PHYSICAL REVIEW B VOLUME 45, NUMBER 10 1 MARCH 1992-II

Temperature dependence of the electron-spin-resonance spectrum of the chain-end $S=\frac{1}{2}$ modes in an $S=1$ antiferromagnetic chain

Partha P. Mitra and Bertrand I. Halperin
Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138

Ian Affleck
Canadian Institute for Advanced Research and Physics Department,
University of British Columbia, Vancouver, B.C., Canada V6T 1Z1

(Received 19 August 1991)

The $S=\frac{1}{2}$ degrees of freedom, which have been predicted to occur at the ends of an $S=1$ Heisenberg-like antiferromagnetic chain, have been observed recently in low-temperature ESR measurements of $Ni(C_2H_8N_2)_2NO_2ClO_4$ (abbreviated NENP) containing selected impurities. The signal was found to decrease rapidly with temperature, at temperatures well below the Haldane gap. We present here a theoretical analysis of the loss of ESR signal due to the presence of thermal spin excitations on the chain, which can at least qualitatively explain the experiment.

I. INTRODUCTION

The theory of $S=1$ Heisenberg antiferromagnetic chains has been largely elucidated over the past decade. Following Haldane's initial suggestion[1] that the excitation spectrum has an energy gap for integer S and that the two-spin-correlation function falls off exponentially with separation in the ground state, many aspects of this problem have been studied theoretically, using both numerical[2-8] and analytical methods.[9-12] A number of experimental systems have been studied[13-19] to observe the gap. Experiments on the organic compound $Ni(C_2H_8N_2)_2NO_2ClO_4$ (NENP), which contains effectively isolated linear chains of antiferromagnetically coupled Ni^{2+} ions, have given some of the most dramatic support for the picture of the Haldane gap, which occurs despite the presence of a substantial uniaxial anisotropy.[15-19]

To explicate the nature of the nontrivial "Haldane" ground state, a related Hamiltonian was proposed in Ref 9 whose exact ground state is known and can be understood as a "valence-bond solid." An interesting feature of this ground state is the presence of fractional spin-$\frac{1}{2}$ degrees of freedom at the ends of a finite chain. It is expected that the ground state of a finite-chain Heisenberg antiferromagnet itself has such terminal degrees of freedom.[6,20] Both numerical[6] and experimental evidence[21,22] for these $S=\frac{1}{2}$ variables have been obtained.

The experimental evidence consists of the electron-spin-resonance (ESR) spectra at low temperatures of $Ni(C_2H_8N_2)_2NO_2ClO_4$ doped with small amounts of either magnetic Cu^{2+} (Ref. 21) or nonmagnetic Zn^{2+}, Cd^{2+}, and Hg^{2+}.[22] The dopants replace some of the Ni^{2+} and break the chains, thus giving rise to terminal sites where the $S=\frac{1}{2}$ degrees of freedom can reside. In the case when the dopant is Cu^{2+}, the spin-$\frac{1}{2}$ copper ion and the two terminal spin-$\frac{1}{2}$ variables of the adjacent chains are coupled together by exchange, and the spectra of three coupled spin-$\frac{1}{2}$ variables is observed. In a more recent experiment, hyperfine splittings of the lines due to the spin $\frac{3}{2}$ of the Cu nuclei have been seen. For the nonmagnetic dopants, one has effectively single spin-$\frac{1}{2}$ degrees of freedom at either end of the chain, and the spectra of isolated spin-$\frac{1}{2}$ variables has been observed in these systems. In both cases the signal can only be observed at very low temperatures and disappears very rapidly with increasing temperature, even at temperatures small compared to the Haldane gap. This rapid loss of intensity is the subject of this paper. We will concentrate on the nonmagnetic dopants for simplicity.

The physical picture is that the thermal excitations are very mobile. For moderate-length chains, excitations can traverse the entire chain several times during the effective time period determined by the width of the ESR line. We find that if even a single excitation is present on the chain, the resonance line is shifted out of the observation window. The observed intensity is therefore proportional to the probability of finding a chain with *no* excitation present. When the chain becomes very long, a single excitation on the whole chain no longer shifts the resonance line out of the observation window. In the limit of infinite chain lengths, the spectrum of excitations is continuous, but the spectral line broadens rapidly as the temperature is increased and excited states get populated whose resonance lines are shifted in a continuous manner from the zero-temperature line. Details then depend on the strength of the interaction between the thermal excitations and $S=\frac{1}{2}$ variables, as represented by their energy-dependent phase shifts.

In any case there should be a rapid loss of ESR signal with increasing temperature, which occurs at temperatures well below the Haldane gap. We derive below quantitative expressions which apply in the two different cases of intermediate chain lengths and infinite chain length, and we also derive formulas for a Poisson distribution of chain lengths. The results are in at least qualitative agreement with experiment.

II. GENERAL CONSIDERATIONS

We consider the Heisenberg Hamiltonian, with axial anisotropy,

$$\mathcal{H}=J\sum_{i=1}^{M-1}\mathbf{S}_i\cdot\mathbf{S}_{i+1}+D\sum_{i=1}^{M}(S_i^z)^2 , \tag{1}$$

with $D>0$, $J>0$, and D/J not too large. According to the current theoretical understanding of this Hamiltonian, the Haldane gap persists up to a finite critical value D_c of D.[23] At D_c the gap closes and reopens for $D>D_c$. The ground state for $D>D_c$ is essentially described by each spin individually being in the $S_z=0$ state, and there should be no free $S=\frac{1}{2}$ variables at the chain ends in this state. Estimates for D in $\mathrm{Ni(C_2H_8N_2)_2NO_2ClO_4}$ show that D is significantly smaller than the numerically estimated D_c. The ground state should therefore be Haldane like.

For an infinite chain, the ground state of the Hamiltonian has no broken symmetry, and the low-lying spectrum is that of a triplet of massive relativistic bosons, the degeneracy of the triplet being lifted by the axial anisotropy. The Hamiltonian (1) is rotationally invariant about the z axis, so that the total spin along the z axis is a good quantum number. The excited states are described by boson excitations which constitute a low-lying doublet and a higher singlet for positive D. The single-boson excited states may be labeled by the total z component of the boson spin S^z and the wave vector k. The energy of the excited state is given by $[E_0^2+(\hbar ck)^2]^{1/2}$ for $S^z=0$ and $[\Delta^2+(\hbar ck)^2]^{1/2}$ for $S^z=\pm1$. In $\mathrm{Ni(C_2H_8N_2)_2NO_2ClO_4}$ the Haldane gap Δ is estimated to be about 14 K, the gap E_0 for the $S^z=0$ excitation to be 31 K, and $\hbar c/a$ to be 110 K from neutron-scattering experiments,[15] where a is the lattice spacing along the chain.

The anisotropy of the chain plays an important role in the observed ESR spectrum at low temperatures. For the isotropic Heisenberg chain, the ESR spectrum would be trivial. Assuming that there is no anisotropy in the g values, all ESR transitions occur at the free-spin Larmor frequency $g\mu_B h$. This is because the total spin is a good quantum number for the isotropic chain and classifies states. ESR transitions conserve the total spin, and therefore transitions are allowed only between states which have the same energy for $h=0$, which are then Zeeman split by the magnetic field. It therefore follows that the transitions would occur at the unperturbed Larmor frequency. The total ESR intensity in the Heisenberg model would be simply proportional to the spin susceptibility, which *increases* monotonically with increasing temperature, in the temperature regime below the Haldane gap. In $\mathrm{Ni(C_2H_8N_2)_2NO_2ClO_4}$ the anisotropy is large enough so that the transitions where a magnon spin is flipped are shifted far out of the observation window, and the spectra of the spin-$\frac{1}{2}$ objects can be observed in isolation. The anisotropy is, however, small enough so that the Haldane-gap state persists, as discussed above.

We shall consider temperatures small compared to Δ. Since E_0 is almost twice Δ, the following inequalities will be satisfied:

$$\exp\left[-\frac{E_0}{T}\right]\ll\exp\left[-\frac{\Delta}{T}\right]\ll1 . \tag{2}$$

In this limit only the low-lying doublet is populated, thus making the analysis simpler. Also, the average kinetic energy of the bosons is small compared to Δ, so that we can make a nonrelativistic approximation. The line-shape problem will then reduce to a problem in nonrelativistic quantum mechanics with conserved boson number, where the boson spectrum is given by

$$E(k)\approx\Delta+\frac{(\hbar k)^2}{2m} , \tag{3}$$

where $mc^2=\Delta$.

The spin-resonance experiment is performed in presence of a static magnetic field. The effects of a magnetic field on the $S=1$ chain have been discussed by various authors.[7,8,11] The Zeeman energies in the magnetic fields we are concerned with here are much smaller than the gap energy, so that the magnetic field is a small perturbation and will be considered as such.

For a finite chain, the ground state, with no bosonic excitations present, is split into four low-lying states corresponding to the two $S=\frac{1}{2}$ degrees of freedom at the two ends of the chain. The spin-$\frac{1}{2}$ variables interact by exchanging virtual bosons in the field-theoretic description. The singlet-triplet splitting in case of the isotropic chain is proportional to $(-1)^N\exp(-N/\xi_0)$, where ξ_0 is the correlation length in units of lattice spacing for the isotropic model, found to be about 7 in numerical simulations.[6] Because of the uniaxial anisotropy in (1), however, the decay length for exchange of an $S_z=0$ boson is shorter than that for a boson with $S_z=\pm1$, so that the exchange constants for the $S=\frac{1}{2}$ variables evidently should be highly anisotropic. To a good approximation, we may write the interaction between the two terminal spin-$\frac{1}{2}$ variables s_1 and s_2 as

$$H_{\mathrm{exch}}=(-1)^{L/a}K\exp(-L/\xi)(s_1^xs_2^x+s_1^ys_2^y) , \tag{4}$$

where $\xi=\hbar c/\Delta$. From the neutron-scattering data in Ref. 15, we may estimate ξ to be about $8a$. We assume that the preexponential factor K is an energy of order Δ, which is at least crudely consistent with the numerical data of Kennedy for the isotropic case.[6] This interaction splits and shifts the spectral line for the individual spin-$\frac{1}{2}$ variables, even at low temperatures, when there are no thermally excited bosons on the chain.

For a finite chain, the spectrum for the excited bosons becomes discrete. Moreover, an excited boson will interact with the $S=\frac{1}{2}$ variables at the end of the chain. In the absence of a detailed description of this interaction, we find it sufficient to parametrize this potential by energy-dependent phase shifts for the bosons, which depend on the spin states of the boson and the spin-$\frac{1}{2}$ variable.

We shall chiefly consider the case when the static magnetic field is along the chain axis, and the rf field is perpendicular to the axis, causing transitions for the $S=\frac{1}{2}$ variables, which gives rise to the spectrum we are interested in. Experimentally, this corresponds to the samples of $Ni(C_2H_8N_2)_2NO_2ClO_4$ doped with nonmagnetic ions, with the static field parallel to the chains, which are along the crystallographic b axis. The total S^z is still a good quantum number which classifies the states. In $Ni(C_2H_8H_2)_2NO_2ClO_4$ there is a small but finite anisotropy present in the plane perpendicular to the chain. We will neglect the effects of this anisotropy for the purposes of this paper.

III. SHORT AND INTERMEDIATE-LENGTH CHAINS

First, consider the case of very short chains or high doping. In this limit, for a fixed chain length, the line is shifted and split even at very low temperatures as a result of H_{exch}, as mentioned earlier. Since there is a distribution of the chain lengths—and the exchange constant depends exponentially on the length—this would also lead to a broadening. For small enough chain lengths, the exchange constants would be so large so as to shift the line out of the observed frequency window. In addition, the dipole-dipole interactions between the spin-$\frac{1}{2}$ variables and any unresolved hyperfine interactions will also broaden the line. Beyond a certain doping, the line would be so shifted and broad as not to be experimentally observable.

Next, we consider the case where the chain is long enough so that we can ignore the interaction of the two $S=\frac{1}{2}$ variables in the ground state, but the spectrum of any excited boson is still discrete on the scale of the observational frequency window $\Delta\omega$. Specifically, the kinetic energy of the bosons have discrete allowed values on the finite chain, whose spacing we may estimate by putting $k=\pi/L$ in (3), to be

$$\delta E \approx \varepsilon_1 \equiv \frac{(\hbar\pi)^2}{2mL^2} \ . \tag{5}$$

To get an idea of the numbers involved, we use the values of the spin-wave velocity and gap energy as measured by inelastic neutron scattering in $Ni(C_2H_8N_2)_2NO_2ClO_4$ (Ref. 15) and obtain $\delta E \approx 0.4$ K for a chain of $L=100a$. This should be compared with the frequency window in which the experiment is being carried out. In the experiments on $Ni(C_2H_8N_2)_2NO_2ClO_4$, $f=9.25$ GHz$=0.44$ K, and the observation window is of the order of $0.3f$. Thus, in chains of length 100, the transitions in which the spin $\frac{1}{2}$ flips and at the same time a boson is scattered from one allowed momentum state to another will be shifted in frequency out of the observation window. In this regime the spectral weight inside a fixed frequency window with width much smaller than δE will go down in temperature as the probability of finding a chain with no boson on it (i.e., in its ground state).

To make a more precise statement, we consider a simple model. First, we assume that the chain is long enough so that interactions between the two terminal $S=\frac{1}{2}$ variables can be neglected. The model problem is the following: At one end of an interval of length L, we place a $S=\frac{1}{2}$ variable. Inside the interval we allow a doublet of bosons to move freely (corresponding to the $S^z=\pm 1$ excited states of the chain). We shall restrict our Hilbert space to this doublet and discard the singlet from our consideration in this model, because this leads to a major simplification, as can be seen below. This assumption if presumably justified at low enough temperatures for the case of $Ni(C_2H_8N_2)_2NO_2ClO_4$. The bosons interact with the spin $\frac{1}{2}$ on one end with an interaction that we will characterize below by means of two phase shifts. We imagine that the boson simply gets reflected on the other end of the chain from a hard wall, and we constrain the boson wave function to vanish there. This assumption does not affect our final conclusions either in the intermediate- or infinite-length case.

Since there is rotational symmetry about the z axis in the original problem, the total z component of the spin, $S^z_{\mathrm{Tot}}=s^z+S^z$, is a good quantum number. The possible values of the total z component are $\frac{3}{2}$, $-\frac{3}{2}$, $\frac{1}{2}$ and $-\frac{1}{2}$. Now, if we constrain our Hilbert space to the lowest occupied doublet, then the value of S^z_{Tot} completely specifies s^z, S^z, so that these two numbers may be used to specify the eigenstates instead of S^z_{Tot}. We make the further approximation that the interaction between the boson and the spin $\frac{1}{2}$ depends only on the product s^zS^z, which can take two values $\pm\frac{1}{2}$. The wave function of a boson with wave vector k is given by

$$\psi_{\pm}(x) \approx C_{\pm}(k)\left(e^{ikx} - e^{-2i\delta_{\pm}(k)}e^{-ikx}\right) \ , \tag{6}$$

where the $\pm$ signs refer to the two signs of s^zS^z, while $C_{\pm}(k)$ is a normalization constant approximately equal to $1/\sqrt{2L}$, and $\delta_{\pm}(k)$ are phase shifts characterizing the interaction of the boson with the $S=\frac{1}{2}$ variable. In our model, $\psi_{\pm}(L)=0$, leading to an equation for the allowed values of the momenta:

$$k_{\pm}^{(n)} = \frac{n\pi}{L} - \frac{\delta_{\pm}(k_{\pm}^{(n)})}{L} \ . \tag{7}$$

In presence of a magnetic field h along the chain, the energy of the system in presence of one boson is given by

$$E = -g_{zz}^{(1)}\mu_B s^z h - g_{zz}^{(2)}\mu_B S^z h + \Delta + \frac{\hbar^2 k^2}{2m} \ . \tag{8}$$

Since we are in the limit of a dilute gas of bosons, we will neglect interactions between the bosons, so that the energy of a many-boson state is simply additive in the individual boson energies. We assume a rf field is switched on in the x direction with frequency ω, described by a perturbation Hamiltonian

$$\mathcal{H}_I = -\left(g_{xx}^{(1)}\mu_B s^x + g_{xx}^{(2)}\mu_B S^x\right)h_x \cos(\omega t) \ .$$

We will only consider the line near the resonance frequency ω_0 of the spin $\frac{1}{2}$ in the absence of the bosons and will therefore disregard in the following the S^x part of $\mathcal{H}_I$. The boson spin needs a large amount of energy to flip (because of the anisotropy), and its spectra are therefore shifted far out of the frequency window of concern. The power absorbed is related to the imaginary part of the susceptibility $I(\omega) \propto \omega\chi''_{xx}(\omega)$, which is given by the fluctuation-dissipation relation

$$2\hbar\chi''_{xx}(\omega)=(1-e^{-\beta\hbar\omega})\int_{-\infty}^{+\infty}\mathrm{Tr}[\rho s^x(t)s^x]e^{i\omega t}dt\ , \tag{9}$$

where $\rho=e^{-\beta\mathcal{H}}/Z$ and Z is the partition function of the system. We are considering temperatures sufficiently low so that $e^{-\beta\Delta}\ll 1$, in which case we may also replace $(e^{\beta\Delta}e^{\beta\varepsilon(k)}-1)^{-1}$ by $e^{-\beta\Delta}e^{-\beta\varepsilon(k)}$, where $\varepsilon(k)$ is the kinetic energy of the boson; i.e., we may consider Maxwell-Boltzman statistics instead of Bose-Einstein statistics for the excitations. In this limit the above expression can be evaluated in a closed form, since each boson acts independently of any other boson on the $S=\frac{1}{2}$ variable. We will calculate only the part of the expression corresponding to the absorption of a single quantum of energy by the $S=\frac{1}{2}$. To do this we need to calculate $\mathrm{Tr}[\rho s_+(t)s_-]$. In trace, we have to sum over different numbers of bosons. The spin-$\frac{1}{2}$ variable has two states $\pm\frac{1}{2}$. To evaluate $\mathrm{Tr}[\rho s_+(t)s_-]$, we need to consider only states in which the spin-$\frac{1}{2}$ variable starts out with $s_z=\frac{1}{2}$, because otherwise the state gets annihilated by s_-. Corresponding to the two relative orientations of the spin $\frac{1}{2}$ and the z component of the boson spin, a single boson can be described by two different Hamiltonians $H_+^{(1)}$ and $H_-^{(1)}$, which act only upon the boson. Since we are assuming that the bosons are independent, the Hamiltonians for the different bosons commute, and therefore the trace restricted to N bosons, $\mathrm{Tr}_N[\rho s_+(t)s_-]$, factorizes into a product over individual bosons, each of the terms of the product being identical. Thus we may write

$$\mathrm{Tr}_N[\rho s_+(t)s_-]=\frac{e^{\beta\hbar\omega_0/2}}{Z}e^{-i\omega_0 t}\frac{Z_1^N}{N!}[f(t)]^N\ , \tag{10}$$

where the factor $N!$ is a remnant of the Bose statistics and $\hbar\omega_0=g_{zz}^{(1)}\mu_B h$. In this expression, Z_1 is the partition function of a single boson, given by

$$Z_1=2e^{-\beta\Delta}\sum_{n=1}^{\infty}e^{-\beta\varepsilon_n}\ , \tag{11}$$

where $\varepsilon_n=n^2\varepsilon_1$ and the function $f(t)$ is given by

$$f(t)=\frac{1}{Z_1}\mathrm{Tr}_1(e^{-\beta H_+^{(1)}}e^{iH_+^{(1)}t/\hbar}e^{-iH_-^{(1)}t/\hbar}+[+\leftrightarrow-]) \tag{12}$$

$$=\frac{e^{-\beta\Delta}}{Z_1}\sum_{n,m}\left[e^{-\beta\varepsilon_+^n}\exp\left[i\frac{\varepsilon_+^n-\varepsilon_-^m}{\hbar}t\right]|\langle n,+|m,-\rangle|^2+[+\leftrightarrow-]\right]\ . \tag{13}$$

It is to be noted that $|n,+\rangle$ and $|n,-\rangle$ are the spatial wave functions for a single boson, given approximately by Eq. (6) and (7), where the + and − signs refer to the two different relative orientations of the boson spin and spin-$\frac{1}{2}$ variable. Note also that we have neglected the corrections to the energies from the phase shifts for the purposes of calculating the partition function and will also do the same in the following. We will also neglect the Zeeman energies of the bosons for purposes of calculating Boltzmann weights. Keeping the Zeeman energies would not make any significant changes in our calculations, but would make the expressions much more cumbersome. Where the corrections from the phase shifts have been kept in the energy, we use the notation $\varepsilon_\pm^n=(\hbar k_\pm^{(n)})^2/2m$. After doing the sum over the number of bosons, we finally obtain

$$\mathrm{Tr}[\rho s_+(t)s_-]=\frac{e^{\beta\hbar\omega_0/2}}{2\cosh(\beta\hbar\omega_0/2)}e^{-i\omega_0 t}e^{-Z_1(1-f(t))}\ . \tag{14}$$

The matrix elements appearing in the formula for $f(t)$ can be calculated from the real-space form in Eq. (6).

For a finite L, the Fourier transform of (14) consists of a δ function at $\omega=\omega_0$, and a set of δ functions at frequencies shifted with respect to ω_0 by the difference of the energies of the bosons in the initial and final states. To illustrate, we can expand the exponential in Eq. (14) and substitute in the susceptibility formula to obtain, for $\omega>0$,

$$2\hbar\chi''_{xx}(\omega)=\frac{1}{4}\tanh\left[\frac{\beta\hbar\omega_0}{2}\right]e^{-Z_1}2\pi\delta(\omega-\omega_0)+(1-e^{-\beta\hbar\omega})\frac{e^{\beta\hbar\omega_0/2}}{8\cosh(\beta\hbar\omega_0/2)}e^{-Z_1}$$
$$\times\sum_{n,m}\left[e^{-\beta\varepsilon_+^n}2\pi\delta\left[\omega-\omega_0+\frac{\varepsilon_+^n-\varepsilon_-^m}{\hbar}\right]|\langle n,+|m,-\rangle|^2+[+\leftrightarrow-]\right]\cdots\ , \tag{15}$$

where ⋯ denotes transitions involving states with two or more bosons.

For $T\approx 0$ nearly all the weight is in the first δ function, but as T increases, the other ones start picking up weight. If $n\neq m$, the kinetic energy change is at least of order ε_1 in notation defined above, and for a chain of length 100 in $\mathrm{Ni(C_2H_8N_2)_2NO_2ClO_4}$, we estimated this to be 0.4 K. Thus these transitions would be shifted out of the frequency window involved in the experiment. If $n=m$, i.e., the boson does not change its principle quantum number, but picks up a phase shift, then in the nth allowed state its energy changes by $2n\varepsilon_1[\delta_+(k_+^{(n)})-\delta_-(k_-^{(n)})]/\pi$ (using the formula for allowed k vectors and assuming $n\pi\gg 2\delta_\pm$). To estimate the phase shifts, we note that for a localized potential next to a reflecting wall, in the absence of a resonance, the phase shifts are linear in k for small k. Therefore, we can approximate

$$\delta_{\pm}(k)\approx D_{\pm}k\xi \; , \tag{16}$$

where $D_{\pm}$ are unknown constants of order unity. Using the parameter values given earlier $[k^{(1)}=\pi/(100a)$, $\xi\approx 8a]$, we obtain for $n=1$ the energy shift to be about 0.07 K. This can be compared with the observed linewidth in Ref. 22, which is about 100 G or about 0.01 K. It therefore seems plausible that the observed signal in these experiments comes solely from the chains with no bosons present (the line being broadened by other means). However, given the crudeness of our estimate of the phase shift and the closeness of the estimated energy shift and observed linewidth, we cannot definitely rule out a possible alternative scenario in which a few of these transitions have smaller energy shifts and contribute to the linewidth.

Let us consider the integrated intensity within a frequency window $\Delta\omega$, which is small enough so that only the line at $\omega=\omega_0$ contributes to the signal. The considerations above show that this is likely to be a meaningful way to interpret the observed intensity in the experiments in $Ni(C_2H_8N_2)_2NO_2ClO_4$ with intermediate chain lengths (e.g., $L=100a$). We are then led to a formula for the temperature dependence of the intensity for a chain of length L with no adjustable parameters (assuming that the gap and spin-wave velocity are known from neutron-scattering measurements), given by

$$I(T)=I(0)\tanh\left[\frac{\beta\hbar\omega_0}{2}\right]e^{-Z_1} \; , \tag{17}$$

where Z_1 is the partition function of a single boson as defined in Eq. (11). Using the Poisson sum formula, we obtain, for Z_1,

$$Z_1=e^{-\beta\Delta}\left[\left[\frac{\pi}{\beta\varepsilon_1}\right]^{1/2}-1 +2\left[\frac{\pi}{\beta\varepsilon_1}\right]^{1/2}\sum_{n=1}^{\infty}e^{-\pi^2 n^2/\beta\varepsilon_1}\right] . \tag{18}$$

If we use the estimate for ε_1 for $L=100$ and set $T=1$ K, the first term in the second sum is $O(\exp(-25))$. We can therefore approximate Z_1 by

$$Z_1=\left[\left[\frac{\pi}{\beta\varepsilon_1}\right]^{1/2}-1\right]e^{-\beta\Delta} = \left[\frac{L}{\pi^{1/2}\lambda_T}-1\right]e^{-\beta\Delta} \; , \tag{19}$$

$$\lambda_T\equiv\hbar c\left[\frac{\beta}{2\Delta}\right]^{1/2} . \tag{20}$$

Note that $2\pi\lambda_T$ is the de Broglie thermal wavelength of the boson.

In the experimental situation, there is a distribution of chain lengths, which one should be able to approximate by means of a Poisson distribution $P(L)\propto\exp(-L/L_0)$. Since very short chains cannot contribute to the signal, we put a lower cutoff on the distribution at some $L_{\min}$. On carrying out the average, the final formula for the intensity reads

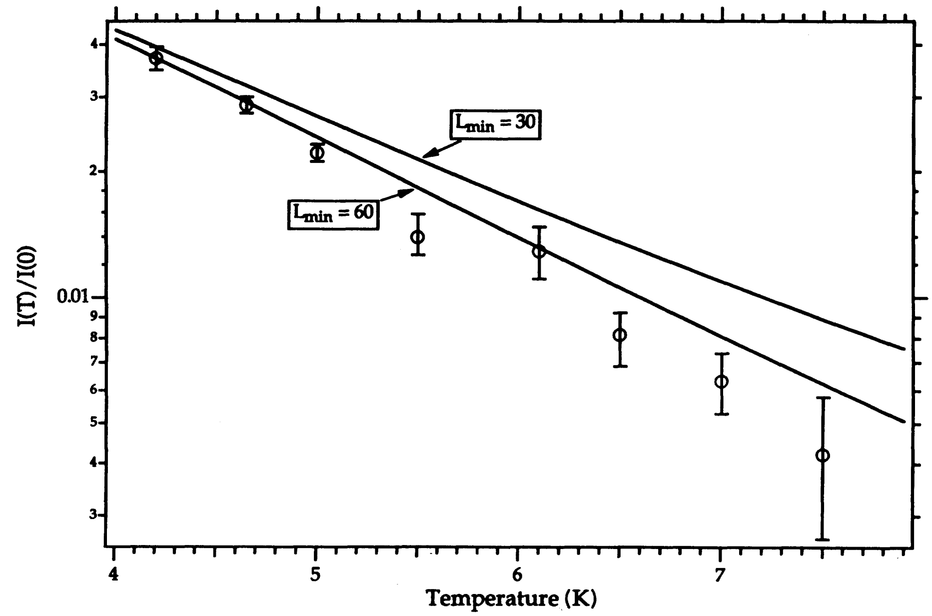

FIG. 1. Formula for the temperature dependence of the intensity for intermediate-length chains is plotted on a semilogarithmic scale against the temperature in K. The intensities are normalized to one at $T=0$. Here $L_0=143$ (corresponding to a impurity concentration of 0.7%), $L_{\min}=30,60$ for two curves as indicated, and $\omega_0=9.25$ GHz. The data points are reproduced from Fig. 3 in Ref. 21. The first datum point has been normalized to fall on the curve for $L_{\min}=60$.

$$I(T)=I(0)\tanh\left[\frac{\beta\hbar\omega_0}{2}\right]\times\frac{\exp[-(\pi^{-1/2}L_{\min}\lambda_T^{-1}-1)e^{-\beta\Delta}]}{1+\pi^{-1/2}L_0\lambda_T^{-1}e^{-\beta\Delta}}\;, \tag{21}$$

where L_0 is the average length of the chain. This temperature dependence of the intensity has been plotted in Fig. 1 for two different values of $L_{\min}$, for a fixed value of $L_0=143$, corresponding to an impurity concentration of 0.7%. It can be seen that the intensity drops sharply as a function of temperature. The curve for $L_{\min}=60$ agrees qualitatively with the data points which are reproduced from Fig. 3 in Ref. 21, although the data points fall somewhat more sharply than the theoretical curve. The first datum point has been scaled to lie on the curve for $L_{\min}=60$. A somewhat better fit (not shown here) can be achieved by using a slightly different normalization constant. The value of $L_{\min}$ to be used in this formula is somewhat arbitrary, but we may estimate it by setting the strength of the interaction (4) between the $\frac{1}{2}$ spins on the same chain to be of the order of the linewidth. If we estimate the interaction very crudely as earlier to be $\Delta\exp(-L/\xi)$, where $\Delta=14$ K, $\xi\approx 8a$, then this yields a value of 57 for $L_{\min}$ for the width $=0.01$ K.

It is to be noted that in the expression obtained above for the intermediate-length case does not depend on the phase shifts of the model, as it just counts the fraction of finite-length chains still in their ground states at temperature T. This prediction should therefore be relatively robust.

IV. INFINITE CHAIN LENGTHS

When the chain length is made larger by making the doping less, some of the lines which were shifted out of the frequency window will move into the window, making the analysis more complicated and model dependent. However, there is another simple limit for the problem, namely, $L\to\infty$, in which the line shape can be calculated in closed form. This can be done by calculating $\phi(t)=\lim_{L\to\infty}Z_1(1-f(t))$. To do this we need the matrix elements in the expression for $f(t)$ up to $O(1/L)$, as can be seen from the formula

$$Z_1(1-f(t))=e^{-\beta\Delta}\sum_{n,m}\left\{e^{-\beta\varepsilon_+^n}\left[1-\exp\left[i\frac{\varepsilon_+^n-\varepsilon_-^m}{\hbar}t\right]\right]|\langle n,+|m,-\rangle|^2+[+\leftrightarrow-]\right\}, \tag{22}$$

which follows from noting that $\sum_m\langle n,+|m,-\rangle\langle m,-|n,+\rangle=1$. The calculations are straightforward and lead to the result

$$\phi(t)=\frac{1}{\pi^2}e^{-\beta\Delta}\int_0^\infty\int_0^\infty\frac{d\varepsilon\,d\varepsilon'}{\sqrt{\varepsilon\varepsilon'}}e^{-\beta\varepsilon}\left[\frac{1-\exp\{i[(\varepsilon-\varepsilon')/\hbar]t\}}{(\varepsilon-\varepsilon')^2}\right][M(\varepsilon,\varepsilon')+M(\varepsilon',\varepsilon)]\;, \tag{23}$$

where

$$M(\varepsilon,\varepsilon')=\{(\sqrt{\varepsilon}+\sqrt{\varepsilon'})\sin([\delta_+(\varepsilon)-\delta_-(\varepsilon')]-(\sqrt{\varepsilon}-\sqrt{\varepsilon'})\sin[\delta_+(\varepsilon)+\delta_-(\varepsilon')]\}^2\;. \tag{24}$$

The real part of $\phi(t)$ is given by

$$\mathrm{Re}[\phi(t)]=\frac{2}{\pi^2}e^{-\beta\Delta}\int_0^\infty\int_0^\infty\frac{dx\,dx'}{\sqrt{xx'}}\beta e^{-x}\left[\frac{\sin[(x-x')t/\tau]}{x-x'}\right]^2\left[M\left[\frac{x}{\beta},\frac{x'}{\beta}\right]+M\left[\frac{x'}{\beta},\frac{x}{\beta}\right]\right], \tag{25}$$

where $(\tau=2\beta\hbar)$. Now we are concerned with a frequency window that is typically much smaller than the temperature (in frequency units) or, in other words, times much larger than τ. In the limit $t/\tau\gg1$, we may replace $\{\sin[(x-x')t/\tau]/(x-x')\}^2$ by $\pi(t/\tau)\delta(x-x')$, to obtain, in the limit of long times,

$$\mathrm{Re}[\phi(t)]\approx\frac{8}{\pi}|t|\frac{e^{-\beta\Delta}}{\hbar\beta}\int_0^\infty dx\,e^{-x}\sin^2\left[\delta_+\left[\frac{x}{\beta}\right]-\delta_-\left[\frac{x}{\beta}\right]\right]. \tag{26}$$

The coefficient of t in the above expression gives an estimate for the linewidth near the center of the line. We cannot proceed further unless we have some information on the phase shifts However, there is a limit in which the formula for the line shape does not depend on the details of the phase shifts. If we assume that the phase shifts in a single collision are large, so that the phase gets completely randomized after one collision, then we may approximately put $\langle\sin(\delta)\rangle=0$, $\langle\sin^2(\delta)\rangle=\frac{1}{2}$, to obtain

$$\mathrm{Re}[\phi(t)]=\frac{4e^{-\beta\Delta}}{\pi^2}\int_0^\infty\int_0^\infty\frac{dx\,dx'}{\sqrt{xx'}}e^{-x}\left[\frac{\sin[(x-x')t/\tau]}{x-x'}\right]^2(x+x')\;, \tag{27}$$

$$\mathrm{Im}[\phi(t)]=-\frac{e^{-\beta\Delta}}{\pi^2}\int_0^\infty\int_0^\infty\frac{dx\,dx'}{\sqrt{xx'}}\frac{e^{-x}-e^{-x'}}{x-x'}\frac{\sin[2(x-x')t/\tau]}{x-x'}(x+x')\;. \tag{28}$$

The integrals can be evaluated exactly to obtain

$$\mathrm{Re}[\phi(t)]=\frac{(32)^{1/2}}{\pi}\frac{|t|}{\tau}e^{-\beta\Delta}\left\{1+\left[1+\left[\frac{\tau}{2t}\right]^2\right]^{1/2}\right\}^{1/2}, \tag{29}$$

$$\mathrm{Im}[\phi(t)]=\frac{(32)^{1/2}}{\pi}\frac{t}{\tau}e^{-\beta\Delta}\left\{\left[1+\left[\frac{\tau}{2t}\right]^2\right]^{1/2}-1\right\}^{1/2}. \tag{30}$$

The corresponding line shapes (Fourier transforms of $\exp[-\phi(t)]$) are plotted in Fig. 2 for two temperatures and clearly show that the line broadens with temperature and also shifts slightly. In the experimental situation, the phase shifts are presumably not large enough for the above approximation to hold, as the temperature, and hence the kinetic energy of the bosons, is smaller than the gap energy, which presumably sets the energy scale of the interaction between the bosons and spin-$\frac{1}{2}$ variable. However, the qualitative conclusion that the line should broaden rapidly with increasing temperature should still be valid for the infinite-chain-length case.

V. DISCUSSION AND CONCLUSIONS

We have considered three regimes for the chain lengths. For very short chains, the line is split and shifted out of the frequency window or too broad to be resolved, even at very low temperatures. For intermediate-length chains, the spectrum of the bosonic excitations on the chain is discrete on the scale of observation, and one obtains a set of δ function peaks (broadened by other means) that are well separated. Only the line corresponding to chains with no excitations remains within the frequency window of observation, and its intensity goes down sharply with increasing temperature as the probability of finding such a chain decreases. For very long chains, where there is a continuous density of states for excitations above the gap, the line broadens rapidly with increasing temperature rather than remaining as a sharp line and going down in intensity. A formula for the line shape that crudely interpolates for the spectrum between the intermediate- and infinite-length cases, and is normalized to unity, is

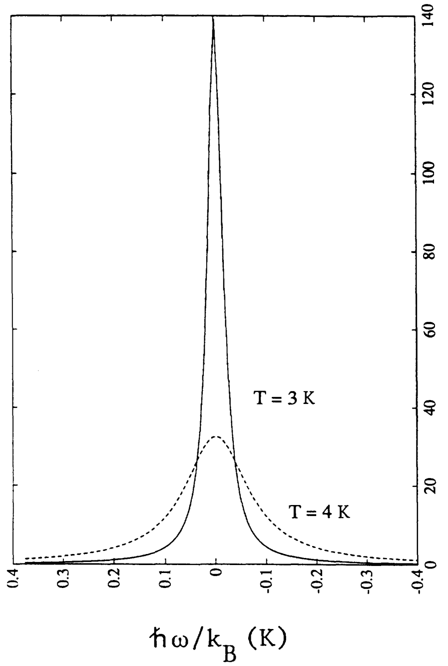

FIG 2. Fourier transform of $\exp[-\phi(t)]$ is plotted against frequency (measured in K). This gives the line shape around the center of the line for an infinite chain in the limit that the phase shifts in a single collision are large. The solid line is for 3 K and the dotted line for 4 K.

$$P(\omega)=e^{-Z_1}\delta(\omega-\omega_0)+(1-e^{-Z_1})P_\infty(\omega), \tag{31}$$

where $P_\infty(\omega)$ is the spectrum for infinite chain lengths as can be calculated from the formulas in the text. For an intermediate-length chain, at high temperatures, the second term is very broad in frequency and does not make a significant contribution in the observed window, while at low temperatures it is too weak to contribute. For very long chains, however, the first term can become small at temperatures low enough so that the second term is still very narrow. Using crude estimates based on Eqs. (21) and (29), we find that the second term of (31) can make a significant contribution to an ESR signal having an observed width of less than 0.01 K only for $T \lesssim 2.2$ K and mean chain lengths $L_0 \gtrsim 5\times10^3 a$.

In our considerations we have replaced one of the ends of the chain by a hard wall for the boson. This does not affect our calculations in the intermediate-length case, because even if we took into account both the spin variables on the two ends of the chain, a single boson would still shift the spectral line out of the observation window, and the only relevant quantity, the probability of finding a chain with no boson on it, would still be the same as in our case. For the case of very long chains, the boson would not have time to reach one end from another during the observation time, and again our considerations would be unaffected by the inclusion of a second $S=\frac{1}{2}$ variable on the other end of the chain.

We have considered only the case of the magnetic field parallel to the chain. Let us briefly discuss the case of the static magnetic field perpendicular to the chain. For intermediate-length chains, our considerations for the temperature-dependence of the intensity do not change. For the infinite-chain case, the corresponding calculation involves the knowledge of additional elements of the S matrix for the interaction between the $S=\frac{1}{2}$ and boson when the field is perpendicular to the chain axis. The calculation becomes more model dependent in this case.

However, the general conclusion that the line broadens rapidly should presumably still be valid.

We have not considered the frequency shifts of the line due to the polarization of the boson. When the magnetic field is perpendicular to the chain axis, the chain is polarized even at zero temperature, because the ground state is not an eigenstate of S_x and S_y.[11] Presumable, the $S=\frac{1}{2}$ interacts with this finite polarization so that its frequency is shifted. Since the polarization is linear in the magnetic field, such a shift would correspond to a shift of the g value for the spin $\frac{1}{2}$. Depending on the nature of the coupling, this shift in g could be either positive or negative. One intriguing aspect of the experiments in Ref. 22 is the observation of two different g values when the magnetic field is perpendicular to the chain, one of which is less than 2 (this being very uncharacteristic of the Ni^{2+} ion, which normally has a g value greater than 2). One might speculate that some consideration such as the above should be able to explain the reduced g values obtained above. However, such an explanation would fall short of explaining why two different g values are observed. It is to be noted that this multiplicity of 2 is left after taking into account the fact that there are two inequivalent chain orientations (the chains are not strictly rotationally invariant about the chain axis) when the field is perpendicular to the chain axis.

ACKNOWLEDGMENTS

The authors are grateful for very helpful discussions with S. Geschwind and K. Katsumata. This research was supported in part by NSF Grant No. DMR-88-17291 and by NSERC of Canada. One of us (P.P.M.) acknowledges support from Schlumberger-Doll Research.

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