Bound-Magnon Dominance of the Magnetic Susceptibility of the One-Dimensional Heisenberg $S=\frac{1}{2}$ Ferromagnet Cyclohexylammonium Trichlorocuprate(II)

Donald N. Haines and John E. Drumheller
Physics Department, Montana State University, Bozeman, Montana 59717
(Received 12 January 1987)

In order to compare linear spin-wave theory with the effects of nonlinear excitations in spin-$\frac{1}{2}$ Ising-Heisenberg ferromagnetic chains, we have studied the differential susceptibility of $(C_6H_{11}NH_3)CuCl_3$ in the region 4.2 K $< T <$ 40 K, in fields of 0, 1, 2, and 3 T. The data are analyzed in terms of linear spin-wave theory and a nonlinear theory which includes bound-magnon effects. Our analysis shows that linear spin-wave theory cannot describe the data, and that the susceptibility is dominated by the bound-magnon contribution. The correspondence between bound magnons and solitons is discussed.

PACS numbers: 75.10.Jm, 75.30.Ds, 75.50.Dd

The detailed theoretical analyses of quantum spin chains which have appeared during the past ten years[1-6] cast serious doubt on the validity of linear spin-wave (SW) theory in one-dimensional (1D) magnets.[2,3] Although very successful in describing the properties of a wide variety of higher-dimensional systems, current theoretical understanding in 1D indicates that the basic assumptions intrinsic to SW theory may be flawed, creating questions about its applicability in certain 2D and 3D systems. For the quantum limit of spin-$\frac{1}{2}$ ($S=\frac{1}{2}$) theoretical analysis of the Heisenberg chain with various anisotropies is largely complete,[1-6] and shows an unusual complex behavior caused by bound SW states, also called bound magnons (BM's), whose energy levels lie below the SW continuum. In many cases analytic calculations predict that the static and dynamic properties are controlled almost entirely by BM's. Our own earlier numerical results, based on the work of Johnson and Bonner,[4] indicate that BM's totally dominate SW's in determining the thermodynamics of the nearly Heisenberg limit of the $S=\frac{1}{2}$, 1D, Ising-Heisenberg ferromagnet ($S=\frac{1}{2}$, 1D, HIF).[7] The importance of BM's is further expanded in light of continued interest in magnetic solitons and recent work dealing with quantum corrections to the classical models.[8-10] A close correspondence has been shown to exist between BM's in quantum spin chains and the classical spin solitons predicted by the sine-Gordon and other soliton models.[11,12] In this Letter we present experimental data which clearly show the existence of BM's in the nearly Heisenberg limit of the $S=\frac{1}{2}$, 1D, HIF, and unambiguously demonstrates that SW theory does not provide an adequate description of the thermodynamics of this system.

Despite the relevance of theories for $S=\frac{1}{2}$ chains, there have been surprisingly few experimental investigations of the analytical predictions, and all of these have concentrated on spectroscopic measurement of BM energy levels, mostly in Ising systems. Bound magnons were first observed by Torrance and Tinkham[13] using far-infrared absorption to measure the first five BM energy levels in the $S=\frac{1}{2}$ quasi 1D Ising ferromagnet $CoCl_2 \cdot 2H_2O$. Other studies using infrared absorption and ESR to measure the energy levels have since been done, not only in $CoCl_2 \cdot 2H_2O$,[14] but also in the $S=\frac{1}{2}$ Ising chain ferromagnets $CoBr_2 \cdot 2H_2O$,[15] $RbFeCl_3 \cdot 2H_2O$,[16] $CoCl_2(NC_5H_5)_2$,[17] and in the $S=\frac{1}{2}$ Ising antiferromagnet $RbCoCl_3 \cdot 2H_2O$.[18] For the more interesting case of isotropic systems, we are aware of only one experimental investigation. Hoogerbeets *et al.*[19] have used ESR to measure the energies of the first seven BM levels in the $S=\frac{1}{2}$ nearly Heisenberg ferromagnetic chain compound $(C_6H_{11}NH_3)CuCl_3$ [cyclohexylammonium trichlorocuprate (II) (CHAC)].[20-22] Until now there has been no experimental study of the effects of BM's on thermodynamic properties.

In order to investigate the effects of BM's on the magnetic susceptibility of quantum spin chains we have measured the differential susceptibility of CHAC as a function of temperature from 4.2 to 40 K in magnetic fields of 0, 1, 2, and 3 T, and fitted our data to the Johnson and Bonner[4] (JB) theory for the $S=\frac{1}{2}$, 1D, HIF. The data and theoretical fits are plotted as χ vs T in Figs. 1(a)–1(d), with data points shown as solid circles and fits to JB theory shown as solid lines. Relative errors in these measurements are less than or equal to the circle radius, and theoretical fits are visual best fits. Also shown, as dashed lines in Figs. 1(b)–1(d), are the JB theory BM and SW contributions to the susceptibility. It is immediately apparent that JB theory semiquantitatively fits the data, confirming the existence of BM's in CHAC. Further, it is clear that BM's dominate the susceptibility and that SW excitation alone cannot account for the observed values.

The sample consisted of 70.0 mg of CHAC powder in a frozen mineral-oil matrix. Differential susceptibility measurements were performed with use of a mutual-inductance bridge which utilizes a SQUID as a null detector. The amplitude of the excitation field used was less than 0.25 Oe, and its frequency was 80 Hz. No re-

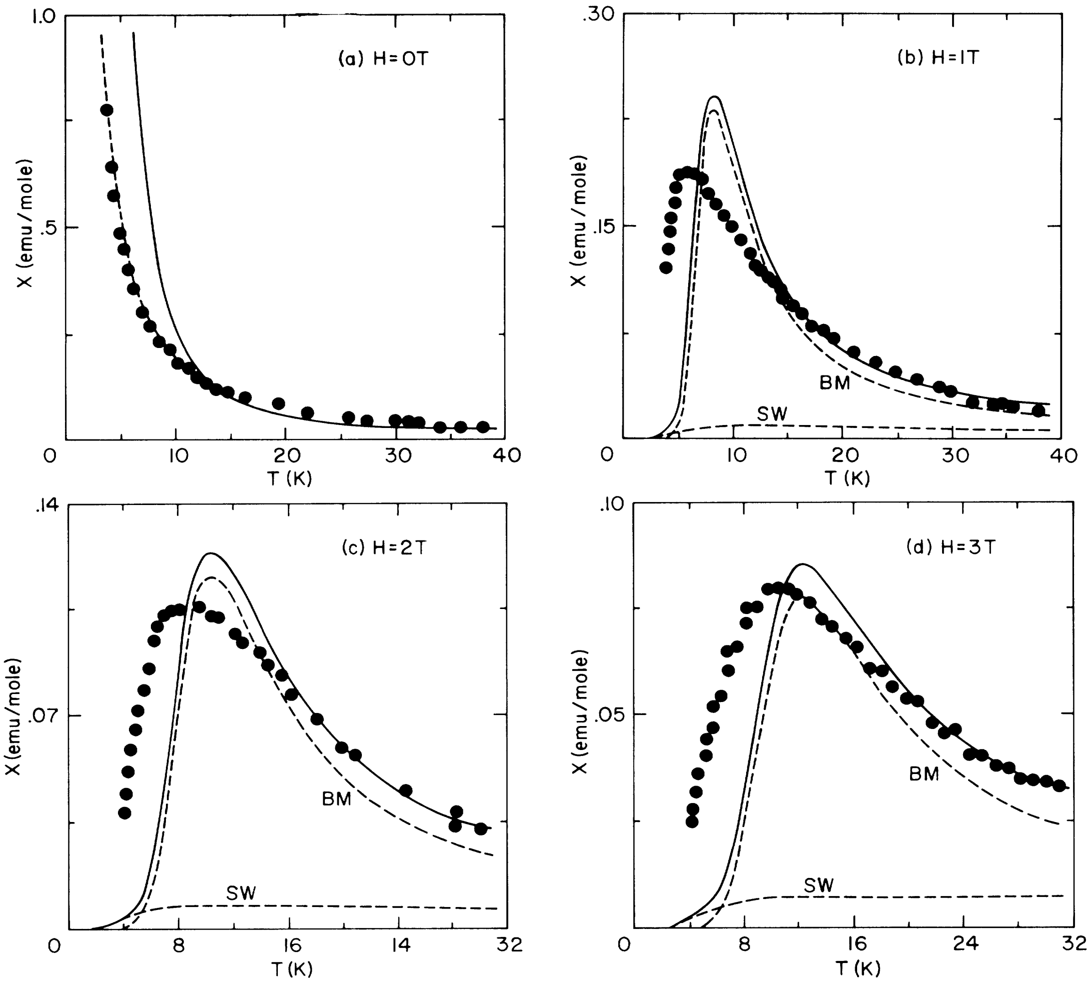

FIG. 1. Differential magnetic susceptibility of CHAC powder vs temperature in fields of 0, 1, 2, and 3 T. Data are indicated by circles, theoretical fits by lines. Solid lines are the Johnson and Bonner susceptibility for $J/k = 78$ K, $\gamma = 0.973$, $g = 2.15$. (a) $H = 0$ T. Dashed line is the Baker *et al.* HTSE susceptibility for $J/k = 55$ K, $g = 2.15$. (b)–(d) $H = 1$ T to $H = 3$ T. Dashed lines are the bound-magnon (BM) and the spin-wave (SW) contributions to the Johnson and Bonner susceptibility, for the same parameters as the total susceptibility.

laxation effects were observed. Although use of a single-crystal sample would have made interpretation of the data more straightforward, the powder clearly displayed the predicted behavior, and a sufficiently large single crystal was not available at the time when the experiments were done. Diamagnetism and temperature-independent paramagnetism in CHAC[20] are more than 2 orders of magnitude smaller than the total susceptibility in this temperature range, and nearly cancel each other, so that corrections for these effects were unnecessary. Measured susceptibilities were small, and the calibration standard was approximately the same shape as the sample, so that no correction for demagnetization was required. Crystallographic and magnetic structure studies of CHAC[20,21] have established it as one of the best $S = \frac{1}{2}$, quasi 1D, nearly Heisenberg ferromagnets currently available, and as a reasonable model compound for use in experimental studies. Ferromagnetic resonance measurements by Phaff *et al.*[22] show a small transverse component in the exchange anisotropy of CHAC, but the analysis by Hoogerbeets *et al.*[19] indicates that the $S = \frac{1}{2}$, 1D, HIF model still provides a good representation of this compound's behavior.

The $S = \frac{1}{2}$, 1D, HIF Hamiltonian is given by

$$H = -2J \sum_i [S_i^z S_{i+1}^z - \tfrac{1}{4} + \gamma(S_i^x S_{i+1}^x + S_i^y S_{i+1}^y)] - g\mu_B H_p \sum_i S_i^z,$$

where J is the exchange energy, γ is the anisotropy parameter, and H_p is the (physical) magnetic field. The anisotropy parameter varies from $\gamma=1$ (Heisenberg model) to $\gamma=0$ (Ising model). Using a thermodynamic Bethe-Ansatz integral-equation formulation,[23] JB[4] calculate the low-temperature asymptotic forms of the susceptibility and specific heat. For the susceptibility they find

$$\chi \simeq T_0^2 \exp[-(\Delta^2-1)^{1/2}/T_0](4\{H_0^2/4+T_0^2\exp[-(\Delta^2-1)^{1/2}/T_0]\}^{3/2})^{-1}+(2\pi T_0)^{-1/2}\exp[-(\Delta+H_0-1)/T_0]$$

valid for $\Delta=1/\gamma>1$ and $T_0 \ll 1$. The dimensionless field and temperature (H_0, T_0) are given in terms of the physical field and temperature (H_p, T_p), the exchange energy J, and the anisotropy parameter γ: $H_0=g\mu_B H_p/2\gamma J$, $T_0=kT_p/2\gamma J$. Parameter values for the JB susceptibility curves shown in Figs. 1(a)–1(d), including the BM and SW susceptibilities in Figs. 1(b)–1(d), are $J/k=78$ K and $\gamma=0.973$, with the same values used for all fields. Previous studies[20] have determined the average (powder) g to be 2.15, and this value was used for all fits. For these parameters $T_0=(0.00659\ \mathrm{K}^{-1})T_p$, and $H_0=(0.00951/T)H_p$, which gives $0.028<T_0<0.26$ and $0<H_0<0.029$ as the dimensionless temperature and field ranges in our data.

The second term of the JB susceptibility is due to SW's, single spin flips in a ferromagnetic chain; the first results from BM's, two or more reversed spins lying on adjacent lattice sites. Spins within a reversed block of spins will interact ferromagnetically, thereby lowering the energy of the chain and giving rise to a state whose energy lies below bottom of the corresponding SW continuum. JB theory predicts that the effective excitation gap, determined by all possible configurations of spin reversals, is a function of anisotropy, field, and temperature. Depending on the values of (H_0, T_0, γ) the effective gap will be governed by either SW's or BM's, and a complex set of crossovers between these two types of behaviors exists for both specific heat and susceptibility. For nearly isotropic systems there are two crossovers, one from BM to SW domination at low field, and one from SW back to BM domination at high field.[7] Low-field crossovers are shown in Figs. 1(b)–1(d) as the intersections of the BM and SW susceptibility curves.

Since the JB exchange and anisotropy ($J/k=78$ K, 2.7%) are larger than the values reported in earlier studies of CHAC[20–22] ($J/k=45$–70 K, 1%–2%), we have fitted our zero-field data with the Baker-Rushbrooke-Gilbert[24] (BRG) Padé-approximant high-temperature series expansion for the Heisenberg chain, as was done in the previous susceptibility study. The resulting fit for $J/k=55$ K and $g=2.15$ is shown as a dashed line in Fig. 1(a). Correlation of this fit to the data is reasonably good, better than that found with JB theory. However, the fit and parameters obtained from BRG must be viewed with caution, since the high-temperature series expansion is strictly applicable only for $J/2kT \ll 1$, and its accuracy depends on the number of Padé approximants used. More importantly, BRG assume a Heisenberg chain and do not include effects due to anisotropy, whereas all theoretical studies of $S=\frac{1}{2}$ anisotropic chains indicate that a small change in anisotropy dramatically affects thermodynamic properties.

In order to compare the JB susceptibility to our data, we first attempted to fit the theory to the peaks in the high-field data, and this analysis gave $J/k=70$ K, $\gamma=0.985$. Correspondence was reasonably good at low temperatures, but the JB peaks were substantially narrower than the peaks in the data, causing all of the data above the peak temperatures to fall significantly off the theoretical curves. To partially normalize peak broadening caused by the powder sample we next fit the JB theory to the data at high temperature, where the measured powder susceptibility and the easy-axis susceptibility are nearly equal. These fits are the ones shown in the figures.

The magnitude of our data is smaller than predicted by JB theory because the measured susceptibility of a powder consists of an average of easy- and hard-axis single-crystal susceptibilities. Also, since crystals with a hard axis oriented along the applied field saturate at a lower temperature than crystals with their easy axis oriented along the field, peaks in the high-field data are broader and occur at a lower temperature than the peaks in the JB theory.

It is clear from the figures that the JB susceptibility expression fits the data satisfactorily, confirming that BM's exist in the $S=\frac{1}{2}$, 1D, HIF. Considering the correspondence which has been established between BM's and solitons as well as the study of Hoogerbeets *et al.*,[19] who were able to fit the first few BM energy levels to an envelope soliton model, our results can be taken as indirect verification of the existence of solitons in this class of quantum spin chains. The relationship between quantum-spin-chain thermodynamics and classical soliton thermodynamics has been studied extensively by Fowler and co-workers (see Ref. 10 and references therein). Most recently, they have used a thermodynamic Bethe-*Ansatz* integral-equation formulation (similar to that used by JB) to calculate the free energy of the sine-Gordon model in the classical limit, and find good agreement with classical transfer integral results, lending further support to the identification of BM's with solitons. A detailed comparison of our data to an appropriate soliton model would provide a more direct proof of the existence of solitons in CHAC.

In addition, the data show that SW theory fails in $S=\frac{1}{2}$, 1D, HIF systems. In Fig. 1(a), for $H=0$ T, the SW susceptibility curve cannot be distinguished from the temperature axis. For the higher-field curves displayed in Figs. 1(b)–1(d) the SW term is quite small, and has only a broad, weak maximum. The SW susceptibility is qualitatively different from the data, and cannot be made to fit for any values of the parameters. On the basis of the data for CHAC, the failure of SW theory would seem to be due not to excitation of too many SW's, as is commonly assumed in 1D, but rather due to the presence of BM's, which are the nonlinear excitations resulting from anharmonic terms in the Hamiltonian. This conclusion is supported by the work of Taylor and Müller,[2] who find that SW theory does not correctly give the $T=0$ dynamic structure factor of certain 1D systems which are ordered at $T=0$. Therefore, it would seem that SW theory should be suspect in any system for which BM's determine the effective excitation gap. The exact analyses by Wortis and co-workers[25] and Hanus[26] (for the two-magnon state) indicate that BM's are mostly limited to large wave numbers in 3D, but that they do exist across the whole Brillouin zone in 2D, and can also be present at zero momentum in 3D if there is sufficient Ising anisotropy. Finally, we note that although SW theory is exact for $S \rightarrow \infty$, the Haldane conjecture,[27] which predicts that half-integer and integer spin chains have drastically different $T=0$ phase behavior, indicates that the approach to the classical limit may be unexpectedly complicated.[3]

The authors are grateful to Professor J. C. Bonner for helpful discussions during preparation of the manuscript. This work was supported by National Science Foundation Grant No. DMR-84-03993.

[1]J. C. Bonner, H. W. J. Blöte, H. Beck, and G. Müller, in *Physics in One Dimension,* edited by J. Bernasconi and T. Schneider (Springer-Verlag, Berlin, 1981).

[2]J. H. Taylor and G. Müller, Phys. Rev. B **28**, 1529 (1983).

[3]J. B. Parkinson and J. C. Bonner, Phys. Rev. B **32**, 4703 (1985). This paper deals primarily with the Haldane conjecture, but contains a short review of $S=\frac{1}{2}$ results and discusses limitations of SW theory.

[4]J. D. Johnson and J. C. Bonner, Phys. Rev. B **22**, 251 (1980).

[5]J. D. Johnson, J. Appl. Phys. **52**, 1991 (1981).

[6]M. Takahashi, Phys. Rev. Lett. **58**, 168 (1987), and references therein.

[7]D. N. Haines, M. Benacquista, and J. E. Drumheller, J. Magn. Magn. Mater. **54–57**, 1145 (1986).

[8]A. M. C. Tinus, W. J. M. de Jonge, and K. Kopinga, Phys. Rev. B **32**, 3154 (1985).

[9]M. D. Johnson and N. F. Wright, Phys. Rev. B **32**, 5798 (1985).

[10]M. D. Johnson, Niu-Niu Chen, and M. Fowler, Phys. Rev. B **34**, 7851 (1986).

[11]H. R. Jauslin and T. Schneider, Phys. Rev. B **26**, 5153 (1982), and references therein.

[12]F. D. M. Haldane, J. Phys. C **15**, L831, L1309 (1982), and references therein.

[13]J. B. Torrance, Jr., and M. Tinkham, Phys. Rev. **187**, 595 (1969).

[14]D. F. Nicoli and M. Tinkham, Phys. Rev. B **9**, 3126 (1974).

[15]J. B. Torrance and K. A. Hay, Phys. Rev. Lett. **31**, 163 (1973).

[16]Q. A. G. van Vlimmeren, C. H. W. Swüste, W. J. M. de Jonge, M. J. H. van der Steeg, J. H. M. Stoelinga, and P. Wyder, Phys. Rev. B **21**, 3005 (1980).

[17]L. A. Bosch, G. J. P. M. Lauwers, K. Kopinga, C. van der Steen, and W. J. M. de Jonge, J. Phys. C **20**, 609 (1987).

[18]E. J. Nijhof, H. van der Vlist, J. A. Puértolas, and G. J. Gerritsma, Phys. Rev. B **33**, 4854 (1986).

[19]R. Hoogerbeets, A. J. van Duyneveldt, A. C. Phaff, C. H. W. Swüste, and W. J. M. de Jonge, J. Phys. C **17**, 2595 (1984).

[20]H. A. Groenendijk, H. W. Blöte, A. J. van Duyneveldt, R. M. Gaura, C. P. Landee, and R. D. Willett, Physica (Amsterdam) **106B**, 47 (1981).

[21]K. Kopinga, A. M. C. Tinus, and W. J. M. de Jonge, Phys. Rev. B **25**, 4685 (1982).

[22]A. C. Phaff, C. H. W. Swüste, W. J. M. de Jonge, R. Hoogerbeets, and A. J. van Duyneveldt, J. Phys. C **17**, 2583 (1984).

[23]M. Gaudin, Phys. Rev. Lett. **26**, 1301 (1971).

[24]G. A. Baker, Jr., G. S. Rushbrooke, and H. E. Gilbert, Phys. Rev. **135**, A1272 (1964).

[25]M. Wortis, Phys. Rev. **132**, 85 (1963); N. Fukuda and M. Wortis, J. Phys. Chem. Solids **24**, 1675 (1963); M. Wortis, Phys. Rev. **138**, A1126 (1965).

[26]J. G. Hanus, Phys. Rev. Lett. **11**, 336 (1963).

[27]F. D. M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983).