interaction between spin waves, which arises from the fact that more $2S+1$ units of reversed spin cannot be attached to the same atom simultaneously, can be neglected in an expansion in powers of $kT/|J|$ (Dyson 1956; Oguchi 1960). The zero point spin reduction in $3D$-HAF is the only quantum effect which deserves to be mentioned. The relative spin reduction is roughly given by $\delta S/S \simeq 1/zS$ where z is the number of neighbours interacting with a given spin. The predicted spin reduction is generally small in true $3D$ system. It is substantially larger in quasi $2D$ – antiferromagnets in which it has been measured by neutron diffraction and nuclear magnetic resonance (Walstedt *et al* 1970; De Wijn *et al* 1973).

In contrast with $3D$ systems, drastic quantum effects are predicted for $1D$ systems. Let us consider, at first, the case of one-dimensional ferromagnets ($1D$-F). The correlation functions of the classical $1D$ Heisenberg system have been determined by Fisher (1964). As T tends to zero, the correlation length diverges as T^{-1} and consequently the magnetic susceptibility of the $1D$-HF proportional to T^{-1}. ξ diverges as T^{-2}. The same T^{-2} susceptibility behaviour is also obtained for the classical $1D$-XY ferromagnet. The magnetic susceptibility of the $S = 1/2$, $1D$-HF cannot be obtained exactly but approximate treatments have been developed by different authors (Bonner and Fisher 1964; Baker *et al* 1964; Lyklema

1982). They indicate a power law divergence $\chi(T) = AT^{-\gamma}$ as $T \to 0$, with an exponent γ lower than the classical value $\gamma_{cl} = 2$. The theoretical estimates presently available range between 1·67 (Baker *et al* 1964) and 1·8 (Bonner and Fischer 1964). The recent synthesis of a few $S = 1/2$, $1D$-F with small magnetic anisotropy allows the testing of the predicted quantum reduction of the exponent γ. First experimental results will be presented in §2.2.

A more striking quantum effect at $D = 1$ concerns the structure of the lowest energy states of the $1D$-HAF. It has been recently conjectured by Haldane (1983) that this structure is completely different for integer and noninteger spin values. The $S = 1/2$, $1D$-HAF has been theoretically investigated by des Cloizeaux and Pearson (dCP) (1962). It exhibits an ordered ground state and a quasi-continuum of excited states without gap from the ground state. The magnetic excitations of lowest energy are $E = \pi/2\,|J|\,|\sin q|$ and appear to be very similar to the classical $1D$-HAF which has also a sine dispersion relation: $E = 2\,|J|\,|S|\sin q\,|$. The neutron diffraction experiments performed in the $1D$-HAF TMMC, with $S = 5/2$ (Hutchings *et al* 1978) and $CuCl_2.2N(C_5D_5)$, (Cu PC) with $S = 1/2$ (Heilmann *et al* 1978) support the theoretical predictions. Subtle quantum effects are revealed from the neutron scans in Cu PC, firstly near the zone boundary $q = 1$, where additional excitations of higher energy than the dCP ones are observed, and secondly in the excitation spectrum in an applied magnetic field. Owing to the similarity between the $S = 1/2$ – and the classical $1D$-HAF, it was thought until recently that the intermediate cases, such as $S = 1$, were of little interest. The interest in the $1D$-HAF with integer spin values has been renewed by Haldane (1983) who predicted, for these systems, an energy gap between the singlet ground state and the first excited states. Botet *et al* (BJK) (1983) investigated in detail the properties of the $S = 1$, $1D$ Heisenberg-Ising antiferromagnet described by the following Hamiltonian

$$\mathcal{H} = \sum_i [-J(S_i^x S_{i+1}^x + S_i^y S_{i+1}^y + \lambda S_i^z S_{i+1}^z) + D(S_i^z)^2], \tag{1}$$

where J represents the intrachain exchange interaction, $1-\lambda$ the exchange anisotropy and D the single-ion anisotropy. For a certain range of λ and D values, there is a novel phase with an unordered singlet ground state and an energy gap to the excited states continuum. The gap exhibits a nontrivial variation with the magnetic anisotropy which is sketched in figure 2. Haldane's predictions and the results of BJK were confirmed by finite size calculations up to $N = 14$ for $S = 1$ (Parkinson and Bonner 1985) and by a Monte Carlo calculation up to $N = 32$ (Nightingale and Blöte 1986). They provide a good estimation for the energy gap of the $S = 1$, $1D$-HAF: $E_G \simeq 0{\cdot}4\,|J|$. These predictions for the $1D$-HAF with $S = 1$, are compared to the experiments on the new model system $Ni(C_2H_8N_2)NO_2ClO_4$ in §2.3.

2.2 *Low temperature magnetic susceptibility of two $S = 1/2$, $1D$ ferromagnets: TMCuC and CHAB*

Among the series of $S = 1/2$, $1D$ ferromagnets recently discovered (Willett *et al* 1983; Willett 1985), $(CH_3)_4NCuCl_3$ (TMCuC) and $(C_6H_{11}NH_3)CuBr_3$ (CHAB) are especially attractive because of their low $3D$ magnetic ordering temperature, $T_N = 1{\cdot}24$ K for TMCuC (Dupas *et al* 1982) and $T_N = 1{\cdot}5$ K for CHAB (Kopinga

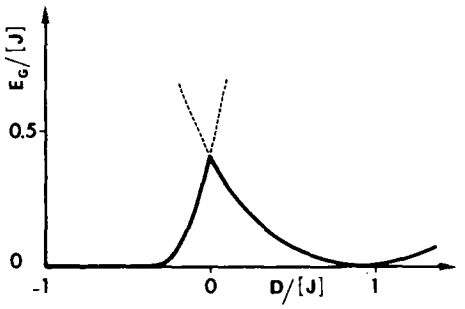

Figure 2. Variation of the energy gap between the ground state and the first excited state of the $S = 1$, 1D–AF, with the single ion anisotropy parameter D ($\lambda = 0$). $D = 0$ corresponds to the pure Heisenberg case, $D < 0$ to XY type anisotropy and $D > 0$ to Ising type anisotropy (after Botet *et al* 1983).

et al 1982), compared to the intrachain interaction of about 100 K (see figure 1a,b). The magnetic anisotropy of TMCuC is not known since single crystals of this compound were not available. It is likely to be small because of the octahedral symmetry of the local environment of the Cu^{2+} ion. For CHAB, the ferromagnetic resonance experiments (Phaff *et al* 1984) show a planar anisotropy of 5% of the isotropic exchange interaction $J/k = 110$ K (Kopinga *et al* 1982).

The magnetic susceptibility of powdered TMCuC at low temperature ($kT/J < 0{\cdot}3$) is shown in figure 3. The experimental data are fairly consistent with the series expansion calculations of Baker *et al* (1964) for the $S = 1/2$, 1D-HF for $J/k = 88$ K. They can be fitted by the power law $T^{-1.58}$ between 2·3 K and 20 K. The deviations from this power law which occur below 2·3 K are certainly related to the 3D interactions with induce antiferromagnetic long range order at $T_N = 1{\cdot}24$ K. From these susceptibility data, it appears that TMCuC behaves as a nearly ideal $S = 1/2$, 1D-HF and exhibits the predicted quantum reduction of the susceptibility critical exponent as T tends to zero. The susceptibility of a small monocrystal of CHAB, grown by Dr C Landee, has been measured with a low field SQUID magnetometer (Beauvillain *et al* 1985), along the crystal axes **c** (easy plane) and **a** (hard axis). The experimental data in figure 4, show the drastic effect of magnetic anisotropy, at temperatures below 30 K, the susceptibility along the hard axis being much smaller than the one along the easy axis, except at the vicinity of the 3D ordering temperature where the interchain interactions become predominant. For the easy direction **c**, the experimental data cannot be described in a wide temperature range by a power law with a unique value of the exponent; in fact, the effective exponent between 20 K and 3 K, varies from 1·75 to about 2. The quantum reduction from the classical exponent 2 is thus less important in CHAB than in TMCuC. This could be related to the planar anisotropy which has been taken into account in the recent quantum Monte Carlo study of Satija *et al* (1985). These authors calculated the susceptibility of CHAB along the easy plane between 5 and 20 K. Their results which are consistent with a $T^{-1.75}$ law, are in good agreement with the experimental data above 8 K; precise calculations at lower kT/J values are clearly needed for an extensive comparison with the experiment.

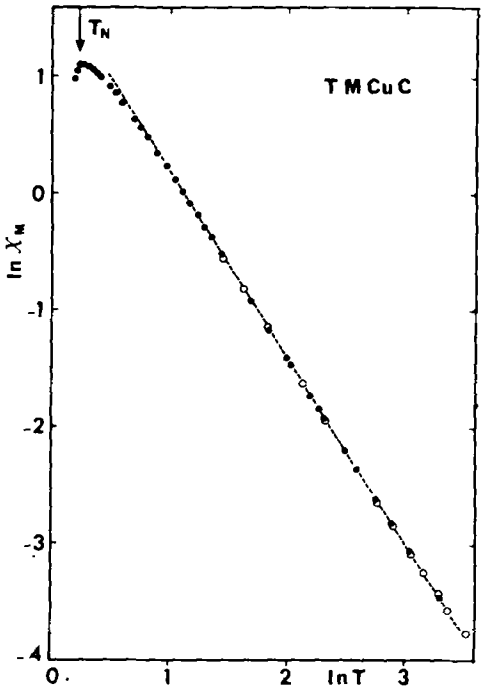

Figure 3. Molar susceptibility of TMCuC powder in cgs emu as a function of temperature, on a double neperian logarithmic scale: (●) experimental data; (○) series expansion of Baker *et al* (1964) for J/k = 88 K. The dotted line represents the power law $T^{-1.58}$.

2.3 *Experimental study of NENP a quasi-1D Heisenberg antiferromagnet with* $S = 1$.

It is surprising that the quantum gap in the quasi-1D-HAF with integer spin value was not observed until very recently. Indeed, the existence of an energy gap E_G between the singlet ground state and the first excited states would produce drastic effects on the magnetic properties. At temperatures below E_G/k, the magnetic susceptibility $\chi(T)$ would exhibit a fast decrease with T and tends to a value, $\chi(0)$, much smaller than the maximum one, χ_{max} at $T \simeq |J|/k$, for all magnetic field orientations. In addition, since the correlation length does not diverge as $T \rightarrow 0$, the quasi 1D-HAF with a gap cannot develop 3D magnetic long range order (LRO) if the interchain exchange interaction J' is sufficiently small.

In fact, until recently, the better 1D-HAF with $S = 1$ was $CsNiCl_3$ for which $|J|/k = 26$ K and $|J'/J| \simeq 10^{-2}$. This compound which is far from ideal, does not exhibit the expected behaviour for a gap system, either in the thermal variation of the susceptibility or in the absence of LRO ($T_N = 4{\cdot}85$ K). Nevertheless, indirect indications for a quantum gap in $CsNiCl_3$ have been recently reported from inelastic neutron scattering experiments (Buyers *et al* 1986).

A possible way to approach the ideal $S = 1$, 1D-HAF is to increase $|J|$ and the interchain distance. This is realized in $Ni(C_2H_8N_2)_2NO_2ClO_4$, hereafter abbreviated as NENP (figure 1c). In the orthorhombic crystal of NENP, the nickel ions are covalently linked by nitrito groups along the **b** crystal axis. This insures a large

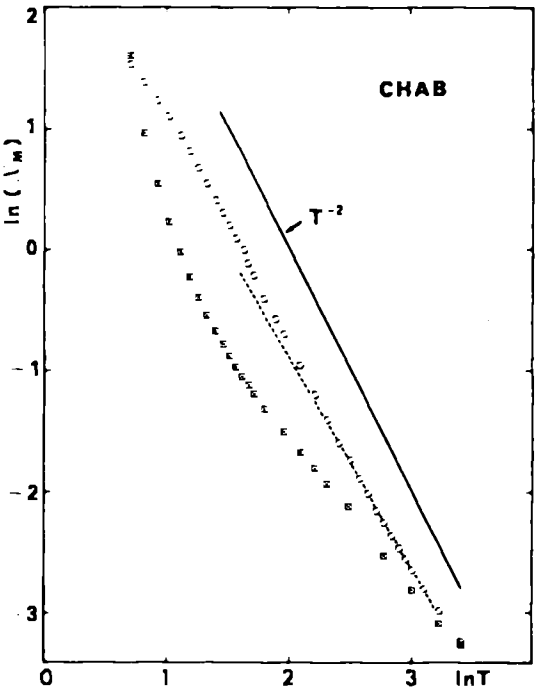

Figure 4. Molar susceptibility of a CHAB single crystal in cgs emu as a function of temperature, on a double neperian logarithmic scale: (○) experimental data for field along c; (—) experimental data for field along a; the dotted line represents the theoretical estimates for $S = 1/2$, 1*D*-*XY* ferromagnet (Satija *et al* 1985); the full line represents the classical law T^{-2}.

antiferromagnetic exchange interaction $J/k = 50$ K, while the planar anisotropy determined from high temperature susceptibility is small, $D/k \simeq 1$ K (Meyer *et al* 1982). The magnetic chains are well separated from each other by ClO_4^- anions, which leads to a small value of the interchain interaction $|J'/J| = 4 \times 10^{-4}$ (Renard *et al* 1987).

The magnetic susceptibilities of a single crystal of NENP, along the three orthogonal crystal axes **a**, **b** and **c** have been measured with a SQUID magnetometer (Beauvillain *et al* 1985) down to 1·7 K (figure 5). For all field orientations, the susceptibility exhibits a rounded maximum at about 60 K, in agreement with the previous measurements and falls down abruptly as the temperature is lowered below 15 K. The ratio $\chi(0)/\chi_{max}$ ranges between 3×10^{-2} and 10^{-1} for the various field orientations. These values are much smaller than the theoretical ones for a gapless 1*D*-HAF [$\chi(0)/\chi_{max} = 0{\cdot}69$ for $S = 1/2$ and 0·83 for $S = \infty$]. The behaviour of the susceptibility of NENP clearly indicates an energy gap E_{ei} between a singlet ground state and the excited states. By fitting the low temperature decay of $\chi(T)$ with an exponential law, $\exp(-E_{ei}/kT)$, a rough estimate of E_{ei}/k of about 14 K is obtained. However the lack of theoretical data relative to the temperature dependence of $\chi(T)$ for the $S = 1$, 1*D*-HAF forbids a quantitative analysis.

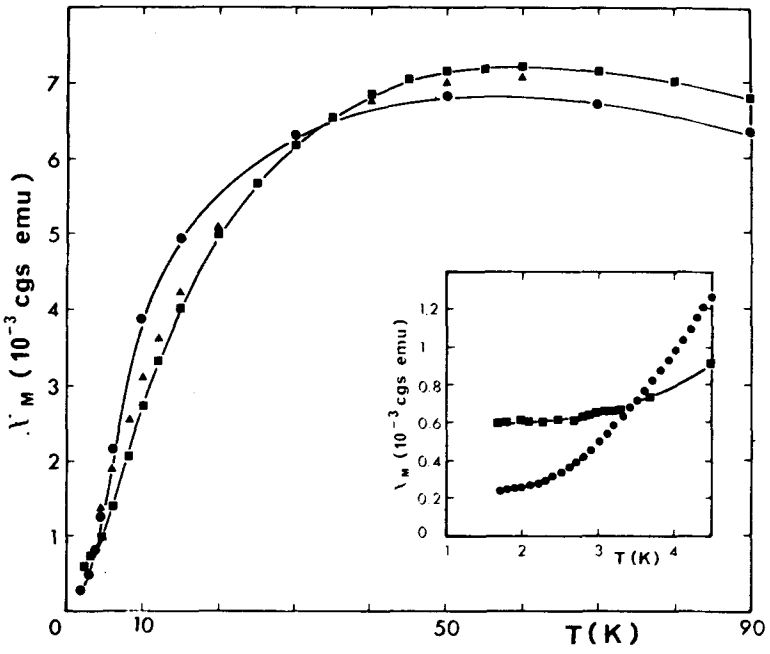

Figure 5. Molar susceptibility of the quasi-1*D*-HAF with $S = 1$, NENP, along the three crystal axes **a** (■), **b** (●) and **c** (▲) as a function of temperature. The solid lines are guides for the eye. Notice the abrupt decrease of the susceptibilities below 15 K due to the quantum energy gap.

A second clear manifestation of the energy gap in NENP is the absence of 3*D*-LRO. For a gapless Heisenberg model with $J/k = 50$ K and $|J'/J| = 4 \times 10^{-4}$, the Néel temperature approximated as $T_N \simeq 2S^2(|J.J'|)^{1/2}/k$, is equal to about 2·5 K. There is no experimental evidence for such a transition in the susceptibility curves of figure 5. In addition, the proton magnetic resonance spectra of a single crystal of NENP were recorded at 77 K and between 1·2 and 4·2 K. The spectra which show negligible temperature dependence of the resonance fields are characteristic of a disordered magnetic phase.

From detailed inelastic neutron scattering experiments, the excitation spectrum of NENP was determined for different scattering vectors (Renard *et al* 1987). These measurements show two energy gaps corresponding to fluctuations of the spin components parallel and perpendicular to the chain axis, at respective values $E_G/|J| = 0{\cdot}26$ and $E_G/|J| = 0{\cdot}58$. The existence of two gaps, instead of one for the pure $S = 1$, 1*D*-HAF is due to the magnetic anisotropy ($D \neq 0$) and is consistent with the predictions of BJK (figure 2). One can reasonably assume that the average of the two gap values, $E_G/J = 0{\cdot}4$ is a good estimate of the unique gap of the 1*D*-HAF. Indeed a good agreement is found with the theoretical predictions $E_G/|J| = 0{\cdot}38$ (Parkinson and Bowner 1985) and 0·41 (Nightingale and Blöte 1986).

3. Low frequency electron spin resonance in 1D magnetic systems

3.1 *High temperature 1D spin dynamics and ESR*

In concentrated paramagnetic exchange coupled systems the ESR lines are Lorentzian in shape and relatively narrow, considering the dipolar interaction between spins. This "exchange narrowing" (Pake 1962) is related to the exchange interaction J between the spins, and can be described as a mechanism which flips the spins at a $|J|/\hbar$ rate and randomizes broadening processes.

More precisely, it can be shown, within linear response theory (Pake 1962), that the ESR absorption from a field $\mathbf{B}_1 \cos \omega t$ linearly polarized along the x-axis is proportional to the Fourier transform of the magnetization correlation function

$$G_x(t) = \langle S_x(t)\, S_x(0) \rangle,$$

$$A_x(\omega) \propto \int_{-\infty}^{+\infty} \langle S_x(t)\, S_x(0) \rangle \exp(-i\omega t)\, \mathrm{d}t, \tag{2}$$

the bracket denoting a statistical average, and the time dependence of the total spin component S_x being due to the spin Hamiltonian of the system (essentially exchange, Zeeman, and dipolar coupling terms).

$G_x(t)$ itself is related to local time-spin correlation functions which, in $3D$ systems, decrease to zero in a very short time $1/J$ so that $G_x(t)$ falls down exponentially with a time constant T_2. A Lorentzian line with half-width (in angular units) $1/T_2 \sim (\omega_d/\hbar)\ (\omega_d/J)$ results, ω_d being a dipolar coupling factor.

Significant deviations from this behaviour are observed in quasi one-dimensional systems such as TMMC. They have been thoroughly studied for the last fifteen years, essentially in the microwave frequency range (Dietz *et al* 1971; Reiter and Boucher 1975; Cheung *et al* 1978; Natsuma *et al* 1980; Siegel *et al* 1982).

The ESR $1D$ spectrum is highly anisotropic and two orientations are of special interest. In the following, θ is the angle between the axis of the chain (**c** axis of the crystal) and the static field $\mathbf{B}_0$. When the static field $\mathbf{B}_0$ points along the chain axis ($\theta = 0°$) a non-Lorentzian broad line is observed while at the magic angle orientation ($\theta = 55°$) the line is narrow and Lorentzian: in this latter case the secular part of the dipolar interaction between spins is cancelled. These features [and other ones: strong sensitivity to impurities (Richards 1974), side band effects (Lagendijk 1978)...] are well-explained by the long-lived local correlation functions. The Heisenberg coupling flips the spins without changing the total magnetization of a chain and the local correlation functions are expected to have a $1D$ diffusive long-time behaviour $t^{-1/2}$. Owing to this very slow decay, the description of the absorption line profile is much more complicated than in $3D$ paramagnets because the damping factor now varies as the static field is swept through the absorption line. It gives rise to shape alteration and a half-width $\sim (\omega_d/J)^{1/3} \cdot \omega_d/\hbar$. At magic angle, however, the non secular dipolar terms are quickly modulated at Larmor frequency and the line remains Lorentzian.

3.2 *Low frequency ESR experiments in $(CH_3)_4N\,Mn\,Cl_3$ (TMMC)*

A recent investigation of the TMMC spectrum at very low frequencies (between 25 and 225 MHz) reveals new, interesting peculiarities (Clement *et al* 1984). In

general, measuring broad lines at low frequency is not an easy matter: the line amplitude varies as ω^2, the square of the angular frequency. This power dependence results from the induction law and from the Boltzmann factor. The situation may even be worse since the lines usually broaden when lowering the frequency; this phenomenon is known as the "10/3 effect" (Pake 1962). In the present study we meet three favourable conditions:

(i) we use large TMMC single crystals (with weighs between 2 and 5·5 g);
(ii) the apparatus sensitivity is such that synchronous detection is unnecessary, and direct interpretation of the results is possible;
(iii) we choose a case study (TMMC) where the symmetry of exchange and dipolar interactions permits large effects, as discussed below.

The field orientation of interest is neither the chain direction, nor the magic angle one, but the one when the field is perpendicular to the chain axis ($\theta = 90°$). In this case, a narrowing of the line is observed when the frequency is lowered, i.e. a phenomenon opposite to the one expected from the "10/3 effect". Moreover, the line amplitude is strongly dependent on the orientation of the oscillating field $\mathbf{B}_1$, defined by the angle $\varphi = (\mathbf{B}_1, \mathbf{c})$ (see figure 6). Relative absorption line amplitudes are measured using free radical DPPH as a standard. In the following, we put aside the ω^2 dependence, since it is common to all lines. When lowering the frequency,
i) the resonance amplitude is enhanced when the oscillating field $\mathbf{B}_1$ is parallel to the chain axis **c**; the enhancement factor is about 4 between 225 and 25 MHz.
ii) the resonance amplitude remains constant when $\mathbf{B}_1 \perp \mathbf{c}$ ($\varphi = 90°$).

These anomalous features can be explained by a simple model, where TMMC is considered as a set of non interacting spin chains, where the spins are coupled only by intrachain exchange H_{ex} and dipolar H_D interactions.

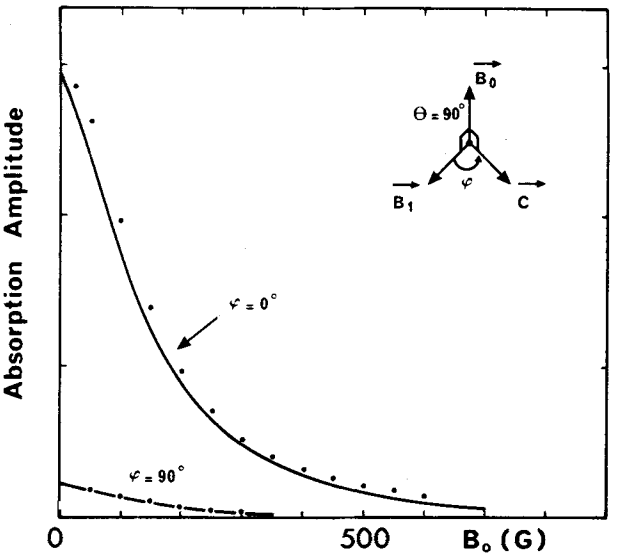

Figure 6. ESR spectrum of TMMC at the frequency $\nu = 25$ MHz for two orientations of the r.f. oscillating field: parallel ($\varphi = 0°$) and perpendicular ($\varphi = 90°$) to the chain axis **c**. For both cases the static field is perpendicular to **c**. The solid lines represent the experimental data and circles the theoretical predictions.

In this frame, the S_x total spin component along the chain axis **c**, supposed to be parallel to the x-direction, is a constant of motion (it commutes with H_{ex} and H_D), while S_y suffers a damping $1/T_2$. If we apply the oscillating field B_1 in the chain direction, in the limit $\omega \to 0$ the line profile is a delta function.

Let us apply the static field $\mathbf{B}_0$ along the z-direction. The S_x motion is coupled to the S_y motion through the Zeeman interaction. At high frequencies, the modulation at Larmor frequency $\omega_z = -\gamma B_0$, where γ is the gyromagnetic ratio, is so fast that anisotropy effects are very small: we recover the usual line profile. At "low" frequencies ($\omega \lesssim 1/T_2$) S_x suffers a damping which is a function of B_0 and T_2: the line is characterized by the enhancement of amplitude, the shift in position and its width narrowing.

If the oscillating field $\mathbf{B}_1$ is applied along the y-direction, the absorption line is related to the motion of S_y: no line amplitude enhancement is expected in this case.

In fact chains of spins are weakly coupled and a resulting damping $1/T_2'$ ($\ll 1/T_2$) occurs. The spectrum may then be accurately described by the following spin motion equations [with (2)], which are Bloch modified equations:

$$\dot{S}_x = \omega_z \cdot S_y - S_x/T_2',$$
$$\dot{S}_y = -\omega_z \cdot S_x - S_y/T_2'. \tag{3}$$

For $\omega \ll 1/T_2$ the main results are the following. At $\varphi = 0°$ ($\mathbf{B}_1 \parallel \mathbf{c}$), interchain interactions give rise to zero field absorption, and the signal is

$$A_x\ (\omega_z = 0) = a \cdot T_2'^{-1}/(\omega^2 + T_2'^{-2}), \tag{4}$$

where a is a constant.

When $\omega < 1/T_2'$, the resonance field is zero. In other cases, the resonance is given by:

$$\omega_z^2 = (\omega - 1/T_2')/T_2, \tag{5}$$

and the resonance signal presents the remarkable property to be almost independent of the damping values:

$$A_x\ (\text{res}) \simeq a/2\omega. \tag{6}$$

This enhancement at low frequencies is inhibited by interchain interactions when $\omega < 1/T_2'$. This is why the experimental resonance amplitude is enhanced four times and not nine when lowering the frequency from 225 MHz to 25 MHz.

At $\varphi = 90°$ there is no shift and the resonance signal A_y is equal to aT_2.

From (4) and (6), it is easy to derive the interchain damping $1/T_2' \simeq 6 \times 10^8$ rad s^{-1}, and from (5), $1/T_2' \simeq 9{\cdot}5 \times 10^9$ rad s^{-1}. Agreement with experiment appears fairly good (figures 6 and 7).

However, $1/T_2'$, and to a lesser extent $1/T_2$, are slowly decreasing functions of the field B_0. This field dependence can be directly observed at the "relaxation configuration" (Lagendijk and Schoemaker 1977), when the oscillating field $\mathbf{B}_1$ is parallel to the static one $\mathbf{B}_0$, along the z-axis. In this case, one measures the longitudinal relaxation of the magnetization towards its equilibrium value which is along the z-axis.

This relaxation occurs with a time constant T_1.

The absorption signal is then

$$A_z = a \cdot T_1^{-1}/(\omega^2 + T_1^{-2}). \tag{7}$$

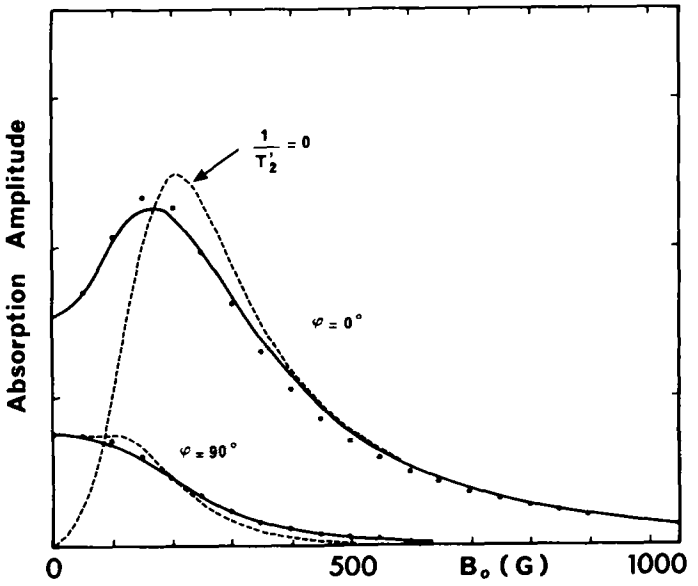

Figure 7. ESR spectrum of TMMC at $\nu = 225$ MHz. The experimental conditions are the same as in figure 6. Solid lines: experiment; circles: theory with $1/T_2' = 0{\cdot}59 \times 10^9$ rad s^{-1}; dashed lines: theory with $1/T_2' = 0$.

Measurements of A_z versus B_0 are shown in figure 8 for two orientations θ of the chain axis **c** with respect to Oz. Amplitude values are unscaled because zero absorption cannot be attained.

T_1 varies with the chain orientation θ. Longitudinal relaxation is produced mainly by the nonsecular terms of the intrachain dipolar interaction (Bourdel *et al* 1981). But when $\theta = 0°$ these terms cancel and the relaxation is caused by interchain interactions: T_1 coincides with T_2' at zero field. At the operating frequency (225 MHz), $A_z \simeq a/\omega^2 T_1$ shows a field dependence somewhat like $1/T_2'$. If the chain axis is perpendicular to the field ($\theta = 90°$) in turns out that $T_1 = T_2$ at zero field, a value $\gg \omega$. Thus $A_z \simeq aT_1$, exhibiting an increase with the field similar to the T_2 dependence.

A microscopic theory (Bize 1987) explains satisfactorily the experimental data for all field orientations and frequencies. This theory is in perfect agreement with the simple model based on modified Bloch equations. So far the same damping constants were used in the Bloch equation (3) though interactions are anisotropic in crystalline solids. This approximation is indeed valid at high frequencies ($\omega \gg 1/T_2$) where spin components suffer a mean damping $(1/T_2 + 1/T_2')/2$, $1/T_2'$ in the oscillating field direction $\mathbf{B}_1$ and $1/T_2$ in the direction perpendicular to both fields $\mathbf{B}_1$ and $\mathbf{B}_0$. But interesting information about local interactions may be obtained from low frequency experiments by varying the oscillating field polarization. To be fair, we must point out that such important effects are observed because TMMC represents an extreme case where the dominant interactions are the exchange ones with spherical symmetry and the intrachain dipolar ones with axial symmetry. This results in extremely small spin damping in the chain direction, hence the magnitude of the observed effects.

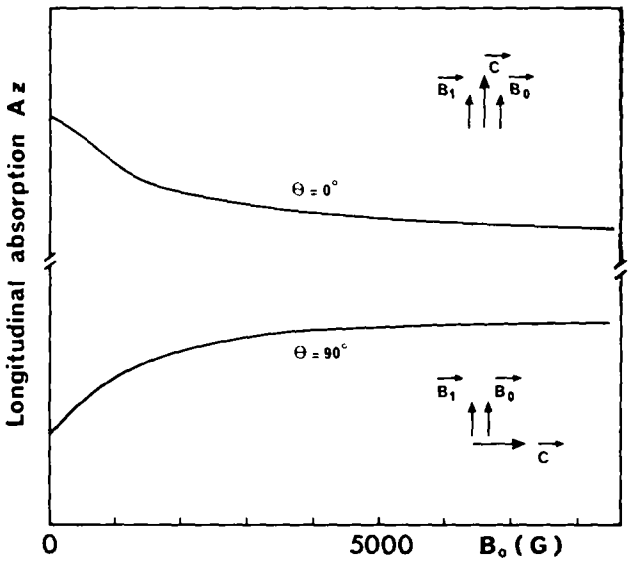

Figure 8. ESR absorption in the "relaxation configuration" i.e. oscillating and static fields parallel to each other. The fields are parallel ($\theta = 0°$) or perpendicular ($\theta = 90°$) to the chain axis. The signals are unscaled.

4. Conclusion

The experimental investigations reported in the preceding sections show how one-dimensional magnetism remains a rich research field in condensed matter. The study of quantum effects in $S = 1/2$, $1D$-materials is yet in rapid development. Indeed, magnetic solitons have been recently observed in the ferromagnetic chains of CHAB (Kopinga *et al* 1984) at low temperature. On the other hand, the study of the $S = 1$, $1D$ antiferromagnets is just at the beginning. It promises interesting developments which include the phase diagram in an applied magnetic field, the low temperature spin dynamics, the direct measurement of the correlation length versus temperature and the effect of magnetic anisotropy on quantum gaps.

The high temperature spin dynamics also remains interesting as shown by the peculiar behaviour of the low frequency ESR. This is a novel method for the direct determination of the interchain exchange interaction, which should be applied to many other $1D$ compounds than the model system TMMC.

Therefore, new progress in 1-D physics demands endeavours in two directions:
(i) development of new instruments and techniques: sensitive magnetometers, versatile ESR spectrometers (low frequency and variable oscillating field direction, Clement *et al* 1984) and low temperature measurements. Instrumental work is underway to make such equipments easily available to the scientific community (Willett 1985);
(ii) synthesis of new compounds with predictable properties, within the chains and between them: this is a challenge for chemists and crystallographers:
$1D$-F are rare. To obtain new species, the synthesis of bimetallic (A, B) compounds, with orthogonal magnetic orbitals (A = d^1; B = d^9 for example) is a possible answer.

The study of quantum gaps necessitates new $S = 1$, or 2, $1D$-AF with smaller J intrachain exchange interaction, with single ion anisotropy of various kinds, Ising and XY, variable D/J and better J'/J ratio (Ribas *et al* 1987).

New quantum effects might be evidenced in the bimetallic ferrimagnetic chains, with different spins, recently synthesized (Drillon *et al* 1983; Gleizes and Verdaguer 1984; Verdaguer *et al* 1984; Pei *et al* 1987), which deserve to be explored.

Finally, interchain interactions have to be carefully controlled: whether to obtain better $1D$ materials with bulky insulating groups, or to build at will $2D$ or $3D$ networks with expected properties, from ferro or ferrimagnetic $1D$ linked by well-conceived connections.

We are working along these lines (Pei *et al* 1987)

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