

Slow dynamics of the magnetization in the ordered state of molecule based magnets with one-dimensional chain structure

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 8881

(<http://iopscience.iop.org/0953-8984/15/50/018>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.125

The article was downloaded on 19/05/2010 at 17:54

Please note that [terms and conditions apply](#).

Slow dynamics of the magnetization in the ordered state of molecule based magnets with one-dimensional chain structure

N V Baranov^{1,2,5}, N V Mushnikov^{2,3}, T Goto³, Y Hosokoshi⁴ and K Inoue⁴

¹ Department of Condensed Matter Physics, Ural State University, Lenin Avenue 51, 620083 Ekaterinburg, Russia

² Institute of Metal Physics, Russian Academy of Science, 620219 Ekaterinburg, Russia

³ Institute for Solid State Physics, University of Tokyo, Kashiwa-shi, Chiba-ken 277-8581, Japan

⁴ Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

E-mail: nikolai.baranov@usu.ru

Received 9 July 2003

Published 3 December 2003

Online at stacks.iop.org/JPhysCM/15/8881

Abstract

The ac susceptibility as a function of temperature, dc magnetic field and frequency as well as the magnetization in quasistatic and pulsed magnetic fields have been measured for new molecule-based heterospin complexes $[\text{Mn}(\text{hfac})_2\text{BNO}_R]$ ($R = \text{H}, \text{Cl}$). These compounds exhibit a quasi one-dimensional chain structure, for which the interchain exchange interaction is small in comparison with the intrachain one ($J/J' \sim 10^{-3}$). A strong frequency dependence of both the real and imaginary parts of the ac susceptibility is found at low frequencies (below 100 Hz) in both antiferromagnetic (AF) $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ and ferrimagnetic (FI) $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{Cl}]$ compounds within the field interval, where the magnetization process is controlled by motion of the domain walls. A number of peculiarities regarding the reversal of magnetization are observed in pulsed fields. In particular, the remanent magnetization appears in the AF compound $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ after application of a unidirectional pulse of field. The remanence relaxes within about 1000 ms through a two-stage thermally activated process associated with the nucleation of the AF phase within the field-induced FI phase and displacement of the domain walls separating AF and FI phases. The activation energies for these two stages are estimated to be about 1.66 and 1.80 meV respectively. The activation energy for domain wall motion in the ferrimagnetic $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{Cl}]$ compound is found to be ~ 3.3 meV. The slow dynamics of the magnetization in these materials is ascribed to the complicated domain wall displacement that presumably includes the lateral motion of the intrachain wall along the separate chains because of the strong 1D character of these compounds.

⁵ Address for correspondence: Department of Condensed Matter Physics, Ural State University, Lenin Avenue 51, 620083 Ekaterinburg, Russia.

1. Introduction

The change of magnetization due to the switching of spins in magnetic materials under the influence of a magnetic field and temperature is of significant practical importance especially for bistable magnetic systems. In the last decades particulate media and low-dimensional systems like thin films, multilayers and quasi one-dimensional (1D) magnetic structures have become attractive subjects for the theoretical and experimental study of switching processes. Much attention has been paid to the investigation of the spin dynamics in these materials [1]. In 1D ferromagnets (F) as well as in 1D antiferromagnetic (AF) compounds soliton-like excitations above the three-dimensional (3D) ordering temperature have been observed using different methods. In particular, neutron scattering experiments have demonstrated the motion of the 1D domain wall ('kink') in such objects in the paramagnetic state [1–4]. One may expect that the 1D structure of such materials will also influence the dynamics of the magnetization below the ordering temperature. In the magnetically ordered state of conventional 3D ferromagnetic or ferrimagnetic materials, the magnetization process occurs via domain wall movement and rotation of magnetization in the domains, which determine the presence of nonzero coercivity and remanence. A powerful tool for studying the magnetic properties of such materials is the measurement of ac susceptibility, since both the real (χ') and imaginary (χ'') components of the ac susceptibility are affected by the magnetization dynamics, peculiarities of the domain structure, microstructure, defects, etc. Most ac susceptibility data have been reported for 3D materials, while the application of ac susceptometry to 1D magnetic systems is rather limited to investigation of the anomalies associated with magnetic phase transitions.

Recent achievements in the construction of molecule-based magnetic materials containing 3d transition metal ions have opened up great possibilities for studying the features of the magnetization process in 1D magnets with different signs and values of the ratio between the intrachain (J') and interchain exchange interaction (J) [5]. In a new series of molecule-based heterospin magnets with general formula $[\text{Mn}(\text{hfac})_2\text{BNO}_R]$ the manganese ions and diradical 5-R-1,3-bis(*N*-*tert*-butyl-*N*-oxy-amino) benzene (BNO_R) molecules ($R = \text{H}, \text{F}, \text{Cl}, \text{Br}$) form helical 1D polymeric chains along the *b*-axis of a monoclinic unit cell. The spins of the NO groups of the diradical in these compounds are ordered ferromagnetically with a large value for the energy of exchange coupling. The exchange interaction between 3d electrons of the divalent Mn ion and the 2p electrons of the NO group is antiferromagnetic. The quasi 1D complex $[\text{Mn}(\text{hfac})_2\text{BNO}_H]$ is ordered antiferromagnetically below 5.5 K owing to a negative interchain exchange interaction between the ferrimagnetic (FI) chains [5–7]. As is suggested in [5], the magnetic moments of Mn and the NO group in $[\text{Mn}(\text{hfac})_2\text{BNO}_H]$ below T_N are directed perpendicular to the *b*-axis. The temperature behaviour of the magnetic susceptibility of the $[\text{Mn}(\text{hfac})_2\text{BNO}_R]$ complexes above their ordering temperature has recently been analysed within the framework of the modified spin-wave theory [8].

Preliminary investigations of the magnetization process in $[\text{Mn}(\text{hfac})_2\text{BNO}_H]$ have shown that this compound exhibits a metamagnetic AF–FI transition at a critical field of about 0.02 T [7]. The small value of the critical transition field indicates that the interchain exchange interaction in this compound is much lower than the intrachain one. The interchain interaction in $[\text{Mn}(\text{hfac})_2\text{BNO}_{Cl}]$ and $[\text{Mn}(\text{hfac})_2\text{BNO}_{Br}]$ is found to be positive, which results in ferrimagnetic ordering of these complexes when the temperature decreases below their Curie temperatures T_C of 4.8 and 5.3 K respectively [5]. The different 3D magnetic ordering in $[\text{Mn}(\text{hfac})_2\text{BNO}_R]$ complexes was attributed to the slight difference in the relative orientation of the chains in the crystals [9, 10]. From analysis of the temperature dependences of the paramagnetic susceptibility, the ratio between interchain (J) and intrachain (J') exchange

Table 1. Crystallographic data for $[\text{Mn}(\text{hfac})_2\text{BNO}_R]$ complexes ($R = \text{H}, \text{Cl}$).

	$[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$	$[\text{Mn}(\text{hfac})_2\text{BNO}_\text{Cl}]$
Empirical formula	$\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_6\text{F}_{12}\text{Mn}$	$\text{C}_{24}\text{H}_{23}\text{Cl}_1\text{N}_2\text{O}_6\text{F}_{12}\text{Mn}$
Formula wt	719.38	753.83
a (Å)	9.212(3)	8.953(4)
b (Å)	16 620(3)	17 020(4)
c (Å)	20.088(2)	20.094(5)
β (deg)	98.46(1)	98.62(2)
V (Å ³)	3042(1)	3027(1)

interaction was estimated to be of the order of 10^{-3} for all the above compounds, which indicates their strong 1D character.

In the present work we study the peculiarities of the magnetization dynamics in 1D antiferromagnetic and ferrimagnetic compounds of the $[\text{Mn}(\text{hfac})_2\text{BNO}_R]$ type below their magnetic ordering temperatures using ac susceptibility and pulsed field magnetization measurements.

2. Experimental details

Powder samples of $[\text{Mn}(\text{hfac})_2\text{BNO}_R]$ ($R = \text{H}, \text{Cl}$) with needle-shaped particles were prepared as described previously in [6]. The x-ray crystal structure analysis was performed using a Rigaku AFC series diffractometer. The main crystallographic data are presented in table 1. The crystal structure of $[\text{Mn}(\text{hfac})_2\text{BNO}_R]$ complexes is described in detail in [10]. The magnetic ac susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ was measured on powder samples using a Quantum Design SQUID magnetometer at an amplitude of the ac field of 5×10^{-4} T within the frequency range from 1 Hz up to 1 kHz at temperatures between 2 and 15 K. The results of the ac susceptibility measurements are presented in arbitrary units, since the demagnetizing field could not be taken into account correctly for powder samples. High magnetic fields up to 42 T were produced using a wire-wound pulse magnet with a duration time of about 20 ms. The magnetization was measured by an induction method with a set of compensated pick-up coils at different temperatures between 1.47 and 4.2 K. The powder samples were tightly packed in the Teflon sample holder so that the particles could not rotate under the influence of an applied field. The relaxation of the remanent magnetization after application of the pulsed field was studied using a half-cycle pulse regime. An ignitron contactor was used to produce a unidirectional pulse of the magnetic field. For the relaxation measurements, the drift of the integrator during the recording time was taken into account. The drift parameters were obtained by the measurement of the magnetization of a piece of the permanent magnet after application of a half cycle of the pulsed field.

3. Results

3.1. Antiferromagnetic complex $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$

Figure 1 shows temperature dependences of the ac susceptibility of $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ at various frequencies for different dc magnetic fields. At zero steady magnetic field, the peaks of χ' and χ'' indicate the Néel temperature $T_N = 5.5$ K that is in agreement with previous results obtained by dc susceptibility measurements [6]. An increase of the frequency of the ac magnetic field from 1 up to 1000 Hz does not affect significantly the $\chi'(T)$ dependence but

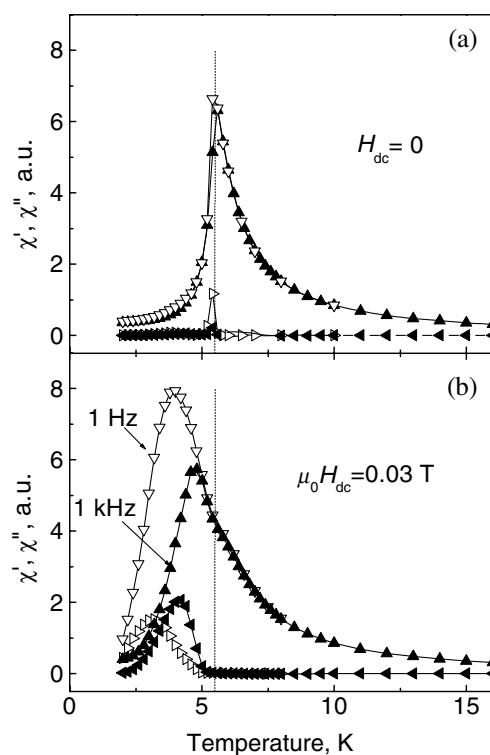


Figure 1. Temperature dependences of the real χ' (down and up triangles) and imaginary χ'' (left and right triangles) parts of the ac susceptibility of $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ measured at different bias fields: $H_{\text{dc}} = 0$ (a) and $\mu_0 H_{\text{dc}} = 0.03$ T (b) and at different frequencies: 1 Hz (open symbols) and 1000 Hz (full symbols).

leads to an appreciable reduction of the χ'' value in the vicinity of the Néel temperature. The peculiarities of the magnetization process caused by antiferromagnetic interaction between ferrimagnetic chains in $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ below T_N are clearly seen from figure 2(a) which displays the M versus H dependence measured at 2 K. An abrupt increase of the magnetization at a critical field H_{c1} of about 0.02 T indicates a metamagnetic transition from antiferromagnetic ordering of the magnetic moments of chains to their parallel alignment in the field-induced state. The magnetization process in the field range 0.02–0.05 T is accompanied by a remarkable hysteresis (of about 0.012 T). Moreover, a small remanent magnetization, M_r , was detected after removal of the field. These features are indicative of a magnetic phase transition of the first order, which occurs through a mixed phase state in a field interval ($H_{c1} < H < H_{c2}$). The presence of an intermediate state, where domains with different magnetic phases coexist, has been demonstrated at the field-induced AF–F phase transition by magneto-optical and neutron diffraction measurements in many antiferromagnetic compounds (see for example [11, 12]).

As follows from figures 2(b) and (c), in the region of the metamagnetic transition, where the AF and FI phases apparently coexist, both the $\chi'(H)$ and $\chi''(H)$ curves reveal a strong frequency dependence. When an applied bias field increases, the ac susceptibility shows a maximum around 0.025–0.030 T. The amplitude of the maximum of both $\chi'(H)$ and $\chi''(H)$ dependences decreases significantly with increasing frequency. A drastic reduction of the maximum of the ac susceptibility in the vicinity of the AF–FI transition occurs mainly in the low-frequency region. Thus, the magnitude of the χ' and χ'' peaks decreases by about 24%

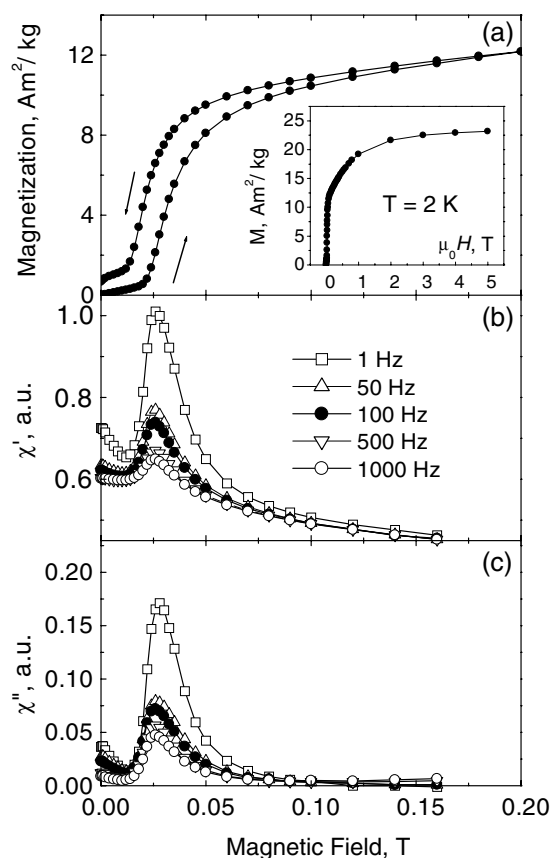


Figure 2. Quasistatic field dependences of the magnetization (a), the real χ' (b) and the imaginary χ'' (c) parts of the ac susceptibility measured at various frequencies of the ac field for the $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ compound at $T = 2$ K.

and 54% respectively with increasing frequency from 1 to 50 Hz. The imaginary component of the ac susceptibility is usually associated with absorption of the energy by material (energy losses) during the change in magnetization in the ac magnetic field. The large value of χ'' at low frequency in the vicinity of the AF–FI transition indicates that the excitation of the domain wall motion occurs more effectively at low frequencies suggesting a slow dynamics of the magnetization.

An application of a bias magnetic field of 0.03 T that corresponds to the middle of the AF–FI transition at $T = 2$ K influences significantly the temperature dependences of the ac susceptibility. As can be seen from figure 1(b), the bias dc magnetic field shifts the maxima of both χ' and χ'' towards lower temperatures. The value of the displacement depends on the frequency: the lower the frequency the larger the shift. Moreover, the narrow peak of χ'' in the vicinity of the Néel temperature broadened significantly in the bias field. The frequency dependences of χ' and χ'' for $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ measured at various temperatures are presented in figure 3 on a logarithmic scale. Above T_N , χ' and χ'' are practically frequency independent, whereas below T_N both the real and imaginary susceptibilities exhibit an appreciable frequency dependence. A weak frequency dependence of the ac susceptibility in the paramagnetic region within the frequency interval 1–1000 Hz may be attributed to the high rate of spin inversion in chains.

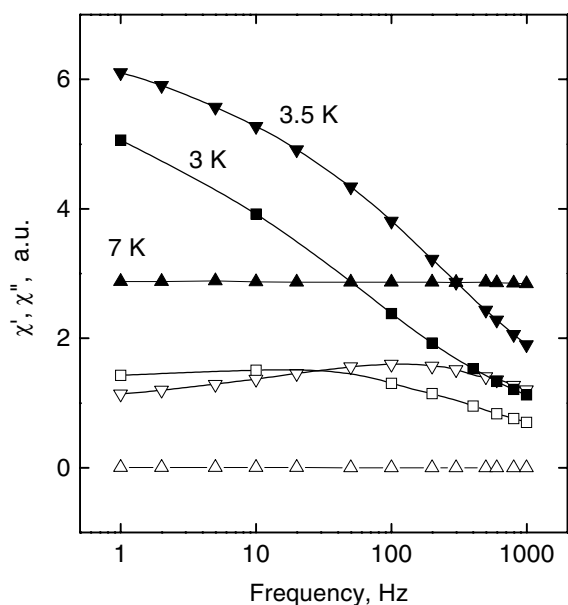


Figure 3. Frequency dependences of χ' (full symbols) and χ'' (open symbols) for $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ in a bias field of 0.03 T at various temperatures.

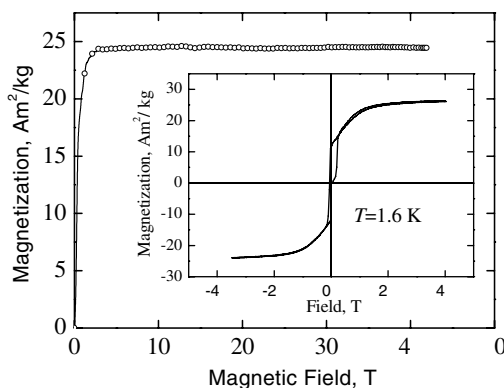


Figure 4. Field dependence of the magnetization of $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ measured in a pulsed field at 1.6 K.

The low rate of change of magnetization in $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ below T_N is clearly evidenced by the unusual magnetization process in pulsed fields. The results of the high-field magnetization measurements in pulsed magnetic fields up to 42 T at 1.6 K are presented in figure 4. The saturation magnetization is found to be in agreement with the measurements in steady fields up to 5 T (see inset in figure 2). The magnetic moment per formula unit in the saturation reaches $3.1 \mu_\text{B}$ at 42 T. This value is close to that expected for the antiparallel alignment of the spins of NO groups of radicals and Mn(II) ions ($M = 2 \mu_\text{B} (S_\text{Mn} - 2S_\text{NO}) = 2 \mu_\text{B} (5/2 - 2/2) = 3 \mu_\text{B}$). These data are also indicative of a strong intrachain exchange interaction in this compound, since the field strength used (42 T) is not enough to destroy the antiparallel alignment of spins of the Mn and NO group and to induce ferromagnetic ordering

in the chains. Nevertheless, in the low-field region we have observed a set of peculiarities of the magnetization process in pulsed fields:

- (i) The value of the critical AF–FI transition field is much higher than that observed in steady fields (about 0.2 T in comparison with 0.03 T).
- (ii) The sample possesses a large remanent magnetization after application and removal of the field.
- (iii) The descending part of the $M(H)$ dependence obtained in negative field (full-cycle measurement, inset in figure 4) does not reveal any critical field which can be associated with a magnetic phase transition.
- (iv) The value of the saturation magnetization in the negative field is lower than that obtained in the positive field by about 10%.

Such features of the magnetic behaviour, in our opinion, originate from slow dynamics of the magnetization in $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ and the high sweep rate of the pulsed magnetic field. A large remanence and absence of any anomalies on the $M(H)$ curve in a negative field may be associated with the magnetization reversal occurring in the metastable field-induced FI state because of a slow kinetics of the FI–AF transition. For pulsed field magnetization measurements we have observed some scattering of the remanent magnetization for different samples (from 8 up to 11 $\text{A m}^2 \text{kg}^{-1}$ at $T \sim 1.6$ K). Such a difference probably originates in the sample preparation. The lower value of the saturation magnetization observed in the negative field (inset in figure 4) can be ascribed to possible heating of the sample owing to the quasi-adiabatic conditions of the magnetization process in pulsed fields. It should be noted that sample heating in pulsed fields was detected for some rare earth antiferromagnetic compounds [13].

Using a half-cycle regime in our pulsed field measurements we could observe the relaxation of the magnetization at the FI–AF transition. Figure 5 shows the change in magnetization with time during and after application of the positive pulse of a 4 T field at $T = 1.61$ K. The time dependence of the field is also presented in this figure. The AF–FI phase transition occurs and the magnetization reaches the saturation value with increasing field within $\sim 2\text{--}5$ ms. The delay of the magnetization relative to the steady field measurements results only in growth of the critical transition field (see above). When the magnetic field decreases to zero, the sample remains in the metastable field-induced FI state with an appreciable remanent magnetization, $M_\text{r} \sim 8 \text{ A m}^2 \text{kg}^{-1}$. The M_r value decreases gradually with time, slowly at the beginning and more quickly after ~ 100 ms; it finally vanishes within about 1000 ms. Time dependences of M_r measured for the same sample at different temperatures (figures 6(a) and (b)) demonstrate how the temperature affects the relaxation process in $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$. As can be seen, the waiting time of the FI–AF transition reduces significantly with increasing temperature, which implies that the relaxation process has a thermal activation nature.

3.2. Ferrimagnetic $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{Cl}]$

Figure 7 displays temperature dependences of the ac susceptibility for the ferrimagnetic compound $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{Cl}]$. Below the ordering temperature $T_\text{C} = 4.8$ K both the real and imaginary parts of the ac susceptibility reveal a strong frequency dependence even in zero bias field. In contrast to the antiferromagnet $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ (figure 1), the influence of the change in frequency on the real part of the susceptibility of $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{Cl}]$ is found to increase with decreasing temperature. Such a difference in the $\chi'(T)$ behaviour for these two compounds exists because the 3D domain structure in the Cl-containing complex appears below T_C with decreasing temperature at zero steady field, while in the compound

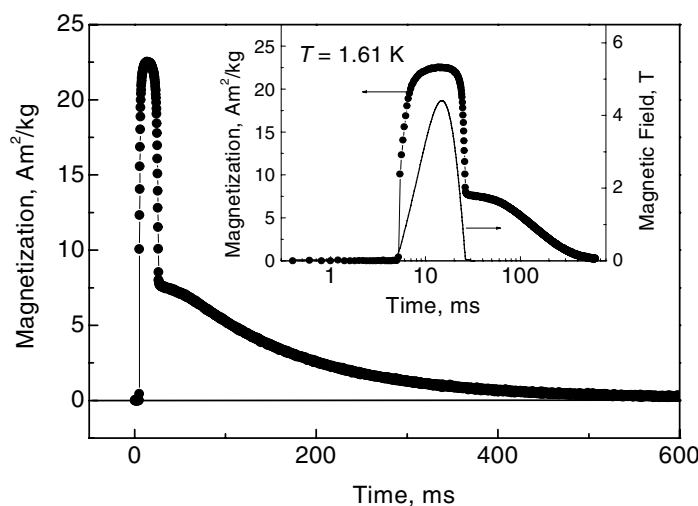


Figure 5. Time dependence of the magnetization of $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ during and after application of the pulsed field up to 4 T at 1.6 K. Inset: the $M(t)$ and $H(T)$ dependences on a logarithmic scale.

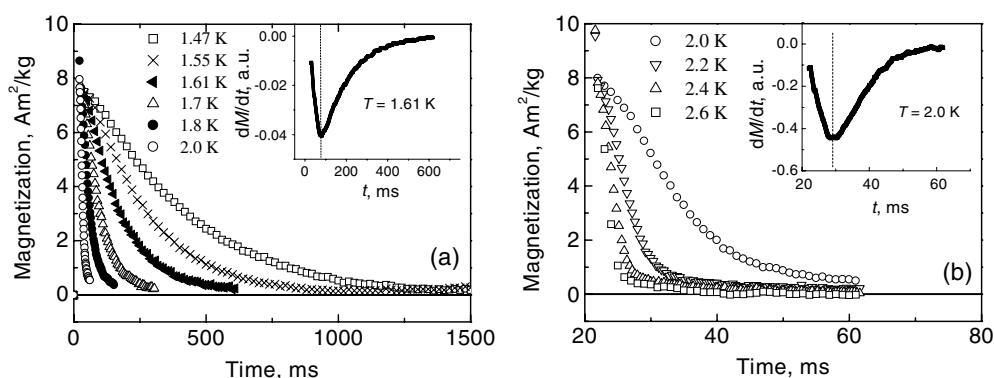


Figure 6. (a), (b) Relaxation of the remanent magnetization of $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ at various temperatures after application of the 4 T pulsed field. Insets show the dM/dt versus t dependences for two different temperatures.

with an AF ground state the AF and F(FI) domains appear only under application of a bias magnetic field. The temperature dependence of the imaginary part of the ac susceptibility of $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{Cl}]$ is also strongly affected by the change in frequency. As follows from figure 7(b), when the frequency of the ac magnetic field increases the $\chi''(T)$ peak shifts towards higher temperatures. Frequency dependences of χ' and χ'' measured at various temperatures below and above T_C are presented in figure 8 on a logarithmic scale. At $T > T_C = 4.8$ K both χ' and χ'' for $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{Cl}]$ are frequency-independent within the range 1–1000 Hz, as for $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$. Below the ordering temperature the frequency dependence of χ'' for $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{Cl}]$ manifests a maximum which shifts towards higher frequencies when the temperature increases.

In figure 9 we show the dc field dependences of the magnetization and ac susceptibility of $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{Cl}]$. The magnetization at 2 K saturates above 3 T and reaches a value of $3 \mu_B$

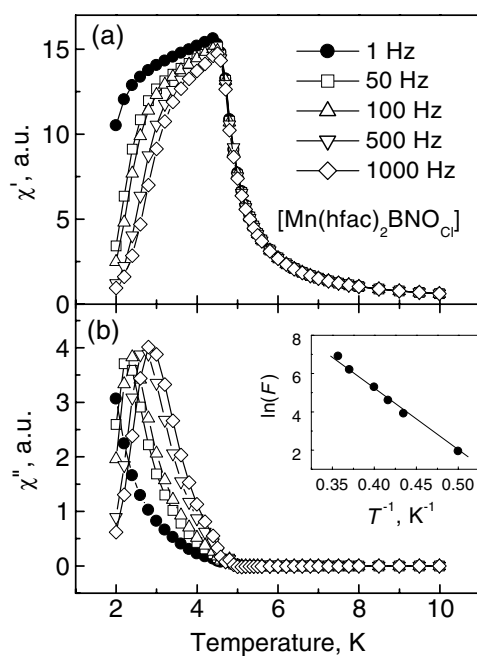


Figure 7. Temperature dependences of the real χ' (a) and imaginary χ'' (b) parts of the ac susceptibility of $[\text{Mn}(\text{hfac})_2\text{BNOCl}]$ measured at various frequencies. The inset shows the $\ln(F)$ versus $1/T$ dependence.

per formula unit, which corresponds to the antiparallel alignment of Mn and NO group spins, as in the AF complex $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$. The ac susceptibility of the Cl-containing compound reveals an appreciable frequency dependence in the low-bias field region (below 0.03 T), where $M(H)$ dependence exhibits a hysteresis and the magnetization process presumably occurs via the displacement of the domain wall. As seen from figure 9, both χ' and χ'' have their strongest frequency dependence in the low-frequency range (1–100 Hz). A slow spin dynamics in $[\text{Mn}(\text{hfac})_2\text{BNOCl}]$ is also sustained by pulsed field magnetization measurements performed in a half-pulse regime. Figure 10 displays the time dependence of the remanent magnetization at 1.5 K for $[\text{Mn}(\text{hfac})_2\text{BNOCl}]$ as well as for $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ for comparison. Unlike the measurements in dc fields, the $[\text{Mn}(\text{hfac})_2\text{BNOCl}]$ compound retains a substantial remanent magnetization ($\sim 30\%$ of the saturation magnetization) after application of a 5 T pulsed field. In zero external field the remanence relaxes during more than 1.5 s, which considerably exceeds the relaxation time in $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ at the same temperature.

4. Discussion

The response of the spin system of a simple two-sublattice antiferromagnet to the application of a low-frequency ac magnetic field below the Néel temperature may be associated with a coherent deviation of magnetic moments in sublattices from the easy magnetization direction. Such a coherent rotation of the magnetization vectors in the antiferromagnet consists of the spatially homogeneous tilting of the magnetic moments within each sublattice. Another contribution to the magnetic susceptibility appears when the measurements are performed in the bias dc magnetic field. If an external bias field approaches a critical value for the AF–FI transition, the ac susceptibility should include a contribution from the new magnetic phase

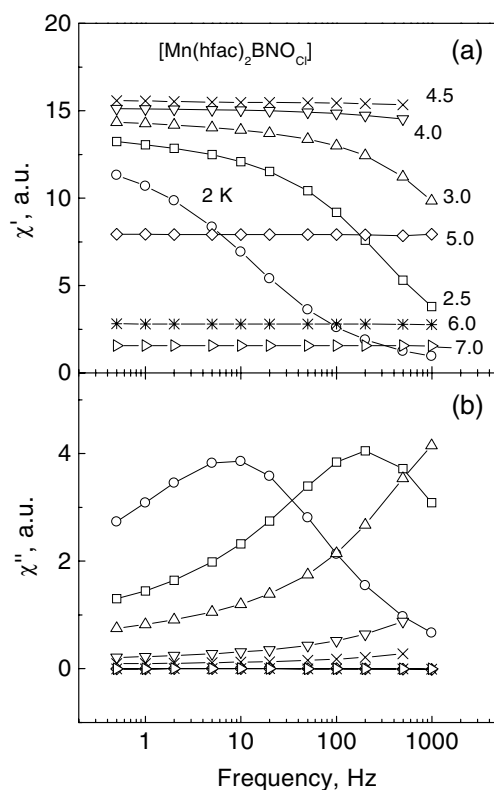


Figure 8. Frequency dependences of χ' (a) and χ'' (b) for $[\text{Mn}(\text{hfac})_2\text{BNOCl}]$ at various temperatures.

and from the motion of the domain walls separating AF and FI phases. The motion of such walls consists in the spatially inhomogeneous rotation of magnetic moments within the wall. These two contributions associated with the coherent rotation of the magnetization within the domain and with the domain wall motion are the constituents of both the real χ' and imaginary χ'' components of the ac susceptibility. At temperatures well above the magnetic ordering temperature, the imaginary part of the ac susceptibility approaches zero, since the relaxation time of magnetic moments is significantly smaller than the period of the ac magnetic field. The value of χ' in this case should be the same as the initial dc magnetic susceptibility. Below the ordering temperature, the imaginary part of the ac susceptibility mainly reflects the energy losses, which occur during the rotation of magnetization within the domains and the movement of the domain walls. The behaviour of χ' and χ'' reflects the magnetization dynamics as a function of temperature, amplitude, frequency and direction of the ac field and the magnitude and direction of the bias field.

The processes of domain wall motion and rotation of the magnetization are usually associated with overcoming the energy barriers at an absolute temperature T with a characteristic relaxation time, τ [14, 15]:

$$\tau^{-1} = 1/\tau_0[\exp(-E/kT)]. \quad (1)$$

Here $1/\tau_0$ is a frequency constant, E is the activation energy and kT is the Boltzmann energy. However, because of the presence of a distribution of energy barrier heights, the thermally activated relaxation can be better approximated, as a rule, by the logarithmic function [16, 17].

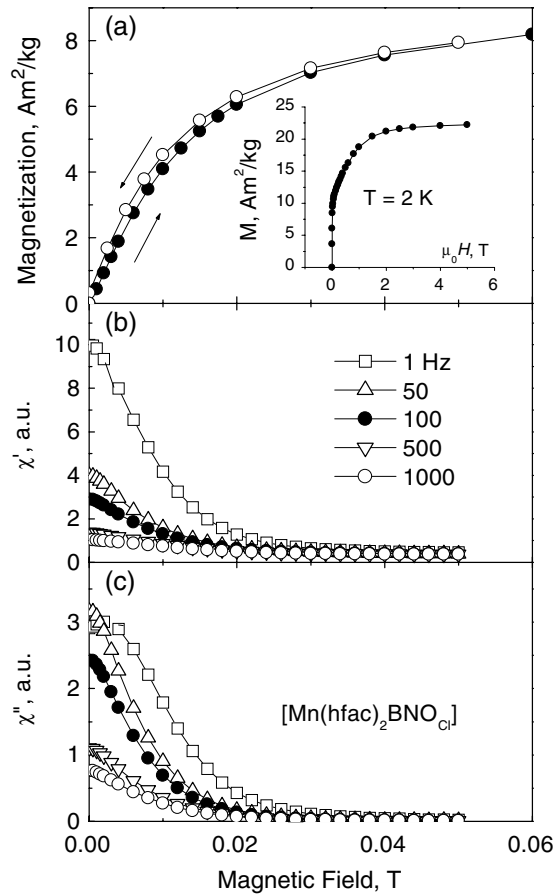


Figure 9. Magnetization curve (a) and the real (b) and imaginary (c) parts of the ac susceptibility at various frequencies of ac field measured for the $[\text{Mn}(\text{hfac})_2\text{BNOCl}]$ compound at $T = 2$ K. The inset shows the field dependence of the magnetization in steady fields up to 5.5 T.

Examination of figure 1 shows that the maximum of the $\chi'(T)$ and $\chi''(T)$ dependences for $[\text{Mn}(\text{hfac})_2\text{BNOH}]$ measured in an applied bias field shifts remarkably towards lower temperatures when the frequency of the ac field decreases. Such a frequency effect is not observed in the case of a zero bias field. Bearing in mind that the applied bias field of 0.03 T corresponds to the average critical field of the AF–FI transition, the frequency effect on the $\chi'(T)$ behaviour may be associated with the appearance of the 3D domain structure when the sample was cooled below T_N . The existence of a mixed state consisting of AF and F domains in the field-cooled sample was observed, in particular, for the metamagnetic compound $\text{Fe}_{0.9}\text{Mg}_{0.1}\text{Cl}_2$ using Faraday rotation contrast [18].

Recently, logarithmic dependence of the ac susceptibility on the frequency was reported for particulate magnetic media [19, 20]

$$\chi'(\omega) \propto -S_{\text{ac}} \ln \omega, \quad (2)$$

where S_{ac} is the ac magnetic viscosity. The S_{ac} value as well as the frequency and temperature range, where the logarithmic law (2) can be observed, should depend on the interactions between magnetic particles and on the distribution of barrier heights within the thermally

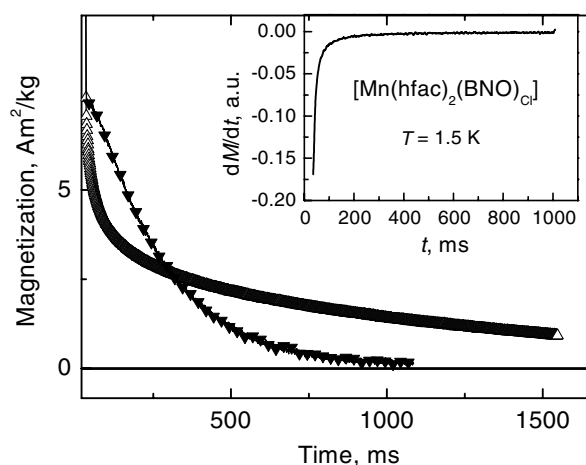


Figure 10. Time dependence of the remanent magnetization for $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{Cl}}]$ (open triangles) measured at 1.5 K after application of the 5 T pulsed field. For comparison, the $M(t)$ dependence measured at $T = 1.55$ K for $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{H}}]$ is also shown (full triangles). Inset: dM/dt versus t dependence for $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{Cl}}]$.

relaxing media. The model considered in [19, 20] can hardly be applied to our systems at low temperatures. Indeed, for both AF and FI systems the $\chi'(\omega)$ dependence is found to be nonlinear in the logarithmic scale at low temperatures (see figures 3 and 8), apparently because of the presence of interchain interaction and the 3D domain structure. However, the frequency range in which the real part of the ac susceptibility follows equation (2) broadens when the temperature of the sample approaches the 3D ordering temperature $T_C = 4.8$ K (see figure 9). Such behaviour may be attributed to a weakening of the interchain coupling in the proximity of T_C .

The fact that the maximum of the $\chi''(T)$ dependence for $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{R}}]$ shifts towards higher temperatures when the frequency of the ac field increases (figures 1(b) and 9) is consistent with generally recognized understanding of the energy loss in ferromagnetic materials (ferrimagnetic in our case) owing to the energy absorption by domain walls during their excitation. This means that excitation of the domain wall oscillations with a higher frequency requires a higher thermal energy. Since the thermally activated process is described by the Arrhenius law (equation (1)), we plotted the logarithm of the frequency of the ac magnetic field versus the inverse temperature of the χ'' peak for $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{Cl}}]$ (inset in figure 7). The observed linear dependence is indicative of the thermally activated process of domain wall motion in this compound. The activation energy associated with such a process and the value of τ_0 are estimated to be about 3.3 meV and 5×10^{-9} s respectively. The domain wall motion in the Cl-containing complex also seems to be a process with slow dynamics as in $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{H}}]$, presumably because of the 1D chain structure of the compound and the low value of the J/J' ratio. Indeed, as can be seen from figure 7, the maximum values of χ' are observed at the minimum frequency used (1 Hz). An increase of the frequency up to 50 Hz is accompanied by a drastic fall of the χ' value (by about 65%) at low temperatures.

Before we consider the magnetization behaviour of the antiferromagnetic compound $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{H}}]$ in pulsed magnetic fields it should be noted that a number of works to date have been devoted to the study of a net spontaneous magnetization that appears in some diluted antiferromagnets with 1D and 2D structures after cooling below the Néel temperature in small applied fields. In particular, remanent magnetization was observed in solid solutions of

$M_{1-x}Zn_xF_2$ ($M = Mn, Fe$) [21, 22], $Fe_{1-x}Mg_xCl_2$ [18, 23], $A_2Fe_{1-x}In_xCl_5 \cdot H_2O$ with $A = K, Rb$ [24, 25] and $(CH_3)_2NH_2Mn_{1-x}Cd_xCl_3 \cdot H_2O$ [26]. The appearance of net magnetization in these diluted antiferromagnetic systems below their ordering temperature is attributed to either the pinning of domain walls separating AF and F phases on nonmagnetic impurities and lattice defects or the lack of compensation of magnetic moments at the ends of magnetically broken chains. The low-temperature remanent magnetization of these compounds relaxes after switching off the field due to the thermally activated process of magnetic relaxation. The small net magnetization that remains in $[Mn(hfac)_2BNO_H]$ after application and removal of the 5 T dc field (see figure 2) can be ascribed mainly to domain wall pinning on lattice defects, since Mn ions are not substituted by nonmagnetic impurities in this compound. However one can suggest that the remanent magnetization in $[Mn(hfac)_2BNO_H]$ will be larger in the case of the dilution of the Mn subsystem by nonmagnetic ions.

The change of magnetization of $[Mn(hfac)_2BNO_H]$ with time during and after application of a pulsed field revealed the large difference in the waiting times for the direct (AF–FI) and inverse (FI–AF) transitions (figures 5 and 6(a), (b)). For the applied pulse with a duration of 20 ms and amplitude of 4 T (the initial sweep rate $\sim 0.7 \text{ T ms}^{-1}$), the direct AF–FI transition starts to occur in a field of $\sim 0.2 \text{ T}$ and is completed within a time of less than 2 ms. Therefore, the high rate of the direct transition is due to the high value of the magnetic field in comparison with the critical field of the AF–FI transition (0.03 T). The large relaxation time after removal of the pulsed field implies very slow dynamics of the magnetization in $[Mn(hfac)_2BNO_H]$ during the inverse transition from the field-induced FI state to the initial AF state in zero field that is close to the critical field of the inverse transition measured in the quasistatic regime. Note that the kinetics of the AF–FI transition may also be controlled by the magnetoelastic interaction, since the value and sign of the interchain exchange interaction in $[Mn(hfac)_2BNO_R]$ compounds were found to be strongly influenced by external pressure. Application of an external pressure significantly increases the critical AF–FI transition field in $[Mn(hfac)_2BNO_H]$ and changes the magnetic order in $[Mn(hfac)_2BNO_{Cl}]$ from the ferromagnetic alignment of the magnetization of chains at ambient pressure to the antiferromagnetic one at hydrostatic pressures above 4 kbar [27]. Therefore, one can suggest that the field-induced AF–FI transition in the $[Mn(hfac)_2BNO_H]$ compound is accompanied by magnetoelastic volume deformations. These deformations should have a significant effect on the stability of AF and FI phases as well as on the kinetics of the AF–FI transition and relaxation process after application of the pulsed field.

The thermally activated change of the remanent magnetization in $[Mn(hfac)_2BNO_H]$ after switching off the field looks quite different from that in ferrimagnetic $[Mn(hfac)_2BNO_{Cl}]$ (see figure 10). Initially, the magnetization decreases fast, as for Cl-containing compounds. It is probably at this stage that the ferrimagnetic domain structure appears in the field-induced FI phase. Then at the level of $11\text{--}8 \text{ A m}^2 \text{ kg}^{-1}$ the magnetization suddenly stops decreasing. We can speculate that at this level the AF phase starts to nucleate and the ferrimagnetic domain walls are pinned at the inclusions of the AF phase. The following relaxation may occur through the nucleation process of the AF phase within the metastable field-induced FI phase followed by growth of the volume of nuclei of the AF phase with zero magnetization by means of displacement of the domain walls separating AF and FI phases. The activation energy for appearance of a nucleus of the new phase may include in our case several contributions associated with the difference in the exchange energy of AF and FI phases, magnetoelastic energy, magnetostatic energy and energy of the interphase domain wall. The relaxation of such a system depends on the barrier height and its energy distribution. The eventual presence of two stages in the evolution of M_r in $[Mn(hfac)_2BNO_H]$ after switching off the field suggests a different rate of change of the magnetization. One can suppose that at the first nucleation

stage the M_r value will show a slow reduction and then M_r will decrease more rapidly via the motion of domain walls. The different rate of change of magnetization during the relaxation of the system through two stages can be seen from the inset in figure 5, which presents the time dependence of the magnetization on a logarithmic scale. In many relaxing magnetic systems the time dependence of the magnetization can be described by the expression

$$M_r(t) = \text{const} - S_{\text{dc}}(T) \ln(t/t_0), \quad (3)$$

where M_r is the remanent magnetization, t is the elapsed time, S_{dc} is the dc viscosity coefficient and t_0 is a constant. The insets in figure 6 display the dM_r/dt versus t dependences obtained at different temperatures. The vertical line indicates the time that may be associated with the change of the relaxation mechanism from nucleation to domain wall displacement during the time evolution of the magnetization. Both these stages are characterized by different viscosity coefficients S_{dc} at the same temperature that implies a remarkable difference in the activation energy. Using equation (1) we can estimate the value of the activation energy from the experimental data of figure 6 since the rate of change of magnetization can be given as:

$$dM_r/dt = C/\tau. \quad (4)$$

Here we will presume that C is a constant. It should be also noted that the value of dM/dt is also influenced by the change of the demagnetizing field that decreases with decreasing remanence. Therefore we have chosen the dM_r/dt values for different temperatures at two values of the remanent magnetization, i.e. at two values of the demagnetizing field:

- (i) at $M_r = 7.2 \text{ A m}^2 \text{ kg}^{-1}$, which corresponds to the first stage in the relaxation process in the temperature interval from 1.47 up to 2.6 K and
- (ii) in the middle of the second stage ($M_r \approx 4 \text{ A m}^2 \text{ kg}^{-1}$) where, in our opinion, the FI–AF transition develops by means of domain wall motion.

Figure 11 shows the temperature dependence of the rate of magnetization as well as $\ln(dM/dt)$ versus $1/T$ dependences (see inset) obtained for the above conditions. For both cases the value of $\ln(dM/dt)$ shows a linear dependence upon $1/T$. This allowed us to estimate the value of the activation energy and pre-exponential factor τ_0 using equations (4) and (1). For the first stage the estimation gives the value $E_I = 1.66 \text{ meV}$ and $\tau_0 \approx 2.2 \times 10^{-7} \text{ s}$, while for the second one $E_{II} = 1.80 \text{ meV}$ and $\tau_0 \approx 1.0 \times 10^{-7} \text{ s}$. The values of E_I and E_{II} are almost two times smaller than the activation energy for the above discussed domain wall motion in ferrimagnetic $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{Cl}}]$. The values of τ_0 for $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{H}}]$ significantly exceed the value of $\tau_0 \sim 10^{-10} - 10^{-12}$ [17] for conventional 3D magnetic materials. Such a discrepancy may be associated with specific dynamics of the magnetization in $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{R}}]$ because of their 1D structure.

Unlike the relaxation of the magnetization in $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{H}}]$, the decay of magnetization in the ferrimagnetic Cl-containing compound after application of a pulsed field is associated with thermally activated domain wall motion only. The difference in the relaxation process for these two compounds is clearly seen from the different shape of the $M_r(t)$ curves at the beginning of the relaxation process (figure 10) and from the dM_r/dt versus t dependence, which is monotonic (inset in figure 10) in contrast with a nonmonotonic curve for $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{H}}]$. The larger value of the relaxation time of the remanent magnetization in $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{Cl}}]$ after switching off the pulsed field is in agreement with the larger activation energy for domain wall motion in this compound, as estimated above from ac susceptibility data.

The slow dynamics of the change in magnetization revealed by ac susceptibility and pulsed field magnetization measurements of both complexes originates, in our opinion, from their

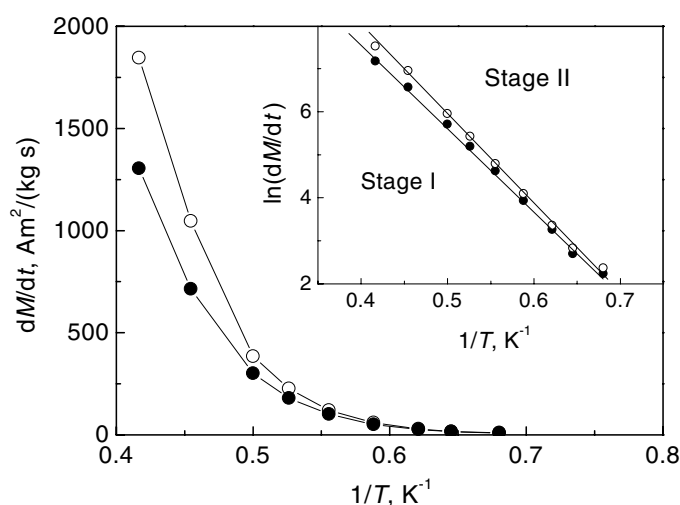


Figure 11. dM/dt and $\ln(dM/dt)$ versus $1/T$ data for the remanent magnetization of $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ for two stages of the relaxation.

chain structure and small value of the interchain exchange interaction in comparison with the intrachain one. Domain wall motion in such compounds may differ significantly from such a process in ordinary 3D magnets. As has been mentioned, theoretical and experimental investigations of nonlinear excitation in 1D magnets above the 3D ordering temperature revealed that the spin dynamics in these materials is associated with the propagation of domain walls along the 1D chain. One can therefore assume that this mechanism is also involved in the magnetization process of the material in the 3D ordered state below the Néel temperature. Displacement of the domain wall parallel to the chain may occur through the lateral motion of the intrachain wall along a separate chain in a perpendicular direction, as is shown schematically in figure 12 for the case of the monoatomic domain wall that separates AF and FI domains. The shape of the domain wall in this material may have a complicated, probably fractal-like, form. In our opinion, the slow dynamics of the change in magnetization in $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{R}]$ may originate from the complicated motion of such a domain wall.

5. Summary

We have measured the ac susceptibility and magnetization in steady and pulsed fields for the new molecule-based magnetic complexes $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{R}]$ ($\text{R} = \text{H}, \text{Cl}$) with ferrimagnetically ordered chains composed of $S = 1$ (biradical) and $S = 5/2$ (Mn). It has been found that the change in magnetization in these compounds under application of a magnetic field below the ordering temperature is a slow dynamical process which presumably originates from their strong one-dimensional character because of the weakness of the interchain exchange interaction in comparison with intrachain one ($J/J' \sim 10^{-3}$). In the antiferromagnetic complex $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ a significant frequency dependence of both χ' and χ'' is found for a low-frequency region below the Néel temperature in the vicinity of the phase transition from the antiferromagnetic to the field-induced ferrimagnetic state. A substantial increase of the critical AF–FI transition field and the appearance of remanent magnetization were revealed by the pulsed field magnetization measurements. The remanence relaxes within about 1000 ms after switching off the field. The relaxation of the remanence is found to proceed in $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ via a two-stage thermally activated process. The first stage may

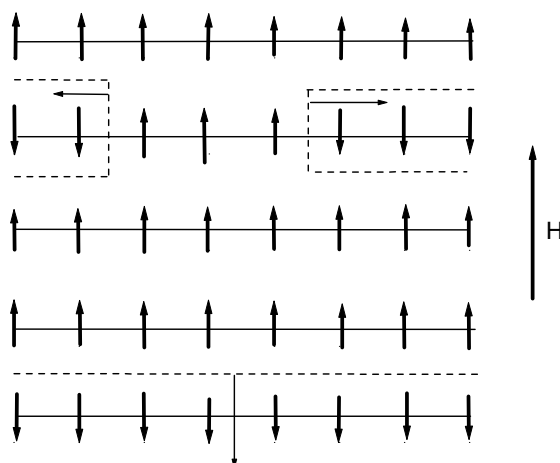


Figure 12. Scheme of the possible domain wall displacement at the AF–FI(F) transition in a material having 1D-chain structure. The position of the domain wall is traced by dashed line.

be associated with the nucleation of the AF phase within the metastable field-induced FI phase and the second one is attributed to the displacement of the domain walls separating AF and FI phases. Each stage is characterized by its own activation energy and the value of τ_0 . For the first stage these characteristics were estimated to be about 1.66 meV and 2.2×10^{-7} s and for the second 1.80 meV and 1.0×10^{-7} s. The values of τ_0 obtained for $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ seem to be of four to five orders larger than those for conventional 3D magnetic materials, which is presumably due to the 1D character of this compound. The ac magnetic susceptibility below the ordering temperature of the ferrimagnetic complex $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{Cl}]$ also reveals a significant frequency dependence in low dc magnetic fields where the magnetization process goes via the domain wall displacement. The activation energy for the domain wall motion in $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{Cl}]$ is found to be about 3.3 meV and the value of $\tau_0 \sim 5 \times 10^{-9}$ s. The larger value of the activation energy in this compound in comparison with that obtained for $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ is confirmed by the larger relaxation time of the remanent magnetization observed after application of the pulsed field.

The slow dynamics of the magnetization in both these compounds may originate from the complicated domain wall motion which occurs apparently parallel to the chains through the lateral motion of the intrachain wall along the separate chains. Such a process is supposed to differ significantly from that for the conventional 3D magnets where domain wall displacement is a result of simple rotation of the magnetization around the direction normal to the plane of the wall.

Acknowledgments

This work was supported by Joint Studies Program of IMS ‘Magnetic Anisotropy and Magnetic Viscosity of Molecule-Based Magnets’ and by the Program ‘Universities of Russia’. NVB and NVM acknowledge the support of IMS and ISSP during their stay in Japan.

References

- [1] Mikeshka H J and Steiner M 1991 *Adv. Phys.* **40** 191
- [2] Kjemis J K and Steiner M 1978 *Phys. Rev. Lett.* **41** 1137
- [3] Yoshizawa H, Hirakawa K, Satija S K and Shirane G 1981 *Phys. Rev. B* **23** 2298

- [4] de Jongh L J 1982 *J. Appl. Phys.* **53** 8018
- [5] Iwamura H and Inoue K 2001 *Magnetism—Molecules to Materials* (part II) ed J S Miller and M Drillon (Weinheim: Wiley-VCH) p 61
- [6] Inoue K and Iwamura H 1994 *J. Chem. Soc. Chem. Commun.* 2274
- [7] Inoue K and Iwamura H 1995 *Synth. Met.* **71** 1793
- [8] Ovchinnikov A S, Bostrem I G, Sinitsyn V E, Boyarchenkov A S, Baranov N V and Inoue K 2002 *J. Phys.: Condens. Matter* **14** 8067
- [9] Inoue K and Iwamura H 1996 *Mol. Cryst. Liq. Cryst.* **286** 133
- [10] Inoue K, Iwahori F, Markosyan A S and Iwamura H 2000 *Coord. Chem. Rev.* **198** 219
- [11] Stryjewski E and Giordano N 1977 *Adv. Phys.* **26** 487
- [12] King A R and Paquette D 1973 *Phys. Rev. Lett.* **30** 682
- [13] Baranov N V, Markin P E, Mushnikov N V and Goto T 2001 *Mater. Sci. Forum* **373–376** 405
- [14] Street R and Wooley J C 1949 *Proc. Phys. Soc. A* **62** 562
- [15] Jacobs L S and Bean C P 1963 *Magnetism* ed G T Rado and H Shul (New York: Academic) p 271
- [16] Street R, Wooley J C and Smith P B 1952 *Proc. Phys. Soc. B* **65** 679
- [17] Gaunt P and Roy G J 1976 *Phil. Mag.* **34** 781
Gaunt P 1986 *J. Appl. Phys.* **59** 4129
- [18] Mattsson J, Kushauer J, Bertrand D, Ferre J and Kleemann W 1994 *J. Magn. Magn. Mater.* **130** 216
- [19] Zhao B, Chow J Y and Yan X J 1996 *Appl. Phys.* **79** 6022
- [20] Klik I, Yao Y D, Yan X and Chang C R 1998 *Phys. Rev. B* **57** 92
- [21] Fries T, Shapira Y, Paduan-Filho A, Becerra C C and Palacio F 1993 *J. Phys.: Condens. Matter* **5** 8083
- [22] Lederman M, Selinger J V, Bruinsma R, Hamman J and Orbach R 1992 *Phys. Rev. Lett.* **68** 2086
- [23] Leitao U A and Kleeman W 1987 *Phys. Rev. B* **35** 8696
- [24] Bacerra C C, Paduan-Filho A, Fries T, Shapira Y and Palacio F 1994 *J. Phys.: Condens. Matter* **6** 5725
- [25] Bacerra C C, Barbeta U B, Paduan-Filho A, Palacio F, Campo J and Gabas M 1997 *Phys. Rev. B* **56** 3204
- [26] Bacerra C C, Paduan-Filho A and Palacio F 2000 *J. Phys.: Condens. Matter* **12** 6207
- [27] Suzuki K, Hosokoshi Y and Inoue K 2002 *Mol. Cryst. Liq. Cryst.* **379** 247