Pis'ma v ZhETF, vol. 85, iss. 12, pp. 774 – 778 © 2007 June 25

On the ac magnetic susceptibility of spin-chains: solitons in one-dimensional systems

S. A. Pikin, Z. Tomkowicz[+], *E. S. Pikina*[*], *W. Haase*[∇]

Shubnikov' Institute of Crystallography RAS, 119333 Moscow, Russia

[+]*Institute of Physics, Jagiellonian University, 30-059 Krakow, Poland*

[*]*Institute for Problems of Oil and Gas RAS, 119333 Moscow, Russia*

[∇]*Institut für Physikalische Chemie, Technische Universität Darmstadt, 64287 Darmstadt, Germany*

Submitted 10 May 2007 г.

It is shown that relatively simple phenomenological considerations of the motion of thermally activated solitons (kinks of various types) in the single spin chains can explain and describe qualitatively and quantitatively the temperature and frequency behaviour of magnetic susceptibility in ac magnetic fields. The comparison of experimental data and theoretical results allows estimate the number of solitons and "weak" places in correlation regions of a sample.

PACS: 75.10.Pq, 75.30.Cr

1. The so-called single molecular magnets [1] (SMM) and single chain magnets [2 – 4] (SCM) are attracting huge interest because of their unusual properties and behavior under the action of magnetic field and temperature. In general, these materials are composed of ferro- or ferromagnetic chains, which are well isolated Ising systems. Recently, the SCM was reported, in which chains are anisotropic Heisenberg systems [5]. It is supposed that at low temperatures, the magnetic behavior of one-dimensional system is better described by such Heisenberg model, which, in the limit of zero field H, predicts Ising-like temperature dependence of the parallel susceptibility [6] $\chi_{dc}T \propto \exp(\Delta/k_BT)$, where Δ is the creation energy of domain wall in the chain [6]. The perpendicular susceptibility at low temperatures is less dependent on that, though it also has singularities at $T = 0$ in connection with the change in transverse H as exact solutions show [7]. The behaviour of such SCM in alternating magnetic field is of great interest. In such systems, slow magnetic relaxations were predicted by Glauber [8] who described the individual dynamics of the spin unit composing a chain and had shown that the relaxation time follows an activation law $\tau(T) \propto \exp(E/k_BT)$. The E energy describes the barrier to reverse the magnetization direction. This approach to SCM was definitely confirmed by the whole series of recent ac and dc measurements for various compounds: on finely grounded polycrystalline sample of Mn(III)-Ni(II) heterometallic chains, [Mn2(saltmen)2Ni(pao)-(L)2](A)2 (see Ref. [9]), and of manganese(III) tetra(*ortho*-fluorophenyl)porphyrin-tetracyanoethylene (see Ref. [10]).

In the present paper, we propose to apply the model of classical solitons (kinks or domain walls), which was developed earlier [11], for the description of temperature and frequency dependences of the magnetic susceptibility of single chain magnets in alternating magnetic fields. We show that basic features of such a magnetic response admit the qualitative and even quantitative explanations at the mentioned phenomenological approach.

2. The model of kinks (domain walls or solitons) [11] was proposed for ferroelectric chiral smectics C at the application of alternating electric field. This model explained some peculiar properties of light scattering (of resonance type) in such compounds. The phenomenological character of this approach allows us to think that a similar model can be applied to the description of magnetic systems, and especially to the explanation of a unusual behaviour of the single spin chain susceptibility. In the continuum approximation for classical spins in the one-dimensional spin chain, we can write the equation for magnetization motion in the analogous form

$$-MH\cos(\omega t)\sin\varphi - U\sin\varphi\cos\varphi + K\frac{\partial^2\varphi}{\partial z^2} = \gamma\frac{\partial\varphi}{\partial t}, \quad (1)$$

where ϕ is the angle in the xy plane between the magnetic moment $\mathbf{M}$ and the magnetic field $\mathbf{H}$, $\mathbf{H}$ changes along the y axis, $H_y = H\cos(\omega t)$, K is the elastic constant, and γ is the viscosity coefficient. The quantity U characterises the energy of anisotropy, we shall assume that U is positive, i.e., the preferential orientations correspond to values $\phi = 0$ and $\phi = \pi$. We suppose that the angle ϕ changes along the z axis (spin chain axis). Equation (1) can describe the motion of the magnetic moment under the action of an alternating magnetic field. We assume that Eq.(1) can be applied to SCM at low temperatures though the spontaneous magnetization does not exist in the one-dimensional system. This assumption is based on the inevitability of sufficiently large fluctuations and big correlation regions at low temperatures even in single spin chains.

It is convenient to introduce the variable $s = z/\eta$ and parameters

$$a = d/\eta, \quad \eta = \sqrt{K/U}, \quad b = \frac{MH}{\gamma} \equiv \frac{1}{\tau_H}, \qquad (2)$$

where d is the distance on which the soliton can arise and move, τ_H is so called rise time during which the field H essentially disturbs the initial orientation of magnetic moment. We suppose that the d distance is of the order of the correlation length ξ characterizing fluctuations in the paramagnetic phase without any defects. If the correlation region has some defects, for example n defects per length ξ, then solitons can only move on distance $d = \xi/n$. One can find, under the mentioned assumptions, the exact solution of Eq.(1),

$$\varphi(s,t) = \arctan\left[\sinh^{-1}\left(\pm s + \frac{b}{\omega}\sin(\omega t)\right)\right]. \qquad (3)$$

Solution (3) describes the solitary kink of function $\phi(s,t)$ which is spreading along the z axis with velocity v_z (see Fig.1),

$$v_z = \mp \eta b \cos(\omega t), \qquad (4)$$

i.e., at very large kink displacements $\pm z$ compared with the kink width η. In practice, the boundary conditions for the fluctuation region with finite length ξ can occur at some defects ("weak" places) in the spin chain where the formation of soliton nuclei can easily arise; in such a case, the mentioned distance $d = \xi/n$ can be less than ξ. Figure 1 presents schematic drawings of spin rotations in various situations: individual kinks (Fig.1). If the time of nucleus (soliton) formation τ^* is smaller than the characteristic time of oscillating soliton displacements, $\tau^* \ll t \sim 1/b \ll 1/\omega$, then we can hope that solution (3), (4) will qualitatively describe the spin reversal. If the time $1/b$ is less than the τ^* time (at very large b values), then solitons (as collective motions of spins) cannot arise, and the corresponding response must disappear (spins behave themselves more or less individually).

One can write the expression for the magnetic susceptibility of a sample containing the identical spin chains

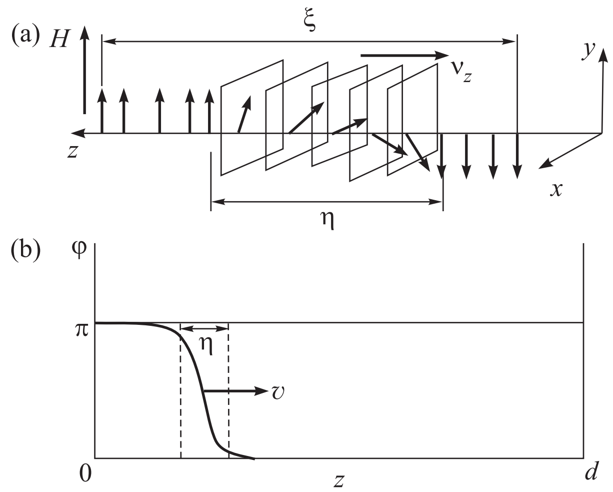

Fig.1. Various types of kinks (solitons) in SCM. (a) General scheme of spin rotations in the kink (soliton); (b) the kink motion from the side of an ideal spin chain

with identical conditions for soliton spreading. Sure, it is an ideal case, since, in reality, there is some distribution of these chains and boundary conditions. The modelled susceptibility of an ideal chain (without defects) takes the form

$$\chi(T,\omega) = \frac{m_{\text{eff}}^2 N}{k_B T}\langle \sin^2\varphi\rangle \equiv \frac{m_{\text{eff}}^2 N}{2\pi k_B}\cdot f(T,\omega), \qquad (5)$$

where the function f is

$$f(T,\omega) = \frac{\omega}{T}\int\limits_0^{2\pi/\omega} dt \cdot \frac{1}{d}\int\limits_0^{d} dz \cdot \sin^2\varphi(z,t) =$$

$$= \frac{1}{aT}\int\limits_0^{2\pi} \tanh\left(a + \frac{b}{\omega}\sin X\right) dX. \qquad (6)$$

Here $X = \omega t$, N is the Avogadro number, k_B is the Boltzmann constant, $m_{\text{eff}} = g\sqrt{J(J+1)}\mu_B$, μ_B is the Bohr magneton. For the substances studied in [10], the factor $m_{\text{eff}}^2 N/2\pi k_B \approx 0.5$ emu/mol, but for substances studied in [9], $m_{\text{eff}}^2 N/2\pi k_B \approx 6$ emu/mol, i.e., 10 times larger as the former. In fact, Eq.(5) describes the real part of the observed susceptibility χ'_{experim}.

We shall assume that all the chain intervals with effective length d can be occupied with solitons (kinks). In the SCM sample with n proper weak places, the maximal magnetic response χ should be proportional to nf. Thus, it is seen from Eqs. (5) and (6) that the function χ, related to correlation regions with n weak places for solitons, has an upper limit which can be written in form $\chi \sim nf < 2\pi n/Ta$. This means that simultaneously as maximum $2n$ kinks can move in different places of the correlated regions (2 solitons from both sides), and, thus, they can increase the discussed magnetic response.

At very small frequencies ω, the $b \equiv \tau_H^{-1}$ parameter does not depend of frequency, but must depend on field H and temperature T drastically. For example, the MH magnitude in Eq.(1) could be proportional to H^2 if we bear in mind that M is proportional to H/T when T approaches zero. If the field change is faster, i.e., the rise time τ_H is larger than the period of field change, then the soliton cannot appear, otherwise the b value and τ_H must depend on the frequency at $\omega \geq \omega_c$ if solitons appear in a high-frequency field. It is hard problem to calculate τ_H as a complicate function of temperature, amplitude, and frequency of the alternating field. Accordingly to the assumption of Glauber, the appearance of kinks has a thermo-activation character. We shall suppose that the τ_H^{-1} value is, roughly speaking, the inverse τ^* time for of nucleus formation, $\tau_H^{-1} \sim 1/\tau^*$, when frequency ω is less than $\omega_c \sim 1/\tau^*$, but $\tau_H^{-1} \sim (\tau^*\omega)^\alpha\omega$ when ω is larger than ω_c. The power index α can be found experimentally. At $\omega \sim \omega_c \sim 1/\tau^*$, τ_H^{-1} becomes of the order $1/\tau^*$.

So, we assume that the soliton solution has the general form given by Eq.(3), where parameter b should be properly selected. We can write the τ^* relaxation time, as a result of thermo-activation, in the form $\tau^* = \tau_0 \exp(E/T)$, where E is the activation energy for a nucleus, and, correspondingly,

$$b = \frac{1}{\tau_H(\omega)} \approx \left(\frac{B\tau_0}{T}\right)\omega^{1+\alpha}\exp\left(\frac{E}{T}\right), \qquad (7)$$

where the constants E, $B\tau_0$ and α will be found from computer simulations. The critical frequency ω_c for the transition to a high frequency regime can be very small if the activation energy E is sufficiently large.

3. For computer calculations, we shall write the function $a \cdot f$ in the form

$$a \cdot f(T,\omega) = \\ = \frac{1}{T}\int_0^{2\pi} \tanh\left[a + \left(\frac{B\tau_0}{T}\right)\cdot\omega^\alpha\cdot\exp\left(\frac{E}{T}\right)\sin X\right]dX, \qquad (8)$$

where parameters a, E, B, and α are chosen numerically. The values of coefficient a were: 1, 2, 3, and 10. We tried different values of α to show the role of this coefficient: 0.1, 0.2, 0.5, and 1. We assume that critical frequency ω_c is small, and the interval of frequencies $\nu = \omega/2\pi$ was $\nu \geq 2/\pi$ Hz, we have taken 4 values of ν: 2, 20, 200, and 2000 Hz. Constant $B\tau_0 \approx 10^{-6}$, the E energy is equal to 110 K to describe the experiment [10], and we tried also the value $E = 60$ K to show the drastic difference in the results. Temperatures $T(K)$ change in the interval $5 \leq T \leq 20$.

The results of numerical calculations are shown on Fig.2, where the values of dimensionless magnitude $af(T,\omega)$ are presented. Fig.2a shows that f has some very characteristic features: the maximum $f_{\max}(\omega) = f(T_0,\omega)$ at $T = T_0 \sim 10$ K, the rapid decrease at temperatures below T_0, and the smooth decrease above T_0. The T_0 value can be considered as the "blocking" temperature [9]. The curves for different ω values are, sure, very close to each other if the coefficient α is small (~ 0.1) (Fig.2b,c). At sufficiently high temperatures, all the curves $af(T,\omega)$ turn to one *universal curve* ($\sim 1/T$) for different frequencies. The presence of this multiplier T in b does not effect strongly on f, only slightly increasing f. Fig.2a shows the effect of the increase in α. It is seen that curves for different frequencies are more separated, but soon turn to one universal curve at high temperatures. Fig.2c shows the effect of the increase of the parameter a ($a_5 = 10$): maximum $f_{\max}(\omega)$ becomes larger and sharper, with more rapid descending below T_0.

Fig.2a shows the $af(T,\omega)$ curves for $\alpha = 1$ and $a = 3$, which are the best in our computer modelling. The values of $f_{\max}(\omega)$, the shapes of curves, the values of $f_{\max}(\omega)$, and the temperature separation of this curves near $T_0(\omega)$ are very similar to the experimental ones [10]. The same qualitative features are valid for the experimental curves [9]. Figure 2b demonstrates that the decrease in activation energy E (here, $E = 60$ K) drastically changes the character of the discussed dependences $f(T,\omega)$: the curves becomes very smooth with small $f_{\max}(\omega)$, and these maxima are shifted far to high temperatures that contradicts to the experiments [9, 10]. Figure 2d presents the ac susceptibility curves in physical units to compare with experimental data [10].

We can compare the results of [9] and [10] using the relation

$$\chi \approx (m_{\text{eff}}^2 N/2\pi k_B)(n/a)f_{\max}(\omega) \approx \chi'_{\text{experim}}. \qquad (9)$$

Since in [10], $\chi'_{\text{experim}} \approx 3.5$, $(m_{\text{eff}}^2 N/2\pi k_B) \approx 0.5$, we can conclude from Eq. (9) that, in this case, the maximum $2n \sim 40 \div 50$ solitons can spread simultaneously in the correlation regions of the studied sample, if $a = 3$, $f_{\max}(10) \approx 0.9$. Accordingly to [9], $\chi'_{\text{experim}} \approx 50$, $m_{\text{eff}}^2 N/2\pi k_B \approx 6$, and we take the same values $a = 3$, and $f_{\max}(10) \approx 0.9$, i.e., approximately 60 solitons are moving simultaneously in this case. We conclude too that kinks are sufficiently wide in the considered substances (their width η is only 2–3 times less than length d), and the number of "weak" places n in correlation regions is of $20 \div 30$. The found effective activation energy

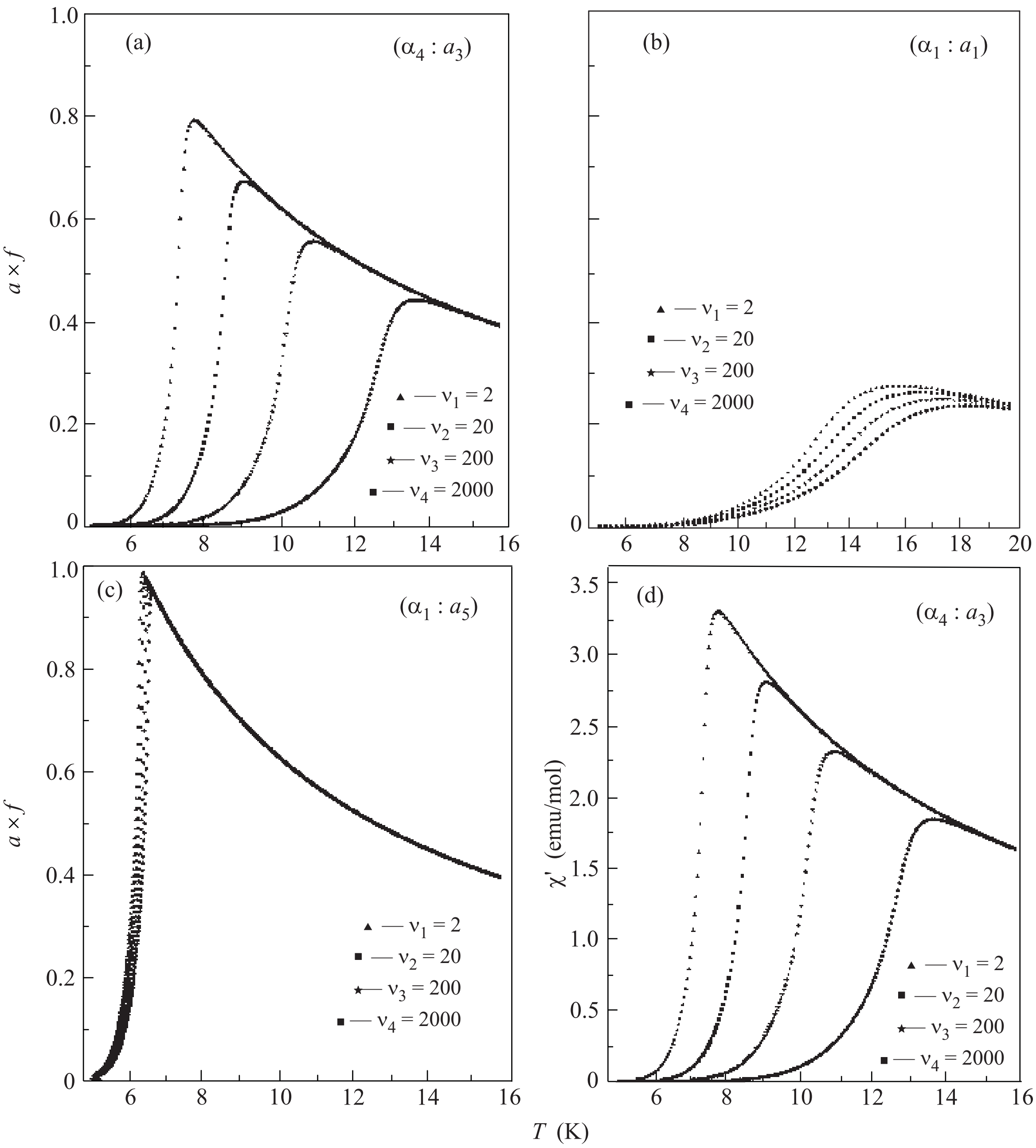

Fig.2. Results of numerical calculations of the ac susceptibility at various values of the main parameters (see the text), the af values in free units. (a) $\alpha_4 = 1$, $a_3 = 3$, $E = 110\,\mathrm{K}$; (b) $\alpha_1 = 0.1$, $a_1 = 1$, $E = 60\,\mathrm{K}$; (c) $\alpha_1 = 0.1$, $a_5 = 10$, $E = 110\,\mathrm{K}$; (d) the ac susceptibility in physical units

$E \approx 110\,\mathrm{K}$ is close to the experimental one found for the dc susceptibility χ_{dc} [10].

4. We have shown that relatively simple phenomenological considerations of the motion of thermally activated solitons (kinks of various types) in the single spin chains can explain and describe qualitatively and quantitatively the temperature and frequency behaviour of magnetic susceptibility in ac magnetic fields. The obtained equations describe well the shapes of the ac magnetic susceptibility curves, as functions of temperature and frequency, with the characteristic rapid decrease at temperature below its blocking value, this blocking value and maximum in the susceptibility, the shift of blocking temperature to higher values at the increase in frequency, the universal curve at high temperatures and any frequency. The comparison of experimental data and theoretical results allows estimate the number of solitons and "weak" places in correlation regions of a sample, and the ratio of the distance between neighbouring weak places to the width of soliton. The magnetization reversal may be strongly influenced by the external magnetic field resulting in the abrupt increase in the number of solitons.

We are thankful to the Division of Physical Sciences of Russian Academy of Sciences (program 5.1 b "New Materials and Structures"), and to the Russian Foundation for Basic Research (project # 05-02-16871) for the support. S.A.P. acknowledges the Alexander von Humboldt Foundation for the support and possibility of working in the Darmstadt University of Technology. W.H. acknowledges the support of the Deutsche Forschungsgemeinschaft.

1. L. Thomas, F. Lionti, R. Ballou et al., Nature (London) **383**, 145 (1996).
2. A. Caneschi, D. Gatteschi, N. Lalioti et al., Angew. Chem. **113**, 1810 (2001).
3. R. Clerac, H. Miyasaka, M. Yamashita et al., J. Am. Chem. Soc. **124**, 12837 (2002).
4. M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer et al., J. Am. Chem. Soc. **127**, 3099 (2005).
5. H. Miyasaka, T. Madanbashi, K. Sugimoto et al., Chem.-Eur. J. **12**, 7021 (2006).
6. K. Nakamura and T. Sasada, J. Phys. C **11**, 331 (1978).
7. S. A. Pikin and V. M. Tsukernik, Sov. Phys. JETP **23**, 914 (1966).
8. R. J. Glauber, J. Math. Phys. **4**, 294 (1963).
9. H. Miyasaka, R. Clerac, K. Mizushima et al., Inorg. Chem. **42**, 8203 (2003).
10. M. Balanda, M. Rams, S. K. Nayak et al., Phys. Rev. B **74**, 224421 (2006).
11. E. Demikhov, S. A. Pikin, and E. S. Pikina, Phys. Rev. E **52**, 6250 (1995).