Distribution of Magnon Modes in a Disordered Magnetic Chain*

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Numerical methods for the calculation of the frequency spectrum of the linearized magnon modes in disordered magnetic chains are outlined. The distribution for the ferromagnetic chain is obtained from the Sturm-sequence algorithm introduced by Dean in the analogous calculation for the one-dimensional crystal lattice. The distribution for the antiferromagnetic chain cannot be calculated by Dean's method. For this case the Sturm sequence obtained from the amplitudes is appropriate (Rosenstock-McGill method). Applications are made to two systems: an amorphous ferromagnetic chain, where comparison is made with the analytic theory of Montgomery, Krugler, and Stubbs, and to an antiferromagnetic chain with parameters chosen to resemble those of $Cu_xCr_{1-x}Cl_2$. The results of numerical studies on chains of 50 000 spins are reported.

I. INTRODUCTION

In recent years the discovery of compounds having magnetic properties which are characteristic of chains of spins coupled by nearest-neighbor exchange interactions has led to increased interest in one-dimensional magnets.[1] Apparently, studies of both the static and dynamic properties of magnetic chains have been limited to crystals having one species of magnetic atom. However, it may be feasible to grow crystals where some fraction of the magnetic atoms are replaced by either nonmagnetic atoms or magnetic atoms with different exchange interactions. Provided there is no interaction between magnetic atoms on different sides of the impurity, the effect of adding the nonmagnetic impurity atoms is simply to break up the long chains of magnetic atoms into chains of differing lengths. The addition of magnetic impurities leads to more complicated effects since the magnetic atoms in the chain are all in communication with one another. In this respect, the one-dimensional systems differ from those of higher dimensions. In the latter, the addition of small numbers of nonmagnetic impurities does not prevent communication between widely separated sites.

In this paper we will focus on one aspect of the properties of disordered magnetic chains, namely, the influence of disorder on the magnon spectrum. Inelastic neutron scattering studies of the linear chain antiferromagnetic $(CD_3)_4NMnCl_3$ (TMMC) have demonstrated the presence of spin waves at low temperatures.[2,3] These excitations, which are well defined as long as the wavelength is less than the correlation length associated with the staggered susceptibility, follow the sinusoidal dispersion curve characteristic of a one-dimensional antiferromagnet with nearest-neighbor, isotropic exchange interactions. As the temperature increases, the spin-wave peaks broaden and the excitations become overdamped, finally disappearing at high temperatures.

The purpose of this paper is to outline numerical procedures for the calculation of the magnon densities of states in one-dimensional ferro- and antiferromagnetic chains with nearest-neighbor interactions. The use of the formalism is illustrated by two examples, an amorphous ferromagnetic chain characterized by a fluctuating exchange interaction, and a substitutionally disordered antiferromagnetic chain resembling $Cu_xCr_{1-x}Cl_2$.

II. THEORY

In a series of remarkable papers[4-6] Dean showed how Sturm's theorem[7] could be used to calculate the phonon density of states in a one-dimensional disordered lattice with nearest-neighbor harmonic interactions. The purpose of this section is to outline how methods similar to those developed by Dean can be applied to magnetic chains.

The first step is to derive the equation of motion of the spin operators. It will be convenient to consider the ferromagnetic and antiferromagnetic cases separately. We begin with the ferromagnetic chain whose Hamiltonian is written

$$\mathcal{H} = -2\sum_{n=1}^{N-1} J_{n,n+1}\vec{S}^n \cdot \vec{S}^{n+1} - \sum_{n=1}^{N} g_n \mu_B H_A^n S_z^n \,. \tag{1}$$

Here $J_{n,n+1}$ is the exchange interaction between sites n and $n+1$, g_n is the g factor associated with the atom on the nth site, H_A^n is the anisotropy field, and $\vec{S}^n$ is the spin. The equations of motion for the operators S_+^n ($S_+ = S_x + iS_y$) are written

$$i\frac{d}{dt}S_+^n = [S_+^n, H] \,. \tag{2}$$

Assuming a ground state of the form $\Pi_n |S_z^n = S^n\rangle$ and carrying out the conventional linearization ($S_z^n \to S^n$) we obtain

$$i\frac{d}{dt}S_+^n = (g_n\mu_B H_A^n + 2J_{n,n+1}S^{n+1} + 2J_{n-1,n}S^{n-1})S_+^n - 2J_{n,n+1}S^nS_+^{n+1} - 2J_{n-1,n}S^nS_+^{n-1}. \quad (3)$$

By postulating a harmonic time dependence $e^{-i\omega t}$, Eq. (3) can be rewritten

$$\omega U_n = A_{n,n}U_n + A_{n,n+1}U_{n+1} + A_{n-1,n}U_{n-1}, \quad (4)$$

where

$$U_n = S_+^n/(S^n)^{1/2} \quad (5)$$

and

$$A_{n,n} = g_n\mu_B H_A^n + 2J_{n,n+1}S^{n+1} + 2J_{n-1,n}S^{n-1}, \quad (6)$$

$$A_{n,n+1} = -2J_{n,n+1}(S^nS^{n+1})^{1/2}, \quad (7)$$

$$A_{n-1,n} = -2J_{n-1,n}(S^{n-1}S^n)^{1/2} = A_{n,n-1}. \quad (8)$$

With the equations of motion written in the form indicated in Eqs. (4)–(8) the evaluation of the magnon frequencies reduces to the calculation of the eigenvalues of the symmetric tridiagonal matrix $\underline{A}$. At this point the problem becomes isomorphic to the calculation of the phonon frequencies, the only difference being that ω in Eq. (4) is replaced by the square of the phonon frequency. In fact if the anisotropy field is zero and all the S^n are the same, then the calculation of the magnon frequencies is identical to the calculation of the squares of the vibrational frequencies of a chain of atoms of unit mass whose force constant $\gamma_{n,n+1}$ is equal to $2J_{n,n+1}S$.

Because of this isomorphism the formalism developed by Dean can be applied directly to the ferromagnetic chain, it being necessary only to express his variables α_i and β_i (Ref. 5) in terms of tha $A_{n,m}$ in Eqs. (6)–(8). In such an analysis it should be kept in mind that the ground state has been postulated to be the state of maximum alignment. If the impurity spins are antiparallel to the majority spins the Dean formalism is not applicable. Furthermore, the magnon frequencies must be positive; negative eigenvalues are to be interpreted as an indication that the postulated ground-state alignment is incorrect.

The calculation of the frequency spectrum of the disordered antiferromagnetic chain is more complicated. The difficulties appear at two levels. First, there is the nature of the ground state, and second, there is the effect of disorder on the low-lying excited states. We will, in effect, circumvent the ground-state problem in the conventional manner. That is, we linearize the equations of motion by replacing S_z^n by $(-1)^nS^n$, having assumed that the odd-numbered spins point in the minus direction, the even-numbered in the plus direction. In the case of TMMC, where $S=\frac{5}{2}$, this procedure is believed to yield frequencies which are in good agreement with experiment. For spin $\frac{1}{2}$, the approximation is more crude. However, it does give the correct wave-vector dependence in the ordered limit; only the over-all normalization is changed (for $S=\frac{5}{2}$ the renormalization factor lies between[3] 1 and 1.1; for $S=\frac{1}{2}$ it is equal to $\frac{1}{2}\pi$).

The Hamiltonian for the antiferromagnetic chain takes the form

$$\mathcal{H} = 2\sum_{n=1}^{N-1} J_{n,n+1}\vec{S}^n\cdot\vec{S}^{n+1} - \sum_{n=1}^{N}(-1)^n g_n\mu_B H_A^n S_z^n . \quad (9)$$

After linearization the equations of motion for the S_+^n can be written

$$\frac{idS_+^n}{dt} = -[2J_{n,n+1}(-1)^{n+1}S^{n+1} + 2J_{n-1,n}(-1)^{n-1}S^{n-1} - (-1)^n g_n\mu_B H_A^n]S_+^n + 2J_{n,n+1}(-1)^n S^nS_+^{n+1} + 2J_{n-1,n}(-1)^n S^nS_+^{n-1}. \quad (10)$$

Writing $V_n = S_+^n/(S^n)^{1/2}$ and assuming a harmonic time dependence we obtain the result

$$(-1)^n\omega V_n = (g_n\mu_B H_A^n + 2J_{n,n+1}S^{n+1} + 2J_{n-1,n}S^{n-1})V_n + 2J_{n,n+1}(S^nS^{n+1})^{1/2}V_{n+1} + 2J_{n-1,n}(S^nS^{n-1})^{1/2}V_{n-1}. \quad (11)$$

The presence of the factor $(-1)^n$ on the left-hand side of Eq. (11) leads to complications. Because of it, the dynamical matrix whose eigenvalues are the magnon frequencies is no longer symmetric. As a consequence, the successive minors no longer form a Sturm sequence with the result that Dean's method is not applicable.

To circumvent this difficulty, we make use of the fact that the amplitudes V_n themselves form a Sturm sequence provided V_1 is set equal to a constant. This was first pointed out in connection with the phonon problem by Rosenstock and McGill.[6] Their analysis also applies to the solution of (11), the main criterion being that the coefficients multiplying V_{n-1} and V_{n+1} have the same sign.

In order to evaluate the distribution of magnon modes we define

$$\epsilon_n(\omega) = V_{n+1}/V_n, \quad (12)$$

and rearrange (11) to read

$$\epsilon_n(\omega) = \frac{-[g_n\mu_B H_A^n + 2J_{n,n+1}S^{n+1} + 2J_{n-1,n}S^{n-1} - (-1)^n\omega]}{2J_{n,n+1}(S^nS^{n+1})^{1/2}} - \frac{J_{n-1,n}(S^{n-1})^{1/2}}{J_{n,n+1}(S^{n+1})^{1/2}\epsilon_{n-1}(\omega)} \quad (13)$$

for $n=2, \ldots, n-1$. For $n=1$, we have (with $V_1=1$)

$$\epsilon_1(\omega)=-\frac{g_1\mu_B H_A^1+2J_{1,2}S^2+\omega}{2J_{1,2}(S^1S^2)^{1/2}}\ . \tag{14}$$

We denote the number of minus signs in the sequence $\epsilon_1, \ldots, \epsilon_n$ by $R(\omega)$. Then, according to Sturm's theorem, the Cauchy index of the function $[\epsilon_{N-1}(\omega)]^{-1}$ over the interval (ω_a, ω_b) is equal to $R(\omega_b)-R(\omega_a)$. In light of the definition of the Cauchy index,[9] we conclude that $|R(\omega_b)-R(\omega_a)|$ is the number of modes with frequencies between ω_a and ω_b in a chain subject to the boundary conditions $V_1=\text{const}$, $V_N=0$.

As with the ferromagnetic chain, the determination of the distribution of magnon modes is reduced to counting the number of minus signs in an appropriate sequence. In connection with this, it should be pointed out that the approach followed for the antiferromagnetic chain (which can also be applied to the ferromagnetic chain[10]) will only work provided the $J_{n,n+1}$ are all nonzero and have the same sign. Also, the frequencies associated with Eq. (11) occur in pairs, one positive and one negative. Imaginary frequencies are an indication that the alternate-spin alignment postulated for the ground state is incorrect.

III. APPLICATIONS

We have carried out detailed calculations of the distribution of modes in two special cases, an amorphous ferromagnetic chain, and a binary antiferromagnetic chain with parameters chosen to resemble those of $Cu_xCr_{1-x}Cl_2$. We consider the former first.

Our interest in amorphous ferromagnets stems from an analytic theory for the density of states in these systems which has been developed by Montgomery, Krugler, and Stubbs (MKS).[11] In their model, the exchange interaction between nearest-neighbor pairs is postulated to be a random function characterized by a mean value and the dispersion about the mean. In one dimension, their approach leads to the result that the density of states $\rho(\omega)$ can be written

$$\rho(\omega)=\frac{N}{2\pi^2}\,\mathrm{Im}\lim_{\epsilon\to 0}\int_{-\pi}^{\pi}dx \times[\omega-i\epsilon-4S\,\mathcal{J}(\omega-i\epsilon)(1-\cos x)]^{-1} \tag{15}$$

for an isotropic exchange interaction. The frequency-dependent effective exchange integral $\mathcal{J}(\omega)$ has the form

$$\mathcal{J}(\omega)=\bar{J}+\Delta(\omega G_0(\omega)-1)/2\bar{J}, \tag{16}$$

where $\bar{J}$ is the mean exchange interaction and

$$\Delta=\langle(J-\bar{J})^2\rangle_{\mathrm{av}}\ . \tag{17}$$

The function $G_0(\omega)$ is the Fourier transform of the spin autocorrelation function for the ordered chain with exchange interaction $\bar{J}$:

$$G_0(\omega)=[(\omega-4\bar{J}S)^2-16\bar{J}^2S^2]^{-1/2}. \tag{18}$$

In order to test the validity of the MKS theory in one dimension, we have undertaken a numerical calculation of the density of states of a ferromagnetic chain of identical spins and zero anisotropy. The exchange integrals were chosen to be of the form

$$J_{n,n+1}=\bar{J}(1-\tfrac{1}{2}B+\tfrac{1}{2}BY)\ , \tag{19}$$

where Y is a random number between zero and one, and $|B|<2$. For this model we have

$$\Delta=\tfrac{1}{12}\bar{J}^2B^2. \tag{20}$$

The results of a numerical calculation based on the Dean algorithm are shown in Fig. 1 for the case $B=1$. The calculations were carried out for a chain of 50 000 spins. On the same graph, we have also plotted the upper-half of the distribution of modes for the ordered chain. It is seen that the effect of disorder is to round out the singularity at the high-frequency end of the spectrum. Although not apparent in the drawing, there is also a slight enhancement in the distribution at low

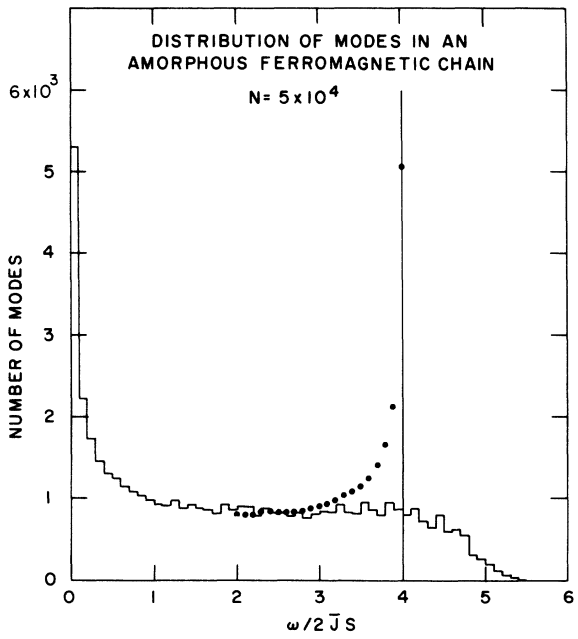

FIG. 1. Histogram of the distribution of magnon modes in an amorphous ferromagnetic chain of 50 000 spins. Shown is the number of modes with frequencies between $\omega-0.2\,\bar{J}S$ and ω. The exchange integral is postulated to vary as $\bar{J}(1-\frac{1}{2}+\frac{1}{2}Y)$, where Y is a random number between zero and one. The upper-half ($\omega\geq 4\bar{J}S$) of the distribution of modes in the ordered chain is indicated by the dotted curve.

frequencies.

In Fig. 2, we have plotted the distribution of modes obtained from the MKS theory with $\Delta = \frac{1}{12}\bar{J}^2$. It is evident that the analtyical approach leads to a density of states which is qualitatively correct, apart from the singularity at the high-frequency end. This singularity, which is a special feature of one dimension, comes about because $\mathcal{J}(\omega)$ is real for $\omega > 8\bar{J}S$. From this we conclude that the MKS expression is a fairly reasonable "first approximation" provided the artificial singularity is smoothed out.

The second application is to an antiferromagnetic chain with the properties similar to the (hypothetical) compound $Cu_xCr_{1-x}Cl_2$. In spite of the fact that it is a quasi-one-dimensional magnet, it is the only system we are aware of where both solvent-solvent and solute-solute exchange integrals are known.[1] According to Ref. 1, we have

$$J_{Cu\text{-}Cu} \simeq 60\,\mathrm{K}, \quad S^{Cu} = \tfrac{1}{2},$$

$$J_{Cr\text{-}Cr} \simeq 6\,\mathrm{K}, \quad S^{Cr} = 2.$$

We approximate $J_{Cu\text{-}Cr}$ by the geometric mean of $J_{Cu\text{-}Cu}$ and $J_{Cr\text{-}Cr}$, i.e.,

$$J_{Cu\text{-}Cr} = (J_{Cu\text{-}Cu}J_{Cr\text{-}Cr})^{1/2} = 19\,\mathrm{K}.$$

We have carried out calculations of the distribution of modes in a chain of 50 000 spins for various values of x between zero and one. Our results for $x = 0.1$, 0.5, and 0.9 are shown in Fig. 3. In compiling the data, we have followed the customary interpretation for negative eigenvalues and have added together the number of modes in the frequency interval $\omega - \Delta\omega \le u \le \omega$ and $-\omega \le u \le -\omega + \Delta\omega$, where $\Delta\omega = 4\,\mathrm{K}$. Particularly interesting here are the data for $x = 0.1$. The modes lying above the Cr band are localized modes associated with Cu impurities. Detailed calculations on chains of 80 spins show that the modes with energies between 136 and 140 K arise from isolated Cu atoms. Their frequency is approximately equal to the precession frequency in the exchange field associated with the two nearest-neighbor Cr atoms. The modes near 114 K come from Cu-Cu pairs, while the modes near 128 and 146 K are associated with Cu-Cr-Cu triplets. The degree of localization is indicated by the fact that more than one Cr atom between a pair of Cu atoms effectively isolates the Cu atoms

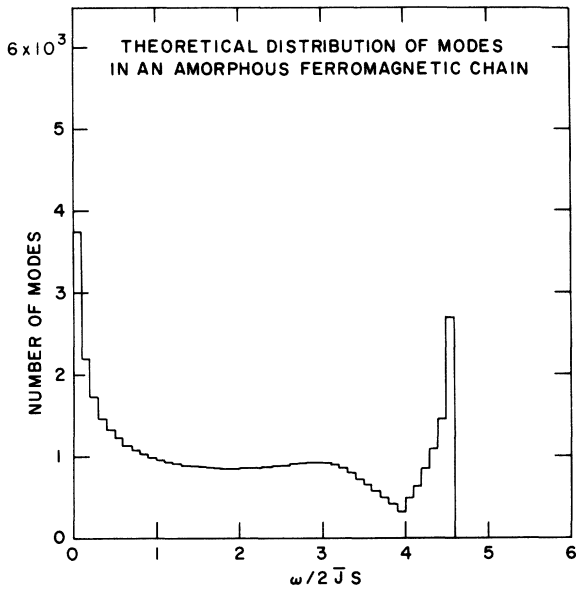

FIG. 2. Histogram of the distribution of magnon modes in an amorphous ferromagnetic chain of 50 000 spins according to the theory of Montgomery, Krugler, and Stubbs (Ref. 11). The number of modes with frequencies between $\omega = 0.2\,\bar{J}S$ and ω for $\Delta = \frac{1}{12}\bar{J}^2$ are shown. The histogram was obtained by calculating the theoretical density of states at the points $\omega/2\bar{J}S = 0.05 + 0.1n$, $n = 0, 1, 2, \ldots$, and multiplying the result by 0.1.

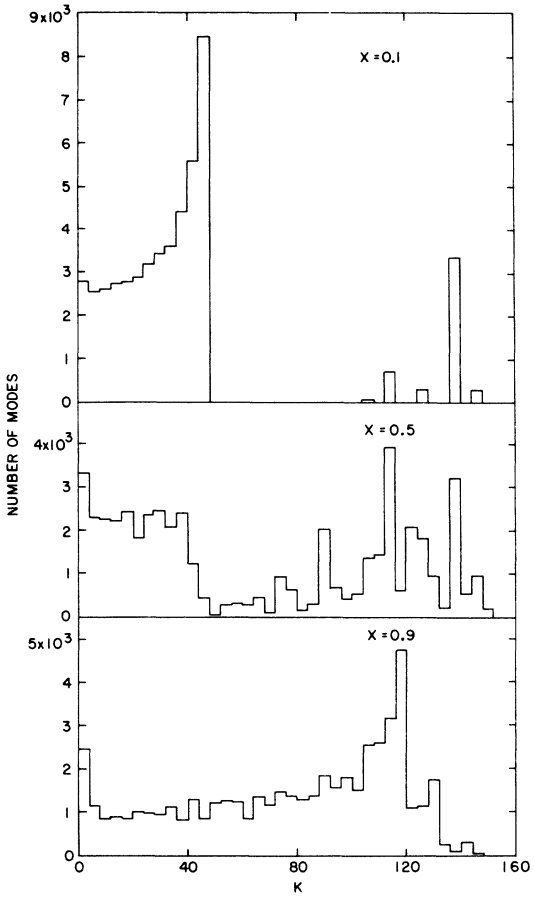

FIG. 3. Histogram of the distribution of magnon modes in $Cu_xCr_{1-x}Cl_2$. Shown is the number of modes with frequencies between ω and $\omega - 4\,\kappa$ in a chain of 50 000 spins for $x = 0.1$, 0.5, and 0.9. Frequencies are measured in K.

from one another leading to two modes with frequencies near 138 K. As the concentration of Cu atoms is increased, more and more modes appear above the Cr band until at $x = 0.9$ the spectrum resembles the Cu density of states with some tailing up to energies on the order of 150 K.

It must be emphasized that our results are obtained with a particular choice of $J_{\text{Cu-Cr}}$. Other choices will lead to quantitatively different distributions. A second point is that the Cu ion has $S = \frac{1}{2}$. As noted above, the linearization in the case of spin $\frac{1}{2}$ is a particularly crude approximation. Even with the correct exchange integrals, the theory may be only qualitatively correct.

IV. DISCUSSION

The purpose of this paper has been to outline methods for the calculation of the magnon density of states in one-dimensional lattices with nearest-neighbor interactions. Apart from the linearization of the equations of motion, the calculations are exact. No further approximations are needed to handle the effects of disorder. Since calculations involving 10^4–10^5 spins are easily handled by a computer, it is possible to simulate the behavior of real systems with great accuracy. This suggests one application, namely, the testing of approximate analytic theories for the density of states in disordered compounds. Such tests are particularly valuable for theories attempting to characterize the behavior of amorphous (as opposed to substitutionally disordered) magnets. The preparation of samples of high quality is often impossible for these systems, making comparison between experiment and theory difficult.

A second area of potential application is in the study of the excitations in real chains with small numbers of impurities. The numerical studies can be of help in identifying the local magnon modes and inferring the strength of the solvent-solute exchange interactions. In connection with this, further theoretical work is needed. Quantitative estimates of the renormalization of the local-mode frequencies would be particularly valuable.

In their studies of the vibrational spectra of disordered lattices Dean and Bacon[12] have shown how Sturm sequence methods can be generalized to two- and three-dimensional lattices. Subsequently, Payton and Visscher have carried out extensive calculations using the Dean-Bacon approach.[13] From the discussion in Sec. II, it is evident that the methods of Dean and Bacon can be applied to the calculation of magnon spectra in disordered two- and three-dimensional ferromagnets.

As a final comment, we would like to point out that considerable theoretical effort has gone into the calculation of phonon distributions in disordered chains.[14] For the most part, these calculations are somewhat artificial since they assume nearest-neighbor interactions. Moreover, in the case of isotopic disorder, the effects associated with realistic changes in the mass are small. On the other hand, magnetic chains do not suffer from either of these drawbacks. The interactions are short range and the relative changes in parameters associated with the impurity are usually large. It is hoped that the possibility of establishing a meeting ground between experiment and theory will stimulate efforts to grow the disordered crystals and study their excitations.

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[10] For the ferromagnetic chain, we have

$$\epsilon_n(\omega) = \frac{g_n \mu_B H_A^n + 2J_{n,n+1} S^{n+1} + 2J_{n-1,n} S^{n-1} - \omega}{2J_{n,n+1} (S^n S^{n+1})^{1/2}} - \frac{J_{n-1,n} (S^{n-1})^{1/2}}{J_{n,n+1} (S^{n+1})^{1/2} \epsilon_{n-1}(\omega)}, \quad n \geq 2$$

$$\epsilon_1 = \frac{g_1 \mu_B H_A^1 + 2J_{1,2} S^2 - \omega}{2J_{1,2} (S^1 S^2)^{1/2}} .$$

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