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^{51}V NMR **study of the doped chain compounds** $PbNi_{2-x}Mg_xV_2O_8$

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Abstract. – ^{51}V NMR has been measured in polycrystalline chain compounds $PbNi_{2-x}Mg_xV_2O_8$ ($x = 0, 0.12, 0.24$) between room temperature and 4 K. A broad strongly shifted resonance has been found in all three cases, suggesting that VO_4 tetrahedra serve as a superexchange bridge between Ni^{2+} chains. The temperature dependence of the first moment of the ^{51}V NMR lines demonstrates the existence of a spin-gap down to very low temperatures even in doped samples. On the other hand, the large inhomogeneous broadening of the ^{51}V NMR spectra and the spin-lattice relaxation data suggest that short-range antiferromagnetic correlations already develop at $T \leq 100$ K and coexist with the 1D magnetic excitations in the Mg-substituted derivatives. In addition, we propose that not all ^{51}V NMR centres remain equivalent after doping. Namely, in Mg-doped samples we find an intense, narrow ^{51}V NMR line whose origin is compatible with the deformed VO_4 tetrahedra.

$PbNi_2V_2O_8$ is a new representative of the one-dimensional (1D) $S = 1$ family of systems exhibiting the Haldane ground state [1]. Its speciality is that it is the first Haldane system that on a D-J_1 phase diagram [2] (where D is the single-ion anisotropy and J_1 is the ratio of the interchain over the intrachain exchange coupling interactions) lays in the extreme vicinity of a phase boundary between the spin-liquid ground state and Ising-like ordered phase [3]. So any slight perturbation can induce a quantum phase transition from the spin-liquid state to a three-dimensional (3D) antiferromagnetic (AF) state. A way to destroy the spin-liquid ground state of $PbNi_2V_2O_8$ is to substitute non-magnetic Mg^{2+} ($S = 0$) ions for Ni^{2+} ($S = 1$) ions [1,4]. The introduction of Mg^{2+} impurities into a Haldane chain releases two $S = 1/2$ spins on each side of the impurity which were detected in $PbNi_{2-x}Mg_xV_2O_8$ by earlier ESR work [5,6]. Substitution of Mg for Ni leads to antiferromagnetically ordered phases for any $x > 0$, at temperatures $T_N \leq 3.5$ K [7], with a magnetic easy c-axis and a staggered moment of $0.9(1)\,\mu_B/Ni^{2+}$ [8].

Despite the fact that the occurrence of long-range AF order in $PbNi_{2-x}Mg_xV_2O_8$ is now well established and confirmed by several investigations, some details still remain unclear.

The competition between the 1D Haldane non-magnetic state and the 3D AF ground state is particularly vague. It is the purpose of this paper to shed some additional light on the transformation of the magnetic correlations from 1D to 3D as a function of doping and temperature. To achieve this goal, we use a local probe technique, *i.e.* ^{51}V NMR, which can detect the magnitude and the dynamics of the local magnetic fields.

The samples were prepared according to standard solid-state reactions [8,9]. X-ray diffraction measurements confirmed the phase purity of each $\mathrm{PbNi_{2-\mathit{x}}Mg_{\mathit{x}}V_2O_8}$ material. ^{51}V NMR has been measured in a magnetic field of 6.3 T. The ^{51}V NMR spectra were obtained by measuring the intensity of the echo signal as a function of resonance frequency.

In a magnetic field $\vec{B}$ the ^{51}V spin, $I = 7/2$, will experience, in addition to the Zeeman interaction, $\mathcal{L}_\mathrm{Z}$, a quadrupolar interaction, $\mathcal{L}_\mathrm{Q}$, and a hyperfine electron-nuclear coupling interaction, $\mathcal{L}_\mathrm{hf}$, namely

$$\mathcal{L} = \mathcal{L}_\mathrm{Z} + \mathcal{L}_\mathrm{Q} + \mathcal{L}_\mathrm{hf}. \tag{1}$$

These three interactions will in general determine the line shape and the center of the ^{51}V NMR line in $\mathrm{PbNi_{2-\mathit{x}}Mg_{\mathit{x}}V_2O_8}$. The temperature dependence of the first moment of the ^{51}V NMR line arises from the hyperfine interaction between the nuclear spin (I) and orbital (L) and spin (S) electronic moments [10]. In the paramagnetic phase, hyperfine interaction can be expressed as $\mathcal{L}_\mathrm{hf} = \hbar\gamma_\mathrm{n} g \mu_\mathrm{B} \vec{I} \cdot \boldsymbol{K} \cdot \vec{B}$. Here γ_n is the nuclear gyromagnetic ratio and μ_B is the Bohr magneton. The isotropic part of the coupling tensor $\boldsymbol{K}$, which determines the position of ^{51}V NMR line, can be decomposed into the sum of orbital, K_orb, and spin, K_spin, contributions as

$$K = K_\mathrm{orb} + K_\mathrm{spin} = 2\langle 1/r^3 \rangle \chi_\mathrm{orb} + A\chi_\mathrm{spin}/\hbar\gamma_\mathrm{n} g \mu_\mathrm{B}. \tag{2}$$

Here $\langle 1/r^3 \rangle$ is the expectation value of $1/r^3$ for $3d$ electrons and A is the hyperfine coupling constant. χ_orb and χ_spin are the orbital and the spin susceptibilities, respectively. At very low temperatures, *i.e.* at temperatures much lower than the Haldane spin-gap Δ, we expect that, at least for the undoped sample, χ_spin is vanishing small and therefore the entire shift of the ^{51}V NMR line at low temperatures arises from the nearly temperature-independent orbital contribution. The position of the ^{51}V NMR line in undoped $\mathrm{PbNi_2V_2O_8}$ at 4 K may thus serve as a reference. On the other hand, the quadrupolar interaction and the anisotropic part of the coupling tensor $\boldsymbol{K}$ determine the actual ^{51}V NMR lineshape. The main contribution to the anisotropic part of $\boldsymbol{K}$ is expected to come from the dipolar interactions between the nuclear spin $\vec{I}$ and the localized electron spin $\vec{S}$.

Figure 1 presents the ^{51}V NMR spectra for $\mathrm{PbNi_{2-\mathit{x}}Mg_{\mathit{x}}V_2O_8}$ ($x = 0, 0.12, 0.24$) at selected temperatures. A sharp resonance at 71.43 MHz is due to the presence of Cu at or around our probe. The lines are significantly shifted for more than 400 kHz from the expected ^{51}V Larmor frequency (70.89 MHz), unambiguously proving that a very large spin density is present at the ^{51}V site. This can be achieved only if $\mathrm{VO_4}$ tetrahedra are contributing to the exchange pathways, acting as a bridge between the $\mathrm{Ni^{2+}}$ spins on adjacent $\mathrm{NiO_6}$ chains. Therefore, $\mathrm{VO_4}$ units are crucial for the understanding of the magnetic phenomena in these systems. The room temperature ^{51}V NMR spectra are inhomogeneously broadened even in undoped $\mathrm{PbNi_2V_2O_8}$ with pronounced shoulders nearly symmetrically placed around the center of the line. Although such a pattern could be a signature of a staggered magnetization along the Ni chains [11–13], this is unlikely to be the case here as the lineshape and the linewidth do not change significantly on cooling. Instead, we find that the lineshape is characteristic of the first-order quadrupole perturbed Zeeman interaction H_Q. The quadrupole coupling constant is rather small, *i.e.* $e^2qQ/h = 60\,\mathrm{kHz}$, suggesting that the ^{51}V is located in a highly symmetric environment, most probably at the center of the $\mathrm{VO_4}$ tetrahedra.

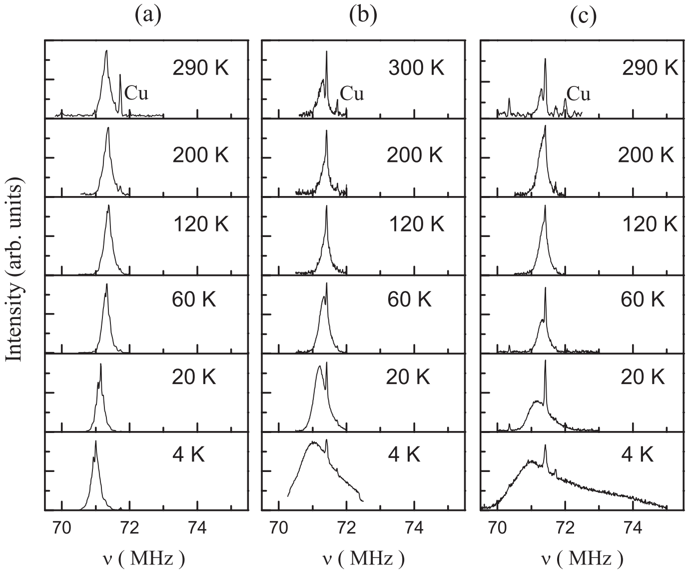

Fig. 1 – Comparison of the temperature-dependent ^{51}V NMR spectra for undoped $PbNi_2V_2O_8$ (a) and Mg-doped $PbNi_{1.88}Mg_{0.12}V_2O_8$ (b) and $PbNi_{1.76}Mg_{0.24}V_2O_8$ (c) samples.

The ^{51}V NMR line of $PbNi_2V_2O_8$ exhibits a large paramagnetic shift ($K \sim 0.6\%$) already at room temperature. The associated first moment, M_1 (fig. 2a), first increases slowly with decreasing temperature until it reaches a broad maximum at around 100 K and finally starts to decrease rapidly at lower temperatures due to the existence of a Haldane spin-gap. At 4 K, the center of the line is close to the ^{51}V Larmor frequency and we assume that at this temperature the entire shift is due to the orbital contributions. In agreement with eq. (2), the ^{51}V NMR M_1 displays nearly the same temperature dependence as the dc spin susceptibility [8]. These observations are fully consistent with a non-magnetic ground state for $PbNi_2V_2O_8$.

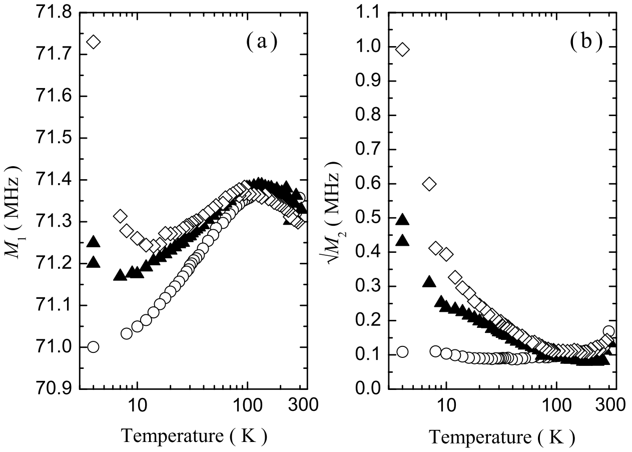

Fig. 2 – The temperature dependence of (a) the first moment and (b) the square root of the second moment of the ^{51}V NMR lines in $PbNi_2V_2O_8$ (○), $PbNi_{1.88}Mg_{0.12}V_2O_8$ (▲) and $PbNi_{1.76}Mg_{0.24}V_2O_8$ (◇).

The linewidth (*i.e.* the square root of the second moment $\sqrt{M_2}$ of the NMR line) for the parent $\mathrm{PbNi_2V_2O_8}$ compound is only very weakly temperature dependent (fig. 2b). This first proves that the main broadening mechanism in the undoped sample is of quadrupolar nature, as was discussed earlier. The anisotropic part of the coupling tensor $\boldsymbol{K}$ is averaged out due to a high mobility of magnetic excitations. It also suggests that there is no further structural deformation of the $\mathrm{VO_4}$ tetrahedra between room temperature and 4 K. Thus in the undoped sample the isotropic hyperfine contact interaction together with a first-order quadrupolar broadening (eq. (1)) are adequate to account for the temperature dependence of the lineshape as depicted by the first and the second moments of the spectra.

In doped $\mathrm{PbNi_{1.88}Mg_{0.12}V_2O_8}$ and $\mathrm{PbNi_{1.76}Mg_{0.24}V_2O_8}$ samples the room temperature ^{51}V NMR spectra (fig. 1) exhibit some important differences with respect to the discussed undoped case. The ^{51}V NMR line is now composed of two components, that is: a broad line identified before in the measurements of the undoped $\mathrm{PbNi_2V_2O_8}$ and a narrow peak. We stress, however, that the relative intensities of the two components illustrated in fig. 1 may not be fully accurate at all temperatures due to very different spin-lattice relaxation times of the two contributions. Because of that, we are unable at this stage to provide any information on the temperature dependence of the relative intensity of the narrow component.

The temperature dependence of the first moment of the broad component of the ^{51}V NMR line for the two Mg-doped samples, between room temperature and 120 K, is nearly the same as in the parent compound (fig. 2a). For $T < 120\,\mathrm{K}$ in both doped samples, M_1 first starts to decrease in a similar manner, with decreasing temperature, providing evidence for the existence of a spin-gap in the magnetic excitation spectrum even in doped samples. Nevertheless, at larger doping levels x, this effect appears to be less prominent. In addition, at $T_{\mathrm{min}} = 7\,\mathrm{K}$ and at $T_{\mathrm{min}} = 14\,\mathrm{K}$ for $\mathrm{PbNi_{1.88}Mg_{0.12}V_2O_8}$ and $\mathrm{PbNi_{1.76}Mg_{0.24}V_2O_8}$, respectively, the "trend" of the M_1 suddenly reverses and on further cooling it becomes enhanced. This result suggests that the 1D excitations characteristic of the Haldane state still exist down to $\sim$ 7–14 K, depending on the Mg content.

The variation of the $\sqrt{M_2}$ of the broad component of the ^{51}V NMR spectra, for doped $\mathrm{PbNi_{1.88}Mg_{0.12}V_2O_8}$ and $\mathrm{PbNi_{1.76}Mg_{0.24}V_2O_8}$ samples, at $T > 100\,\mathrm{K}$ is again rather reminiscent of the one measured for the undoped material (fig. 2b). This may indicate that Mg doping at the Ni sites does not appreciably distort the $\mathrm{VO_4}$ tetrahedra. This conclusion holds at least for the fraction of ^{51}V sites that are responsible for the broad signal. However, below 100 K the $\sqrt{M_2}$ of the ^{51}V NMR lineshape in $\mathrm{PbNi_{1.88}Mg_{0.12}V_2O_8}$ and $\mathrm{PbNi_{1.76}Mg_{0.24}V_2O_8}$ starts to increase tremendously and for $\mathrm{PbNi_{1.76}Mg_{0.24}V_2O_8}$ it reaches almost $\sqrt{M_2} = 1\,\mathrm{MHz}$ at 4 K. The lineshape becomes strongly asymmetric (fig. 1) and resembles a powder lineshape for a uniaxial-type coupling tensor. The electronic spins that couple to the ^{51}V centre and affect the ^{51}V NMR lineshape must therefore be localized at least in the NMR time-scale. Contrary to the undoped ones, doped samples show evidence for localized $S \neq 0$ spins already far above T_{N}. Therefore, such localized spins are induced by non-magnetic Mg-doping and the large increase in the $\sqrt{M_2}$ below 100 K suggests the development of AF correlations.

To get further insight into the excitation spectrum of the doped compounds, we also measured the ^{51}V spin-lattice relaxation time. The magnetization recovery curves for $\mathrm{PbNi_2V_2O_8}$ and $\mathrm{PbNi_{1.88}Mg_{0.12}V_2O_8}$ were found to be single exponential over the entire temperature range except for very low temperatures. On the other hand, in $\mathrm{PbNi_{1.76}Mg_{0.24}V_2O_8}$ compound the magnetization recovery curves were deviating from pure exponential. When fitted with a stretch-exponential form, we found an exponent $\alpha \approx 0.85(4)$. In fig. 3 we report the temperature dependence of the spin-lattice relaxation rate $1/T_1T$ for all three compounds. It coincides between room temperature and 100 K for all samples. However, important differences are found at lower temperatures where the relaxation rates are enhanced for larger

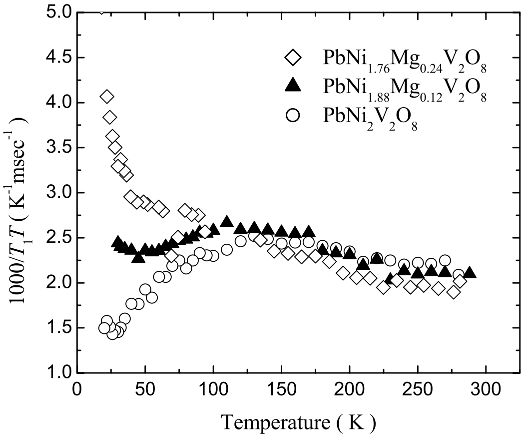

Fig. 3

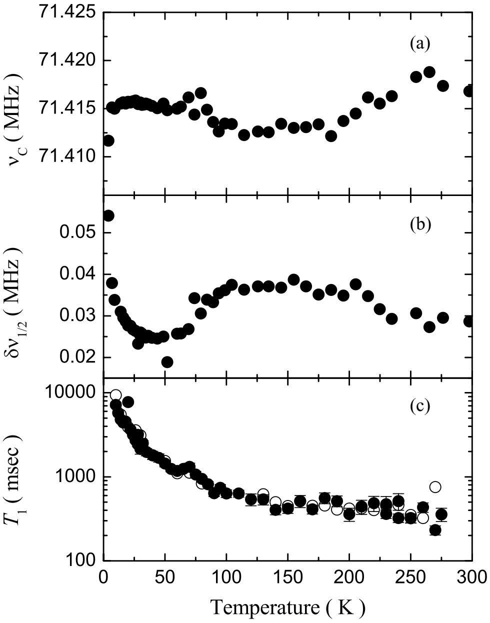

Fig. 4

Fig. 3 – The temperature dependence of the ^{51}V spin-lattice relaxation rates, $1/T_1T$, for the broad ^{51}V NMR component in $PbNi_2V_2O_8$ (○), $PbNi_{1.88}Mg_{0.12}V_2O_8$ (▲) and $PbNi_{1.76}Mg_{0.24}V_2O_8$ (◇).

Fig. 4 – The temperature dependence of the (a) center, (b) linewidth, and (c) spin-lattice relaxation time of the narrow component in the ^{51}V NMR spectra of $PbNi_{1.88}Mg_{0.12}V_2O_8$. For comparison the T_1 data for the $x = 0.24$ composition (open circles) are shown in panel (c).

doping. An appropriate starting point for the analysis of the nuclear spin-lattice relaxation time data is the expression [14]

$$T_1^{-1} = \sum_{\substack{\alpha=j,k \\ 0\le q\le\pi}} \left|K_\alpha(q)\right|^2 S_\alpha(q,\omega_\mathrm{N}) n_\alpha(q), \tag{3}$$

where $K_\alpha(q)$ is the electron-nuclear coupling, $S_\alpha(q,\omega_\mathrm{N})$ is the dynamic structure factor of the magnetic excitations, ω_N is the nuclear resonance frequency, and $n_\alpha(q)$ is the corresponding occupation function for the magnetic excitations. It has been shown [15, 16] that at least at low temperatures, in the Haldane state, eq. (3) for the relaxation can be expressed as $1/T_1 = (1/T_1^m)\exp[-\Delta_\mathrm{r}/T]$, with $\Delta_\mathrm{r} \sim 2\Delta(0)$ when the relaxation is dominated by spin-fluctuations at $q = \pi$ [15,16]. Fitting leads to $\Delta_\mathrm{r} = 82 \pm 2\,\mathrm{K}$ for the $PbNi_2V_2O_8$ compound. The obtained value for the zero-temperature Haldane gap, $\Delta(0) = 41\,\mathrm{K}$, is in good agreement with previous estimates of the spin-gap in $PbNi_2V_2O_8$ [1,3,8]. The analysis of the spin-lattice relaxation data in doped samples is, on the other hand, not so straightforward. If we use a high-temperature approximation for eq. (3),

$$T_1^{-1} = \gamma_\mathrm{N}^2 k_\mathrm{B} T \sum_{\substack{\alpha=j,k \\ 0\le q\le\pi}} \left|K_\alpha(q)\right|^2 \frac{\chi''_\alpha(q,\omega_\mathrm{N})}{\omega_\mathrm{N}}, \tag{4}$$

and assume that the dissipative part of the dynamic spin susceptibility $\chi''_\alpha(q,\omega_\mathrm{N})$ is simply proportional to the static susceptibility χ_spin, which determines the M_1 of the line (fig. 2a), we can successfully describe the data between room temperature and 100 K. However, at temperatures below 100 K, additional relaxation mechanisms must be considered in doped samples. In $\mathrm{PbNi_{1.88}Mg_{0.12}V_2O_8}$ one can still witness the presence of a spin-gap by observing a decrease in the $1/T_1T$ rate with decreasing temperature down to 50 K. This activated type of behaviour completely disappears in $\mathrm{PbNi_{1.76}Mg_{0.24}V_2O_8}$, where we find a monotonic increase in $1/T_1T$ rate with decreasing temperature (fig. 3). It may well be that enhanced AF fluctuations determine the low-temperature relaxation in doped samples. Such spin correlations, at $T < 100\,\mathrm{K}$, may indicate the tendency towards the formation of short-range ordered regions and explain the extreme broadening (fig. 2b) of the ^{51}V NMR lines as well as "less pronounced" decrease of M_1 below 100 K in doped samples (fig. 2a).

Let us now consider the occurrence of the narrow line in doped samples (fig. 1). In $\mathrm{PbNi_{1.88}Mg_{0.12}V_2O_8}$ and $\mathrm{PbNi_{1.76}Mg_{0.24}V_2O_8}$, the line is centred at 71.418 MHz, has a linewidth of about 25 kHz and a paramagnetic shift of about 470 kHz from the expected ^{51}V Larmor frequency. The intensity of this line represents $\sim 19\%$ ($x = 0.12$) and $\sim 50\%$ ($x = 0.24$) of the total ^{51}V NMR signal intensity at room temperature and roughly scales with the level of Mg doping as $2x$. This suggests that these ^{51}V sites are introduced by doping. The temperature dependence of the centre, ν_C (fig. 4a), and the linewidth, $\delta\nu_{1/2}$ (fig. 4b), are much less pronounced, when compared to the previously discussed broad line. While the ν_C of the narrow line does not shift appreciably with temperature (it changes only by about 5 kHz), the $\delta\nu_{1/2}$ seems to change in a similar manner to the spin susceptibility, *i.e.* it shows a broad maximum at around 100 K, then reaches a shallow minimum at 40–50 K and below this temperature is significantly increased. We also measured the spin-lattice relaxation time of the narrow component. We stress here that the relaxation magnetization curves over the entire temperature range are strongly non-exponential and were fitted with a stretch-exponential form: $M_Z(t) = M_Z(0)(1 - r\exp[-(t/T_1)^\alpha])$ with exponent $\alpha \approx 0.50(5)$ over the entire temperature range. T_1 evolves similarly for both Mg-doped samples (fig. 4c), *i.e.* $T_1 = 400\,\mathrm{ms}$ is nearly constant for $T > 175\,\mathrm{K}$. For $T < 175\,\mathrm{K}$, T_1 starts to increase and at 10 K is as long as $T_1 \sim 7\,\mathrm{s}$.

The origin of the narrow component in the ^{51}V NMR spectra is at the moment unclear. Its high intensity rules out the possibility that this line simply comes from impurity phases (structural data suggest less than 1% of impurity in the samples). Possibly, it represents the ^{51}V NMR centers in distorted $\mathrm{VO_4}$ tetrahedra. In such a case the electric-field gradients will be much larger when compared to those in undistorted $\mathrm{VO_4}$ tetrahedra. The expected satellite transitions then become very broad and difficult to detect. However, the central transition $-1/2 \leftrightarrow 1/2$ is in first order unaffected by the $\mathrm{VO_4}$ tetrahedral imperfections and should be thus observable [10]. If this assumption is plausible, then the rather long T_1 and the absence of strong temperature dependence for the M_1 suggest that the Fermi contact interaction with the magnetic excitations characteristic of the Haldane state is strongly suppressed at these ^{51}V sites. Therefore, the ^{51}V nuclei responsible for this narrow signal do not provide a superexchange bridge between the neighbouring $\mathrm{Ni^{2+}}$ chains. We suggest that they are coupled to the electronic spins only via dipolar interactions [17].

In conclusion, we measured the ^{51}V NMR response in the chain compounds $\mathrm{PbNi_{2-x}Mg_xV_2O_8}$ ($x = 0, 0.12, 0.24$). A broad strongly shifted resonance has been found in all cases, suggesting that $\mathrm{VO_4}$ tetrahedra serve as a superexchange bridge between $\mathrm{Ni^{2+}}$ chains. The temperature evolution of the first moment of the ^{51}V NMR line in all three samples supports the existence of a spin gap in the excitation spectrum down to T_min. T_min is vanishing small ($\sim 0\,\mathrm{K}$) in the undoped compound $\mathrm{PbNi_2V_2O_8}$ and rises from $\sim 7\,\mathrm{K}$ ($x = 0.12$) to 14 K ($x = 0.24$) in doped samples. On the other hand, the large anisotropic broadening of the ^{51}V NMR spectra for Mg-doped samples is attributed to the presence of the localized $S \neq 0$ spins. Our T_1 data are also consistent with enhanced AF fluctuations at $T < 100\,\mathrm{K}$ and together with the temperature dependence of the second moment suggest the formation of a short-range AF order even at temperatures far above T_{N}. The results thus imply the co-existence of 1D magnetic excitations and the development of short-range AF spin correlations already at elevated temperatures. Finally, a new insight with respect to the inhomogeneous local magnetic-field distribution along the NiO_6 chains is provided by the evolution of a narrow, intense ^{51}V NMR line, suggesting that not all ^{51}V sites remain equivalent after doping. Although the precise relation between these sites and the modulated local fields along the Ni chains is not clear at this stage of our work, we find that the ^{51}V sites corresponding to the narrow line are compatible with a deformed VO_4 tetrahedra.

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