High-m spin excitations in the one-dimensional Ising ferromagnet $[(CH_3)_3NH]FeCl_3\cdot 2H_2O$

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(Received 19 August 1991)

The differential magnetic susceptibility of $[(CH_3)_3NH]FeCl_3\cdot 2H_2O$ has been measured as a function of temperature in the range 4.2 K $< T <$ 20 K in fields of 0, 500, 1000, and 1500 Oe. To interpret the data, a simple model for a fermion gas of noninteracting clusters of various sizes is presented. The analysis suggests that single-spin reversals make only a small contribution to the susceptibility and that to obtain even qualitative agreement with data the effects of large spin clusters and interaction between spin clusters must be included.

In this paper we present ac susceptibility data for the one-dimensional (1D), spin one-half ($S=\frac{1}{2}$), Ising ferromagnet $[(CH_3)_3NH]FeCl_3\cdot 2H_2O$ (FeTAC)[1] and compare the results to the Ising model for a 1D ferromagnet. Employing simple calculations for the Ising model, we conclude that the presence of large domains of reversed spins and interactions between these domains are necessary for a correct description of the susceptibility. Exploiting the equivalence of these domains to Ising bound magnons and classical Ising solitons, and examining the Heisenberg$\rightarrow$Ising limit, we qualitatively extend these conclusions to bound magnons and classical solitons in the nearly isotropic case.

A single crystal of FeTAC weighing 0.403 mg and measuring 1.7 mm$\times$0.6mm$\times$0.4mm was selected using a polarizing microscope. The crystal was mounted with its long (z) axis, the magnetic easy axis, parallel to the applied field. ac susceptibility measurements were made using an off-balance mutual inductance method which utilized an rf SQUID as a flux detector. The amplitude and frequency of the excitation field were 6 mOe and 80 Hz. No relaxation effects were observed. Temperature was measured using a calibrated carbon glass resistor. The data were corrected for demagnetization effects. Figure 1 shows the susceptibility data for FeTAC (zero field data not shown) and fits of the exact Ising model[2] to the data using the previously reported values $J/k=17.5$ K, $g=7.5$ (Ref. 1) for FeTAC. Relative error bars fall within the symbol indicator for each data set.

Greeney *et al.*[1] and Landee, Kuentzler, and Williams[3] have characterized FeTAC as a nearly ideal $S=\frac{1}{2}$, Ising ferromagnetic chain (IF). Interchain coupling is $z'J'/zJ\sim-10^{-3}$, and there is no overt spin canting. Zero-field 3D ordering occurs at $T_N=3.12$ K, and the magnetic phase diagram is metamagnetic with $H_c(0)=90$ Oe. The Ising model fits our data nicely in zero field, but as is apparent from Fig. 1, shows systematic deviations at high fields. Mean-field corrections using J' to account for interchain coupling does not improve the fits. However, variations of the data from the Ising model may be due to field enhanced interchain coupling.[4]

To understand how spin dynamics affects susceptibility, we consider Ising excitations. The Hamiltonian for an N-spin, $S=\frac{1}{2}$, IF is

$$\mathcal{H}=-2J\sum_{i=1}^{N}S_i^zS_{i+1}^z-g\mu_BH\sum_{i=1}^{N}S_i^z\ ,$$

where $J>0$ is the exchange energy and H is the magnetic field. Dispersion curves are given by the energies of spin clusters (domains of reversed spins, antiparallel to the applied field). For m spins in a cluster,

$$\tilde{E}_m=1+m\tilde{H}+\tilde{E}_0\ ,$$

where all quantities are dimensionless, with energy $\tilde{E}_m=E_m/2J$, field $\tilde{H}=g\mu_BH/2J$, $m=1, 2, 3, \ldots$, and ground-state energy $\tilde{E}_0=(-N/4)-(N\tilde{H}/2)$. In an IF, spins within a reversed cluster couple with an exchange energy identical to that in the ground state, so $\Delta\tilde{E}=1$ is entirely due to domain wall interactions. The zero field

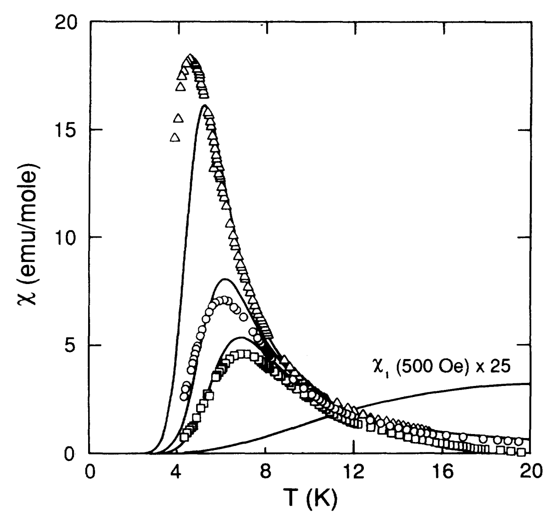

FIG. 1. Susceptibility vs temperature for a single crystal of FeTAC, with the applied field along the easy axis, for fields of 500 (△), 1000 (○), and 1500 (□) Oe. Theoretical fits of the exact susceptibility for the Ising chain ferromagnet with $J/k=17.5$ K, $g=7.5$ are shown as solid lines. The curve labeled χ_1(500 Oe) is for single-spin reversals, and is multiplied by a factor of 25.

energy of a cluster equals that of an isolated reversed spin, so at finite temperature multispin clusters will be more numerous than single spin flips. Spin clusters in the IF have been observed in ESR[5,6] and FIR[7] absorption experiments. An IF spin cluster is the extreme anisotropic limit of a sine-Gordon kink-antikink soliton pair in the *XY* chain.

Ising excitation are dispersionless, i.e., $\tilde{E}_m$ is wave vector independent. Since they have zero group velocity, they can only undergo thermally activated diffusion, and possess no intrinsic dynamics. If anisotropy is reduced slightly, more interesting processes are possible. For the nearly IF cluster mobility decreases as size increases, so thermally activated dynamics still predominates, but noncommuting spin components allow forbidden IR and ESR transitions.[8] Calculations by Ishimura and Shiba[9] and experiments by El Massalami *et al.*[10] reveal a spin structure consisting of very long, thermally activated, essentially static kink-antikink pairs, with excitations involving only a few spins rapidly traversing the static structure. An analogy between spin-lattice and spin-spin relaxation and kink-lattice and kink-kink relaxation has been suggested.[10] By contrast, for the nearly Ising antiferromagnetic chain, creation of a kink-antikink pair of any length requires reversal of only two spins, producing excitations which are dispersive and display an interesting intrinsic dynamics.[9,11]

To study how various sizes of spin clusters affect statistical mechanics in the pure IF, we examine a simple model in which a fermion gas of noninteracting clusters of size *m* are taken to be the only excitations in the chain. This is formally analogous to an $m=1$ (magnon) model, except that the Zeeman energy per excitation is increased by a factor of *m*, and the maximum possible number of excitations is reduced by a factor of $1/m$. For general *m* the dimensionless susceptibility per spin is found to be

$$\tilde{\chi}_m = \frac{\exp(-\tilde{\varepsilon}_m/\tilde{T})}{\tilde{T}[1+(1/m)\exp(-\tilde{\varepsilon}_m/\tilde{T})]^2} ,$$

where the dimensionless excitation energy and temperature are given by $\tilde{\varepsilon}_m = 1+m\tilde{H}$ and $\tilde{T}=kT/2J$. $\tilde{\chi}_m$ includes effects of kinematic interactions,[12] so that no spin can be reversed more than once, and no more than *N* spins in the chain can be reversed (clusters are treated as fermions). Dynamic interactions,[12] however, which would allow clusters to break apart, combine to form new clusters, etc., are not accounted for. The line labeled χ_1(500 Oe) in Fig. 1 shows the susceptibility for single-spin flips in 500 Oe. Comparing this curve to the exact IF susceptibilities, it is clear that $m=1$ clusters cannot account for the magnitude and temperature dependence of the exact result. Unlike the exact zero field susceptibility, $\chi_m(H=0)$ does not diverge at $T=0$. To obtain this divergence the $m\to\infty$ limit must be taken before the $(H,T)\to 0$ limits, further indicating that the large *m* excitations determine the behavior of χ.

$\chi_m(T)$ for $m=2,6,10,20,50,100,200,300$, with $H=1000$ Oe is shown in Fig. 2. General behavior is similar for other fields. The (m,H,T) dependence of χ_m is summarized in Fig. 3, where the magnitude of the susceptibility at the peak, $(\chi_m)_{\max}$, is plotted as a function of the temperature at which the peak occurs for a series of (m,H) values. Peaks in susceptibility correspond to the largest possible change in magnetization δM for a field change δH. As the temperature is decreased from the paramagnetic regime, a peak in $\chi_m(T)$ is expected, qualitatively, when the sum of the exchange, Zeeman, and kinematic interaction energies exceed the thermal energy. At this temperature, clusters of reversed spins begin to fall back into the ground state, thereby saturating the magnetization and reducing the susceptibility from its maximum.

Small clusters, $m \lesssim 20$, have small susceptibilities which decrease uniformly as applied field is increased. The temperatures of the maxima (for a given *m*) increase only slightly as field increases, but (for a particular field) decrease with increasing *m*. Since these excitations carry small magnetizations and have minimal Zeeman energies, the small peak heights and weak dependences of peak temperatures on field are expected. The decrease in the

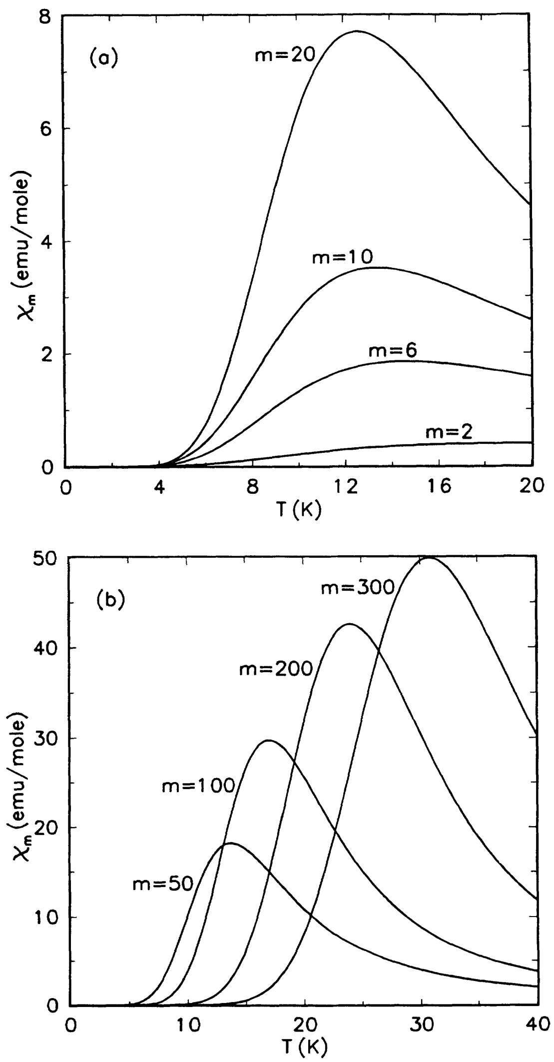

FIG. 2. Theoretical susceptibility vs temperature for a gas of noninteracting, Fermi-like *m*-fold spin clusters in an applied field of 1000 Oe. (a) $m=2,6,10,20$. (b) $m=50,100,200,300$.

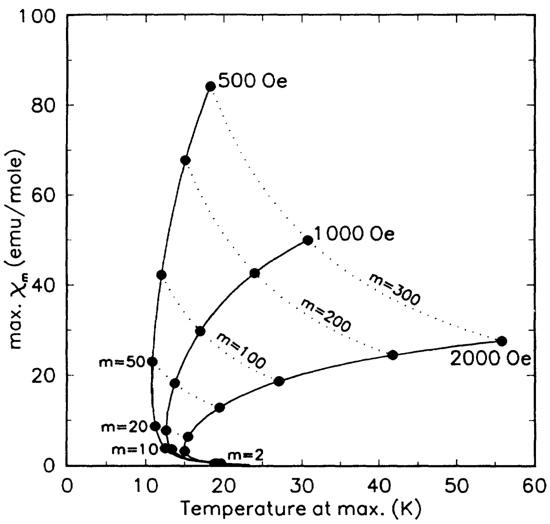

FIG. 3. Maximum (peak) values of theoretical susceptibility vs temperature at peak for a gas of noninteracting, Fermi-like, m-fold spin clusters, as a function of cluster-size m and applied field H. Lines are guides to the eye.

temperature of $(\chi_m)_{\max}$ as m is increased is apparently due to kinetic interactions. With small Zeeman energy, the main limitation on the number of spin clusters becomes the availability of excited state energy levels, i.e., the number of spins available to be reversed. When $5 \leq m \leq 20$ comparatively few excitations are allowed, so that the required thermal energy is small, and the peaks occur at lower temperature. For $m=1$ and $m=2$ a larger number of clusters can be excited, so more thermal energy is required, giving rise to peaks at higher temperatures. The range $10 \lesssim m \lesssim 20$, where the bends occur in Fig. 3, is a crossover region between kinetic interaction and Zeeman interaction dominated behavior.

Zeeman energy appears to exceed kinetic interaction energy for clusters of size $m \gtrsim 20$. Large thermal energies are required for excitation, giving rise to high-temperature peaks in $(\chi_m)_{\max}$, with peak temperatures which increase as m is increased. As expected, the increased Zeeman energies in higher fields allows fewer excitations, so susceptibilities decrease monotonically with field. Peak height increases indefinitely as cluster size is increased, attaining values much larger than the exact susceptibility. This feature results not only from the large magnetizations carried by large cluster, but also from a fundamental flaw in the model.

Considering the temperature dependence and magnitude of χ_m, it is clearly not possible to reproduce the exact susceptibility by any simple combination of cluster sizes. For a particular field all χ_m peaks occur at temperatures above the exact χ peak temperatures. The high-m excitations must be mixed with the small-m excitations in a way which will drastically reduce the temperature of the high-m peaks, but still retain much of their magnitude. Examining the response of the high-m clusters to a magnetic field provides insight into the underlying difficulty.

When a large cluster is thermally excited at a given temperature in a dc magnetic field it is part of an equilibrium distribution of clusters. If the field is increased by an amount $\delta\tilde{H}$, as in an ac susceptibility experiment where $\tilde{\chi}=\delta\tilde{M}/\delta\tilde{H}$, the cluster's energy will increase by an amount $m\,\delta\tilde{H}$, and it will (temporarily) be out of equilibrium. In the cluster gas model described above the only remedy is a complete reversal of the whole cluster back to the ground state. The resultant energy decrease is $m(\tilde{H}+\delta\tilde{H})$, which overcompensates by $m\tilde{H}$. In the real physical system it is possible for the cluster to be reduced in size, presumably by an amount $\Delta m = m\,\delta\tilde{H}$, rather than being entirely eliminated. Alternatively, in order to reduce energy by $m\,\delta\tilde{H}$, $\Delta p+1$ clusters can combine to provide the decrease $m\,\delta\tilde{H}=\Delta p$. Obviously, cluster-size reductions or increases and cluster combinations or splittings can provide the required equilibration without the need for large cluster destruction or creation which gives excessively large susceptibilities at unreasonably high temperatures. Spin cluster interactions must play an crucial role in determining the observed susceptibility.

We have also partially developed a cluster gas model for an isotropic chain, the $S=\frac{1}{2}$, Ising-Heisenberg ferromagnet (HIF), and preliminary results indicate that conclusions drawn from the IF are also valid in this more complex system. The correspondence is not unexpected.[13,14] Johnson and Bonner[13] have noted that the exact dispersion relation for the HIF becomes Ising-like as the number of reversed spins (m) in a bound state becomes large: The excitation gap increases monotonically to a constant value, and the dispersion curves flatten. (This limiting process is *not,* however, applicable in the pure Heisenberg case.) Our analysis reveals that for 1% anisotropy this limit is >99% complete when $m \geq 40$. High-m clusters (bound magnons) are virtually Ising even in nearly isotropic chains. Therefore, the above conclusions for an IF should also be valid in much of the isotropic regime. Since spin clusters in the IF are just highly anisotropic kink-antikink solitons, this correspondence with isotropic chains corroborates theoretical arguments for the existence of quantum solitons in spin one-half isotropic chains.[15,16]

The striking importance of interactions between spin excitations in determining the essential physics of the IF chain is also relevant to the difficult problem of soliton interactions in the classical XY ferromagnetic chain.[17] Magyari[18] has shown that as anisotropy is increased the wall width in 180°-Bloch-type solitons gradually decreases, reaching a single lattice spacing—identical to an Ising kink soliton—when the anisotropy becomes $\frac{2}{3}$ of the exchange. Consequently, it appears that spin cluster (kink-antikink) interactions, shown here to be essential for a proper description of thermodynamics in the Ising ferromagnetic chain, should also be important in isotropic soliton bearing systems.

The authors wish to thank R. E. Greeney and Professor C. P. Landee for providing crystals of FeTAC. This work was supported by NSF Grant No. DMR-90-11072. One of us (D.N.H.) was supported by ONR Contract No. N00014-88-K-0094 during the later stages of the work.

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