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Solid State Communications, Vol.53,No,7, pp.573-577, 1985.
Printed in Great Britain.

0038-1098/85 $3.00 + .00
Pergamon Press Ltd.

FIELD-DEPENDENT MÖSSBAUER RELAXATION STUDY OF DOMAIN WALLS IN THE QUASI 1-d ANTIFERROMAGNET $RbFeCl_3.2H_2O$

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(Received November 1984 by R.A. Cowley)

Domain walls (narrow solitons) in the Ising-type quasi 1-d antiferromagnet $RbFeCl_3.2H_2O$ have been studied by means of Mössbauer relaxation experiments in magnetic fields strong enough (1.5 T) to suppress the 3-d long-range ordering. Excellent agreement is obtained with the Blume - Tjon model, assuming stochastic relaxation due to the propagation of wall-pairs. In still higher fields (6 T) the excitation of walls is found to be suppressed by the generation of a staggered field on the (slightly canted) antiferromagnetic chains.

Introduction

In the last few years the dynamics of non-linear excitations has become of considerable theoretical interest. Moreover, experiments to test the applicability of these theoretical concepts are still rather scarce. In this respect the study of quasi 1-d magnetic systems can be quite rewarding, since it has been recently recognized that they provide excellent examples of soliton bearing systems. The Ising-type magnets are of particular interest, since they allow the presence of solitons (domain-walls) both in zero- and in applied magnetic fields[1].

In a previous letter Thiel et al.[2] have studied the anomalous broadening observed in the Mössbauer spectra of the Ising-type quasi 1-d antiferromagnet $RbFeCl_3.2H_2O$, and other compounds. They showed that the behaviour above the transition temperature, $T_c \approx 11.96$ K, could be well explained by the propagation of π-domain walls along the individual chains. Such π-walls separate degenerate ground state configurations of the antiferromagnetic chain, which are obtained by a simultaneous rotation over an angle π of the two sublattices (fig. 1.b), analogous to the Bloch-wall in the ferromagnetic case (fig. 1a). A passing π-wall flips the electron spin of the Mössbauer atom (Fe^{2+}), and thereby the direction of the hyperfine field that the electron spin exerts on the nuclear spin. The flipping rate Γ_ω is proportional to the product $n_w v_w$ of wall density and average wall velocity. If the corresponding fluctuation time is either very fast or very slow compared to the inverse nuclear Larmor frequency, $\omega_N^{-1} \approx 10^{-7}$ s, no observable line-broadening will occur. For Γ_ω of the order of ω_N, however, a spectrum will be observed that is partially split magnetically, with linewidths that vary strongly with temperature. As discussed in ref. 2 the ensuing excess linewidth $\Delta\Gamma$ will be given approximately by:

$$\Delta\Gamma \propto \Gamma_\omega/(\Gamma_\omega^2 + \omega_N^2) ,$$

so that $\Delta\Gamma \propto \Gamma_\omega$ for $\Gamma_\omega \ll \omega_N$, and $\Delta\Gamma \propto \Gamma_\omega^{-1}$ for $\Gamma_\omega \gg \omega_N$. A maximum excess linewidth occurs for $\Gamma_\omega = \omega_N$. Since the walls are thermally excited, the density n_w will correspond to an activated process, so that $\Gamma_\omega \propto \exp(-E_o/k_BT)$, where E_o is the excitation energy. This implies an exponential increase and subsequent decrease of $\Delta\Gamma$ as the temperature is lowered through the range at which Γ_ω becomes of the order of ω_N.

In the initial work of Thiel et al.[2] such an exponential increase of $\Delta\Gamma$ was indeed observed in the (wide) temperature range $T_c \lesssim T \lesssim 3\ T_c$. However, the relaxation maximum in $\Delta\Gamma(T)$ and the subsequent exponential decrease could not be detected in their experiment due to the occurrence of 3-d magnetic order between the chains at a temperature T_c higher than that corresponding to $\Gamma_\omega = \omega_N$. Below T_c the weak interchain coupling leads to a 3-d ordered structure, in which the domains are static. This implies that the contribution $\Delta\Gamma$ from the wall propagation is simply "switched off" below T_c, and $\Delta\Gamma$ decreases very steeply to zero. In fact, this observation constitutes an important argument for the interpretation of the excess linewidth in terms of the propagation of domain walls in the individual chains.

Notwithstanding, one would also like to study the relaxation phenomenon over the whole frequency range including $\Gamma_\omega \ll \omega_N$, and in order to do so the value of T_c should be reduced in

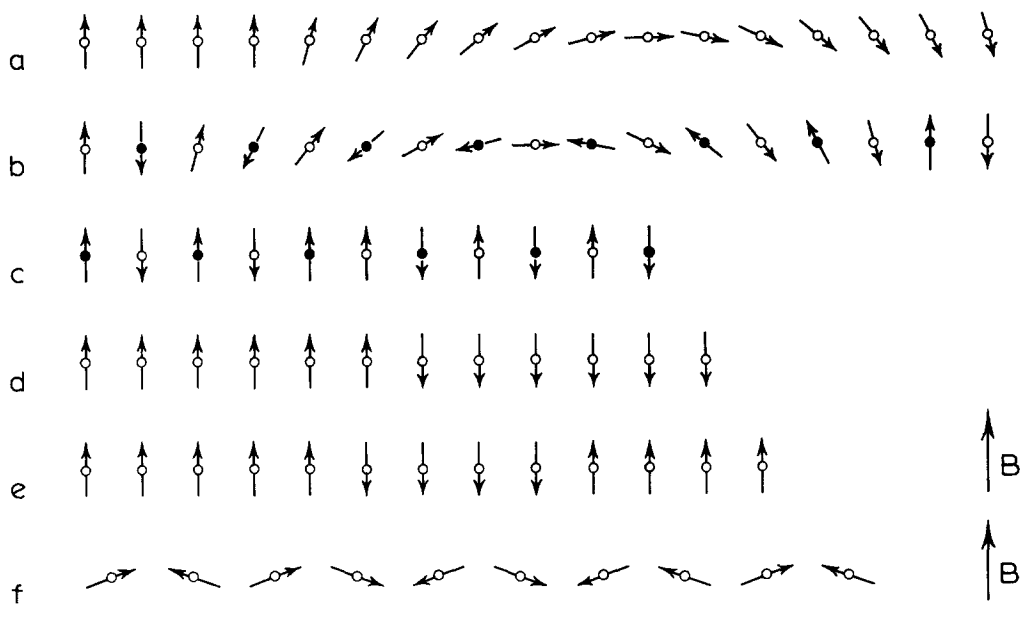

Fig.1 Non-linear excitations in magnetic chains:
a, b) π-soliton in a classical ferro- and antiferromagnetic chain
c, d) π-domain wall in a quantum mechanical S = ½ antiferro- and ferromagnetic chain
e, f) magnon bound states in a ferromagnetic chain and in $RbFeCl_3.2H_2O$.

one way or the other. In a recent study on an analogous ferromagnetic chain system, De Groot et al.[3] succeeded in lowering T_c to a sufficient extent by doping the magnetic (Fe^{2+}) chains with small (0.5 - 1.0 %) amounts of non-magnetic Cd^{2+} atoms. They were indeed able to detect the complete relaxation maximum in this way. However, their method has some disadvantage in that the chains are cut into smaller segments, so it remained of interest to lower T_c by another trick. In case of an antiferromagnetic system, this possibility is provided by the application of a magnetic field of sufficient strength to overcome the weak interchain coupling that produces the 3-d order. For $RbFeCl_3.2H_2O$ a field $B_c > 1.24$ T along the c-axis suffices[4] to saturate the system at T = 0 K. In this note we present Mössbauer data taken in such a field (B_c = 1.5 T), showing that the wall-relaxation phenomenon now extends to the lowest temperatures where a meaningful linewidth could still be determined. In addition we shall discuss data taken in a much higher applied field of 6 T, in which we found the wall relaxation to have almost completely disappeared. This result is at first sight surprising, since even at 6 T the field energy is still small compared to the antiferromagnetic intrachain exchange energy. We will show this to be due to the particuliar magnetic structure of the chains in $RbFeCl_3.2H_2O$, in which the antiferromagnetic spins are slightly canted towards the c-axis. This implies that the application of a uniform field along this direction entails a staggered field along the axis of antiferromagnetic alignment (a-axis). It is this staggered field which suppresses the π-wall formation and thus the corresponding line-broadening. The physical process becomes immediately clear by realizing that a staggered field in an antiferromagnet is a field that changes sign in going from one sublattice to the other, so that it corresponds to a uniform field in a ferromagnet. The fact that the ferromagnetic domain structure can be driven out by a sufficiently strong uniform field is of course well known[5].

Experiment and Analysis

The magnetic structure of $RbFeCl_3.2H_2O$ as reported in the literature[4] is shown in fig. 2a. The antiferromagnetic chains are along the a-axis, with intrachain exchange constant $J_a/k_B = -39$ K. The chains are weakly coupled by interactions smaller than 2×10^{-2} J_a in the remaining directions. The magnetic moments are slightly canted by an angle of 19° from the a-

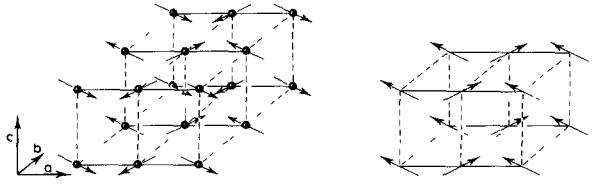

Fig.2 Representation of the magnetic structure of $RbFeCl_3.2H_2O$
a) At zero field and temperature.
b) The proposed magnetic structure at $B_c > 1.24$ T and zero temperature.

axis towards the c-direction. This results in weak ferromagnetic components in the ac-planes, which are however alternating in going from one plane to the other along b, so that in zero-field no net moment results. For a field B_c = 0.81 T along c a metamagnetic transition occurs[6] and for B > B* ≈ 1.24 T all the weak ferromagnetic components are aligned parallel to the field in a structure shown in fig. 2b (at T = 0 K).

The important point to note is that the application of such a field thus transforms the uniaxial Ising anisotropy as present for the antiferromagnetic components in zero field, into a unidirectional anisotropy in the high-field (paramagnetic) phase. In other words the (gradual) saturation of the weak ferromagnetic (c) component of the spins by a uniform field B > B* entails a staggered field of increasing strength for the antiferromagnetically coupled a-components. As already mentioned this peculiarity of the magnetic structure of $RbFeCl_3.2H_2O$ yields a rather unique means of eliminating the π-domain walls.

Field dependent Mössbauer spectra were recorded in the installation in Liverpool, which allows the application of magnetic fields up to 6 T by means of a superconducting solenoid. Typical spectra measured for B_c = 1.5 T at different temperatures are shown in fig. 3. In the letter of Thiel et al.[2], linewidths were extracted from selected lines in these spectra. As explained elsewhere[3] this method has serious disadvantages, and a much better method is to analyse the full spectrum by means of the Blume - Tjon model, in which it is assumed that the hyperfine field jumps stochastically between the two possible values $\pm H_{hf}$. Application of this model to the present compound is justified by the strong Ising anisotropy which leads to narrow domain-walls. Since the passage time of a wall is very short (≈ 10^{-11} s) compared to the inverse Larmor frequency $\omega_N^{-1} \approx 10^{-7}$ s, the Mössbauer probe will experience the passage of the wall as an instantaneous event, i.e it is not sensitive to the internal structure of the wall. It is in fact the average time between successive passages of kinks and antikinks, corresponding to $\Gamma_\omega = n_w v_w$ that is responsible for the relaxation process. In applying the Blume - Tjon model our Mössbauer spectra can be fully fitted at all temperatures, with the flipping rate Γ_ω and the ratio of probabilities that H_{hf} jumps to $-H_{hf}$ and vice versa, as the only adjustable, temperature dependent parameters. The fits are shown as the solid curves in fig. 3. In these fits the other Mössbauer parameters were kept at the values determined at low temperatures, i.e.

H_{hf}=7.5 T, Q.S.=1.43 mm/s, I.S.=1.33 mm/s,

η=0.8, B_c=1.5 T, θ_H=30°, ϕ_H=32°,

θ_B=120°, ϕ_B=45°, θ_γ=77°, and ϕ_γ=124°,

where the indices H, B, and γ of the polar coordinates θ and φ refer to the directions of hyperfine field, the applied field and the gamma rays, respectively.

As may be seen from the figure, the fits reproduce the observed spectra remarkably well over the whole temperature range. The resulting values for Γ_ω are plotted in fig. 4 on a logarithmic scale versus the inverse temperature. The earlier zero-field spectra were similarly analysed, and the results are compared with the in-field data in the same figure. Below T_c the zero-field data show the expected sharp drop in Γ_ω due to the wall-freezing. For T > T_c the expected exponential dependence with a slope E_o/k_B = 115 ± 5 K is observed. The data for B_c = 1.5 T on the other hand, follow the expo-

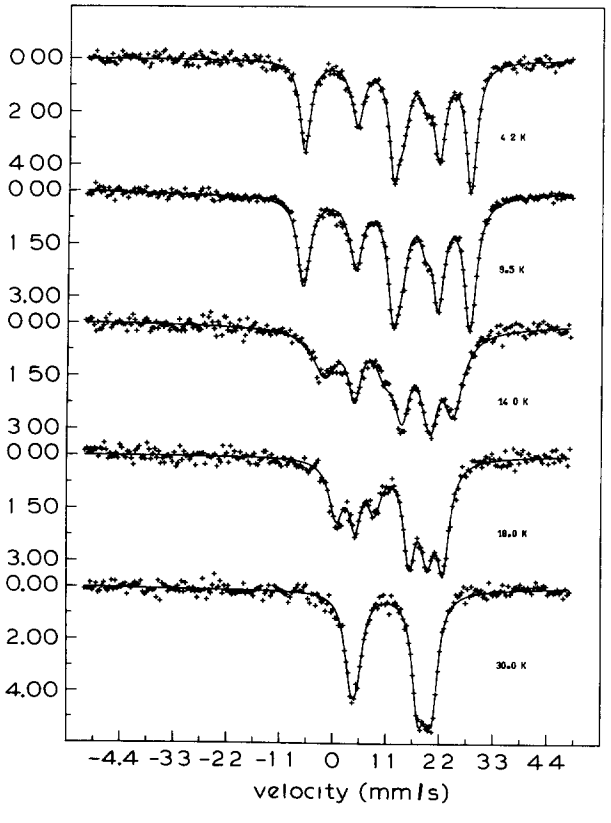

Fig.3 Some representative Mössbauer spectra for B_c = 1.5 T. The solid lines correspond to the fits according to the model of Blume - Tjon.

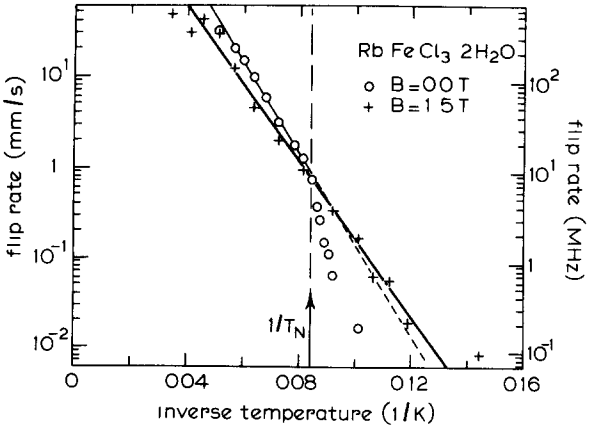

Fig.4 Flipping rate versus the inverse temperature obtained from the measurements in zero field and in 1.5 T.

nential law over the whole frequency window of the Mössbauer probe, i.e. from 0.2 MHz up to 400 MHz (to be compared to $\omega_N \simeq 10$ MHz). The slope in this case yields a slightly smaller value, $E_o/k_B = 105 \pm 5$ K, than for $B_c = 0$ T.

We may compare these excitation energies to theoretical predictions for soliton models. In ref. 2 the classical Sine-Gordon model was used, based upon the Hamiltonian for classical spins:

$$\mathcal{H}^{SG} = -2J \sum_i \vec{S}_i \cdot \vec{S}_{i+1} - D_x \sum_i S_{ix}^2 ,$$

where $J < 0$, $D_x > 0$. In that case the soliton energy becomes $E_w/k_B = 4\, S^2 (D_x |J|)^{\frac{1}{2}}$ where the spin value $S = 2$. However, for $RbFeCl_3.2H_2O$ a narrow soliton model is probably more appropriate, in view of the effective spin $S = \frac{1}{2}$ and the associated strong Ising anisotropy at low temperatures. In that case the formalism of Villain may be used[7], which is based upon the Ising-type hamiltonian ($\sigma = \pm \frac{1}{2}$):

$$\mathcal{H}^{I} = -2J \sum_i \sigma_i^z \sigma_{i+1}^z - 2\varepsilon J \sum_i \left(\sigma_i^x \sigma_{i+1}^x + \sigma_i^y \sigma_{i+1}^y\right) ,$$

where $\varepsilon \ll 1$. The excitation energy of a single kink is to a good approximation given by $E_w \simeq -J$, and the kink-structure is shown in figs. 1c and d for the antiferromagnetic and the analogous ferromagnetic case, respectively. Experimentally, however, we find values for the activation energy E_o of the order of $-2J_a$ instead of $-J_a$. We believe this to be due to the fact that the kinks are mainly excited in the form of kink-antikink pairs (cf. fig. 1e) rather than as single kinks. In case of a single kink, the chain segment on one side of the kink has to be rotated by an angle π, which will be opposed by the interchain interactions. In case of a kink-pair state, only the spins in between the two walls have to be reversed. However, also for the ideal case of an isolated chain, the statistical weights of the kink-pair and the single kink are N^2 and N, respectively, where N is the number of spins along the chain. Therefore, the single-kink excitations can be safely neglected for sufficiently long chains. It has lately become recognized[8,9,10] that a soliton in a magnetic system can be regarded as a bound state of a number of magnons. Indeed, for the analogous $S = \frac{1}{2}$ ferromagnetic Ising-type chain, the non-linear excitations correspond to the magnon-bound states, which have been considered earlier by Torrance and Tinkham[11], and which are likewise kink-antikink pairs (cf. fig. 1e) with a thermal excitation energy gap of about $2J_a$. In the limit that the number of bound magnons reduces to 1, the single spinflip is obtained, which is the basic excitation of the Ising chain. We note that for this case the correlation energy gap is smaller by a factor of two than the thermal excitation gap, since for the Ising chain the susceptibility varies as $\exp(-J_a/k_BT)$. Similar differences between thermal and magnetic excitation gaps have recently been found for the anisotropic Ising-Heisenberg ferromagnet by Johnson and Bonner[12]. The same considerations should apply to the Ising-type antiferromagnetic chain, as confirmed by recent experimental and theoretical work[8,9,13]. Thus, according to which type of experiment is performed, one of the two energy gaps should be measured. In a quasi-elastic neutron scattering experiment the correlation length is measured and the corresponding energy gap will be J_a. In an inelastic neutron scattering experiment one measures the excitation energy, which should correspond to $2J_a$[14,15,16]. The thermal excitation energy gap should also apply to the specific heat. On the other hand, in a Mössbauer experiment (and also in a NMR - T_1^{-1} experiment), the autocorrelation function is measured, which should be determined by the density n_w of excitations. In our view this density should be given by the number of excited wall pairs n_{wp} rather than by twice the number of singly excited walls as is usually assumed[17,18]. That is we should have $n_{wp} \propto \exp(-2E_w/k_BT)$, rather than $n_w \propto 2\exp(-E_w/k_BT)$. This was in fact also found for the ferromagnetic chain compound $FeCl_2(pyridine)_2$, where the Mössbauer data yielded an energy gap twice as large as that found from the ferromagnetic susceptibility[3].

Lastly, we turn to the experiment in $B_c = 6.0$ T. In fig. 5 the excess linewidth is shown as a function of the inverse temperature. For comparison the results of the zero-field measurements have also been plotted. We believe the high base linewidth found in the $B_c = 6$ T measurements is due to a misalignment of the crystal of about 5 degrees. However, the temperature dependent excess linewidth is almost completely absent in this case. We attribute this to the effect of the staggered field B_{st} that is induced by the applied field and acts upon the antiferromagnetic a-components of the spins (cf. fig. 1f). In a ferromagnet the application of a uniform field will reduce the down-domains with respect to the up-domains. For an antiferromagnet in a staggered field, an analogous reduction of one of the two domain-types should occur. This means that the average interpair distance between kink-antikink pairs will become very large, and consequently the intrapair distance ℓ_o of a kink and antikink very small. Upon the passage of such a pair, the spin will return to its original state quickly, so that the long-time correlations will not be disturbed. The associated fluctuation times $\tau_o \propto \ell_o/v_w$ will become too short relative to the inverse nuclear Larmor frequency ω_N^{-1} to contribute to the autocorrelation function, and therefore these exci-

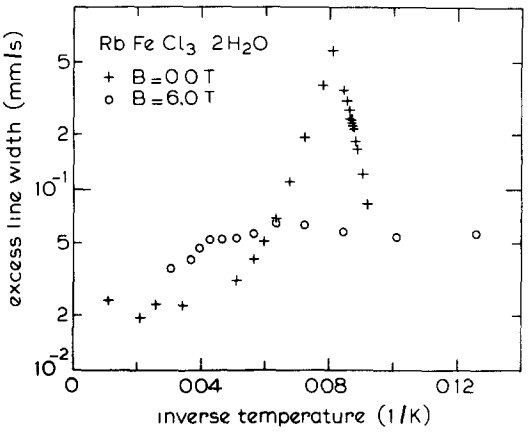

Fig.5 Excess linewidth versus the inverse temperature obtained from the measurements in zero field and in 6.0 T.

tations will not cause any line broadening.

Acknowledgements - We would like to thank the group of Prof. W.J.M. de Jonge of the Technical University of Eindhoven for providing the single crystals. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) and was made possible by financial support from the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Pure Research).

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