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Deuterium NMR in YMn_2D_x compounds

H. Figiel, A. Budziak, and P. Mietniowski
Department of Solid State Physics, Faculty of Physics and Nuclear Techniques, University of Mining and Metallurgy, Al. Mickiewicza 30, 30-059 Cracow, Poland

M. T. Kelemen and E. Dormann
Physikalisches Institut, Universität Karlsruhe (TH), Wolfgang Gaede Str. 1, D-76128 Karlsruhe, Germany

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The NMR investigations of YMn_2D_x $(x=0.65,1.0,1.5,2.0,2.5)$ deuterides are presented and discussed. The observations of ^2D spin echo signals were made for the samples in the paramagnetic state in the temperature ranges close above their magnetic ordering temperatures. The temperature dependencies of ^2D resonance frequency, T_1 and T_2 relaxation times at the ordering temperature show a divergence which is dependent on the deuterium concentration. It is shown that the mechanisms of conduction electron interaction and of dipolar or orbital interactions are responsible for the observed relations between Knight shift and the susceptibility. The observed concentration dependent relaxation rates are explained on the basis of extended theory of spin fluctuations.

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I. INTRODUCTION

Hydrogen is readily absorbed by the rare-earth and yttrium compounds and induces strong modifications of their structural and magnetic properties. For example, the compounds with manganese show an especially broad variety of transformations induced by hydrogen. These phenomena are not completely understood and need further research. One of the most suitable compounds to study the influence of hydrogen on the magnetic properties of the manganese sublattice is the YMn_2 Laves phase compound.

The magnetic properties of the YMn_2 compound are already well known.[1] At room temperature it crystallizes in the cubic $C15$-type structure ($Fd\overline{3}m$ space group) and is an enhanced paramagnet with $\mu_{Mn}\sim 2.7\mu_B$ and giant spin fluctuations. At $T\sim 100$ K the compound undergoes a first-order magnetic transition to a complicated helicoidal magnetic structure with a period of about 400 Å.[2] This magnetic transition is accompanied by a large increase of the unit-cell volume by about 5% with a small tetragonal distortion. The magnetic properties of RMn_2 compounds are closely related with the Mn-Mn distance, where for the distances greater than the critical distance ($d_c\sim 2.67$ Å) localization of Mn moments is observed[3] together with the onset of magnetic structures of antiferromagnetic type.

The magnetism and structure of YMn_2 compound are very sensitive to hydrogen absorption. Hydrogen causes expansion of the unit cell favoring better localization of the Mn magnetic moments and causing distinct increase of the magnetic ordering temperature. As it was shown in Ref. 4, for the YMn_2H_x hydrides with very low hydrogen concentrations $(x<1)$, the temperatures of magnetic ordering are in the vicinity of 240 K. In the range from $x\sim 1$ up to $x\sim 4$ the ordering temperature increases linearly reaching values above the room temperature.[5,6] For this hydrogen concentration range a small ferromagnetic contribution $(0.1–0.3\mu_B)$ is observed, which suggests that hydrogen to some extent modifies the antiferromagnetic, noncollinear structure of the pure compound. The crystallographic structure of the hydrides is very sensitive to temperature and the hydrogen content.[4] For concentrations $x<1.1$ tetragonal distortions appear at temperatures below the magnetic ordering temperature, whereas for $x>1.2$ up to about 3.5 the cubic structure remains unchanged in both paramagnetic and magnetically ordered phase. As it was deduced from the decrease of the expansion coefficient in the hydride as compared with pure YMn_2, the spin fluctuations in the hydrides are smaller in the paramagnetic range.[7]

Substitution of hydrogen by deuterium in general does not influence the magnetic and structural properties, but gives additional possibilities of experiments not possible on samples with hydrogen. In particular it enables neutron diffraction studies to trace spatial ordering of deuterium, and in the case of NMR observations using ^2D saves the discrimination of proton signals from the environment of the sample. The neutron experiments performed on the YMn_2D_x samples proved appearance of the deuterium ordering in temperature range below 100 K.[8–10]

In the muon spin rotation (μSR) experiments[11] the muon relaxation rates at the paramagnetic range above the ordering temperatures for $x=1$ and 2 were analyzed. Muons locate in the same interstitial positions (96g) as hydrogen (deuterium) atoms. It was found that at temperatures relatively far above the ordering temperature the relaxation rates follow the simple relation $(T/T_N-1)^{-\eta}$ of the critical character. The η value was found to increase with the deuterium concentration in contradiction to theoretical expectations that the critical exponent do not depend on the chemical composition of the material. To check this behavior the NMR measurements of spin-lattice and spin-spin relaxation times were performed and are presented in this work together with the Knight shift analysis. Since the deuterium magnetic moments interact with the same fluctuating fields as the muons, the temperature-dependent behavior of deuterium relaxation rates and muons relaxation rates ought to be the same.

II. EXPERIMENTAL DETAILS

The YMn_2D_x samples with compositions $x=1$ and 2 were the same as those used in the μSR experiments.[11] The samples with $x=0.65$, 1.5, and 2.5 were prepared specially for the NMR experiment. All specimens were prepared from high-purity starting elements and the sample preparing procedure was analogous to that described in Ref. 4. The sample with deuterium concentration $x=3$ was not measured by NMR because its magnetic ordering temperature was above the room temperature ($T_c=325$ K).

The NMR measurements were performed using the BRUKER CXP 200 spectrometer with the quadrature detection. The capacitively tuneable probehead with the coil of 5 mm diameter and 25 mm length and with 18 turns was placed in the cryostat equipped with superconducting magnet ($B=4.6975$ T). Due to Knight shift in our samples the corresponding resonance frequency of ^{2}D was smaller than that of free isotope (30.701 MHz). The spin-spin relaxation times T_2 were measured with two pulse spin-echo sequence with pulses 3 and 6 μs long and the shortest distance between pulses enabling us to detect echo signals was 20 μs. The spin-lattice relaxation times T_1 were measured using the three-pulse stimulated echo technique. In the T_1 measurements the shorter distances between the third pulse and the echo were limited by the effect of overlapping of the other echoes which appear,[12] and were about 50 μs. It caused, that in T_2 measurements we were able to approach closer the magnetic ordering temperature than in T_1 measurements. To observe temperature shifts of the resonant frequency the probe head was appropriately tuned. The precise values of resonant frequencies were obtained from the position of the Fourier transformed echo signals. The temperature of the sample was stabilised at accuracy better than 0.2 K. Typically the signals were accumulated to get proper signal/noise ratio.

The deuterium nuclei possess a quadrupole moment, however, in the obtained results we have found no traces of quadrupole splitting. The temperature-dependent x-ray measurements, with the SIEMENS D5000 diffractometer using Cu-$K\alpha$ radiation ($\lambda=1.540\,56$ Å), as well as the magnetic measurements using the Quantum Design MPMS superconducting quantum interference device magnetometer were performed for the samples with $x=0.65$, 1.5, and 2.5.

III. EXPERIMENTAL RESULTS AND INTERPRETATION

A. Frequency shifts

The temperature dependencies of the resonant frequency appeared to be correlated with the hydrogen concentration as it is visible in Fig. 1. The corresponding Knight shifts are clearly temperature dependent for deuterium concentrations $x>1$. It is worth noting here that in this concentration range the hydrides do not undergo any structural transition at the ordering temperature, remaining cubic with no evidence of any distortion.[4] This was also observed in x-ray-diffraction measurements for samples with $x=1.5$ and 2.5.

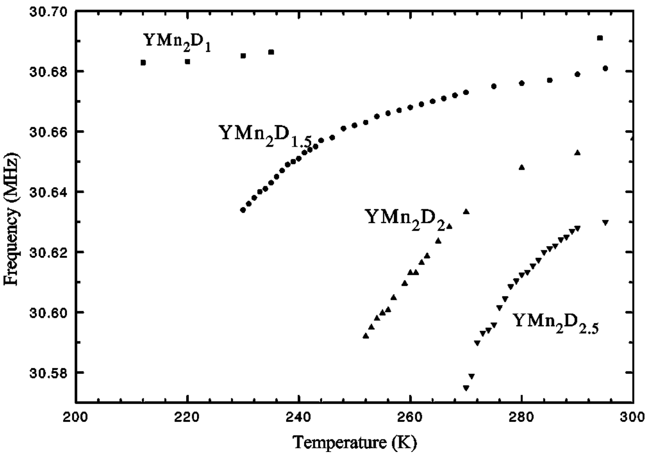

FIG. 1. The ^{2}D resonant frequencies as function of temperature for the investigated hydrides.

The temperature dependence of the magnetic moment for the samples under investigation shows field dependency and cannot be converted to a field-independent magnetic susceptibility. Figure 2 shows the temperature dependence of the weight related magnetization of $YMn_2D_{1.5}$ and $YMn_2D_{2.5}$ for magnetic flux densities of 4.7 and 0.01 T as an example. Thus, instead of standard relation:[13]

$$K(T)=K_0+\frac{\alpha}{N_A\mu_B}\chi(T) \tag{1}$$

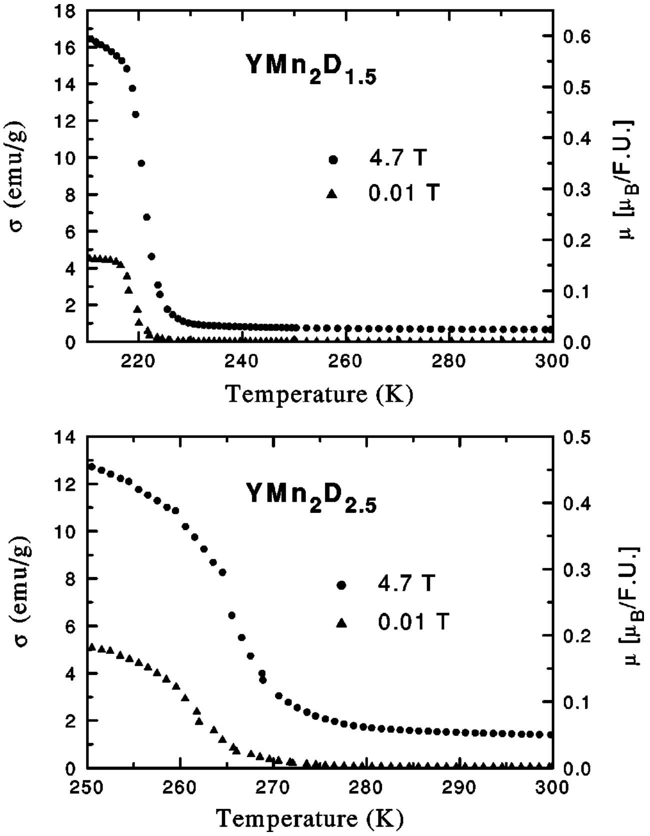

FIG. 2. The temperature changes of magnetization for $YMn_2D_{1.5}$ and $YMn_2D_{2.5}$ measured at $H=4.7$ T and $H=0.01$ T.

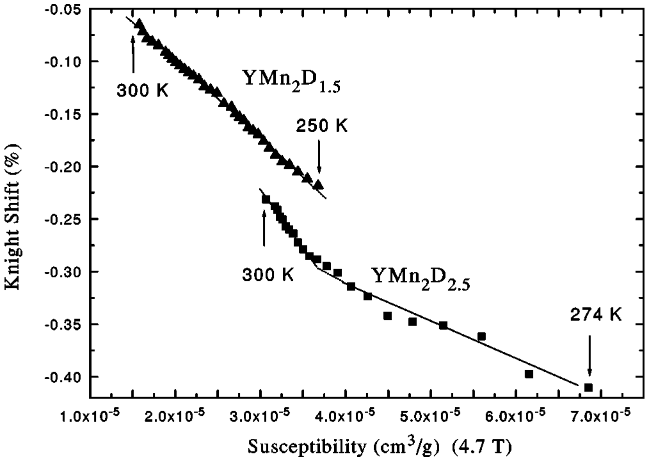

FIG. 3. Relations between Knight shift and susceptibility for $YMn_2D_{1.5}$ and $YMn_2D_{2.5}$.

the Knight shift and the high-field susceptibility obtained from the magnetization at the same field strength as the NMR signals have to be correlated:

$$K(T)=K_0+\frac{\alpha}{N_A\mu_B}\frac{M(T)}{H}. \tag{2}$$

The Knight-shift values were calculated from the resonant frequencies presented in Fig. 1 with the reference frequency ν_0 being the resonant frequency of ^{2}D in $YMn_2D_{1.5}$ at room temperature. The correlation between the Knight shift and the high-field susceptibility is presented in Fig. 3 according to Eq. (2) with the temperature as an implicit parameter. The same general trend was observed for all deuterium concentrations studied: there is a break in the slope of the Knight shift versus susceptibility, with the larger, negative slope for the high temperature, i.e., for the weak magnetic moments. In all cases the shift is negative. The slope for $YMn_2D_{1.5}$ amounts to $\alpha=-0.202T/\mu_B$ in the whole temperature range, whereas for $YMn_2D_{2.5}$ $\alpha=-0.303T/\mu_B$ in the high-temperature range, and $\alpha=-0.101T/\mu_B$ for the low-temperature range. These values are comparable with those obtained for other compounds, e.g., for $CeAl_2$.[13] The evident change in slope for $YMn_2D_{2.5}$ reveals two different coupling mechanisms contributing to the correlation of magnetic moments and Knight shift. These contributions predominate in the different temperature ranges, e.g., that related to conduction electron contact interaction in the high-temperature range whereas a dipolar (orbital) field contribution in the low-temperature range. This conclusion can be related to results of NMR on ^{55}Mn in the ordered state in YMn_2H_x (Ref. 14) and $GdMn_2H_x$ (Ref. 15) hydrides. An increase of Mn magnetic moments and their orbital contribution was deduced from an increase of Mn hyperfine fields following the increase of hydrogen concentration. The difference between high- and low-temperature coupling constants of the 2.5 deuteride shows also nicely that even in the 4.7-T external field the transferred fields must compensate partially.

B. Relaxation times

In Figs. 4 and 5 the temperature dependences of T_1 and T_2 relaxation rates for all hydrogen concentrations are presented. Figures 4 and 5 show the systematic variation of ordering temperatures, spin-lattice, and spin-spin relaxation rates with increase of the deuterium concentration in YMn_2D_x. This behavior qualitatively follows the trend observed for the relaxation rate in μSR experiment.[11]

Figure 4 shows separately the variation of $1/T_1$ and $1/T_2$ with temperature for $YMn_2D_{0.65}$. For this deuterium concentrations range the occurrence of two structural transitions $\alpha-\beta'$ and $\beta'-\gamma$ was established.[4] The irregularity in the $1/T_2$ temperature dependence visible in Fig. 4 reveals that the spin-echo decay may indeed be influenced at about 240 K by such a structural anomaly. Thus the temperature dependence of $1/T_1$ and $1/T_2$ for this concentration range (below $x\sim 1$, where structural transitions take place[4]) must be discussed with care due to the possible interference of structural and magnetic transition characteristics.

The temperature dependence of $1/T_1$ and $1/T_2$ was analyzed within the recently introduced model describing quasicritical behavior.[16] The model of relaxation caused by spin fluctuations, introduced by Moriya,[17] gives for antiferromagnets, at temperatures close above the ordering temperature, the following expression for the spin-lattice relaxation rate:

$$\frac{1}{T_1}=\frac{1}{T_0}\left(\frac{T-T_N}{T_N}\right)^{-1/2}. \tag{3}$$

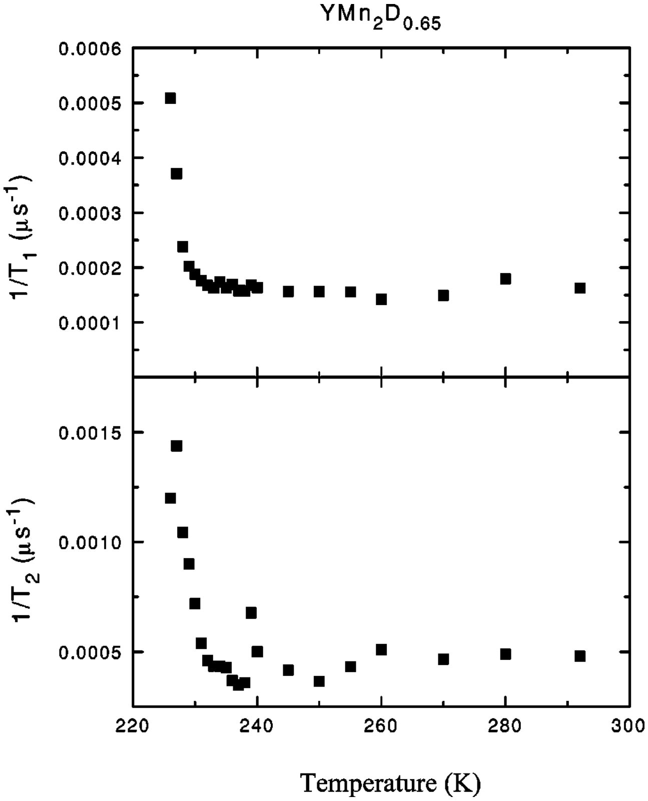

FIG. 4. The relaxation rates $1/T_1$ and $1/T_2$ in function of temperature for $YMn_2D_{0.65}$.

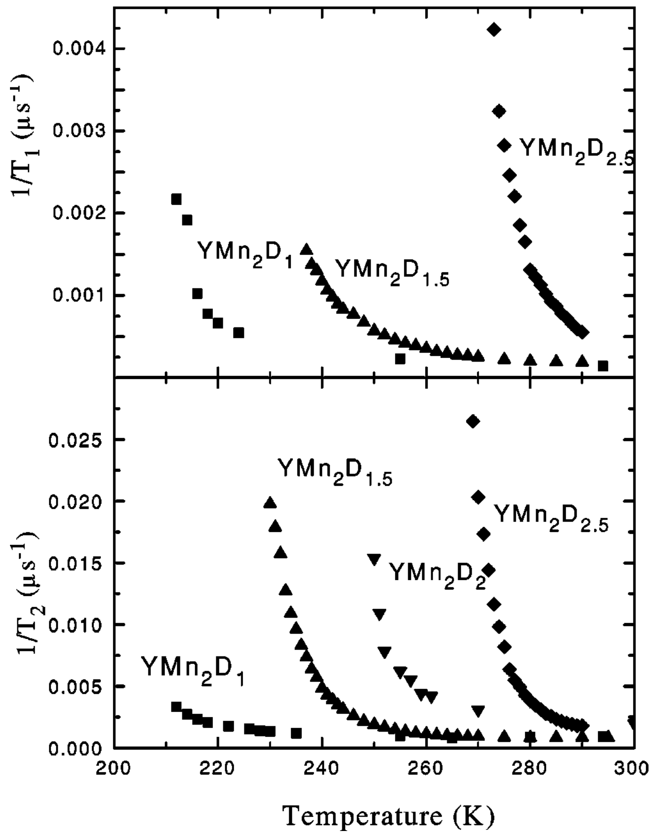

FIG. 5. The relaxation rates $1/T_1$ and $1/T_2$ in function of temperature for YMn_2D_x, $x=1.0,1.5,2.0,2.5$.

For the YMn_2D_x deuterides (hydrides) the muon[11] and NMR relaxation rates show divergence at the ordering temperature, but instead of Eq. (3) with fixed exponential factor 1/2, the formula with the free exponential factor η may be used:

$$\frac{1}{T_1}=\frac{1}{T_0}\left(\frac{T-T_N}{T_N}\right)^{-\eta}. \tag{4}$$

Fitting this formula to our experimental data gives linear dependence of η versus hydrogen concentration as visible in Fig. 6(a). However, this behavior cannot be understood in terms of existing theories which predict that such divergences of critical type at the ordering temperature should not depend on chemical composition, and here in particular on the hydrogen (deuterium) concentration in the compound. This leads to the idea of the model,[16] which improves the Moriya's approach based on spin fluctuations.[17]

The relaxation rates are generally proportional to $\Sigma(\chi(\mathbf{k})/\Gamma_k)$ term. Starting from this expresion, the proposed model takes into account different wave-vector dependencies (dispersion) of the staggered susceptibility $\chi(k)$ and the $\Gamma(k)$ parameter of the relaxing (correlation) function, which is a width of the spin-fluctuation excitation spectrum. In the result of calculations a formula for the relaxation rate was proposed:[16]

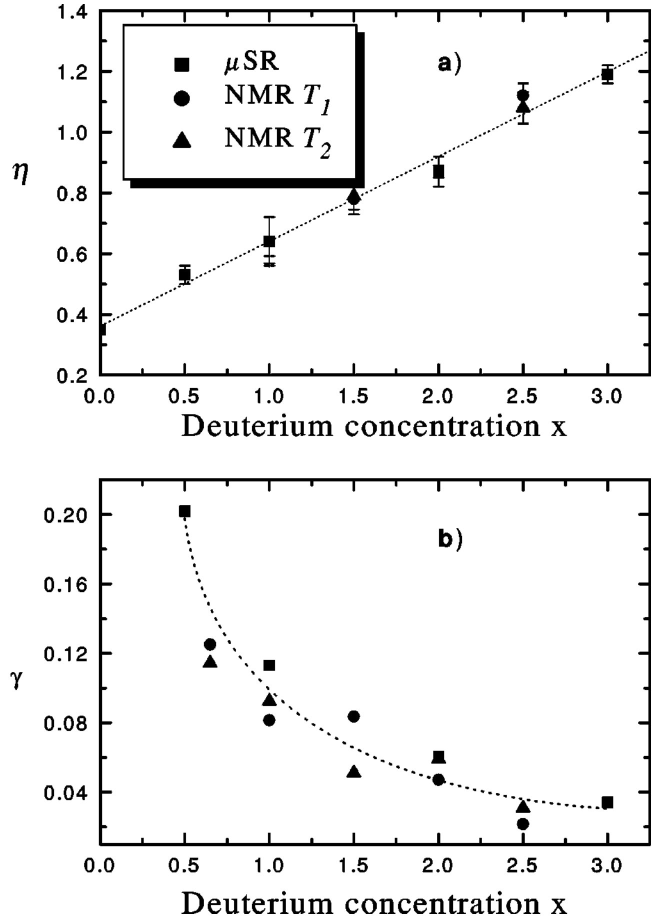

FIG. 6. (a) Dependence of the parameter η on the hydrogen concentration. (b) Dependence of the parameter γ on the hydrogen concentration.

$$\frac{1}{T_1}=\mathrm{const}\cdot T\cdot\left(\frac{\delta}{\gamma}\right)^{-1/2}\left\{\frac{1}{1-\alpha}\arctan\left[k_{max}\left(\frac{\delta}{\gamma}\right)^{-1/2}\right]+\frac{\alpha^{1/2}}{\alpha-1}\arctan\left[k_{max}\left(\frac{\alpha\delta}{\gamma}\right)^{-1/2}\right]\right\}, \tag{5}$$

where γ results from the dispersion form of the susceptibility:

$$\chi(\mathbf{k})=\frac{C_1}{\delta+\gamma\kappa^2} \tag{6}$$

with $\kappa=\mathbf{k}-\mathbf{K_0}$, $\mathbf{K_0}$ the antiferromagnetic wave vector, k_{max} being a cutoff parameter, $\alpha \ll 1$ and

$$\delta\equiv\frac{T-T_N}{T_N}. \tag{7}$$

The physically most important is the γ parameter, which describes the strength of wave vector influence on the susceptibility dispersion.

Table I collects the parameters of Eq. (5) for YMn_2D_x compounds derived from the analysis of the μSR,[10,18] $1/T_1$, and $1/T_2$ data. The γ parameter decreases while increasing deuterium concentration as visible in Fig. 6(b). Because it is

TABLE I. The fit parameters of the Eq. (5) for YMn_2D_x.

x	0.5	0.65	1	1.5	2	2.5	3
γ (μSR)	0.20179		0.112		0.0607		0.034
γ (T_1)		0.125	0.081	0.0835	0.0471	0.0215	
γ (T_2)		0.114	0.092	0.051	0.059	0.0308	

related with the wave-vector dependent susceptibility, the larger dispersion parameter γ for the low concentration compounds indicates that here $\chi(k)$ is much stronger k dependent at the wave vector K_0 of antiferromagnetic ordering, with other contributions comparatively suppressed.

It is noticeable that γ dependence of hydrogen concentration is reflected in the susceptibilities. The measured susceptibilities (see Fig. 3) are smaller for low concentration of hydrogen (higher γ) and bigger for higher hydrogen content (smaller γ) corresponding to Eq. (6). As it comes out from theoretical considerations, γ is related with the exchange coupling constant J according to the relation:[16]

$$\frac{J(\mathbf{k})}{J(\mathbf{K_0})}=1-\gamma(\mathbf{k}-\mathbf{K_0})^2. \tag{8}$$

Thus the decrease of the γ value with increasing deuterium concentration means that the exchange interactions in the system become more uniform.

This is also in good agreement with the observation that a much more pronounced shift of resonance line was observed (Knight shift) for the high deuterium concentration compounds. Since the shift reflects the response to the uniform external field, i.e., $\chi(0)$, it is larger for low γ values (more uniform exchange interaction), i.e., high deuterium concentration.

IV. CONCLUSIONS

The combined analysis of the NMR line shift proportional to the uniform susceptibility and the relaxation behavior reflecting the critical and quasicritical contributions gives an important piece of evidence for the magnetic interactions of these fascinating YMn_2 hydride and deuteride compounds. From the relation between the Knight shift and susceptibility it was concluded that two types of interaction are responsible for the observed behavior. Namely, hyperfine interactions with exchange polarized band electrons and dipolar (or orbital) interactions with the manganese moments for higher concentration of hydrogen are responsible for the observed temperature changes of K and χ. Analysis of the temperature changes of the relaxation rates for different deuterium concentrations supported by the theoretical model gave evidence of the importance of the excitation spectrum of spin fluctuations for proper understanding of the dynamics of these deuterides at temperatures close to the ordering temperature. According to our experimental results and analysis, for increasing deuterium concentration, not only does the ordering temperature increase, but also the dispersion characterizing the exchange enhancement of the wave-vector-dependent magnetic susceptibility is modified in a characteristic way. It also proves that the dependence of the exchange interactions on the wave vector is related with the hydrogen content.

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