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Spin dynamics of the one-dimensional magnet Na_2MnF_5

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The spin dynamics of the one-dimensional (1D) magnet Na_2MnF_5 have been investigated by inelastic neutron scattering. Measurements of the spin-wave dispersion resulted in values of the exchange constant $J/k_B = -8.5(1)$ K and the anisotropy constant $D/k_B = -2.70(2)$ K, respectively. The temperature dependence of the magnetic correlation length showed significant deviations from the Heisenberg/ Fischer behavior at low temperatures. The observed exponential increase of the inverse correlation length upon temperature is a typical feature of strongly anisotropic systems. Soliton excitations have been measured directly by high-resolution neutron spectroscopy. From these measurements, a soliton activation energy of $E_s/k_B = 65(5)$ K has been determined. The results are discussed with respect to other 1D magnetic systems among the fluoromanganates.

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I. INTRODUCTION

One-dimensional (1D) magnetic systems have attracted considerable interest in solid state physics. Based on topological reasons, short range order effects of interacting spins and nonlinear excitations are essential in describing the spin dynamics of these compounds. The physical realization of a 1D magnet are compounds in which the magnetic ions are arranged along chains. Consequently, the exchange interaction J along the chains is much stronger than the exchange constant J' perpendicular to it. The ratio J'/J can be taken as a measure of the onedimensionality of a system. The existence of a nonvanishing interchain coupling J' necessarily leads to a three-dimensional long-range magnetically ordered state at sufficiently low temperatures. In any case, the typical features of 1D magnetic behavior can be observed over a large temperature range above the ordering temperature. A recent review on the elementary excitations in prototypical examples of antiferromagnetic chain compounds can be found in Asano *et al.*[1] and references therein.

The fluoromanganates are antiferromagnetic chain compounds which may serve as model systems for 1D magnets. In this class of compounds, the basic structural unit of MnF_6 octahedra are trans-corner-linked to form magnetic chains which are separated by the cations. The magnetic species Mn^{3+} is in its high-spin configuration with $S=2$. Depending on the cation, the metal-metal distance and the Mn-F-Mn bridge angle β can be modified in a controlled way, whereas the local geometry of the MnF_6 octahedra remains unchanged. According to the Kanamori-Goodenough rules, the fluoromanganates offer the unique possibility of changing the exchange interaction of the 1D magnetic chains within the accessible range of the bridge angle $110^o \leqslant \beta \leqslant 180^o$ from almost ferromagnetic to purely antiferromagnetic.

Previously, the spin dynamics of $A_2^I/A^{II}MnF_5(H_2O)(A = Li^+, Na^+, NH_4^+, ND_4^+, K^+, Sr^{2+}, Ba^{2+}$ and enH_2^{2+}, $en =$ ethylene diamine) was studied on 2% ^{57}Fe doped compounds by means of Mößbauer spectroscopy.[2–7] The Mössbauer spectra could be successfully fitted for all compounds by adopting the Blume-Tjon model[8–10] in which it is assumed that the hyperfine field jumps stochastically with a flipping rate $\Gamma(T)$ between two possible states $+H_{hf}$ and $-H_{hf}$. Thus the hyperfine interaction is replaced by a fluctuating effective field, and the increase in the fluctuation rate causes line broadening, asymmetric spectra and related phenomena. The spin fluctuation rate changes from 10^6 to 10^{12} Hz in the temperature region $T_N \leqslant T \leqslant JS(S+1)/k_B$. This points toward a dominating influence of nonlinear spin excitations due to the thermal activation of magnetic solitons. Therefore, the relaxation spectra were calculated and interpreted on the basis of classical soliton theory for $T_N \leqslant T \leqslant 3T_N$.[11] For Na_2MnF_5, the spin fluctuation rate $\ln[\Gamma(T)]$ versus the inverse temperature $1/T$ results in a thermal activation energy of $E_A = 132(5)$ K. From a knowledge of the spin correlation functions as derived by Mössbauer relaxation spectra, the single crystal susceptibility measurements of Na_2MnF_5 could be perfectly described by an anisotropy constant $D/k_B = 2.75(4)$ K, an exchange coupling constant $J/k_B = -8.8(2)$ K, and a Néel temperature of $T_N = 9.2(2)$ K.[11] A central issue, relevant to all compounds investigated, represents the question whether the magnetic fluctuation rate, as observed by Mössbauer spectroscopy, is indeed due to magnetic solitons.

Therefore recently, the magnetic properties of the homologue compound $(ND_4)_2MnF_5$ have been investigated independently in detail by neutron scattering experiments.[12] The deuterated sample has been chosen in order to avoid strong incoherent background scattering from hydrogen. From a crystallographic point of view, both deuterated and protonated compounds are equivalent. From the spin wave dispersion, the exchange and anisotropy constants of $(ND_4)_2MnF_5$ have been determined as $J/k_B=-10.3(1)$ K and $D/k_B=-2.78(2)$ K, in excellent agreement with the results of single crystal susceptibility measurements.[11,12] The measurements of the nonlinear spin excitations resulted in a single soliton activation energy of $E_s/k_B=81(3)$ K which is half of the value of the thermal activation energy as obtained from Mössbauer spectroscopy.[12]

Here we report on a systematic study on the spin dynamics of Na_2MnF_5 by means of inelastic neutron scattering. Compared to the ammonium compound, Na_2MnF_5 has a smaller Mn-F-Mn bridge angle due to the smaller ionic radius of the sodium ions which results in a weaker antiferromagnetic exchange interaction.

II. EXPERIMENTAL DETAILS AND RESULTS

Sample preparation and characterization

Large single crystals of Na_2MnF_5 were synthesized by the evaporation method of a saturated solution of Na_2MnF_5 in hydrofluoric acid. Single crystal x-ray diffraction measurements revealed a monoclinic structure characterized by space group $P2_1/c$.[13] The magnetic chain direction is along the crystallographic *a*-axis. For the inelastic neutron scattering experiments, single crystals with dimensions of $5\times7\times20$ mm^3 and a corresponding mass of 1.3 g were used. Neutron diffraction confirmed the monoclinic structure of Na_2MnF_5, and revealed the perfect homogeneity and excellent quality of the samples. The crystallographic parameters of Na_2MnF_5 are space group $P2_1/c$, lattice constants $a=7.719(1)$ Å, $b=5.236(1)$ Å, $c=10.862(2)$ Å, and monoclinic angle $\beta=109.0(1)^o$.

Spin wave excitations

A suitable Hamiltonian for the description of trans corner linked MnF_6 octahedra forming quasi onedimensional magnetic chains is given by

$$\hat{H}=\sum_i -2JS_iS_{i+1}+D\left(S_{i,z}^2-\frac{1}{3}S_i(S_i+1)\right)+E(S_{i,x}^2-S_{i,y}^2)-g\mu_B HS_i \qquad (1)$$

The chain direction is along the z direction. The first term represents an isotropic Heisenberg exchange interaction between two neighboring spins with exchange constant $-2J$, D and E are the axial and rhombohedral anisotropy constants, respectively, and the last term is the Zeeman interaction in the presence of an external magnetic field. In the present case we consider only the first two terms, since for Mn(III) chain compounds it has been shown[11] that $|D|\gg|E|$ and $|J|\geqslant|D|$, and no field has been applied.

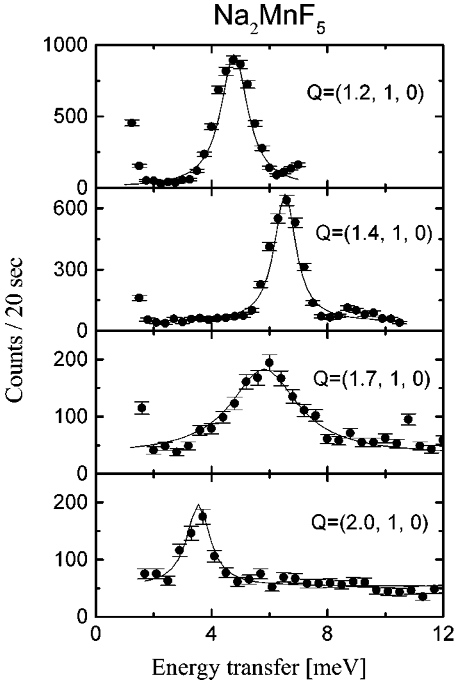

FIG. 1. Spin wave excitations of Na_2MnF_5 along the magnetic chain direction at $T=1.7$ K. The varying excitation energies (peak positions) for different Q values nicely illustrate the spin wave dispersion.

To measure the spin wave excitations and the magnetic correlation length of Na_2MnF_5, inelastic neutron scattering experiments have been performed on the thermal three-axis spectrometer IN22 at the Institute Laue Langevin, Grenoble. A standard configuration of the instrument has been chosen with vertically focused pyrolythic graphite monochromator and doubly focused analyzer in constant final wave vector mode with $k_f=2.662$ Å^{-1}. The sample was mounted in a cryostat allowing for temperatures $1.5\leqslant T\leqslant300$ K with the reciprocal lattice vectors **a*** and **b*** lying in the horizontal scattering plane. The neutron spectra along **a*** revealed well defined spin wave excitations which could be fitted by a single Lorentzian line convoluted with the instrumental resolution, as shown in Fig. 1. The different width of the excitations are caused by resolution effects. The corresponding magnon dispersion has been established by measuring the spin wave excitations throughout two Brillouin zones at $T=1.7$ K. The resulting dispersion curve is displayed in Fig. 2. Within the classical spin wave approximation, the data were analyzed according to a 1D antiferromagnetic chain (full line in Fig. 2):

$$\hbar\omega=[4S^2D^2+16S^2|J||D|+16(SJ)^2\sin^2(\pi q_b)]^{1/2}. \qquad (2)$$

The fit results in an exchange constant $J/k_B=-8.5(1)$ K, an anisotropy constant $D/k_B=-2.70(2)$ K, and a corresponding spin wave excitation energy gap of $\Delta_{magnon}=39.8(2)$ K. These values are in excellent agreement with the results of single crystal susceptibility measure-

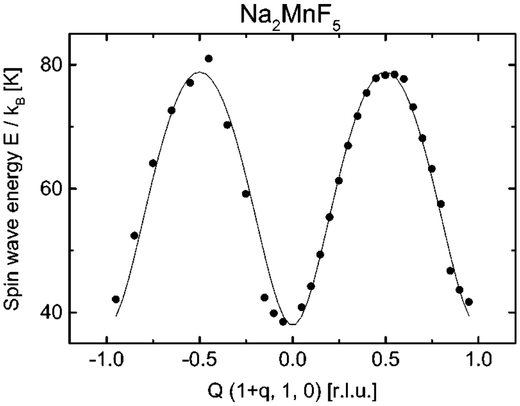

FIG. 2. Spin wave dispersion relation of Na_2MnF_5 at $T=1.7$ K. The full line corresponds to a fit according to an antiferromagnetic chain as described in the text.

ments and Mößbauer spectroscopy of the iron-doped compound[11] (also see Table I). The spin wave measurements perpendicular to the chain direction did not reveal any significant dispersion, thus yielding to an upper limit of the interchain exchange constant of $J'/k_B \leqslant 0.02$ K, thereby confirming the good one-dimensionality of the compound.

TABLE I. Magnetic properties of Na_2MnF_5 as determined by magnetic susceptibility measurements[11] (χ), neutron scattering (N. S.), and Mössbauer spectroscopy (Ref. 11) (M. S.). Listed are the anisotropy constant D, the magnetic intrachain constant J, the magnetic inter-chain constant J', the magnetic ordering temperature T_N, the magnon energy gap Δ_{magnon}, the single soliton energy E_s, and the thermal activation energy E_A.

Parameter	χ[a]	N. S.	M. S.[b]
D/k_B (K)	$-2.85(4)$	$-2.70(2)$	$-2.75(10)$
J/k_B (K)	$-8.8(2)$	$-8.5(1)$	
J'/k_B (K)	$1.4\ 10^{-3}$	$\leqslant 2\ 10^{-2}$	
T_N (K)	9.2(3)[c]	11.5(3)[c]	
Δ_{magnon}/k_B (K)		39.8(2)	
E_s/k_B (K)		60(4)/65(5)[d]	66(3)[e]
E_A/k_B (K)		130(9)[e]	132(5)

[a] From Ref. 6.

[b] From Ref. 6. Compounds were doped with ^{57}Fe.

[c] The different values of T_N originate from different measuring conditions. The magnetic measurements have been performed employing a SQUID magnetometer in an applied field of 1 T whereas the neutron experiments are zero-field measurements. Indeed, particular details of the low-temperature three-dimensional magnetic ordering process of Na_2MnF_5 give rise to pronounced field effects that are currently being investigated.

[d] Depending on the fitting procedure; see the text.

[e] From the assumption $E_s = E_A/2$.

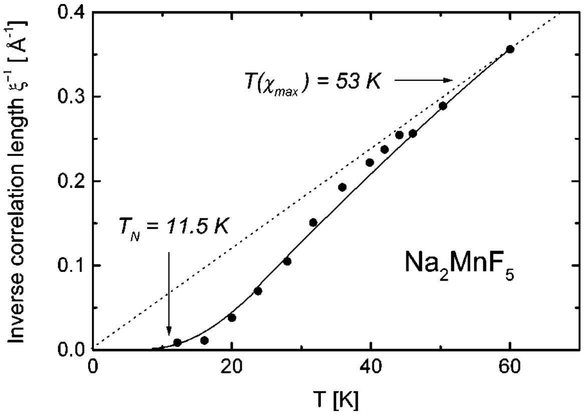

FIG. 3. Temperature dependence of the inverse correlation length of Na_2MnF_5. The full line corresponds to a fit according to classical soliton theory, whereas the dashed line represents a classical Heisenberg / Fischer behavior. The Néel temperature and the temperature of the susceptibility maximum are indicated as well to illustrate the temperature region of the 1D magnetic behavior of Na_2MnF_5.

Magnetic correlation length

By removing the analyzer crystal from the three-axis spectrometer, one can measure in an energy integrative mode, i.e., all neutrons are detected for a given scattering angle irrespective of their energy. A scattering geometry with $\mathbf{k}_f$ parallel to a^* has been chosen, and corresponding scans have been performed in such a way as to cross the one-dimensional magnetic ridge and to integrate over the inelastic signal. From the width of the energy integrated scattering cross section in reciprocal space we have determined the temperature dependence of the magnetic correlation length of Na_2MnF_5, as shown in Fig. 3. At low temperatures, the inverse correlation length exhibits significant deviations from the Heisenberg/Fischer behavior (dashed line in Fig. 3). The exponential increase upon temperature is a typical feature for strongly anisotropic systems. The temperature dependence of the inverse correlation length can be well described by classical soliton theory (solid line in Fig. 3), according to which the inverse correlation length ξ^{-1} and the thermal soliton activation energy E_s are related by

$$\xi^{-1} = 2\sqrt{\frac{8}{\pi}}\sqrt{\frac{D}{J}}\sqrt{\frac{E_s}{kT}}\exp\left(\frac{-E_s}{kT}\right). \tag{3}$$

With given parameters D and J as resulting from the spin wave dispersion, the fit of the temperature dependent magnetic correlation length according to Eq. (3) yields to a single soliton activation energy of $E_s = 65(5)$ K. The temperature dependent magnetic correlation length as shown in Fig. 3 is in good agreement with the results of Mössbauer relaxation spectra and single crystal susceptibility measurements.[11] This is a strong indication that the spin dynamics of Na_2MnF_5 above the ordering temperature is indeed dominated by the presence of soliton excitations.

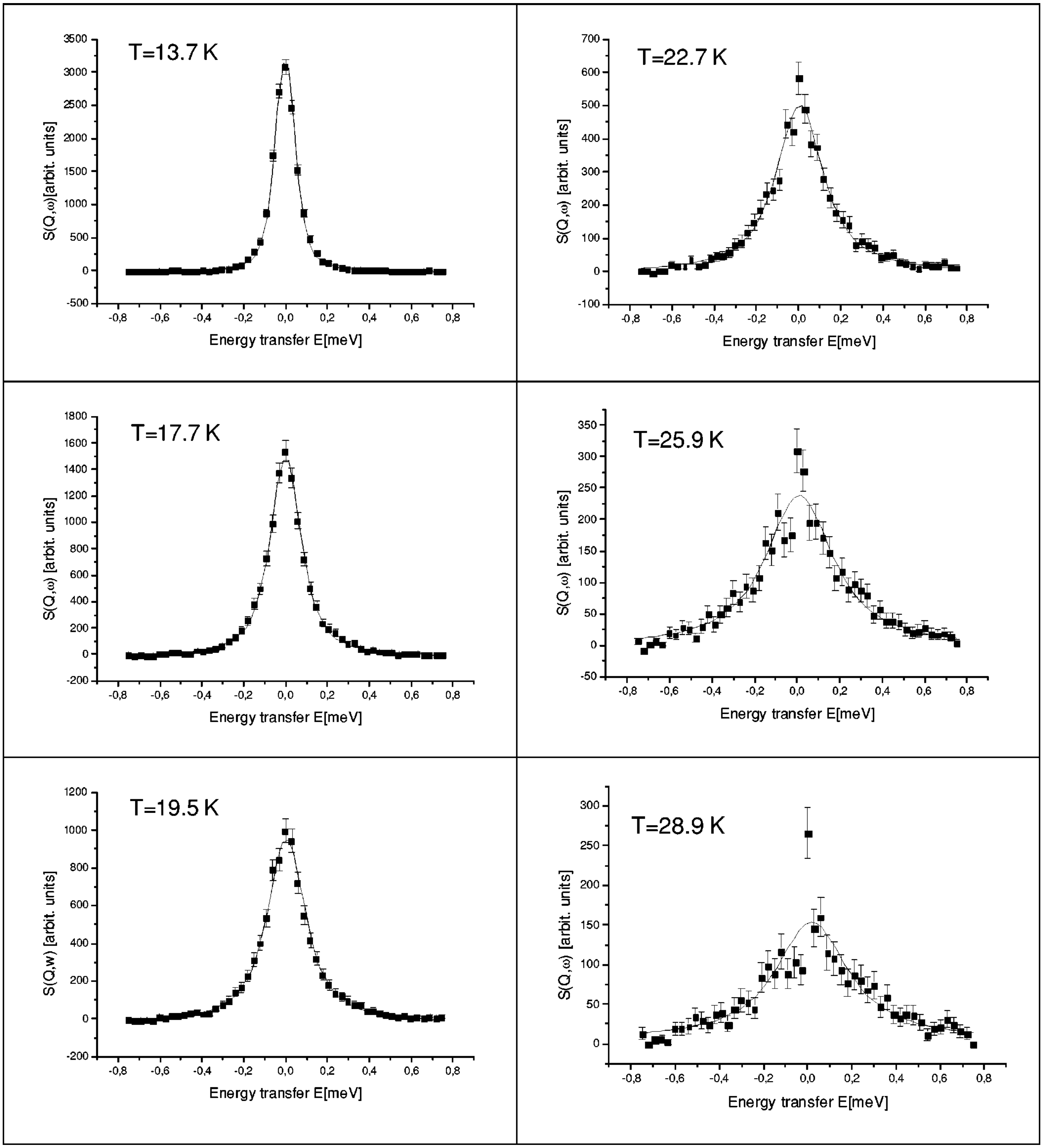

FIG. 4. Temperature dependent residual quasielastic scattering intensity $S(Q,\omega)$ of Na_2MnF_5 due to magnetic soliton excitations.

Nonlinear excitations

High-resolution neutron spectroscopy is the most direct experimental access to study non-linear magnetic excitations. Neutron scattering by solitons gives rise to a weak quasielastic intensity hidden by a large incoherent elastic background signal. Therefore, high neutron flux, high resolution, and large single crystalline samples of high quality are the prerequisites for a successful experimental determination of soliton excitations. High-resolution inelastic neutron scattering experiments have been performed on the cold three-axis spectrometer IN12, also located at the Institute Laue Langevin, Grenoble. The instrument operated in final wave vector mode with $k_f = 1.4$ Å^{-1} and a corresponding energy resolution of $\Delta E(\text{full width at half maximum}) = 100\ \mu\text{eV}$. A Be-filter was inserted to suppress higher order contamination. The sample was again oriented with the reciprocal lattice vectors **a*** and **b*** lying in the horizontal scattering plane. In order to determine the incoherent background properly, additional measurements have been performed, either at $T = 1.5$ K deep within the magnetically ordered state of Na_2MnF_5 or at $T = 75$ K $[T \geqslant T(\chi_{max})]$ where magnetic correlations have been destroyed by the thermal energy.

After the background correction, a residual quasielastic signal could be observed in the temperature range $T_N \leqslant T \leqslant 30$ K. The decreasing intensity upon increasing momentum transfer confirms its magnetic origin. The data could be successfully fitted by either a single Lorentzian line or a pseudo-Voigt profile, convoluted with the instrumental resolution. The quasielastic scattering intensities measured at $Q = (1,0.9,0)$ and the corresponding fits are shown in Fig. 4. The width of the signal strongly increases with increasing temperature, whereas its intensity becomes heavily suppressed (compare with Fig. 4). The classical soliton model describing a non-interacting soliton gas predicts an exponential temperature dependence of the line width upon temperature,

$$\Gamma_D = \xi^{-1} v_s = \frac{2^5}{\sqrt{\pi}}\ SJ\sqrt{\frac{D}{J}}\exp\left(-\frac{E_s}{k_B T}\right), \tag{4}$$

with the average thermal soliton velocity

$$v_s = \frac{4SJ}{\sqrt{E_s/2k_B T}}, \tag{5}$$

and the single soliton activation energy given by

$$E_s = 4S^2\sqrt{DJ}. \tag{6}$$

From the knowledge of the anisotropy and exchange constants J and D, as derived by the measurements of the spin wave dispersion, the only adjustable parameter is the soliton activation energy E_s. Therefore, attributing our measured quasielastic scattering signal solely to soliton excitations, the observed temperature dependence of the linewidth determines the soliton activation energy, as displayed in Fig. 5. The slope of $\ln[\Gamma_D(T)]$ versus the inverse temperature $1/T$ corresponds to a soliton activation energy of $E_s/k_B = 65(5)$ K when employing a single Lorentzian line and to $E_s/k_B = 60(5)$ K when performing the fit by a pseudo-Voigt profile (as shown in Fig. 5).

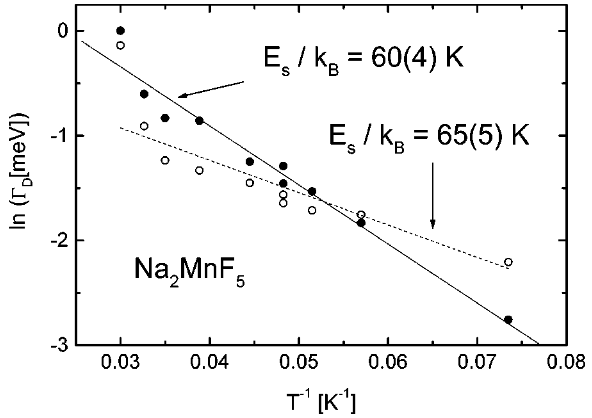

FIG. 5. Semilogarithmic plot of the residual quasielastic line width vs the inverse temperature of Na_2MnF_5. The slope determines the single soliton activation energy.

III. DISCUSSION AND CONCLUSION

We have investigated the spin dynamics of the 1D magnet Na_2MnF_5 by means of inelastic neutron scattering. The magnetic properties of Na_2MnF_5 are summarized in Table I. The values of the exchange constant J and anisotropy constant D have been determined by measuring the spin wave dispersion and are in excellent agreement with the results of single crystal susceptibility measurements and Mößbauer spectroscopy.[11] The slightly smaller values of the magnetic ordering temperature T_N and the intrachain constant J of Na_2MnF_5 as compared to $(NH_4)_2MnF_5$ are due to a weaker antiferromagnetic exchange as resulting from a smaller Mn-F-Mn bridge angle. The temperature dependent magnetic correlation length is consistent with a soliton activation energy of $E_s = 65(5)$ K, which has been confirmed by direct measurements of the soliton excitations in high-resolution neutron scattering experiments. Within the experimental accuracy, these values are a factor of two smaller than the spin fluctuation rate obtained by Mössbauer spectroscopy (see Table I). These results are in agreement with systematic studies on Fe(II) linear chain compounds by de Jongh and co-workers.[14] The activation energy E_A, as determined by the electronic flipping rate Γ_D of the Mössbauer relaxation spectra was systematically found to be twice the energy of a single soliton, that is, it corresponds to a soliton pair excitation.[15] Since the soliton pair excitations are thermally activated, a coupling between the spin system and the phonon bath is required which may be provided by spin-orbit coupling. The difference between the single soliton energy E_s as determined by neutron scattering experiments and the thermal activation energy E_A established from Mössbauer relaxation spectra has also been observed in $(NH_4)_2MnF_5$.[12] However, this difference is in contrast to the classical description within an ideal gas of non-interacting solitons, and is presently examined theoretically.[16]

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