

# Quantum dissipation theory of slow magnetic relaxation mediated by domain-wall motion in the one-dimensional chain compound $[\text{Mn}(\text{hfac})_2\text{BNO}_H]$

A. S. Ovchinnikov,\* I. G. Bostrem, V. E. Sinitsyn, A. S. Boyarchenkov, and N. V. Baranov†  
*Department of Physics, Ural State University, 620083 Ekaterinburg, Russia*

K. Inoue

*Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*  
 (Received 29 June 2006; revised manuscript received 19 September 2006; published 22 November 2006)

Based on a quantum dissipation theory of open systems, we present a theoretical study of slow dynamics of magnetization for the ordered state of the molecule-based magnetic complex  $[\text{Mn}(\text{hfac})_2\text{BNO}_H]$  composed from antiferromagnetically coupled ferrimagnetic  $(5/2, 1)$  spin chains. Experimental investigations of the magnetization process in pulsed fields have shown that this compound exhibits a metamagnetic AF-FI transition at a critical field in the order of the interchain coupling. A strong frequency dependence for the ac susceptibility has been revealed in the vicinity of the AF-FI transition and was associated with an AF-FI interface kink motion. We model these processes by a field-driven domain-wall motion along the field-unfavorable chains correlated with a dissipation effect due to a magnetic system-bath coupling. The calculated longitudinal magnetization has a two-step relaxation after the field is switched off and are found in good agreement with the experiment. The relaxation time determined from the imaginary part of the model ac susceptibility agrees qualitatively with that found from the remanent magnetization data.

DOI: [10.1103/PhysRevB.74.174427](https://doi.org/10.1103/PhysRevB.74.174427)

PACS number(s): 72.25.Rb, 61.20.Lc, 67.40.Fd

## I. INTRODUCTION

Magnetic resonance effects due to switching of spins by a time-dependent magnetic field and relaxation measurements are widely used to study magnetic materials. They may give information about the main mechanism of the magnetization change in samples. When a magnetic field varies, magnetic materials which exhibit a hysteresis present a characteristic time dependence of the magnetization due to the multiplicity of available metastable states. In many relaxing magnetic systems the time dependence can be described by  $M = M_0 - S \ln t$ , where  $S$  is the magnetic viscosity of the system. The viscosity is a consequence of thermal activation of irreversible domain processes such as the domain wall motion and the nucleation of domains of the reverse magnetization. The logarithmic change with time  $M \sim \ln t$  is predicted if there is a distribution of energy barriers or time-dependent activation energies present in the material. A simple Debye relaxation  $M = M_0 \exp(-t/\tau)$  arises from a single-barrier activation mechanism.<sup>1,2</sup> The barriers associated with the relaxation process are of two types. The intrinsic barriers arising, for example, from the magnetic anisotropy contribute to the reversal of magnetization, whereas the barriers due to the pinning of domain walls are generally attributed to the defects in the materials. Both types of barriers are responsible for the pronounced metastability (hysteresis phenomena) of magnetic systems.

Recent efforts in synthetic chemistry provide a number of low-dimensional magnetic systems that show the slow relaxation of the magnetization, for example, this effect was found in one-dimensional (1D) anisotropic ferrimagnetic chains named as single chain magnets (SCM).<sup>3</sup> The slow magnetic relaxation in the paramagnetic phase has been observed with ac susceptibility and SQUID magnetometry measurements in the real quasi-1D ferrimagnetic compound

$[\text{Co}(\text{hfac})_2\text{NITPhOMe}]$ .<sup>4</sup> An Arrhenius behavior with the activation energy  $\Delta \sim 152$  K, which is of order of the intrachain exchange interaction between alternating  $\text{Co}^{2+}$  and organic NITPhOMe spins, has been observed for 10 decades of relaxation time and found to be consistent with the Glauber model.<sup>5</sup> The relaxation was also studied by monitoring the decay of the longitudinal magnetization, which was found to be exponential. The slow relaxation is governed by the uniaxial anisotropy seen by each spin on the chain and magnetic correlations between the spins.

Recently, the ac susceptibility and magnetization in steady and pulsed fields have been measured for the molecule-based magnetic complexes  $[\text{Mn}(\text{hfac})_2\text{BNO}_R]$  ( $R = \text{H}, \text{Cl}$ ) with ferromagnetically (Cl) or antiferromagnetically (H) ordered ferrimagnetic chains composed of  $S = 1$  (biradical) and  $S = 5/2$  ( $\text{Mn}^{2+}$ ).<sup>6</sup> It has been found that the change in magnetization in these compounds under application of a magnetic field below the three-dimensional (3D) ordering temperature [ $T_N = 5.5$  K (H) and  $T_C = 4.8$  K (Cl)] is a slow dynamical process which presumably originates from their strong one-dimensional character, i.e., because of the weakness of the interchain exchange ( $J$ ) interaction in comparison with intrachain ( $J'$ ) one ( $J/J' \sim 10^{-3}$ ). The thermally activated change of the remanent magnetization in  $[\text{Mn}(\text{hfac})_2\text{BNO}_H]$  after switching off the field looks quite different from that in  $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{Cl}}]$ . Figure 1 displays time dependence of the remanent magnetization at 1.5 K for these compounds for comparison. The large value of the relaxation times of both processes and their existence well below  $T_{3D}$  lead to the suggestion that these relaxation processes are related to the development and motion of magnetic domains either with a wide distribution of energy barriers ( $R = \text{Cl}$ ) or a single energy barrier height ( $R = \text{H}$ ).

Indeed, the change of the magnetization of  $[\text{Mn}(\text{hfac})_2\text{BNO}_H]$  with time during and after application of

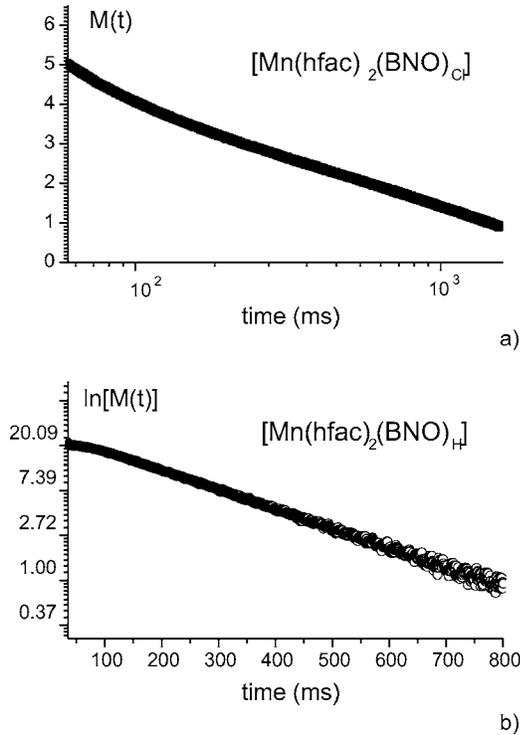


FIG. 1. Time dependence of the magnetization of  $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{Cl}}]$  (a) and  $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{H}}]$  (b) compounds at 1.5 K after application of the 5 T pulsed field. The logarithmic curve in the first case results from a relaxation mechanism that involves a distribution of energy barriers. The exponential decrease for the second case arises from a single-barrier activation mechanism.

a pulsed field is controlled by the direct AF-FI and inverse FI-AF transitions. For the applied pulse with a duration of 20 ms and amplitude of 4 T, the direct AF-FI transition is completed within a time of less than 2 ms. 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 in steady fields and about 0.2 T in pulsed fields). The large relaxation time ( $\sim 500$  ms) after removal of the pulsed field implies very slow dynamics of the magnetization during the inverse transition from the field-induced FI state to the initial AF state in zero field. The slow dynamics of the magnetization in this material was suggested to be controlled by the domain wall motion along the separate field-unfavorable chains.<sup>6</sup> The energy barrier which hampers the reversal of the magnetization is originated by the antiferromagnetic interchain coupling that is reminiscent of the molecular clusters or single cluster magnet (SCM) where the energy barrier is due to the magnetic anisotropy.

The fast relaxation during the field change and the slow relaxation due to the transitions between the different metastable states involves the release of the magnetic energy which cause local heating. The process of energy losses in  $[\text{Mn}(\text{hfac})_2\text{BNO}_{\text{H}}]$  is likely due to the motion of domain boundaries within the chains and is connected with the coercivity losses and the radiation of phonons. Finally, the energy of the magnetic system is transformed into the phonon energy, that is, into the heat. Due to the magnetic system-

bath coupling we may explain the experiments under the condition of isothermal relaxation, and, as a consequence, in an assumption that self-heating in the magnetic relaxation does not destroy 3D order.

## II. PRELIMINARIES

The choice of a proper formalism of the quantum dissipation theory depends essentially on the real physical media and real process of the energy transfer. The interaction between a quantum system and its environment is the physical factor responsible for the relaxation process in the system. Such a relaxation process can be provided by the environment if it acts as a bath. This arises the fundamental problem of description of the relaxation dynamics for a system simultaneously interacting with a heat bath and a time-dependent driving field.

The question now arises as to what is a nature of heat bath. We note that the spin system in the external dc bias field in ac-susceptibility measurements or in the pulsed field in magnetization measurements consists of two weakly interacting parts, i.e., field-favorable ( $S_1$ ) and field-unfavorable ( $S_2$ ) chains. Then, two distinct models for the bath are assumed. The first one identifies the bath with a crystal lattice (phonon bath). In this case, the energy levels of the bath are populated according to the conventional Gibbs distribution. When a rapidly varying strong pulsed field causes the AF-FI transition the spin temperature of the  $S_2$  part becomes much higher than the lattice and the  $S_1$  part temperatures (saturation process). After the field is off the whole spin quantum system is driven to the thermal equilibrium characterized by Gibbs's density matrix owing to energy exchange between the  $S_1$ ,  $S_2$  systems and the heat bath. Following the fundamental Bogoliubov's procedure of the contraction of description with the accompanying hierarchy of relaxation times<sup>7</sup> we may conclude that the weak interchain interactions are related to long-time relaxation process with the characteristic time equal to the characteristic time scale of the experiment 1– $10^3$  ms. It is assumed that another interaction, including usual spin-phonon ones, are strong enough and have associated correlation effects with shorter relaxation times, i.e., much smaller than the duration of the experiment. We should eliminate them as irrelevant information to characterize the macrostate. Apparently, a possible approach to this irreversible process may be performed within the nonequilibrium statistical operator (NSO) method largely elaborated by Zubarev and co-workers,<sup>8,9</sup> which is a large generalization of the Gibbs's theory. The results of the NSO analyses will be given by us elsewhere.

The second model of the bath is based on the suggestion that the relaxation process is related with the development and motion of magnetic domains in the field-unfavorable chains  $S_2$  in a driving field. The recent study of the behavior of domain walls in Ising ferromagnetic chains yields the following picture.<sup>10</sup> In zero field the interface between two domains of oppositely oriented spins, a kink, moves left or right with the probability  $p=1/2$ , which may be interpreted as a random walk. Two such kinks can meet via diffusive motion. Once there is only one spin left between two kinks

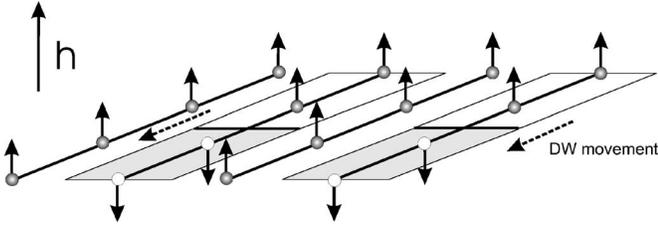


FIG. 2. In an external positive field the system consists of field-favorable (white) and field-unfavorable (shaded) chains. Interface kinks (domain walls) in the second-type chains can move only along the dotted arrows.

they annihilate with probability  $p \sim 1$  in the next time step and the two domains merge. Switching on the external driving field causes domains with spins parallel to the field to start growing. The kinks at the end of such a cluster move outwards one step during each time step where the field remains favorable. If the field switches into an unfavorable direction, the cluster shrinks again (breathing behavior). In this process the small domains and the kinks associated with them will be eliminated rapidly. In the Ising model a domain wall width is simply the lattice constant. On the contrary, the domain walls in the Heisenberg chains are much wider due to the strong exchange interactions involved. The closest analog of such a wall is the soliton in a magnetic chain.<sup>11</sup> Therefore another model, appropriate for this domain wall relaxation dynamics, may be applied for the bath. In this model a quantum system (the field-unfavorable chain with a kink) interacts weakly with the environment, i.e., with the nearest surrounding field-favorable chains and the lattice (Fig. 2). The bath is again considered as a quantum statistical system being at equilibrium. The domain walls oscillate around their equilibrium position under a varying ac field (the process far from a saturation) or move reversibly under a time-dependent pulsed field (the saturation process). The bath provides an existence of random fields (Langevin forces) created by the environment which interacts with variables of the quantum system (Langevin dissipative modes). Due to the system-bath interactions the domain wall dynamics become irreversible and the system relaxes from its initial nonequilibrium state to the equilibrium one when the field is off.

A quantum dissipative theory (QDT) with the system-bath interaction being treated rigorously at the second-order cumulant level for reduced dynamics has been recently constructed for open quantum systems.<sup>12</sup> The theory belongs to a class of widely used quantum master equations, such as the Bloch-Redfield theory<sup>13,14</sup> and a class of Fokker-Plank (FP) equations,<sup>9,15</sup> and is valid for arbitrary bath correlation functions and time-dependent external driving fields. The QDT-FP formulation constitutes a theoretical framework for the present study of dissipative processes in the molecule-based magnetic complexes  $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ .

### III. QUANTUM DISSIPATION THEORY

The key theoretical quantity in a quantum dissipation is the reduced density operator  $\rho(t) \equiv \text{Tr}_B \rho_T(t)$ , i.e., the partial

trace of the total system and bath composite  $\rho_T(t)$  over all the bath degrees of freedom. For a system dynamical variable  $A$ , its expectation value

$$\langle A(t) \rangle = \text{Tr}[A\rho_T(t)] = \text{Tr}[A\rho(t)]$$

can be evaluated with the substantially reduced system degrees of freedom. Quantum dissipation theory governs the evolution of the reduced density operator  $\rho(t)$ , where the effects of bath are treated in a quantum statistical manner.

The total composite Hamiltonian in the presence of classical external field can be written as

$$H_T = H(t) + H_B - \sum_a Q_a F_a. \quad (1)$$

Here  $H(t)$  is the deterministic Hamiltonian that governs the coherent motion of the reduced system density matrix and involves interaction with an arbitrary external classical field  $h(t)$ . The system is embedded in a dissipative bath ( $H_B$ ) and the last term in Eq. (1) describes the system-bath couplings, in which  $\{Q_a\}$  are Hermite operators of the primary system and can be called the generalized dissipative modes. The generalized Langevin forces

$$F_a(t) = e^{iH_B t} F_a e^{-iH_B t}$$

are Hermite bath operators in the stochastic bath subspace assuming Gaussian statistics. Without loss of generality, their stochastic mean values are set to  $\langle F_a(t) \rangle_B = 0$ , where  $\langle \dots \rangle_B$  denote the ensemble average over the initially stationary bath density matrix  $\hat{\rho}_B(0)$ . The effects of Langevin forces on the reduced primary system are therefore completely characterized by their correlation functions  $\tilde{C}_{ab}(t) = \langle F_a(t) F_b(0) \rangle_B$ . They satisfy the boundary conditions  $\tilde{C}_{ab}(\pm\infty) = 0$ , and the detailed-balance and the symmetry relations  $\tilde{C}_{ab}^*(t) = \tilde{C}_{ab}(t - i\beta) = \tilde{C}_{ba}(-t)$ , where  $\beta = 1/kT$ . This admits the Meier-Tannor parametrization  $\tilde{C}_{ab}(t)$  in terms of exponential functions<sup>16</sup>

$$\tilde{C}_{ab}(t \geq 0) \equiv \sum_m \nu_m^{ab} e^{-\zeta_m^{ab} t}$$

with the adjustable parameters  $\nu_m^{ab}$ ,  $\zeta_m^{ab}$ . These parameters are in general complex but, for simplicity, we take  $\zeta_m^{ab}$  to be real and positive.

The frequency-domain symmetry relation reads as  $C_{ab}^*(\omega) = C_{ba}(\omega)$ , and the detailed-balance relation in terms of spectral functions is  $C_{ba}(-\omega) = e^{\beta\omega} C_{ab}(\omega)$ . Using the generalized bath interaction spectral density function  $J_{ab}(\omega) = C_{ba}(-\omega) - C_{ab}(\omega)$  obeying the symmetry relations  $J_{ab}(\omega) = -J_{ba}(-\omega) = J_{ba}^*(\omega)$  we have  $C_{ab}(\omega) = J_{ab}(\omega)/(e^{\beta\omega} - 1)$ .

We will use the reduced Liouville equation, i.e., the equation of motion for the reduced density matrix  $\rho(t)$ , in the partial ordering prescription<sup>17</sup>

$$\dot{\rho}(t) = -iL(t)\rho(t) - R(t)\rho(t), \quad (2)$$

which is characterized by the local-time kernel  $R(t)$ . The Liouvillian  $L$  is the commutator of the reduced system Hamiltonian  $H(t)$  in the presence of external classical field

$$L(t)\hat{A} \equiv [H(t), \hat{A}], \quad (3)$$

and the superoperator  $R(t)$  can be formulated in terms of the system-bath interaction. In the standard approximation of the weak-coupling limit in which the system-bath interaction is considered only up to second order the dissipation term is

$$R(t)\rho(t) \equiv \sum_a [Q_a, \tilde{Q}_a(t)\rho(t) - \rho(t)\tilde{Q}_a^\dagger(t)], \quad (4)$$

where  $\tilde{Q}_a(t)$  is the non-Hermitian relaxation operator in the Hilbert space

$$\tilde{Q}_a(t) = \sum_b \int_{-\infty}^t d\tau \tilde{C}_{ab}(t-\tau)G(t, \tau)Q_b. \quad (5)$$

The Liouville-space propagator  $G(t, \tau)$  associated with  $L(t)$  is defined via

$$i \frac{\partial}{\partial t} G(t, \tau) = L(t)G(t, \tau).$$

It can be defined in terms of the Hilbert-space Green's function  $\tilde{G}(t, \tau)$  via the relation for an arbitrary operator  $\hat{A}$ ,

$$G(t, \tau)\hat{A} \equiv \tilde{G}(t, \tau)\hat{A}\tilde{G}^\dagger(t, \tau),$$

where we treat  $\hat{A}$  on the left-hand side as a vector in Liouville space.

The reduced system Hamiltonian in the presence of external classical field can be written as

$$H(t) = H_s + H_{sf}(t),$$

where  $H_s$  is the time-independent, field-free Hamiltonian, whereas  $H_{sf}(t)$  is the interaction between the system and the external classical field  $h(t)$ . We further define similarly to Eq. (3) the Liouville superoperators  $L_s$  and  $L_{sf}(t)$  corresponding to the reference Hamiltonians. The identity

$$G(t, \tau) = G_s(t, \tau) - i \int_{\tau}^t d\tau' G(t, \tau')L_{sf}(\tau')G_s(\tau', \tau) \quad (6)$$

obtained from the definitions

$$G(t, \tau) \equiv \hat{T} \exp\left(-i \int_{\tau}^t [L_s + L_{sf}(\tau')]d\tau'\right),$$

where the symbol  $\hat{T}$  implies a time ordering, and

$$G_s(t, \tau) = G_s(t-\tau) = e^{-iL_s(t-\tau)}$$

allows us to separate the dissipation effects in Eq. (5) into the field-free part and the correlated driving-dissipation part. This yields

$$\begin{aligned} \tilde{Q}_a(t) &= \tilde{Q}_a^s - i \sum_b \int_{-\infty}^t d\tau \int_{\tau}^t d\tau' \tilde{C}_{ab}(t-\tau)G(t, \tau')L_{sf}(\tau') \\ &\quad \times G_s(\tau', \tau)Q_b, \end{aligned} \quad (7)$$

where the field-free contribution  $\tilde{Q}_a^s$  is time independent and given explicitly by

$$\begin{aligned} \tilde{Q}_a^s &= \sum_b \int_{-\infty}^t d\tau \tilde{C}_{ab}(t-\tau)G_s(t-\tau)Q_b \\ &= \sum_b \int_0^{\infty} d\tau \tilde{C}_{ab}(\tau)e^{-iL_s\tau}Q_b = \sum_b C_{ab}(L_s)Q_b. \end{aligned} \quad (8)$$

Equation (2) together with Eqs. (4), (7), and (8) provide a prescription for obtaining the reduced density operator up to the second order in system-bath interaction. The underlying assumption is that the system-bath coupling is not strong enough, which makes the second order cumulant expression reasonable. It is known that this approximation applies well to most dissipative systems in quantum optics, and in transport in mesoscopic systems.<sup>18</sup> In the strong system-bath regime a special technique is required, which goes beyond the second order approximation.<sup>19,20</sup>

One of the traditional approaches to treat the problem is based on the associated quantum master equations. It focuses on the relation among various matrix elements of the density operator in the time-independent  $H$ -eigenstate representation and is well suitable for the finite systems. For larger systems (spin chains, for example) the number of many-particle states increases dramatically and we cannot generally solve all the microscopic equations. However, we can describe the system by macroscopic variables (domain wall position, total magnetization of a chain) which fluctuate in a stochastic way. The Fokker-Plank (FP) equation arises as an equation of motion for the distribution function of the fluctuating macroscopic variables.<sup>21</sup> Equations (2), (4), (7), and (8) will serve as starting formulations for deriving FP equations for observables of the reference system.

#### IV. PROCESS FAR FROM A SATURATION: DYNAMIC ac SUSCEPTIBILITY

Magnetic systems exhibiting relaxation phenomena can be characterized by the complex ac susceptibility,  $\chi(\omega) = \chi' - i\chi''$ , where the dispersion  $\chi'$  and the absorption  $\chi''$  are frequently dependent. Before moving on to the technical details of the calculation, we mention briefly some of the experimental results in the ac-susceptibility measurements for the  $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$  compound that support the domain-wall motion picture.

A strong frequency dependence both for  $\chi'(\omega)$  and  $\chi''(\omega)$  has been revealed in the bias dc fields of 0.025–0.03 T. The magnetization process in the field range 0.02–0.05 T is accompanied by a remarkable hysteresis (of about 0.012 T), and, in addition, a small remanent magnetization 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, from antiferromagnetic ordering of the chain magnetic moments to their parallel alignment in the field-induced state.<sup>22</sup> In the region of the metamagnetic transition, where the AF and FI phase coexist, the amplitude of a maximum of both  $\chi'$  and  $\chi''$  decreases significantly with increasing frequency, especially in the frequency region from 1 to 50 Hz. From the large values of  $\chi(\omega)$  for  $\omega \sim 1$  Hz in the vicinity of the AF-FI transition, we may suggest that excitation of domain wall motion by a

small oscillating field occurs more effectively at low frequencies.

The complex magnetic ac susceptibility can be explained within approach, where the magnetization  $M$  is controlled by the field-induced sideways motion of domain walls. In this case, the contribution of one domain wall to the susceptibility is

$$\chi = \frac{\partial M}{\partial h} = \frac{\partial M}{\partial x} \frac{\partial x}{\partial h},$$

and taking approximately  $M \propto x$  as the magnetization increases due to a wall displacement along the  $x$  axis, one finds  $\chi \propto \partial x / \partial h$ .

A periodic domain wall motion caused by the external ac-field  $h(t) = h_0 \cos \omega t$  is modeled by a well studied system, a driven Brownian oscillator (DBO), with the Hamiltonian

$$H_s = \Omega(a^\dagger a + \frac{1}{2}),$$

where the number of oscillator excitations  $a^\dagger a$  corresponds to an instant magnetization. The dissipation coupling mode  $\hat{Q}$ ,

$$\hat{Q} = \frac{1}{\sqrt{2}}(q_+ \hat{a}^\dagger + q_- \hat{a})$$

interacts with a stochastic bath force. Here,  $q_+ = q_-^*$  are complex numbers, and  $\hat{a}(\hat{a}^\dagger)$  are the annihilation (creation) operators of the oscillator with the frequency  $\Omega$  determined by the interchain coupling in an applied bias field, i.e., in the vicinity of the AF-FI transition, and we hold only a single Langevin mode  $Q$  in study. The operator  $\hat{\mu} = \frac{1}{\sqrt{2}}(\hat{a}^\dagger + \hat{a})$  interacts with the ac field and describes periodic domain wall movement caused by  $h(t)$ . After introducing these definitions, Eq. (7) can be transformed as follows:

$$\tilde{Q}(t) = \tilde{Q}^s - \frac{i}{2} \int_0^\infty d\tau \lambda(\tau) h(t - \tau), \quad (9)$$

where the system-bath coupling response

$$\lambda(\tau) = \int_\tau^\infty d\tau' \tilde{C}(\tau') (q_+ e^{i\Omega(\tau' - \tau)} - q_- e^{-i\Omega(\tau' - \tau)})$$

is given explicitly as

$$\lambda(\tau) = \frac{q_+ \nu_m}{\zeta_m - i\Omega} e^{-\zeta_m \tau} - \frac{q_- \nu_m}{\zeta_m + i\Omega} e^{-\zeta_m \tau} \quad (10)$$

with the aid of Meier-Tannor parametrization. As usual, a summation is to be made for the repeated index  $m$ . In the following calculation we choose  $q_\pm = 1$  for simplicity, i.e., the dissipation is the same both for left and right domain-wall displacements.

Substituting (10) into Eq. (9), followed by some minor algebra, we get

$$\tilde{Q}(t) = \tilde{Q}^s + \frac{h_0 \Omega \nu_m}{(\zeta_m^2 + \Omega^2)(\zeta_m^2 + \omega^2)} (\zeta_m \cos \omega t + \omega \sin \omega t).$$

The time-local dissipation superoperator is

$$R(t)\rho(t) \equiv [Q, \tilde{Q}(t)\rho(t) - \rho(t)\tilde{Q}^\dagger(t)] = R_s \rho(t) + i\xi(t)[Q, \rho(t)],$$

where  $R_s$  is the field-free dissipation

$$R_s \rho(t) \equiv [Q, \tilde{Q}^s \rho(t) - \rho(t)(\tilde{Q}^s)^\dagger].$$

The effective local-field correction, acting on the system via  $Q$  is

$$\xi(t) = \frac{2h_0 \Omega \nu_m''}{(\zeta_m^2 + \Omega^2)(\zeta_m^2 + \omega^2)} (\zeta_m \cos \omega t + \omega \sin \omega t)$$

and determined by the imaginary part of the bath correlation function  $\tilde{C}(t)$ . Hence, the final QDT formulation is

$$\dot{\rho}(t) = -i[H_s - \hat{\mu}h(t) + \hat{Q}\xi(t), \rho(t)] - R_s \rho(t). \quad (11)$$

The static superoperator  $R_s$  is

$$R_s \rho(t) = [Q, Q^s \rho - \rho(Q^s)^\dagger],$$

where the field-free time-independent dissipation coupling mode  $Q^s$  is

$$Q^s = C(\hat{L}_s)Q = \frac{1}{\sqrt{2}}[C(-\Omega)a + C(\Omega)a^\dagger] = \frac{1}{\sqrt{2}}(k_+ a + k_- a^\dagger),$$

where  $k_+ = C(-\Omega)$  and  $k_- = C(\Omega)$  are defined by the bath interaction spectrum  $C(\Omega)$ . Using the results of Sec. III we have  $C(\Omega) = J(\Omega)n(\Omega)$  and  $C(-\Omega) = J(\Omega)[n(\Omega) + 1]$ , where  $n(\Omega) = [\exp(\beta\Omega) - 1]^{-1}$ . Then the dissipation superoperator  $R_s$  has the conventional formulation

$$R_s \rho(t) = \frac{k_-}{2} a a^\dagger \rho - \frac{1}{2} (k_- + k_-^*) a^\dagger \rho a + \frac{k_-^*}{2} \rho a a^\dagger \\ + \frac{k_+}{2} a^\dagger a \rho - \frac{1}{2} (k_+ + k_+^*) a \rho a^\dagger + \frac{k_+^*}{2} \rho a^\dagger a.$$

After some simple algebra, we obtain

$$R_s \rho(t) = J(\Omega)[n(\Omega) + 1] \left( \frac{1}{2} \{a^\dagger a, \rho\} - a \rho a^\dagger \right) \\ + J(\Omega)n(\Omega) \left( \frac{1}{2} \{a a^\dagger, \rho\} - a^\dagger \rho a \right).$$

Using the differential representation for the Bose superoperator, one can convert master equation (11) into Fokker-Plank equations (see the Appendix for details) for the Wigner function  $f$ ,

$$\dot{f} = \left( i\Omega + \frac{\gamma}{2} \right) \frac{\partial}{\partial z} (z f) + \left( -i\Omega + \frac{\gamma}{2} \right) \frac{\partial}{\partial z^*} (z^* f) \\ + \gamma \left( n(\Omega) + \frac{1}{2} \right) \frac{\partial^2 f}{\partial z \partial z^*} - \frac{i\tilde{h}(t)}{\sqrt{2}} \left( \frac{\partial f}{\partial z} - \frac{\partial f}{\partial z^*} \right), \quad (12)$$

where  $z, z^*$  are the complex variables,  $\tilde{h}(t) = h(t) - \xi(t)$  and  $\gamma = J(\Omega)$ . To derive differential equations for Weyl symbols  $\langle a \rangle_W, \langle a^\dagger \rangle_W$  of the boson operators  $a$  and  $a^\dagger$  we multiply Eq. (12) by  $z$  or  $z^*$ , respectively, and integrate over the complex plane. Supposing that  $f \rightarrow 0$  at  $|z|^2 \rightarrow \infty$ , we obtain the system

$$\frac{\partial \langle a \rangle_W}{\partial t} = - \left( i\Omega + \frac{\gamma}{2} \right) \langle a \rangle_W + \frac{i\tilde{h}(t)}{\sqrt{2}}, \quad (13)$$

$$\frac{\partial \langle a^\dagger \rangle_W}{\partial t} = - \left( -i\Omega + \frac{\gamma}{2} \right) \langle a^\dagger \rangle_W - \frac{i\tilde{h}(t)}{\sqrt{2}}. \quad (14)$$

Using the coordinate  $x = \langle a + a^\dagger \rangle_W / \sqrt{2}$  and the conjugated momentum  $p_x = -i \langle a - a^\dagger \rangle_W / \sqrt{2}$  we get the equation of the damped harmonic oscillator,

$$\frac{\partial^2 x}{\partial t^2} + \gamma \frac{\partial x}{\partial t} + \omega_0^2 x = \Omega \tilde{h}(t) \quad (15)$$

with  $\omega_0^2 = \Omega^2 + \gamma^2/4$ , which is the dynamic equation for the Bloch wall.<sup>23</sup>

The magnetic ac susceptibility was measured within the frequency range from 1 Hz up to 1 kHz (slow varying ac field). In assumption that the characteristic time scale of the experiment of order  $10^{-3} - 1$  s is much greater than the characteristic relaxation times  $\zeta^{-1}$  of the bath ( $\omega \ll \zeta$ ), we obtain

$$\xi(t) \approx \frac{2\Omega \nu_m''}{(\zeta_m^2 + \Omega^2) \zeta_m} h(t) = \sigma h(t),$$

i.e., the effective local-field correction  $\xi(t)$  depends on the incident field.

Now we use Eq. (15) to evaluate the range of relaxation time  $\tau \sim 1/\gamma$ . We note first that without an applied bias dc field the oscillator frequency  $\Omega$  is determined by the inter-chain coupling, whereas in the bias fields of the experiment, approaching a critical value of the AF-FI transition,  $\Omega$  is reduced to much smaller values, when a leading contribution to the ac-susceptibility results from the motion of domain walls separating AF and FI phases. To reach a consistency with the data on a time evolution of the longitudinal magnetization in pulsed fields (see Sec. V), we suppose  $\Omega \ll \gamma$  and consider a small ac-field frequency  $\omega \ll \omega_0 \sim \gamma$ . Then the solution of Eq. (15) has a relaxation character that yields the expressions for  $\chi'(\omega)$  and  $\chi''(\omega)$  in the usual Debye form

$$\chi'(\omega) = \frac{(1-\sigma)\Omega}{\omega_0^2} \frac{1}{1+\omega^2\tau^2},$$

$$\chi''(\omega) = \frac{(1-\sigma)\Omega}{\omega_0^2} \frac{\omega\tau}{1+\omega^2\tau^2}, \quad (16)$$

where the relaxation time  $\tau = \gamma/\omega_0^2$ . The maximum of the imaginary part of the ac susceptibility  $\chi''(\omega)$  is reached at  $\omega_{\max} = \tau^{-1} = \omega_0^2/\gamma \sim \gamma$ . According to the available experimental data<sup>6</sup>  $\omega_{\max} \sim 10 - 100$  Hz ( $T = 3 - 3.5$  K) that yields  $\tau \sim 10 - 100$  ms for the small frequencies  $\sim 1$  Hz. This agrees qualitatively with the  $\tau$  values found from the relaxation of the remanent magnetization (Fig. 3).

## V. SATURATION PROCESS: STRONG MAGNETIC FIELD PULSES

The key moment distinguishing this case from previous consideration is the value and time dependence of the external driving field. The ac-field being of order  $10^{-4}$  T is weak in the sense that the system remains near global equilibrium at all times. This is not the case for a strong field ( $\sim 5$  T)

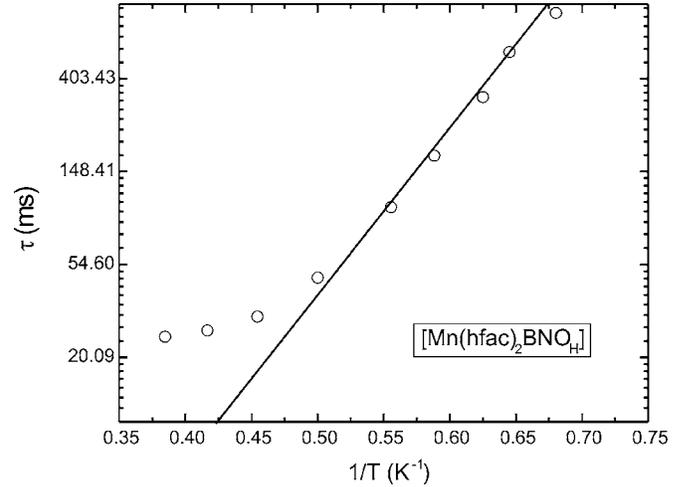


FIG. 3. Temperature dependence of the relaxation time obtained from the remanent magnetization  $M_r$  at the value  $M_r = 1$  A m<sup>2</sup>/kg after application of the 4 T pulsed field. The solid line shows Arrhenius behavior at lower temperatures.

changing fast in comparison with relaxation to global equilibrium. A long time scale of a driving field  $H(t)$  ( $\sim 10$  ms) prohibits the normal evolution towards a Boltzmann distribution of states due to dynamical non-Markovian effects. This feature is intrinsically built into the QDT, hence we can similarly construct a FP equation to evaluate the time evolution of a longitudinal magnetization.

We introduce the operator  $\hat{\mu} = a^\dagger a$  interacting with an external pulsed field

$$h(t) = h_0 \sin\left(\frac{\pi}{T}t\right) [\theta(t) - \theta(t-T)],$$

where  $T$  is the time period of the external field and other definitions are identical to that used for the ac field. This choice ensures a saturation of magnetization by pulsed field measurement performed in a half-pulse regime.

Unlike the ac case the commutator contained in the integrand of Eq. (7) now becomes an operator

$$L_{sf}(\tau') G_s(\tau' - \tau) Q = -h(\tau') [\hat{\mu}, G_s(\tau' - \tau) Q]$$

$$= \frac{h(\tau')}{\sqrt{2}} (e^{i\Omega(\tau' - \tau)} a - e^{-i\Omega(\tau' - \tau)} a^\dagger).$$

Further simplicity arises from that

$$G(t, \tau) \hat{a} = \exp\left(i \int_\tau^t [\Omega - h(\tau')] d\tau'\right) a$$

and

$$G(t, \tau) \hat{a}^\dagger = \exp\left(-i \int_\tau^t [\Omega - h(\tau')] d\tau'\right) a^\dagger.$$

Thus, we have

$$G(t, \tau') L_{sf}(\tau') G_s(\tau' - \tau) Q = \frac{h(\tau')}{\sqrt{2}} (e^{i\Omega(t-\tau) - ih_0 g(t, \tau')} a - e^{-i\Omega(t-\tau) + ih_0 g(t, \tau')} a^\dagger), \quad (17)$$

where  $\int_{\tau'}^t h(\tau'') d\tau'' \equiv h_0 g(t, \tau')$ . Substituting (17) into Eq. (7) we obtain

$$\tilde{Q}(t) = \tilde{Q}^s - \frac{i}{\sqrt{2}} \int_0^\infty d\tau \lambda(\tau) h(t - \tau), \quad (18)$$

where the system-bath coupling response becomes an operator

$$\lambda(\tau) \equiv \int_\tau^\infty d\tau' \tilde{C}(\tau') [e^{i\Omega\tau' - ih_0 g(t, t-\tau)} a - e^{-i\Omega\tau' + ih_0 g(t, t-\tau)} a^\dagger].$$

The explicit expression for  $\lambda(\tau)$  can be easily carried out as

$$\lambda(\tau) = \frac{\nu_m}{\zeta_m - i\Omega} e^{i\Omega\tau - \zeta_m\tau} e^{-ih_0 g(t, t-\tau)} a - \frac{\nu_m}{\zeta_m + i\Omega} e^{-i\Omega\tau - \zeta_m\tau} e^{ih_0 g(t, t-\tau)} a^\dagger$$

via Meier-Tannor parametrization.

The convolution in Eq. (18) is simplified as

$$\int_0^\infty d\tau \lambda(\tau) h(t - \tau) = \begin{cases} h_0 \int_{t-T}^t d\tau \lambda(\tau) \sin\left(\frac{\pi}{T}(t - \tau)\right), & t \geq T, \\ h_0 \int_0^t d\tau \lambda(\tau) \sin\left(\frac{\pi}{T}(t - \tau)\right), & 0 \leq t < T, \\ 0, & t < 0. \end{cases}$$

The dissipative mode is then defined as follows:

$$\tilde{Q}(t) = \frac{1}{\sqrt{2}} (\tilde{k}_+ a + \tilde{k}_- a^\dagger),$$

where

$$\tilde{k}_+ = k_+ - i \frac{h_0 \nu_m}{\zeta_m - i\Omega} \Phi(t), \quad \tilde{k}_- = k_- + i \frac{h_0 \nu_m}{\zeta_m + i\Omega} \Phi^*(t), \quad (19)$$

and

$\Phi(t)$

$$= \begin{cases} \int_{t-T}^t d\tau \sin\left(\frac{\pi}{T}(t - \tau)\right) e^{i\Omega\tau - \zeta_m\tau} e^{-ih_0 g(t, t-\tau)}, & t \geq T, \\ \int_0^t d\tau \sin\left(\frac{\pi}{T}(t - \tau)\right) e^{i\Omega\tau - \zeta_m\tau} e^{-ih_0 g(t, t-\tau)}, & 0 \leq t < T, \\ 0, & t < 0. \end{cases} \quad (20)$$

The coefficients  $k_+ = J(\Omega)[n(\Omega) + 1]$  and  $k_- = J(\Omega)n(\Omega)$  are

determined as for the ac case. The dissipation superoperator (4) reads as

$$R(t)\rho(t) = \frac{\tilde{k}_-}{2} a a^\dagger \rho - \frac{1}{2} (\tilde{k}_- + \tilde{k}_-^*) a^\dagger \rho a + \frac{\tilde{k}_-^*}{2} \rho a a^\dagger + \frac{\tilde{k}_+}{2} a^\dagger \hat{a} a - \frac{1}{2} (\tilde{k}_+ + \tilde{k}_+^*) a \rho a^\dagger + \frac{\tilde{k}_+^*}{2} \rho a^\dagger a.$$

The Liouville equation

$$\dot{\rho}(t) = -i[H_s - \hat{\mu}h(t), \rho(t)] - R\rho(t)$$

takes the final form

$$\dot{\rho}(t) - i\tilde{\Omega}[\rho, a^\dagger a] = -\frac{\tilde{k}_-}{2} a a^\dagger \rho + \frac{1}{2} (\tilde{k}_- + \tilde{k}_-^*) a^\dagger \rho a - \frac{\tilde{k}_-^*}{2} \rho a a^\dagger - \frac{\tilde{k}_+}{2} a^\dagger a \rho + \frac{1}{2} (\tilde{k}_+ + \tilde{k}_+^*) a \rho a^\dagger - \frac{\tilde{k}_+^*}{2} \rho a^\dagger a, \quad (21)$$

where  $\tilde{\Omega} = \Omega - h(t)$ .

Then we convert Eq. (21) into the equivalent Fokker-Plank equation using the Wigner functions for the density matrix  $\rho$  and Bose operators

$$\frac{\partial \bar{n}}{\partial t} = -\frac{1}{\sqrt{2}} (\tilde{k}_+ + \tilde{k}_+^* - \tilde{k}_- - \tilde{k}_-^*) \left( \bar{n} + \frac{1}{2} \right) + \frac{1}{2\sqrt{2}} (\tilde{k}_+ + \tilde{k}_+^* + \tilde{k}_- + \tilde{k}_-^*), \quad (22)$$

where  $\bar{n} = \langle a^\dagger a \rangle_t$  is the number of oscillator excitations corresponding to the instant magnetization. In the complete absence of the external field ( $h_0 = 0$ ) Eq. (22) amounts to

$$\frac{\partial \bar{n}}{\partial t} = -\frac{1}{T_1} (\bar{n} - n_0),$$

and the net magnetization relaxes from an initial value to the equilibrium one  $n_0 = n(\Omega) = (e^{\beta\Omega} - 1)^{-1}$  with the spin-lattice relaxation rate  $T_1^{-1} = \sqrt{2}\gamma$ . In general, by using the coefficients (19), we can recast Eq. (22) as

$$\frac{\partial \bar{n}}{\partial t} = -\frac{1}{T_1} (\bar{n} - n_0) - \sqrt{2} \bar{n} f_1(t) + f_2(t) - f_1(t), \quad (23)$$

where the time-dependent coefficients are

$$f_1(t) = \frac{\sqrt{2} h_0 \nu_m''}{\zeta_m^2 + \Omega^2} [\zeta_m \Phi'(t) - \Omega \Phi''(t)],$$

$$f_2(t) = \frac{\sqrt{2} h_0 \nu_m'}{\zeta_m^2 + \Omega^2} [\Omega \Phi'(t) + \zeta_m \Phi''(t)].$$

As can be inferred from Eq. (20),  $f_{1,2}(t)$  decreases exponentially with time and falls to zero as  $t > \zeta^{-1}$ .

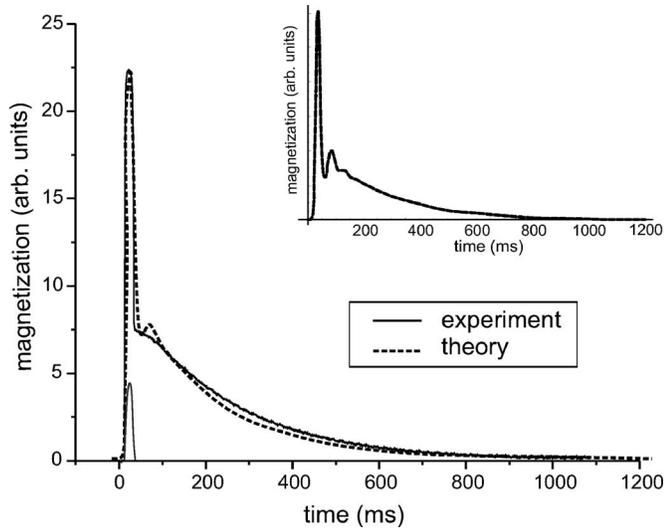


FIG. 4. Model time dependence of the magnetization during and after application of the pulsed field found from the Fokker-Plank equation (dotted line). The experimental magnetization curve for  $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$  at  $T=1.61$  K presented for comparison is shown as a solid line. The profile of the pulsed field used in the measurement is also plotted. The model parameters are  $\nu'_m=0.3$ ,  $\nu''_m=0.95$ ,  $T=12$ ,  $\gamma=0.004$ ,  $\Omega=1.3$ ,  $\zeta_m=0.7$ , and  $h_0=1.3$ . Inset, time dependence of the longitudinal magnetization when  $\gamma=0.003$ ,  $\zeta_m=0.4$ , and  $\nu''_m=0.35$ . The damped domain wall oscillations are resolved more clearly.

The differential equation (23) can be solved numerically with the initial condition  $\bar{n}(t_0)=0$  ( $t_0 < 0$ ). The results for the simplest one-exponential case  $m=1$  are presented in Fig. 4 where the experimental data are plotted for comparison. We can see how the magnetization, following the  $h(t)$  variation, increases initially with time. After switching off the field, the magnetic moment of the system has a two-step evolution. The first, rapid stage ends when the system arrives at the critical state due to the balance of the magnetic driving force and the coercive force on the domain walls. The second, slow stage of the evolution is due to backward domain wall movement accompanied with damped oscillations around the moving center position. The damping indicates the effect of spin-lattice coupling. At rather low temperatures below 3D ordering, most of the system energy is lost to the bath because of dissipation. It is obviously seen from the inset of Fig. 4 that the damping is governed by the force fluctuation decay  $\zeta$  in the bath. The slower the decay rate the more prominent domain wall oscillations.

## VI. CONCLUSIONS

In conclusion, we summarize briefly the results presented in the paper. Measurements of the magnetization in pulsed fields for the molecule-based magnetic complex  $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$  composed from antiferromagnetically ordered ferrimagnetic chains show that the change in the magnetization in this compound below 3D ordering temperature is a slow dynamical process controlled by motion of magnetic domains with a single energy barrier height. As a criti-

cal field for the direct AF-FI transition is approached during application of a pulsed field, the domain wall motion along the separate field unfavorable chains start to develop. After the field is switched off, the inverse transition from the field-induced FI state to the initial AF state in zero field provides very slow dynamics of the magnetization. The energy barrier hampering the reversal of the magnetization is originated from the antiferromagnetic interchain coupling. The latter thus plays an analogous role to that of magnetic anisotropy in a molecular cluster or a single chain magnet. The measurements of the ac susceptibility in the region of the metamagnetic transition, where the AF and FI phase coexist, show that a leading contribution to the ac susceptibility results from the motion of domain walls separating the AF and FI phases.

The domain-wall motion in both the ac and pulsed fields is accompanied by energy losses that causes a local heating of the samples. This is because the energy of the magnetic system transforms into the phonon energy, and, as a consequence, 3D magnetic ordering holds. Thus the system-bath coupling is crucial in the description of the relaxation dynamics in  $[\text{Mn}(\text{hfac})_2\text{BNO}_\text{H}]$ .

On the basis of quantum dissipative theory in the standard second-order approximation for the system-bath Hamiltonian, we derive Fokker-Plank equations for observables of the reference system. It is known that this well-justified approximation makes applicable the resultant FP equation in a large number of dissipative systems provided the system-bath coupling is not strong. The QDT-FP formalism has advantages of application convenience and straightforwardness, as well as the ability to address both saturation processes caused by strong magnetic field pulses and processes far from a saturation by a small oscillating ac field.

The complex magnetic ac susceptibility is calculated within an approach, where the magnetization is controlled by the field-induced sideways motion of domain walls. The expressions for  $\chi'(\omega)$  and  $\chi''(\omega)$  have the usual Debye form for small frequencies. From the maximum of the imaginary part of the ac susceptibility we evaluate the relaxation time that agrees qualitatively with that found from the remanent magnetization data.

In the case of a small oscillating field the system remains near global equilibrium at all times, whereas a strong long-time driving field changing fast in comparison with relaxation to global equilibrium prohibits the normal evolution towards a Boltzmann distribution due to dynamical non-Markovian effects. In order to obtain a reliable understanding of the physics of the process we derive a FP equation in the framework QDT. The study of a time relaxation of a longitudinal magnetization shows that it experiences a two-step evolution after the field is switched off. The first rapid stage ends when the system arrives at the critical state where the magnetic driving force and the coercive force acting jointly on the domain wall are balanced. The second slow stage of the evolution corresponds to backward domain wall movement together with damped oscillations around the moving domain-wall center. The damping is managed by a decay of force-force correlations of Langevin dissipative modes acting on the system from the bath.

ACKNOWLEDGMENTS

The authors would like to thank E. Z. Kuchinskii for discussions. This work was partly supported by Grant No. NREC-005 of US CRDF (Civilian Research and Development Foundation). Two of the authors (V.E.S. and A.S.B.) thank the Foundation Dynasty (Moscow) for support.

APPENDIX

As a method for expressing the density operator in terms of  $c$ -number functions, the Wigner functions often lead to considerable simplification of the quantum equations of motion, as for example, by transforming operator master equations into more amenable Fokker-Plank differential equations. By the Wigner function one can express quantum-mechanical expectation values in the form of averages over the complex plane (the classical phase space), the Wigner function playing the role of a  $c$ -number quasiprobability distribution

$$f(z, z^*; t) = \text{Tr}[\rho(t) \hat{\delta}_W(a - z)],$$

where

$$\hat{\delta}_W(a - z) = \int \frac{d^2x}{\pi^2} \exp[ix^*(a - z) + ix(a^\dagger - z^*)]$$

is the operator delta function with  $d^2x = dx_1 dx_2$ ,  $x = x_1 + ix_2$ ,  $z = z_1 + iz_2$ . The Wigner function has the following property:  $\int f(z, z^*; t) d^2z = 1$ , and allows to easily evaluate expectations of symmetrically ordered products of the field operators, corresponding to Weyl's quantization procedure<sup>24</sup>

$$\int (z^*)^m z^n f(z, z^*; t) d^2z = \langle [(a^\dagger)^m a^n] \rangle,$$

where

$$[(a^\dagger)^m a^n] = \frac{1}{(m+n)!} \sum_P P(a^\dagger)^m a^n$$

and the symbol  $P$  denotes a permutation of the Bose operators.

Using the last identity one obtains

$$\int z^* f(z, z^*; t) d^2z = \langle a^\dagger \rangle_t, \quad \int z f(z, z^*; t) d^2z = \langle a \rangle_t,$$

and

$$\int z^* z f(z, z^*; t) d^2z = \langle a^\dagger a \rangle_t + 1/2.$$

The Weyl symbol for any operator  $\hat{O}$  is determined by

$$(\hat{O})_W(z, z^*) = \pi \text{Tr}[\hat{O} \hat{\delta}_W(\hat{a} - z)],$$

and the inversion formula is

$$\hat{O} = \int (\hat{O})_W(z, z^*) \hat{\delta}_W(\hat{a} - z) d^2z.$$

The Wigner functions of multiplication of two operators  $\hat{A}\hat{B}$  can be easily obtained from those of  $(\hat{A})_W$  and  $(\hat{B})_W$  using the following identities:

$$(\hat{A}\hat{B})_W(z, z^*) = (\hat{A})_W\left(z + \frac{1}{2} \frac{\partial}{\partial u^*}, z^* - \frac{1}{2} \frac{\partial}{\partial u}\right) (\hat{B})_W(u, u^*)|_{u=z},$$

$$(\hat{A}\hat{B})_W(z, z^*) = (\hat{B})_W\left(z - \frac{1}{2} \frac{\partial}{\partial u^*}, z^* + \frac{1}{2} \frac{\partial}{\partial u}\right) (\hat{A})_W(u, u^*)|_{u=z}$$

and Weyl symbols for Bose operators

$$(a^\dagger)_W(z, z^*) = z^*, \quad (a)_W(z, z^*) = z.$$

The relation between the Wigner function and the Weyl symbol of the density operator is the following:

$$f(z, z^*; t) = \pi^{-1} [\rho_S(t)]_W(z, z^*).$$

\*Corresponding author.

<sup>†</sup>Also at: Institute of Metal Physics, 620219 Ekaterinburg, Russia.

<sup>1</sup>R. Street and J. C. Wooley, Proc. Phys. Soc., London, Sect. A **62**, 562 (1949).

<sup>2</sup>P. Gaunt, J. Appl. Phys. **59**, 4129 (1986).

<sup>3</sup>M. A. Novak, W. S. D. Folly, J. P. Sinnicker, and S. Soriano, J. Magn. Magn. Mater. **294**, 133 (2005).

<sup>4</sup>A. Caneschi, D. Gatteschi, N. Laloti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini, and M. A. Novak, Angew. Chem., Int. Ed. **40**, 1760 (2001).

<sup>5</sup>R. J. Glauber, J. Math. Phys. **4**, 294 (1963).

<sup>6</sup>N. V. Baranov, N. V. Mushnikov, T. Goto, Y. Hosokoshi, and K. Inoue, J. Phys.: Condens. Matter **15**, 8881 (2003).

<sup>7</sup>N. N. Bogoliubov, *Lectures in Quantum Statistics* (Gordon and Breach, New York, 1970).

<sup>8</sup>D. N. Zubarev and V. P. Kalashnikov, Teor. Mat. Fiz. **1**, 137 (1969) [Theor. Math. Phys. **1**, 108 (1970)].

<sup>9</sup>D. N. Zubarev, V. Morozov, and G. Röpke, *Statistical Mechanics of Nonequilibrium Processes*, Vols. 1 and 2 (Akademie Verlag, Berlin, 1996 and 1997, respectively).

<sup>10</sup>J. Hausmann and P. Ruján, J. Phys. A **32**, 75 (1999).

<sup>11</sup>L. J. de Jongh, J. Appl. Phys. **53**, 8018 (1982).

<sup>12</sup>R. Xu and Y. J. Yan, J. Chem. Phys. **116**, 9196 (2002).

<sup>13</sup>R. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1953); F. Bloch, *ibid.* **102**, 104 (1956); **105**, 1206 (1957).

<sup>14</sup>A. Redfield, IBM J. Res. Dev. **1**, 19 (1957).

<sup>15</sup>H. Dekker, Phys. Rep. **80**, 1 (1981).

<sup>16</sup>C. Meier and D. J. Tannor, J. Chem. Phys. **111**, 3365 (1999).

<sup>17</sup>Y. Yan, Phys. Rev. A **58**, 2721 (1998).

<sup>18</sup>X.-Q. Li, J. Luo, Y.-G. Yang, P. Cui, and Y. J. Yan, Phys. Rev. B **71**, 205304 (2005).

<sup>19</sup>R.-X. Xue, P. Cui, X.-Q. Li, Y. Mo, and Y. J. Yan, J. Chem. Phys. **122**, 041103 (2005).

<sup>20</sup>H. Schoeller and G. Schon, Phys. Rev. B **50**, 18436 (1994).

<sup>21</sup>H. Risken, *The Fokker-Plank Equation, Methods of Solution and Applications* (Springer, Berlin, 1989).

<sup>22</sup>It goes without saying, the field strength used, up to 5 T in the ac-susceptibility measurements and up to 42 T for magnetization measurements in pulsed fields, is not enough to destroy the

antiparallel alignment between spins of the Mn and the NO group and to induce ferromagnetic ordering in the chains.

<sup>23</sup>L. Néel, *J. Phys. Radium* **13**, 249 (1952).

<sup>24</sup>A. Perelomov, *Generalized Coherent States and Their Applications* (Springer, Berlin, 1986).