Soliton Contribution to the Electron Paramagnetic Resonance Linewidth in the Two-Dimensional Antiferromagnetic

C. E. Zaspel,* T. E. Grigereit,† and John E. Drumheller
Department of Physics, Montana State University, Bozeman, Montana 59717
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An observed exponential decay in the electron paramagnetic resonance linewidth of the nearly classical two-dimensional antiferromagnet as a function of temperature is shown to be the result of solitons interacting with magnons, and provides an experimental confirmation of these excitations. The temperature dependence of the linewidth is calculated using the dynamic spin correlation function derived from soliton-magnon scattering in the Born approximation. Data in the critical regime for (n-propylammonium)$_2$ tetrachloromanganese (II) are presented and compared to the theory.

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A large class of layered magnetic insulators has been shown to exhibit the experimental characteristic of two-dimensional (2D) magnetism and has been useful in testing theories pertinent to 2D systems. Many of the magnetic systems show 2D critical fluctuations with corresponding critical exponents [1] in the temperature range immediately above the 3D ordering temperature. In this paper we will focus on these fluctuations as observed through electron paramagnetic resonance (EPR) line broadening, which occurs in a narrow temperature range just above the Néel temperature T_N, in the nearly 2D antiferromagnetic case. About ten years ago Waldner [2] experimentally showed that nearly classical ($s = \frac{5}{2}$) layered antiferromagnets exhibited an Arrhenius EPR linewidth $\Delta H \sim \exp(E/T)$ temperature dependence immediately above T_N. It was also proposed that E was a soliton excitation energy and further that the observed Arrhenius behavior indicated that solitons contribute to the EPR linewidth. Later Waldner [3,4] proposed that this 2D soliton was a static type, which was first investigated by Skyrme [5] about thirty years ago. Finally Belavin and Polyakov [6] applied Skyrme's solution to the 2D classical Heisenberg magnet in the continuum approximation and showed that topologically the solitons correspond to a mapping of the spin space sphere onto the lattice plane. The soliton energy $E_s = 4\pi J s^2$ is obtained by the minimization of the classical Heisenberg Hamiltonian $H = J\sum_{\langle i,j\rangle} \vec{S}_i \cdot \vec{S}_j$, where J is the exchange constant, and $\vec{S}_i$ is the spin vector at site i of magnitude s. In Refs. [2,4] it was shown that the measured E in the EPR linewidth temperature dependence agreed with E_s to within a few percent for four different compounds with known values of J, and it was implied that solitons contribute to the EPR linewidth in the critical fluctuation region. However, there are two difficulties with this interpretation. First, since the EPR linewidth is related to the time-dependent spin correlation function, static solitons cannot contribute to the linewidth. Second, the theoretical basis for the Arrhenius behavior derives from a calculation by Mikeska [7] for the 1D magnet, rather than the 2D, with the time dependence resulting from moving sine-Gordon solitons. Indeed, Waldner [4] has remarked that, since the soliton contribution to the EPR linewidth for the 2D magnet was not known, the agreement between the observed Arrhenius behavior and the excitation energy E_s is perhaps fortuitous.

To interpret the observed Arrhenius behavior it is necessary to calculate the dynamic soliton contribution to the EPR linewidth or equivalently the time-dependent correlation function in the critical fluctuation region. Previous work on the dynamics of 2D magnetic solitons is scant. Mobile vortices rather than solitons were considered by Gouvea *et al.* [8] with the result that motion gives rise to a central peak in the frequency-dependent correlation function. Later we showed [9] that soliton motion also results in a central peak. The soliton-magnon interaction is another mechanism that will affect the dynamics, but was considered only for the 1D sine-Gordon system by Allroth and Mikeska [10]. In the 2D magnet only the vortex-magnon interaction has been investigated [11]. Recently, the EPR linewidth has been calculated for the 2D quantum ($s = \frac{1}{2}$) antiferromagnet (AFM) by Chakravarty and Orbach [12] with the result that the dominant temperature dependence is $\exp(3E_s/2T)$ rather than $\exp(E_s/T)$, and this has been experimentally confirmed by Castner and Seehra [13]. Chakravarty and Orbach's results, however, cannot be applied with great accuracy to the nearly classical ($s = \frac{5}{2}$) spin systems in which solitons are expected.

In this Letter the dynamic spin correlation function owing to the soliton-magnon interaction is calculated using the technique of Refs. [8–11]. Next, the temperature-dependent EPR linewidth is calculated and shown to have the form $\exp(E_s/T)$. Finally, the calculated temperature dependence is then compared with EPR linewidth data on several previously measured $s = \frac{5}{2}$ layered manganese compounds as well as our new data on n-propylammonium tetrachloromanganate, (n-PA)$_2$MnCl$_4$.

We begin with the Lagrangian for the two sublattice antiferromagnet, which is described by the magnetization vector $\vec{m} = \frac{1}{2}(\vec{S}_1 + \vec{S}_2)$ and the sublattice magnetization

vector $\vec{l} = \frac{1}{2}(\vec{S}_1 - \vec{S}_2)$, where the subscripts refer to the different sublattices. In the critical fluctuation region with negligible external magnetic field, the condition $|\vec{l}| \gg |\vec{m}|$ is satisfied and the Lagrangian can be expressed in terms of $\vec{l}$ only [14],

$$L = \frac{Js^2}{2} \int \left[\frac{1}{c^2}\theta_t^2 + \frac{1}{c^2}\sin^2\theta\varphi_t^2 - (\nabla\theta)^2 - \sin^2\theta(\nabla\varphi)^2 \right] d^2x , \quad (1)$$

where $\theta(x,y)$ and $\varphi(x,y)$ are polar and azimuthal angles of the vector $\vec{l}$, which has length s, and c is the magnon velocity. Static soliton solutions are obtained by integration of the nonlinear equations of motion for the two dependent variables

$$(\varphi_t \sin\theta)_t/c^2 = \nabla^2\theta - (\nabla\varphi)^2 \sin\theta\cos\theta$$

and

$$\theta_{tt}/c^2 = \nabla\cdot(\sin^2\theta\nabla\varphi) ,$$

where the subscript t indicates a partial time derivative. A particular solution $\theta_0(r) = 2\tan^{-1}(r_0/r)$ and $\varphi = \phi$ is easily obtained by integration of these equations in a polar (r,ϕ) coordinate system. As mentioned previously, either soliton motion or soliton-magnon scattering must be considered to obtain the dynamic spin correlation function. Soliton motion results in a central peak at zero frequency, which is far removed from the EPR resonance frequency, therefore, the soliton-magnon interaction will be the time-dependent mechanism considered here.

In order to determine how the soliton-magnon interaction affects the time-dependent spin correlation function, it is first necessary to calculate the time dependence of the dependent variables θ and φ which appear in Eq. (1). We do this by assuming that the spin polar and azimuthal angles can be expressed as $\theta(r,t) = \theta_0(r) + \chi(r,t)$ and $\varphi(r,\phi,t) = \phi + \xi(r,t)$. Here χ and ξ are assumed to be small quantities which reduce to magnon solutions if no solitons are present. In the presence of a soliton, χ and ξ give the change in the soliton structure as a result of the soliton-magnon interaction. As a further simplification we use the results of Ref. [11] where it was shown that s-wave scattering gives the main contribution to the vortex-magnon interaction. Therefore we assume that χ and ξ are independent of ϕ. Then to first order in small quantities the equations for θ and φ become first order equations to be solved for χ and ξ. Next, the ansatz $\chi(r,t) = rf(r)\sin\theta_0(r)\cos\omega t$ and $\xi(r,t) = -rf(r)\sin\omega t$ is useful in that it results in the equations for χ and ξ decoupling into a single equation to be solved for $f(r)$. These substitutions give

$$f_{rr} + \frac{1}{r}(3 - 2\cos\theta_0)f_r + \left(\alpha^2 + \frac{1}{r^2}(1 - 2\cos\theta_0)\right)f = 0 , \quad (2)$$

where $\alpha = \omega(q)/c$ and $\omega(q) = c|q|$ is the magnon frequency. The absence of a soliton corresponds to $\cos\theta_0 = 1$, resulting in Bessel function magnon solutions $f(r) = J_1(\alpha r)$ and $Y_1(\alpha r)$. In the presence of a soliton, $f(r)$ is obtained from the solution of Eq. (2) when magnons scatter from the outer part ($r \gg r_0$) of the soliton as was done in Ref. [11] for the vortex-magnon interaction. Equation (2) is solved in the Born approximation with the assumption that q is small, resulting in the large radii solution

$$f(r) = \frac{2\alpha r_0^2}{\pi^2 r^3} . \quad (3)$$

To calculate the spin correlation function we use the soliton structure factor

$$g(q,t) = \int l^x(r,t)e^{-i\vec{q}\cdot\vec{r}}\, d^2r , \quad (4)$$

where $l^x(r,t)$ is the x component of the sublattice magnetization with the time dependence resulting from the soliton-magnon interaction. This structure factor contains a static contribution from the static solution and a time-dependent contribution from soliton-magnon scattering. Both of these parts are evaluated in the large-r approximation ($\cos\theta_0 \cong 1, \sin\theta_0 \cong 2r_0/r$) by substituting Eq. (3) into the dependent variable transformations which are then used in Eq. (4) to get

$$g(q,t) = [g_0(q) + g_1(q)\cos\omega t]\cos\gamma , \quad (5)$$

where $g_0 = 4\pi i r_0/q$, $g_1 = -4\alpha i r_0^3 q/\pi$, and γ is the direction of $\vec{q}$ relative to the x axis.

Finally, the structure factor can be used in Eq. (4) to get $l^x(r,t)$ from which the spin correlation function and the EPR linewidth will be calculated. The linewidth is the temporal integral of the four-spin correlation function and is given by

$$\Delta H = \frac{T}{2\chi_\perp \hbar^2} \sum_{q,q'} A(k_0)\,\mathrm{Re} \int e^{i\omega_0 t}\langle l_q^x(t) l_{-q'}(t) l_{-q}^x l_{q'}^x\rangle\, dt . \quad (6)$$

Here $A(k_0)$ is related to the Fourier coefficients of the dipolar interaction evaluated at the antiferromagnetic wave vector ($k_0 = \pi/a$), and ω_0 is the resonance frequency. At this stage it is possible to evaluate the soliton contribution to the four-spin correlation function without use of the usual decoupling procedure in which the four-spin correlation function is expressed as a product of two-spin correlation functions. Assuming that $l^x(r,t)$ is from solitons at different centers r_μ, then $l^x(r,t) = \sum_\mu l^x(r - r_\mu, t)$, and the sums over the soliton centers yield [15] $n\langle g(q,t)g(-q,t)g(q,0)g(q,0)\rangle$ for the correlation function, where $n \sim 1/R^2$ is the soliton density in terms of the correlation length [12]. Referring to Eq. (5), it should be noted that the four-spin correlation function in Eq. (6) will contain time-independent terms which will integrate to zero because of the oscillatory $e^{i\omega_0 t}$ factor. Since the dominate contribution [12] to the sum over q in Eq. (6) will be in the small q region, we only retain terms linear in g_1. This results in the leading soliton contribution to the linewidth

$$\Delta H_s \sim n\frac{T}{\chi_\perp}\frac{S^4}{(2\pi)\sum_q^2}\int_0^\infty \langle g_0^2\rangle\langle g_0 g_1\rangle\cos\omega(q)t^{i\omega_0 t}\, dt . \quad (7)$$

First, the time integration in Eq. (7) is performed by assuming that the magnetization relaxes by diffusion, which is expected for manganese compounds [16]. The complex magnon frequency is $\omega(q) = cq + iDq^2/2$, where D is the diffusion coefficient. Next, the sums over q are converted to integrals and evaluated by use of the following two approximations. First, the temperature-dependent soliton sizes $\langle r_0^n \rangle$ are assumed to be independent of the wave vector integral. Second, since well-defined spin waves [17] exist if $qR > 1$, the lower limit of the q integral is $1/R$. These assumptions lead directly to $\langle g_0^2 \rangle \sim 4^2\pi^2\langle r_0^2 \rangle \ln R$ and $\langle g_0 g_1 \rangle \sim 32(T/c)\langle r_0^4 \rangle$. Finally, the temperature-dependent soliton sizes are estimated by performing the thermal average $\langle r_0^n \rangle = (1/z)\sum r_0^n e^{-E_s/T}$, where z is the partition function for a single excitation. The sum can be converted to an integral by including a "density of states" factor as was done in Ref. [9], but the form of this factor is not critical here. The upper limit of this integral is determined by the requirement that $\theta_0(R) \leq |\max\theta_{0r}|$, so that the "gap" at the soliton edge at $r = R$ will be consistent with the continuum approximation giving the final temperature dependent factor $\langle r_0^2 \rangle \sim R/2$ and $\langle r_0^4 \rangle \sim R^2/3$. The remaining temperature-dependent factors are the diffusion coefficient obtained through dynamic scaling by Chakravarty, Halperin, and Nelson [17], $D = R\sqrt{T/\chi_\perp}$, and the correlation length from Takahashi's [18] modified spin wave theory for the 2D AFM, $R = (1/8\sqrt{2}\, e^{\pi/2})e^{E_s/2T}$. These result in the following soliton contribution to the EPR linewidth:

$$\Delta H_s \sim \frac{T}{c\chi_\perp}\frac{16s}{3\sqrt{2}}\left(\frac{T}{Js^2}\right)^{3/2} R^2 \ln R\,,$$

where $c = \sqrt{8}\,Js$ and $\chi_\perp = 1/8J(\hbar = 1)$. The magnon contribution to the linewidth which was calculated in Ref. [12] can be applied to the classical AFM using Takahashi's [18] $q = 0$ spin correlation function which gives

$$\Delta H_M \sim \frac{T}{c\chi_\perp}\sqrt{\frac{E_s}{2T}}\left(\frac{T}{Js^2}\right)^4 R^3.$$

Combining these we obtain the final expression for the temperature-dependent EPR linewidth,

$$\Delta H \sim \frac{T}{c\chi_\perp}\left[\frac{16s}{3\sqrt{2}}\left(\frac{T}{Js^2}\right)^{3/2}\ln R + \left(\frac{T}{Js^2}\right)^4\sqrt{\frac{E_s}{2T}}\,R\right]R^2, \tag{8}$$

which has the observed Arrhenius behavior if the second term is small compared to the first.

For experimental confirmation we chose $(n\text{-PA})_2MnCl_4$ because it is a good approximation to the classical 2D AFM [19]. In particular, this is a layered compound with the MnCl layers separated by n-PA cations, resulting in a very small interlayer exchange coupling of the order of 10^{-5} J while the intralayer exchange is 9.2 K. Also since Mn(II) has $s = \frac{5}{2}$, it is well approximated by a classical spin model so that nonlinear excitations should indeed follow from Eq. (1). Temperature-dependent EPR data were obtained with a Varian E109 series X-band spectrometer. At room temperature the compounds exhibited similar angular and temperature-dependent EPR linewidth characteristics of spin diffusion in a 2D system [16]. Below room temperature the linewidth decreases linearly with decreasing temperature until a minimum linewidth is reached at approximately 70 K owing to exchange narrowing. At lower temperatures the increasing correlation length results in an increasing EPR linewidth beyond T_N ($T_N = 39.2$ K) to the lowest measured temperatures in the ordered state. It was in this region that the temperature-dependent linewidth for other manganese compounds in Refs. [2,4] was attributed to static solitons. Figure 1 shows the temperature-dependent linewidth from 54 K down to 46 K on a semilog plot versus T_N/T so that the dominant exponential dependence can be clearly seen. The temperature-dependent EPR linewidth is calculated from Eq. (8) and compared with these data for first the classical soliton energy $E_s = 725$ K, resulting in the calculated linewidth from the soliton-only contribution represented by the dashed curve in Fig. 1. The solid curve represents both the soliton and magnon contributions to the linewidth from Eq. (8). Throughout the observed temperature range it should be noted that the soliton contribution is the main source of the linewidth temperature dependence. We have also included the Chakravarty-Orbach theory from Ref. [12] which is indicated by CO in Fig. 1. Finally, it should be noted that this theory is only valid in the narrow temperature range where the hydrodynamic description of the AFM is applicable and broadening begins. Experimentally this region begins at approximately $T_N/T \sim 0.7$, where $R = 10$, but in the vicinity of $T_N/T \sim 0.86$ the line broadens to the extent that we can no longer accurately measure the linewidth.

The temperature-dependent linewidth given by Eq. (8) appears to fit the experimental data of all of the nearly classical layered compounds studied. This is seen because of the near equality of the measured excitation energy, obtained from the slope of the $\ln\Delta H$ versus T_N/T graph, and the calculated soliton energy E_s. This agreement

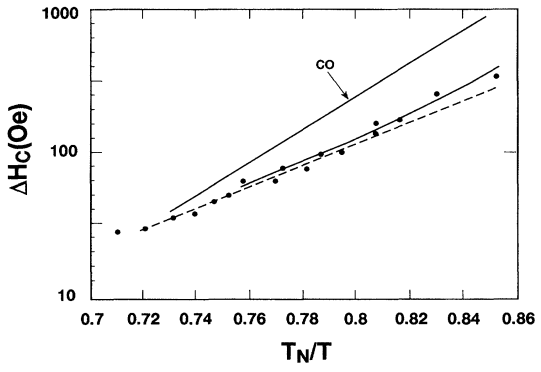

FIG. 1. ΔH versus T/T_N for $(n\text{-PA})_2MnCl_4$. The dashed curve is the calculated temperature-dependent linewidth due to solitons only, and the solid curve is the calculated linewidth with magnon effects included. The linewidth calculated from the Chakravarty-Orbach (CO) theory is also indicated.

TABLE I. Measured and calculated excitation energies for various Mn^{2+} compounds.

Mn^{2+} compounds ($s = \frac{5}{2}$)	Measured E (K)	$E_s = 4\pi Js^2$ (K)
K_2MnF_4	620	653
Rb_2MnF_4	650	591
$(CH_3NH_3)_2MnCl_4$	760	784
$(C_2H_5NH_3)_2MnCl_4$	770	700
$(n\text{-PA})_2MnCl_4$	727	710

between the measured and calculated excitation energies is presented in Table I for the four compounds previously measured by Waldner as well as our result for $(n\text{-PA})_2MnCl_4$.

In summary, solitons interacting with magnons in the classical 2D AFM result in an EPR linewidth with a dominant $\exp(E_s/T)$ temperature dependence. Since this dependence can occur only if solitons are present in the fluctuation region, EPR linewidth measurements provide an indirect method to experimentally detect solitons. Finally, experimental data confirm that solitons dominate the thermodynamics in the fluctuation region immediately above T_N.

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*Permanent address: Western Montana College, Dillon, MT 59725.

†Present address: Reactor Radiation Division, National Institute of Standards and Technology, Gaithersburg, MD 20899 and Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, MD 20742.

[1] D. L. Huber and M. S. Seehra, Phys. Lett. **43A**, 311 (1973).
[2] F. Waldner, J. Magn. Magn. Mater. **31–34**, 1203 (1983).
[3] F. Waldner, J. Magn. Magn. Mater. **54–57**, 873 (1986).
[4] F. Waldner, J. Magn. Magn. Mater. **104–107**, 793 (1992).
[5] T. H. R. Skyrme, Proc. R. Soc. London **262**, 237 (1961).
[6] A. A. Belavin and A. M. Polyakov, JETP Lett. **22**, 245 (1975).
[7] H. J. Mikeska, J. Phys. C **13**, 2913 (1980).
[8] M. E. Gouvea, G. M. Wysin, A. R. Bishop, and F. G. Mertens, Phys. Rev. B **39**, 11 840 (1989).
[9] C. E. Zaspel, Phys. Rev. B **48**, 926 (1993).
[10] E. Allroth and H. J. Mikeska, Z. Phys. B **43**, 209 (1981).
[11] B. V. Costa, M. E. Gouvea, and A. S. T. Pires, Phys. Lett. A **165**, 179 (1992).
[12] S. Chakravarty and R. Orbach, Phys. Rev. Lett. **64**, 224 (1990).
[13] T. G. Castner and M. S. Seehra, Phys. Rev. B **47**, 578 (1993).
[14] B. A. Ivanov and D. D. Sheka, Phys. Rev. Lett. **72**, 404 (1994).
[15] F. G. Mertens, A. R. Bishop, G. M. Wysin, and C. Kawabata, Phys. Rev. B **39**, 591 (1989).
[16] P. M. Richards and M. B. Salamon, Phys. Rev. B **9**, 32 (1974).
[17] S. Chakravarty, B. I. Halperin, and D. R. Nelson, Phys. Rev. B **39**, 2344 (1989).
[18] M. Takahashi, Phys. Rev. B **40**, 2494 (1989).
[19] H. A. Groenendijk, A. J. Van Duyneveldt, and R. D. Willett, Physica (Amsterdam) **98B**, 53 (1979).