Low-Temperature Electron Spin Resonance Theory for Half-Integer Spin Antiferromagnetic Chains

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A theory of low-temperature (T) electron spin resonance (ESR) in half-integer spin antiferromagnetic chains is developed using field theory methods and avoiding previous approximations. It is compared to experiments on Cu benzoate. Power laws are predicted for the linewidth broadening due to various types of anisotropy. At $T \to 0$, zero width absorption peaks occur in some cases. The second ESR peak in Cu benzoate, observed at $T < 0.76$ K, is argued not to indicate Néel order as previously claimed, but to correspond to a sine-Gordon "breather" excitation. [S0031-9007(99)09424-7]

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In electron spin resonance (ESR) a static magnetic field is applied and the absorption of radiation polarized along the field direction is measured, as a function of frequency. The absorption intensity is proportional to the Fourier transform of the correlation function of the (zero wave-vector) total spin operator, $G(t) \equiv \langle S^+(t)S^-(0)\rangle$, when the field is along the z axis. (Here $\mathbf{S} \equiv \sum \mathbf{S}_j$.) We write the Hamiltonian:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' + \mathcal{H}_Z , \tag{1}$$

where $\mathcal{H}_0$ is the isotropic Heisenberg Hamiltonian, $J\sum \mathbf{S}_i \cdot \mathbf{S}_{i+1}$, $\mathcal{H}_Z$ is the Zeeman term, $-H\sum S_i^z$, and $\mathcal{H}'$ represents various possible small anisotropic terms. (We set $g\mu_B = 1$.) When $\mathcal{H}' = 0$, $[\mathcal{H}, S^-] = HS^-$, implying that the absorption spectrum consists only of a δ-function peak at the Zeeman energy, H. The shift and nonzero width of this peak are caused by the small anisotropic terms in the Hamiltonian, $\mathcal{H}'$.

In this paper we develop a new approach to calculating the ESR intensity for one dimensional antiferromagnets (1D AF's) of 1/2-integer spin. Using bosonization and the standard Feynman-Dyson self-energy formalism we are able to avoid making assumptions about the relaxation function as in the previous treatment [1].

We then calculate the width and shift perturbatively, avoiding previous Hartree-Fock approximations which are generally invalid in 1D. This perturbation theory generally breaks down due to infrared divergences at low T where universal scaling functions give the shift and width, whose calculation requires more powerful methods, based, for example, on exact integrability. We study the case where $\mathcal{H}'$ corresponds to a staggered field [2]. We show that the width is proportional to $(H/T)^2$ and the shift to $(H/T)^3$ at intermediate temperatures. The predicted dependence on T, H and field direction is shown to agree with experiments on Cu benzoate. We argue that the low-temperature ESR experiments are observing excitation of a sine-Gordon breather above the ground state, rather than Néel order as previously claimed.

We bosonize the spin operators, with $\mathcal{H}_0$ corresponding to a free boson Lagrangian, $(1/2)\int dx\, \partial_\mu\phi\, \partial^\mu\phi$ and

$$\begin{aligned} S_j^z &\approx \frac{1}{\sqrt{2\pi}}\frac{\partial\phi}{\partial x} + \text{const} \times (-1)^j \cos(\sqrt{2\pi}\,\phi), \\ S_j^- &\approx e^{i\sqrt{2\pi}\,\tilde{\phi}}[\text{const} \times \cos\sqrt{2\pi}\,\phi + C(-1)^j]. \end{aligned} \tag{2}$$

Here, the fields may be decomposed into left and right movers as $\phi = \phi_L + \phi_R$ and $\tilde{\phi} = \phi_L - \phi_R$ and we set the spin-wave velocity to 1. Noting that $\mathcal{H}_Z = -(H/\sqrt{2\pi})\partial\phi/\partial x$, we see that $\mathcal{H}_Z$ may be eliminated by the field redefinition,

$$\phi \to \phi + (H/\sqrt{2\pi})x . \tag{3}$$

This shift must be applied to the bosonization formulas of Eq. (2). Upon Fourier transforming the spin operators, this means that some momenta get shifted by $\pm H$. Writing the low-momentum parts of the spin operators in terms of left and right spin currents, $(\mathbf{J}_L + \mathbf{J}_R)$, we see that the ESR absorption intensity can be written in terms of the Green's functions of these operators. The effect of shifting ϕ is to shift the Fourier modes of the currents as $J_R^\pm(k) \to J_R^\pm(k + H)$, $J_L^\pm(k) \to J_L^\pm(k - H)$. Note that the bosonized version of $\mathcal{H}_0 + \mathcal{H}_Z$ is apparently independent of H and hence SU(2) invariant; it is only the mapping from the lattice spin operators to the field theory which depends on H. [Actually, it is known that the correlation exponents vary with H, corresponding to a change in the compactification radius of ϕ. However, this can be seen to be irrelevant to ESR, which probes the finite energy $\sim H$. The effective SU(2) symmetry is manifested by the zero linewidth of the ESR peak.) The ESR intensity is determined by the Green's functions of $J_{L,R}^\pm$, which are given by exponentials of $\phi_{L,R}$. On the other hand, the Green's functions of $J_{L,R}^z$ are easier to deal with since these fields are linear in $\phi_{L,R}$. In particular, we may use the standard Dyson result to write the retarded Green's function for ϕ in terms of the self-energy, $\Pi(q, \omega, T)$: $G_\phi = [\omega^2 - k^2 - \Pi]^{-1}$. This is a very useful formula

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for ESR because, in the limit where we may treat $\mathcal{H}'$ perturbatively, the shift and width are simply given by the real and imaginary parts of $\Pi(H,H)$. Using the effective SU(2) symmetry of the bosonized theory we may express the ESR intensity in terms of the Green's functions of $J^z_{L,R}$. Note that the validity of Dyson's formula is a highly nontrivial result of the structure of perturbation theory to all orders, resulting from the multiple insertions of one-particle irreducible diagrams and free propagators. In our new approach, this essentially replaces the previous assumptions [1] about the relaxation functions.

We consider the particular example of a transverse staggered field:

$$\mathcal{H}' = h\sum_j (-1)^j S^x_j \,. \tag{4}$$

This term arises, with $h \propto H$, from either a staggered off-diagonal component of the g tensor or from a Dzyaloshinskii-Moriya (DM) interaction [2]; both of these occur in Cu benzoate. The bosonized interaction is $\mathcal{H}' = hC\int dx \cos(\sqrt{2\pi}\,\tilde{\phi})$, which is unaffected by the field redefinition. In the case $H = 0$, $\mathcal{H}_0 + \mathcal{H}'$ is invariant under rotation about the z axis by π. It then follows that the Green's function giving the ESR intensity can be expressed as $G^{+-} = G^{xx} + G^{yy}$, since $G^{xy} = 0$. (Here $G^{ab} \equiv -i\langle[S^a, S^b]\rangle$.) We now use the SU(2) symmetry of $\mathcal{H}_0$ to prove that G^{xx} for a staggered field in the x direction is the same as G^{zz} for a staggered field in the z direction and G^{yy} for a staggered field in the x direction is the same as G^{zz} for a staggered field in the y direction. As argued above, this SU(2) symmetry remains present in the bosonized version of $\mathcal{H}_0 + \mathcal{H}_Z$ for nonzero H. Thus we have succeeded in expressing the ESR intensity in terms of $\langle\phi\,\phi\rangle$ although we apparently must consider two different forms of $\mathcal{H}'$. In fact these two different $\mathcal{H}'$s differ only by the interchange of $\phi \leftrightarrow \tilde{\phi}$, corresponding to $J^z_R \leftrightarrow -J^z_R$. Thus, the contribution to the ESR intensity, $\propto \langle J^z_L J^z_L\rangle + \langle J^z_R J^z_R\rangle$, is identical in both cases. Thus our formula for the ESR intensity, $I(\omega, H, T)$ becomes

$$I \propto -\omega\,\mathrm{Im}\left[\frac{H^2 + \omega^2}{\omega^2 - H^2 - \Pi(\omega, H, T)}\right]. \tag{5}$$

This fundamental formula replaces the more *ad hoc* ones generally used in ESR theory. It will be particularly useful when $\mathcal{H}'$ can be treated as a small perturbation, resulting in a small value of $\Pi(H,H)/H \ll H, T$. In this case Eq. (5) predicts an approximately Lorentzian line shape with shift $\mathrm{Re}\Pi(H,H)/2H$ and width $-\mathrm{Im}\Pi(H,H)/2H$.

Note that h is a relevant coupling constant of scaling dimension $3/2$. It produces an excitation gap, $\Delta \propto J^{1/3}h^{2/3}$. Thus perturbation theory in h will be valid only at high T; infrared divergences occur for $T \leq \Delta$. It follows from general scaling arguments that the shift and width both have the form $Tf_i(\Delta/T, H/T)$, for two different scaling functions f_i. We first consider the case $T \gg \Delta$ where we may use lowest order perturbation theory in h; we consider the low T case later. The first nonvanishing term is $O(h^2)$. We must amputate the external lines from the Green's function $\langle\phi\exp[i\sqrt{2\pi}\,\phi]\exp[-i\sqrt{2\pi}\,\phi]\phi\rangle$. This can easily be done by Taylor expanding the exponentials and gives two terms corresponding to Feynman diagrams in which the external lines are attached to the same or different vertices. This gives

$$\Pi(H,H) \approx 2\pi(Ch)^2[G'(H,H) - G'(0,0)], \tag{6}$$

where G' represents the retarded Green's function of $\sin(\sqrt{2\pi}\,\phi)$ in the free theory. We also performed a field-theory calculation using the traditional approach [1] to find the same result as above, in the lowest order of perturbation. Of course, the higher order perturbative terms from our new formulation, and in particular the nonperturbative low T behavior, go beyond the traditional approach.

G' has been evaluated by Schulz [3]. In general for a normalized primary field with left and right scaling dimensions $x_L = x_R = x/2$ the retarded Green's function is given by, using $\omega_\pm = \omega \pm q$,

$$G(\omega, q)_x = -(2\pi T)^{2x-2}F_x\left(\frac{\omega_-}{T}\right)F_x\left(\frac{\omega_+}{T}\right)\sin\pi x\,; \tag{7}$$

$$F_x(\epsilon) \equiv \Gamma(x/2 - i\epsilon/4\pi) \times \Gamma(1-x)/\Gamma(1 - x/2 - i\epsilon/4\pi), \tag{8}$$

where Γ is Euler's Gamma function. For the staggered field case, $x = 1/2$. Also considering the limit $H \ll T$, we may Taylor expand $F_x(\epsilon)$. Although the proportionality factor, C, in the bosonization formula, Eq. (2) is not universal it was recently evaluated exactly using Bethe ansatz results [4]. Because of a marginally irrelevant operator in the Hamiltonian, so far ignored, C^2 is effectively proportional to $\ln T$ (for $T \gg H$). This finally gives the results for the shift, $\delta\omega$ and width η:

$$\begin{aligned}\delta\omega &\approx 0.42596(\ln J/T)Jh^2H/T^3,\\ \eta &\approx 0.685701(\ln J/T)Jh^2/T^2.\end{aligned} \tag{9}$$

The effective staggered field, h, is determined by a linear combination of the staggered component of the g tensor and the DM interaction. It takes the form $h = cH$ where the proportionality constant, c, is a strong function of the direction of the applied field. Thus the shift and width should scale as essentially $(H/T)^3$ and $(H/T)^2$, respectively, with strong field-direction dependence, in the temperature range $\Delta, H \ll T \ll J$. (In experiments, usually the frequency is kept fixed; the frequency dependence corresponds to the H dependence.) Note that the width and shift *increase* with decreasing T. The increase of the shift (but not the width) due to the staggered g tensor was already discussed by Nagata [5] using a classical spin approximation, although our result is quite different from his.

Such a peculiar behavior of the width was actually observed in Cu Benzoate [6]. We choose the DM vector, $(D_{a''}, D_{c''}) = (0.13, 0.02)J$, which seems consistent with most of the experimental data on Cu benzoate [2]. Figures 1 and 2 show the dependence of the width on field direction, T and H. [There we replaced the logarithmic factor in Eq. (9) by unity.] We see from Fig. 1 that while the direction dependence and magnitude of the width are roughly reproduced, there appears to be an additional smaller contribution to the width with weaker dependence on field direction. We expect such a contribution from exchange anisotropy (discussed below); there may be other contributions as well. In Fig. 2, the temperature dependence of the linewidth for $H \parallel c''$ is shown for several resonance frequencies (i.e., field magnitude H). We see that the dependence of the width on H and T are well reproduced by our theory of the staggered field effect, although an additional contribution to the width, depending less strongly on H and T, is evident.

Another possibility is that the increasing width with decreasing T is related to the onset of Néel order at low T due to interchain couplings ignored in our theory. However, there is no evidence for Néel order from neutron scattering or susceptibility measurements [7]. (As we argue below, the interpretation [8] of ESR at still lower T as evidence for Néel order seems incorrect.) Furthermore, it seems unlikely that the peculiar dependence of the width on the three different variables, T, H and direction, captured by our purely 1D theory, could be explained in this way.

For $T \leq \Delta$, the above perturbative analysis breaks down. In the extreme low T limit, $T \ll \Delta$, we can nonetheless make some statements about the ESR intensity based on general principles and on exact results on the sine-Gordon model [2]. The simple picture of a Lorentzian line shape characterized by just a shift and a width is no longer very useful. Instead at very low T, ESR experiments should, in principle, be able to resolve some of the same excitations above the ground state as seen in neutron scattering. (Related observations were made independently by Boucher *et al.* recently [9].) Using the SU(2) rotation trick discussed above, we see that the radiation can create the excitations of the sine-Gordon model produced from the ground state by the scalar field, ϕ. This includes the first breather as well as a multiparticle continuum. Thus the ESR intensity, $I(\omega)$ at $T = 0$ should contain a zero width peak at the energy of the breather with momentum H,

$$\omega = \sqrt{H^2 + \Delta(h)^2}, \tag{10}$$

in addition to a continuum at higher energies. Calculations of the ϕ form factor [10] based on the exact integrability of the sine-Gordon model indicate that the intensity of the multiparticle contribution is very small and that the spectrum is dominated by the first breather peak at zero temperature. This breather peak can get broadened only by collisions with thermally excited particles, so we expect that its width should vanish as $\exp[-\Delta/T]$. As the temperature is raised other contributions to the ESR intensity should appear corresponding to additional processes involving thermally excited particles.

Experimentally [8] a noticeable change in ESR spectrum occurs at T of $O(\Delta)$. In particular, a two-peak structure is observed for an intermediate range of T. At lower T only the higher energy peak survives. A possible interpretation of this behavior is that the higher energy peak represents excitations from the ground state, perhaps primarily the first breather whereas the lower energy peak, which disappears with decreasing T, corresponds to other processes involving thermally excited particles. This hypothesis can be tested by fitting the shift to the breather energy of Eq. (10). Note that this leads to a characteristic direction dependence of the shift due to the strong direction

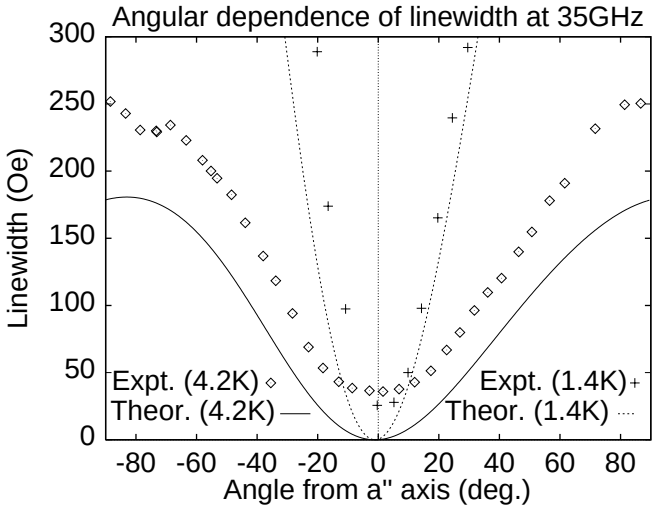

FIG. 1. The field-direction dependence of the ESR linewidth in the *ac* plane at frequency 35 Hz [6] compared to Eq. (9).

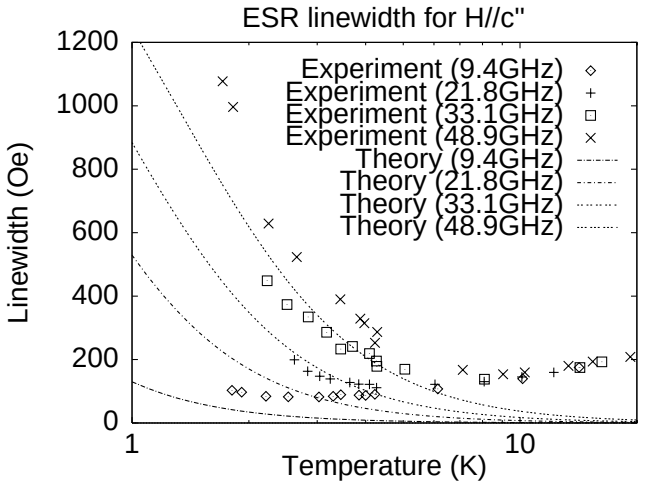

FIG. 2. The temperature and frequency dependence of the ESR linewidth for $H \parallel c''$ [6], compared to Eq. (9).

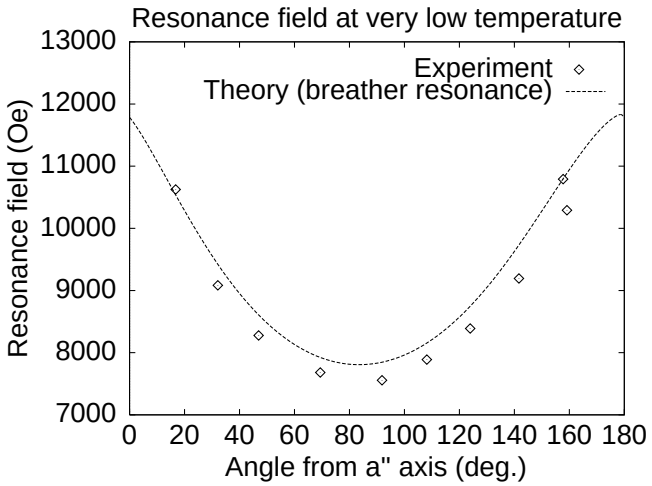

FIG. 3. The resonance field at very low temperature for various field directions in the *ac* plane. The experimental data were taken from the "antiferromagnetic resonance" in Ref. [8] at 0.41 K, and the theory refers to the lowest breather excitation at zero temperature (10).

dependence of the effective staggered field, h, and hence of the gap, Δ. Using the previously determined parameters, we obtain the dependence of resonance field (i.e., shift) on direction which is compared to experimental data at low T in Fig. 3. The agreement looks quite good. On the other hand, the observed width of this low T peak appears to go to a nonzero value at low T, which appears inconsistent with the breather interpretation. This may be due to an additional broadening mechanism which is effective at low T such as quenched disorder. Further experiments at higher field would help to clarify the situation. In any event, the previous interpretation of the low T peak as a signal of Néel order seems unjustified. Instead it can perhaps be explained entirely within the 1D theory taking into account the nontrivial evolution of the ESR intensity with T and H. This would then resolve the contradiction between the claimed observation of Néel order from ESR and its nonobservation in neutron scattering. It is worth emphasizing that the staggered field, by producing a gap and a staggered moment, tends to suppress the interchain coupling effects.

We have also analyzed the contribution to the width from exchange anisotropy (and/or dipolar interaction) $\sim \sum_j S_j^\alpha M_{\alpha\beta} S_{j+1}^\beta$ using field theory, based on our new formulation as well as the traditional one [1]. We emphasize that it is not necessary to use a Hartree-Fock approximation to calculate the Green's function, as has been commonly done in the past, even when the operator is quadratic in the lattice spin operators. Indeed such Hartree-Fock approximations are generally qualitatively wrong in the 1D case. Since $\mathcal{H}'$ is marginal it follows from scaling that $\eta \propto T f(\delta, H/T)$, where $|M| \propto \delta$ and f is a scaling function. Using Eqs. (7) and (8) in the limit of $x \to 2$, and including the effect of the large isotropic marginal operator gives the width

$$\eta \propto (\delta/J)^2 [\ln(J/T)]^2 T \,. \tag{11}$$

Such a linear T-dependence of the width is observed approximately, over an intermediate range of T, in a variety of quasi-1D antiferromagnets [11–13]. As far as we know, ours is the first derivation of this behavior from first principles.

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