

## High-Field NMR Insights into Quantum Spin Systems

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Possibilities of NMR technique will be illustrated by a selection of high-field NMR results on antiferromagnetic quantum spin systems, obtained at the Grenoble High Magnetic Field Laboratory. We present results for two well known systems, doped Haldane spin chain  $\text{Y}_2\text{BaNi}_{1-x}\text{Mg}_x\text{O}_5$  and spin-Peierls compound  $\text{CuGeO}_3$ , as well as two newly studied compounds, the  $\text{NaCu}_2\text{O}_2$  chain (or zigzag ladder) and the 2D dimer compound  $\text{BaCuSi}_2\text{O}_6$  ("Han purple").

### §1. Introduction

Nuclear Magnetic Resonance (NMR), being a microscopic probe for magnetism naturally performed in magnetic field ( $H$ ), is therefore particularly appropriate for studies of quantum spin systems (QSS).<sup>1)</sup> It is relatively simply implemented in the high field and low temperature ( $T$ ) environment, providing a uniquely broad access to the  $H$ - $T$  phase diagram of these compounds. NMR spectra can provide detailed "image" of the spatially non-homogeneous spin polarization (commensurate and incommensurate spin modulations, impurity effects), while the relaxation rates ( $T_1^{-1}$ ,  $T_2^{-1}$ ) reflect the low-energy excitations, and are typically used to follow the  $H$ - and  $T$ -dependence of the gap, revealing its nature.

In the high-field NMR group at Grenoble High Magnetic Field Laboratory (GHMFL) we have focused our attention on those QSS for which the value of the "critical" magnetic field  $H_c$  bringing the system into its "interesting" phase is higher than standard fields ( $\lesssim 9$  T) used for Solids NMR. A number of systems have been studied in the past decade, as summarized in Table I. In this paper we will present a short résumé of two oldest QSS studied at GHMFL, the doped Haldane chain  $\text{Y}_2\text{BaNi}_{1-x}\text{Mg}_x\text{O}_5$  and the spin-Peierls system  $\text{CuGeO}_3$ , as well as preliminary results on two new topical systems under study, the  $\text{NaCu}_2\text{O}_2$  chain and the 2D coupled dimers system  $\text{BaCuSi}_2\text{O}_6$ .

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Table I. Quantum Spin System studied by NMR at the GHMFL, classified by their dimensionality. Systems marked by asterisk \* are discussed in this paper.

dimensionality	formula and “title” <sup>NMR Ref.)</sup>
0D	“Fe10”, “Fe6” and “Cr8” molecular spin rings <sup>2)</sup>
1D	Y <sub>2</sub> BaNi <sub>1-x</sub> Mg <sub>x</sub> O <sub>5</sub> , doped Haldane chain <sup>3)*</sup>
	CuGeO <sub>3</sub> , spin-Peierls chain <sup>4)*</sup>
	Azurite Cu <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub> , diamond chain <sup>5)</sup> NaCu <sub>2</sub> O <sub>2</sub> , J <sub>2</sub> -J <sub>1</sub> chain or zigzag ladder <sup>6)*</sup>
2D	SrCu <sub>2</sub> (BO <sub>3</sub> ) <sub>2</sub> , Shastry-Sutherland system <sup>7)</sup>
	“Han purple” BaCuSi <sub>2</sub> O <sub>6</sub> , coupled dimers <sup>8)*</sup>
?D	Cu <sub>2</sub> (C <sub>5</sub> H <sub>12</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>4</sub> “ladder”, rather coupled dimers <sup>9)</sup> CuBrTeO <sub>5</sub> , (chain of) tetrahedra <sup>10)</sup>

## §2. Doped Haldane chain Y<sub>2</sub>BaNi<sub>1-x</sub>Mg<sub>x</sub>O<sub>5</sub>

The Y<sub>2</sub>BaNiO<sub>5</sub> compound appears to be an excellent model system for a Haldane spin chain:<sup>11)</sup> spins  $S = 1$  are carried by Ni<sup>2+</sup> ions, the intra-chain exchange coupling is  $J = 285$  K while the other inter-chain (3D) couplings are more than 1000 times smaller, and the Haldane gap anisotropy is quite small, the gap values being  $\Delta_H(\parallel \text{ to } a, b, c\text{-axis}) = 89, 102, 112$  K. When doping the system by Mg impurities, the Ni<sup>2+</sup>  $S = 1$  spins are substituted by the zero spin Mg<sup>2+</sup> ions thus cutting the ideally infinite spin chains into finite-size segments. As in any antiferromagnetic (AF) system, the impurities induce around them a staggered response. The particularity of this system is that this alternating spin-polarization surrounding each impurity could be directly observed by <sup>89</sup>Y NMR spectra; it is resolved site by site as satellite peaks developing around the main NMR line (in a certain temperature range), as shown in Fig. 1 and in Fig. 1 of Ref. 3). In this way one could *experimentally* establish that impurity induced spin polarization is indeed staggered (i.e., AF) and exponentially decreasing, defining an “impurity induced” correlation length, which turned out to be the same as the theoretically predicted correlation length of a pure system.<sup>3), 12)</sup> The same result was recently obtained<sup>13)</sup> for two other types of impurities, the  $S = 0$  Zn doping, but also for the  $S = 1/2$  Cu doping. The observed NMR spectra have been successfully compared to exact, Quantum Monte Carlo (QMC) numerical results — taking into account that in a real system there is a distribution of chain segments, and that the impurity induced response somewhat depends on the length of each segment.<sup>14)</sup> However, the QMC simulations of NMR spectra have been presented only for a random distribution of impurities, and their doping dependence shown in Fig. 1 predicts a strong suppression of the main NMR peak (coming from spins far away from impurities) towards 10% doping. In the NMR spectra this suppression is slower, which can be attributed to a mutual repulsion of impurities, increasing the percentage of longer chain segments in the samples.

We must also stress that the satellite lines in <sup>89</sup>Y NMR spectra could be resolved only down to  $\sim 80$  K, which is of the order of the Haldane gap. This corresponds to a regime where a classical description is still approximately valid, and the observed impurity induced spin polarization could also be well accounted for by simpler *clas-*

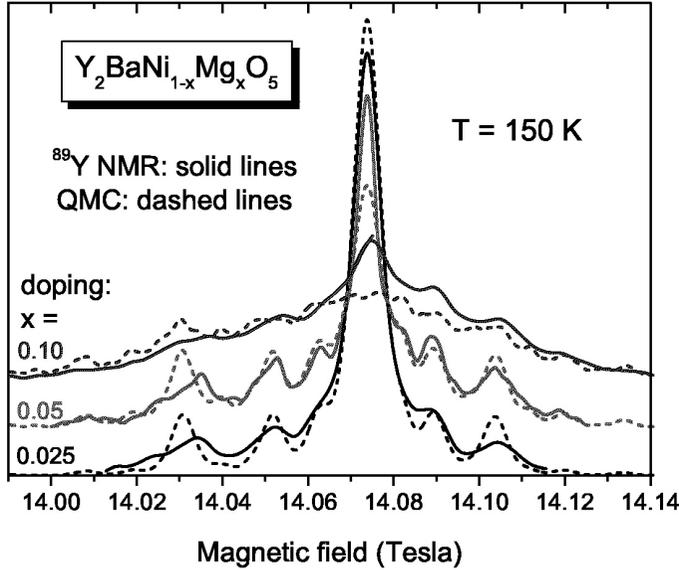


Fig. 1. Doping dependence of the  $^{89}\text{Y}$  NMR lineshape in  $\text{Y}_2\text{BaNi}_{1-x}\text{Mg}_x\text{O}_5$  at 150 K, and the corresponding Quantum Monte Carlo theoretical simulations.<sup>15)</sup> Resolved satellite peaks allow the site by site reconstitution of the local staggered spin polarization induced around Mg impurities.

sical Monte Carlo numerics.<sup>16)</sup> In the true quantum regime at lower temperature, unexpectedly, the satellite peaks of NMR spectra merge into a broad distribution, and the understanding of NMR results in this regime is still missing. It seems that the spectra are modified by increasing transversal relaxation rate  $T_2^{-1}$ , pointing to some dynamical, fluctuations effect.

### §3. Spin-Peierls chain $\text{CuGeO}_3$

Second example deals with the spin-Peierls chain, i.e., a Heisenberg, AF, spin 1/2 chain on an elastic lattice.<sup>17)</sup> At low temperature, this spin chain can gain energy by spontaneous dimerization (deformation) of the lattice, which allows the opening of a gap in magnetic excitations (absent in simple Heisenberg half integer spin chains). The dimerized state is non-magnetic, with a collective singlet state and an energy gap towards triplet excitations. Application of magnetic field will reduce the gap and, above the critical field  $H_c$ , drive the system into a magnetic phase with spatially inhomogeneous magnetization. In this field-induced phase, magnetization appears as an incommensurate (IC) lattice of magnetization peaks (solitons), where each soliton is bearing a total spin 1/2. The subject of our investigation was the NMR imaging of the magnetic field dependence (at nearly zero temperature) of the soliton lattice, followed from the limit of nearly independent solitons just above  $H_c$ , up to the limit of strongly overlapping solitons at high magnetic field, where the modulation of spin polarization is nearly sinusoidal.

By NMR we have studied<sup>20),21),4)</sup> the first and the most studied inorganic spin-Peierls system  $\text{CuGeO}_3$ ,<sup>22)</sup> presenting a spin-Peierls transition at 14–10 K (depending

on  $H$ ), and a critical field  $H_c \cong 13$  T. While in the high-temperature and in the dimerized phase symmetric NMR lines are observed<sup>20)</sup> reflecting spatially uniform magnetization, above  $H_c$  each line is converted to a very wide asymmetric spectrum (inset to Fig. 4, Fig. 1 in Ref. 4)) corresponding to a non-uniform distribution of magnetization, a soliton lattice. As for 1D spin modulation NMR lineshape can be directly converted into the corresponding real-space spin-polarization profile,<sup>21),4)</sup> we have thus obtained a full *quantitative* description of its  $H$  dependence in the range from  $H_c$  to  $2H_c = 26$  T.<sup>4)</sup> Analysis of these data proved that the staggered component of magnetization is reduced in the NMR image by phason-type motion of the soliton lattice.<sup>23),18)</sup> The magnetic correlation length (measuring the width of solitonic magnetization peaks) is found to be smaller than the correlation length of the corresponding lattice deformation measured by X-rays.<sup>19)</sup> This is recognized as a direct consequence of the frustration, i.e., the second neighbor interaction in the system.<sup>23)</sup> In Fig. 2 one sees that above 14 T the correlation length is close to the theoretically predicted value ( $\sim 8$  lattice units), the observed field dependences by NMR and neutrons are weak and of opposite sign, and may be very well only due to experimental errors or/and different crystal orientations. However, approaching  $H_c$  both techniques indicate a strong increase of the correlation widths, which remains to be understood theoretically.

We also mention some important theoretical results “motivated” by the efforts to understand NMR and other data on  $\text{CuGeO}_3$ . First, one should remember that behind the simplest Hamiltonian describing the spin-Peierls system there is an adi-

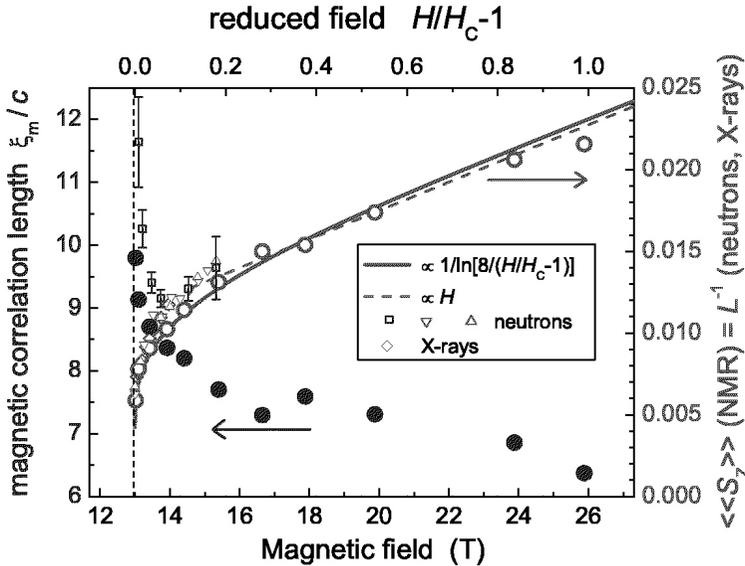


Fig. 2. Magnetic field dependence of the magnetic correlation length of solitons in the incommensurate high magnetic field phase of the spin-Peierls compound  $\text{CuGeO}_3$ , as determined by NMR<sup>4)</sup> (solid dots) and neutrons<sup>18)</sup> (open squares). Average spin polarization  $\langle\langle S_z \rangle\rangle$  (by NMR,<sup>4)</sup> open dots), which is equal to the incommensurability  $L^{-1}$  (neutrons,<sup>18)</sup> open triangles and X-rays,<sup>19)</sup> open diamonds), is compared to the mean-field prediction (full line, nearly linear at high fields).

abatic approximation, which is probably not valid in the real  $\text{CuGeO}_3$ . Next, the Hartree-Fock (HF) approximation with the *constant* HF term converts the XYZ spin Hamiltonian into the much simpler XY spin Hamiltonian, and therefore changes strongly the predicted spin-polarization profile in the high-field IC phase. When AF character of the system is correctly taken into account in the HF treatment, the XYZ character is preserved and the *true* HF description is quite close to descriptions taking into account the interactions completely, in the effective bosonic continuum model or numerically. In the bosonic model the sine-Gordon equation (defining the same correlation length for both spin-polarization and the lattice deformation) is obtained in the approximation of spatially homogeneous phase fluctuations. Numerical studies showed that this is not true, and that adding frustration (i.e., the second neighbor interaction) generates different correlation lengths for the spin-polarization and the lattice deformation,<sup>23)</sup> as observed experimentally.

#### §4. $\text{NaCu}_2\text{O}_2$ spin chain

The copper oxide compound  $\text{NaCu}_2\text{O}_2$  is an interesting candidate for a frustrated, quantum,  $S = 1/2$  spin chain or possibly a double chain with a zigzag ladder structure. This compound is isostructural to  $\text{LiCu}_2\text{O}_2$ , for which a helically ordered, incommensurate (IC) magnetic phase has been observed by neutron diffraction.<sup>24)</sup> The double-chain spin structure proposed for the Li-based compound implies a quantum, gapped, spin-liquid state with dominant commensurate, antiferromagnetic correlations, in contrast to the observed classical ( $S = \infty$ ), IC, helical solution of the same model. Masuda et al.<sup>24)</sup> proposed that an important parameter for stabilizing the classical IC state is the intrinsic chemical disorder, since the real composition of the compound is  $\text{Li}_{1+0.16}\text{Cu}_{2-0.16}\text{O}_2$ , in which 16% of Cu spins in the chains are replaced by zero spin Li ions. However, the chemical disorder in the isostructural  $\text{NaCu}_2\text{O}_2$  does not exist, yet below 13 K the “classical” helically ordered state is also observed.<sup>25)</sup> These results suggest that another spin structure is more appropriate for the description, namely the one of strongly frustrated chains with  $J_2 \gg J_1$ . The anomalously small size of the nearest neighbor coupling  $J_1$  is then associated to the Cu-O-Cu bond angle being close to  $90^\circ$ .

The aim of this NMR investigation of the  $\text{NaCu}_2\text{O}_2$  compound was to consolidate the neutron determination of the magnetic structure,<sup>25)</sup> which suffers from relatively weak signal to noise ratio. In particular, NMR can clearly distinguish IC from commensurate spin structures. The latter are characterized by splitting of NMR lines into resolved multiplets, as compared to broad continuous distributions reflecting IC phases. For a simple sinusoidal IC modulation of spin polarization, the NMR line-shape is expected to be given by the corresponding density of states,  $\propto 1/\sqrt{a^2 - x^2}$ , convoluted with a Gaussian (or Lorentzian) to account for the linewidth. Copper NMR spectra in the ordered phase of  $\text{NaCu}_2\text{O}_2$  were found to be of that shape, with overlapping signals from two isotopes  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ . In Fig. 3 we can see the temperature dependence of the half-width of this distribution, which directly reflects the spin modulation amplitude, i.e., the order parameter. The temperature dependence is found to be the same as in the  $\text{CuGeO}_3$  spin-Peierls chain, which is the standard

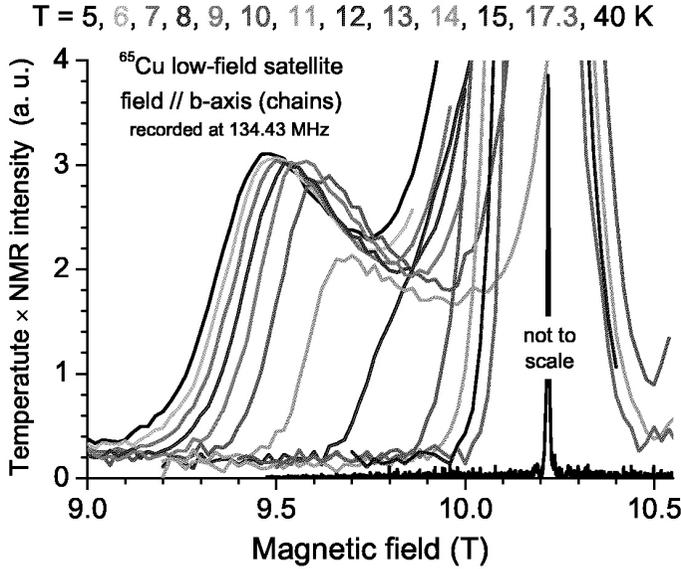


Fig. 3. Temperature dependence of the incommensurate spin polarization developing in the  $\text{NaCu}_2\text{O}_2$  spin chain compound, as revealed by copper NMR spectra. The phase transition into the ordered phase is recognized by a rapid broadening of the IC line-shape just below 13 K. Only the low-field half of one of the  $^{65}\text{Cu}$  NMR lines is shown out of a very broad field-sweep spectra, the other half being hidden by the overlapping  $^{63}\text{Cu}$  signal.

dependence for a 3D ordered phase with a two-component order parameter. The extrapolated low temperature value (scaled by the hyperfine field) corresponds to an amplitude of the spin modulation of  $0.30 \mu_B$ . To compare this value to the one determined in neutron experiments, we note that NMR observes only one of the two Cu sites present in the system, namely the Cu1 site (in the closed shell configuration). The NMR signal from the spin carrying Cu2 site is unobservable because of strong spin fluctuations. As each Cu1 site is coupled to two neighboring spins in two neighboring chains, the NMR always observes an average over four spins. This reduces the spin value measured by neutrons,  $0.64 \mu_B$ , by  $\cos(81.7^\circ/2) \times \cos(90^\circ/2)$ , where the angles are the pitch of the helical structure along and perpendicular to the chains. Neutron data corrected by this factor lead to  $0.34 \mu_B$ , a spin value very close to the one observed by NMR. As this value depends on both the amplitude and the pitch angle, the NMR result should be considered as a strong confirmation of the helical spin structure determined by neutrons.

By comparing the temperature dependence of the NMR line-shift above 13 K to the macroscopic magnetic susceptibility, we are able to precisely determine the spin susceptibility (and the hyperfine field). Its temperature dependence is found to be quite close to the theoretical “Bonner-Fisher” dependence of a simple Heisenberg chain. Altogether, the data support the model of a strongly frustrated chain,  $J_2 \gg J_1$ , for which both quantum and classical descriptions predict IC spin correlations.

### §5. 2D dimer compound $\text{BaCuSi}_2\text{O}_6$

The ancient pigment known as “Han purple”,  $\text{BaCuSi}_2\text{O}_6$ , has recently been recognized as a potentially ideal model system for the Bose-Einstein condensation of triplet excitations as a function of external magnetic field.<sup>26)</sup> Indeed, in the crystal structure of this compound one can recognize dimers of  $\text{Cu}^{2+}$  ions, i.e., spins  $S = 1/2$ , arranged in regular square lattice in planes, with negligible out-of plane coupling. This gives an apparently ideal 2D system of weakly coupled dimers, and from magnetization measurements the values of the intra-dimer, inter-dimer and out-of plane couplings have been found to be 51.6, 6.7 and 1.3 K, respectively. The singlet-triplet gap is closed by a magnetic field of  $H_{c1} \cong 23.5$  T and the full polarization is reached at  $H_{c2} \cong 49$  T. According to the specific heat and magnetization measurements, the phase appearing between  $H_{c1}$  and  $H_{c2}$  at low temperature ( $\max(T_c) = 3.8$  K) corresponds well to a Bose-Einstein condensate (BEC) of triplet excitations.<sup>26)</sup>

We have performed the first NMR investigation of  $\text{BaCuSi}_2\text{O}_6$  at very low temperature and close to  $H_{c1}$ ,<sup>8)</sup> in order to identify and characterize  $H_{c1}$  as a quantum critical point, and to give microscopic characterization of the “BEC” phase above  $H_{c1}$ . The experiment turned out to be technically very difficult, with extremely slow relaxation rate of  $^{29}\text{Si}$  nuclei (incompatible with time-limited high-field measurements), so that only a few preliminary results are available. The relaxation rate  $T_1^{-1}$  of  $^{29}\text{Si}$  at 23.4 T  $\cong H_{c1}$  is found to be nearly temperature independent in the 0.3–1.1 K range, confirming that the gap is well closed at this point. At 0.04 K the  $T_1^{-1}$  is found to be smaller, possibly due to some residual gap, smaller than 0.3 K. As shown in Fig. 4, on crossing  $H_{c1}$  the  $^{29}\text{Si}$  NMR lineshape changes dramatically

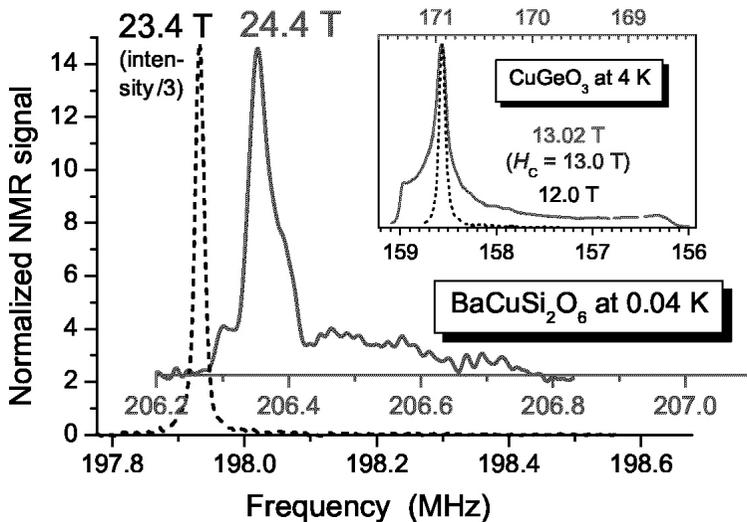


Fig. 4. “Zero” temperature ( $T = 0.04$  K)  $^{29}\text{Si}$  NMR spectra taken just below  $H_{c1}$  (dashed line) and in the supposedly “BEC” phase (solid line) of  $\text{BaCuSi}_2\text{O}_6$ . Unexpectedly, the latter phase seems to be incommensurate, as suggested by the comparison to the  $^{65}\text{Cu}$  spectra in the dimerized (dashed line) and the IC phase (solid line) of  $\text{CuGeO}_3$  given in the inset.

from a symmetric to a much broader and asymmetric spectrum, resembling what has been observed in  $\text{CuGeO}_3$  when entering the IC phase. The signal to noise ratio of spectra above  $H_{c1}$  is rather poor and needs to be improved, but these spectra do seem to indicate the presence of an *incommensurate* spin modulation. This is in contrast to simple line-splitting corresponding to a Néel-type order expected for the “BEC” phase. That is, in this phase the in-plane components of each spin in a dimer are staggered,<sup>27)</sup> and the BEC corresponds to ordering of that staggered moment. If the IC modulation in  $\text{BaCuSi}_2\text{O}_6$  is confirmed by further measurements, one should wonder what is stabilizing this structure. Higher temperature NMR data might give a hint to answer this question as well; they indicate that below 100 K there is a structural phase transition which might break the highly ideal tetragonal symmetry of the room temperature structure. Further NMR experiments are planned to shed more light on these questions.

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