Soliton Contribution to the Mössbauer Linewidth in Quasi-One-Dimensional Antiferromagnets with Ising Anisotropy: Theory Versus Experiment

R. C. Thiel, H. de Graaf, and L. J. de Jongh
Kamerlingh Onnes Laboratory, University of Leiden, 2300-RA Leiden, The Netherlands
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A discussion is given of the contribution to the Mössbauer linewidth in quasi-one-dimensional antiferromagnets with Ising anisotropy due to thermal excitation of moving domain walls ("kinks" or "solitons"). Experimental data on Fe^{2+} chain compounds are presented that confirm the predicted exponential temperature dependence of the linewidth.

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The study of solitary excitations is an exciting new topic that has an impact on a great many branches of physics.[1] In contrast to the rapid development of theoretical understanding of nonlinear dynamics, very few experimental results bearing upon this problem have been obtained up till now. It is therefore of great importance to find new ways in which to probe the presence of these nonlinear excitations and to establish their influence on experimentally measurable quantities.

It has recently become apparent that magnetic chains offer quite promising possibilities in this respect. Following a suggestion of Mikeska,[2] an inelastic neutron scattering study on the quasi-one-dimensional (1D) XY ferromagnet $CsNiF_3$ was performed by Kjems and Steiner,[3] who found an anomalous increase in intensity of the central peak attributed to scattering of the neutrons by the solitons.

It has subsequently been shown,[4] that analogous local excitations exist in a 1D XY antiferromagnet. In a series of field-dependent neutron inelastic scattering and NMR studies on $(CH_3)_4NMnCl_3$ (TMMC), contributions ascribed to solitons have been observed which were very much more pronounced than those found in $CsNiF_3$.

It is the purpose of this note to point out that Mössbauer spectroscopy can provide an additional tool for studying such nonlinear excitations. Similarly to NMR, the Mössbauer effect measures the hyperfine interaction between electronic and nuclear spins. Spin fluctuations arising from linear as well as from nonlinear excitations may contribute to the Mössbauer linewidths, just as they contribute to the NMR nuclear spin lattice relaxation time T_1. After a brief outline of the formal analogy between the Mössbauer linewidth Γ, the $1/T_1$ in NMR, and the neutron scattering cross section, we present experimental linewidth data on a number of linear chain Fe^{2+} antiferromagnets with different Ising-type spin anisotropy. In this class of soliton-bearing systems solitons have not been studied before experimentally. Because of the Ising type of anisotropy there is no need for a symmetry-breaking applied magnetic field.[5] The contribution to Γ from the solitons reveals itself as an anomalous line broadening that extends to temperatures far above the 3D magnetic ordering temperature T_c (brought about by the weaker interchain couplings), and shows an exponential dependence on temperature.

In theoretical treatments of spin fluctuations, one considers the space-time correlation between spins via the pair correlation functions $G^{\alpha\alpha}(\vec{r},t) = \langle S^\alpha(\vec{r},t)S^\alpha(0,0)\rangle$. By taking the space-time Fourier transform of $G^{\alpha\alpha}(\vec{r},t)$, the dynamical structure factor (Van Hove scattering function)

$$S^{\alpha\alpha}(\vec{k},\omega) \propto \int d^3r\, e^{i\vec{k}\cdot\vec{r}} \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \langle S^\alpha(\vec{r},t)S^\alpha(0,0)\rangle$$

is obtained. In the case of uniaxial symmetry, we have

$$S^{zz}(\vec{k},\omega) = S_\parallel(\vec{k},\omega)$$

and

$$S^{xx}(\vec{k},\omega) = S^{yy}(\vec{k},\omega) = S_\perp(\vec{k},\omega).$$

The magnetic neutron scattering cross section is related to the $S^{\alpha\alpha}(\vec{k},\omega)$ via

$$d^2\sigma/d\Omega\, d\omega \propto [c_\parallel S_\parallel(\vec{k},\omega) + c_\perp S_\perp(\vec{k},\omega)], \tag{1}$$

where $c_\parallel$ and $c_\perp$ are constants determined by the geometry of the scattering arrangement. Furthermore, the nuclear spin lattice relaxation time in NMR may be expressed as $1/T_1 \propto A f^z(\omega_n) + Bf^+(\omega_e)$. Here the A and B are geometrical constants describing the dipolar coupling between electronic and nuclear spins; ω_n and ω_e are the nuclear and electronic Larmor frequencies, respectively; the f^α refer to the autocorrelation functions $\langle S_j^\alpha(t)S_j^\alpha(0)\rangle$. Written in the high-temperature approximation in terms of the dynamical structure factors, this becomes[4]

$$1/T_1 \propto \sum_k [A_k S_\parallel(\vec{k},\omega_n) + B_k S(\vec{k},\omega_n)]. \tag{2}$$

In a Mössbauer experiment, we have to consider the excess linewidth Γ which comes in addition to the natural linewidth Γ_0. Provided that the observed line shape is Lorentzian, we may put $\Gamma \sim \tau$ where τ is the electron spin correlation time. For $\omega_n \tau \ll 1$ we may relate Γ to the autocorrelation functions by[6,7]

$$\Gamma = \int_{-\infty}^{+\infty} dt [C\langle S^z(t)S^z(0)\rangle + D\langle S^+(t)S^-(0)\rangle], \qquad (3)$$

since it arises from variations in the hyperfine field due to the fluctuations of the electron spins. The constants C and D are determined by the hyperfine interaction. Equation (3) can be written in terms of the dynamical structure factors as

$$\Gamma \propto \sum_k [C' S_\parallel(\vec{k},0) + D' S_\perp(\vec{k},0)], \qquad (4)$$

an expression that is equivalent to Eqs. (1) and (2).

In calculating the contribution to the linewidth due to the solitons, we refer to the classical spin model for 1D magnets (in the continuum approximation) used by Mikeska and others.[5] In spite of the approximations inherent to this model, it accounts quite well for the effects observed in the experiments.[3,4] Here we briefly summarize its application to the case of an antiferromagnet with Ising-type anisotropy, which is directly related to the experiments presented below. The Hamiltonian is

$$\mathcal{H} = -J\sum_n \vec{S}_n \cdot \vec{S}_{n+1} + D\sum_n [(S^z)_n]^2,$$

with $D < 0$. The polar representation $S = S(\sin\theta \times \cos\varphi,\ \sin\theta \sin\varphi,\ \cos\theta)$ is used. The chain direction is along the z axis, which is also the preferential axis for the spins. The boundary condition $\theta = 0$ at infinity leads to $\varphi = \text{const}$, so we take $\varphi = 0$. For the polar angle θ, one then has the equation $\partial^2\theta/\partial z^2 - c^{-2}\partial^2\theta/\partial t^2 = (D/|J|)\sin 2\theta$, i.e., the sine-Gordon equation for 2θ, with mass parameter $m = (2D/|J|)^{1/2}$. The soliton width is a/m, where a is the lattice constant; its rest energy is $E_0 = 2S^2(2D|J|)^{1/2}$, and $c = 2|J|Sa$ is the magnon velocity for $k \to 0$. The soliton is thus a moving domain wall which separates the two degenerate ordered configurations of the antiferromagnetic Ising chain, corresponding to $\theta = 0$ and π. A passing soliton yields a variation in the transverse (x) and longitudinal (z) components of the spin vectors. The situation in the 1D Ising antiferromagnet is formally analogous to the correlations in the 1D XY antiferromagnet in the directions perpendicular and parallel to the applied symmetry-breaking field, respectively.[5] For the transverse dynamical structure factors, Mikeska found

$$S^{xx}(k,\omega) = \pi^{-2}\Gamma_D{}^2(\omega^2 + \Gamma_D{}^2)^{-1}\Gamma_s(k^2 + \Gamma_s{}^2)^{-1}.$$

After integrating over k, and setting $\omega \simeq 0$, one obtains $S^{xx}(k,\omega) \simeq 1/\pi\Gamma_D = (4\pi\beta m)^{1/2}/4\pi n_0 c$. Here n_0 is the density of solitons, given by $n_0 = 4m(\beta m/\pi)^{1/2}\exp(-8\beta m)$, and $\beta = |J|S^2/4k_BT$. The contribution to Γ coming from the transverse fluctuations is therefore $\Gamma_{xx} \propto \sum_k S^{xx}(k,\omega) \propto A_{xx}\exp(E_0/k_BT)$. The longitudinal fluctuations lead to a contribution to Γ, the temperature dependence of which is given by $S^{zz}(k,\omega) \propto \beta e^{-8\beta m}$, so that $\Gamma_{zz} \propto T^{-1}\exp(-E_0/k_BT)$, and, finally

$$\Gamma_{tot} = \Gamma_{xx} + \Gamma_{zz} \propto A_{xx}\exp(+E_0/k_BT) + T^{-1}B_{zz}\exp(-E_0/k_BT). \qquad (5)$$

It follows that at low temperatures (but above the 3D ordering temperature T_c) the linewidth is dominated by the transverse fluctuations, leading to an exponential dependence of Γ on T.

The compound $Fe(N_2H_5)_2(SO_4)_2$ ($T_c = 6.02 \pm 0.05$ K) has been shown from susceptibility and specific heat[8] data to be a quasi-1D antiferromagnet with $S = 2$ and an intrachain exchange $J/k_B \simeq -4.4 \pm 0.4$ K. The spin anisotropy is orthorhombic, with a main XY-type component $D^{xy}/k_B \simeq +5$ K establishing an easy plane, and a weaker Ising-type component, D^I/k_B, that leads to an easy direction within the XY plane. Although an accurate value for D^I/k_B is missing, we may estimate it to be of the order of 1 K on basis of earlier crystal-field studies.[9] Thus there is a substantial Ising anisotropy within the XY plane. By contrast, $Co(N_2H_5)_2(SO_4)_2$ has been found[8] to be an excellent example of an $S = \frac{1}{2}$ XY antiferromagnet ($J/k_B \simeq -14$ K, $T_c \simeq 1.60$ K), so that there $|D^I| \ll |D^{xy}|$. Interchain interactions are estimated[8] to be of order $10^{-2}J$ in these hydrazinium (N_2H_5) compounds.

We also present data on $RbFeCl_3 \cdot 2H_2O$ ($T_c = 12.6$ K) and $CsFeCl_3 \cdot 2H_2O$ ($T_c = 12.6$ K) which are also[10] antiferromagnetic chains with $S = 2$. For $RbFeCl_3 \cdot 2H_2O$, the exchange $J/k_B \simeq -5.4$ K, and the Ising type spin anisotropy is very strong, $D^I/k_B \simeq -21$ K. The chains are coupled into layers by interchain interactions of order $10^{-2}J$, and the interactions between these layers are weaker still. The magnetic properties of $CsFeCl_3 \cdot 2H_2O$ are apparently quite similar.[10]

The linewidth data presented below have been obtained from earlier reported powder measurements,[11] from reanalyses of such measurements, and from hitherto unpublished results. The analyses were restricted purposely to those temperature regions for which the line shapes could be well represented by Lorentzians. Plots of the individual linewidths versus T, broadest and narrowest, left- and right-hand spectrum, in all cases gave four essentially parallel curves. In the interest of clarity, the averages of these widths are presented in the figures below. The analyses of the magnetically split spectra ($T < T_c$) were performed using a Hamiltonian containing both a magnetic interaction and an electric quadrupole term for determining peak positions and relative intensities. The linewidths were plotted versus T and again a set of essentially parallel curves resulted. For the figures below we have therefore arbitrarily taken the averages of the widths of the outermost peaks in the spectra.

The anomalous linewidths Γ were obtained by subtraction of the natural linewidth $\Gamma_0 = 0.194$ mm/s. The error bars in the figures represent a combination of the statistical errors in the linewidths indicated in the computer fits and the spreads observed when averaging the widths. In most cases the latter were considerably larger than the former. The excessive widths observed for the source measurements were due to the use of a too thick single line absorber. This lead directly to slightly non-Lorentzian line shapes, and an ensuing larger χ^2. Furthermore, the sources used were relatively weak, so that the statistics were certainly not optimal. None the less, for comparison purposes we feel these results to be useful, especially since the absorber measurements could be used for delimitation of the relaxation region.

The data are presented in Figs. 1(a) and 1(b) for the N_2H_5 and the Cl_3 compounds, respectively. In both figures, one observes the linewidths to be essentially constant in the ordered region, rising sharply for $T \to T_c^-$, and decreasing exponentially with temperature in the paramagnetic phase. The exponential dependences predicted on basis of Eq. (5) are given by the solid lines labeled S, and correspond to $E_0/k_B = 120$ and 22 K for $RbFeCl_3 \cdot 2H_2O$ and $Fe(N_2H_5)_2(SO_4)_2$, respectively. The corresponding values, calculated on basis of the values for J/k_B and D^I/k_B given above, are 120 and 23.7 K. We should perhaps stress the fact that there is no adjustable parameter in the fit of theory to experiment. The fact that the linewidth is varying with T at temperatures so far above T_c is already quite unusual in itself.

As explained in Ref. 11 the effects cannot be ascribed to spin lattice relaxation or to the usual superparamagnetic behavior of 3D systems. In

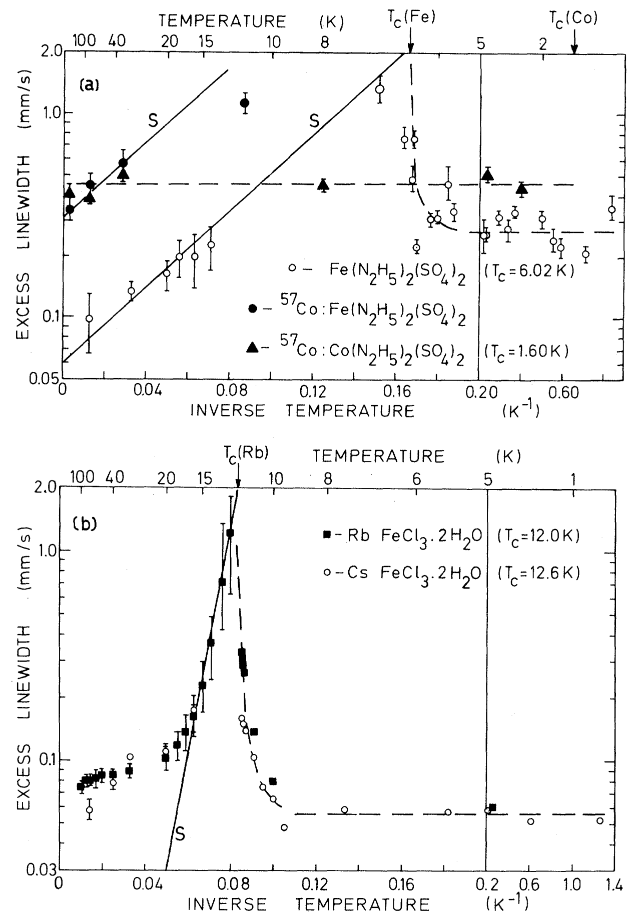

FIG. 1. Excess linewidths vs inverse temperature for the (a) hydrazinium and the (b) Cl_3 compounds. Only Lorentzian lines were considered, explaining the gap in the data for $Fe(N_2H_5)_2(SO_4)_2$ for $0.07 < 1/T < 0.15$ K^{-1}. Solid curves (S) are discussed in the text; dashed curves are guides to the eye.

the neighborhood of T_c one expects critical fluctuations[12] arising from the divergence of the susceptibility. The relevance of these to the Mössbauer linewidth has been recently discussed by Hohenemser.[13] Even in 3D materials, these contributions are limited to an extremely narrow range around the ordering temperature ($|T - T_c| \simeq 0.1T_c$), so that they are difficult to study with the Mössbauer technique. In our quasi-1D magnets, the size of the critical region will be even smaller, so that we must conclude that critical fluctuations cannot explain the peaks in Γ observed near T_c. The soliton contribution, on the other hand, is expected to be strongly peaked at T_c, since it rises exponentially with decreasing T for $T \to T_c^+$, and will be absent below T_c, where the movements of the solitons become blocked by the gradual establishment of 3D magnetic order. This agrees completely with our observations.

As another mechanism we might consider the contribution to Γ due to linear 1(D) excitations, e.g., the spin waves. From the neutron scattering and NMR $1/T_1$ experiments on quasi 1D Heisenberg and XY antiferromagnets,[14] we may conclude that the spin-wave contribution to the linewidth will depend only weakly on the temperature. This agrees with our own observations, since in the ordered regions we see no appreciable temperature dependence of Γ. Furthermore, for ^{57}Co $:Co(N_2H_5)_2(SO_4)_2$ we also observe a constant linewidth at all temperatures studied. Since this compound is an XY chain with very weak Ising anisotropy, one does not expect a soliton contribution (for $H=0$), but magnonlike excitations will certainly exist for this compound. In contrast, the data on $^{57}Co{:}Fe(N_2H_5)_2(SO_4)_2$ show an exponential dependence on temperature similar to the pure Fe^{2+} compound. In conclusion, we remark that magnonlike excitations will be suppressed by the Ising anisotropy, in particular for the Cl_3 compound, and that even if they should contribute to Γ, this contribution would be only weakly dependent on temperature.

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