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Biquadratic exchange from susceptibility data in classical one-dimensional Heisenberg systems

B. D. Gaulin and M. F. Collins
Physics Department, McMaster University, Hamilton, Ontario L8S 4M1, Canada

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We have investigated the magnetic susceptibility of three quasiclassical one-dimensional magnetic systems, $CsMnBr_3$, $(CH_3)_4NMnCl_3$ (TMMC), and $CH_3NH_3MnCl_3{\cdot}2H_2O$ (MMC), in their paramagnetic regimes. We find that a previous analysis in terms of a classical Heisenberg Hamiltonian does not provide an adequate description of the data at low temperatures where short-range correlations are high. We show that approximate quantum-mechanical corrections to this exact treatment do not account for the discrepancies systematically. A classical treatment which includes exchange interactions biquadratic in the spins is applied to this problem, resulting in a marked improvement of the description of experiments by theory at all temperatures. We include weak dipolar terms in the Hamiltonian, in addition to both bilinear and biquadratic exchange terms, for the case of $CsMnBr_3$ by means of a Monte Carlo simulation. To within the quoted accuracy, the simulation describes the susceptibility completely for the temperature range considered. Our results show that the strength of the biquadratic exchange interactions, relative to the strength of the bilinear interactions, is strongest in MMC and weakest in TMMC, but that the absolute magnitude is greatest for $CsMnBr_3$. Quantitatively, we find that our calculations produce a biquadratic exchange strength for $CsMnBr_3$ which is in agreement with neutron spectroscopic measurements of transition energies in Mn^{2+} linear triads.

I. INTRODUCTION

The interaction between S-state magnetic moments in solids is most often represented by the Heisenberg Hamiltonian, which is bilinear in spin operators. This provides a reasonably good description of many magnetic systems; however, it has long been realized that the Hamiltonian should contain terms of higher order in the spin operators. The physical origin of these higher-order terms is twofold. They have been shown to be present as a direct consequence of the superexchange mechanism.[1] In addition, and what is believed to be more important, is the fact that any magnetostrictive system with a bilinear Heisenberg interaction between spins and a Hooke's-law—type interaction between atoms can be represented by a Hamiltonian with an effective interaction biquadratic in spin operators.[2,3]

To see this, consider the Hamiltonian

$$H=k(a-a_0)^2-2\left[J_0+\frac{\partial J}{\partial a}(a-a_0)\right]\mathbf{S}_i\cdot\mathbf{S}_j \tag{1}$$

for two spins $\mathbf{S}_i$ and $\mathbf{S}_j$ separated by a distance a. Minimizing the Hamiltonian with respect to the separation distance a, between the spins we get

$$\frac{\partial H}{\partial a}=0=2k(a-a_0)-2\frac{\partial J}{\partial a}\mathbf{S}_i\cdot\mathbf{S}_j\ ,$$

which gives

$$a-a_0=k^{-1}\frac{\partial J}{\partial a}\mathbf{S}_i\cdot\mathbf{S}_j\ ,$$

and replacing this in the Hamiltonian (1) gives

$$H=-2J_0\mathbf{S}_i\cdot\mathbf{S}_j-k^{-1}\left[\frac{\partial J}{\partial a}\right]^2(\mathbf{S}_i\cdot\mathbf{S}_j)^2\ , \tag{2}$$

where we have assumed $\partial J/\partial a$ is a constant. Note that as k must be positive, the biquadratic term must give a negative contribution to the total energy.

Interest in biquadratic exchange interactions in solids has been present throughout the last three decades. However, it resurfaced after somewhat of an experimental dormancy recently, because of direct spectroscopic neutron measurements of the transitions between Mn^{2+} pair and triad levels in the magnetic system $CsMn_{0.28}Mg_{0.78}Br_3$.[4,5] This system has essentially the same crystal structure as $CsMnBr_3$ and is a very good representation of a one-dimensional magnetic system. Inclusion of diamagnetic Mg^{2+} ions in the crystal matrix at the Mn^{2+} site means it is very easy to isolate magnetically pairs and triads of Mn^{2+} ions.

Since these measurements show that biquadratic exchange effects are appreciable in $CsMnBr_3$, we seek in this work to investigate whether biquadratic exchange effects can be discerned in the magnetic properties of pure one-dimensional magnetic systems consisting of unbroken chains of Mn^{2+} ions. It was pointed out by Falk *et al.*,[4] and is somewhat ironic, that the most powerful probe for investigating the details of magnetic systems, neutron scattering, is inappropriate for observing effects from biquadratic exchange in these pure systems. This is because the biquadratic exchange term has the same spin symmetry as the bilinear term and, hence, to a good approximation, the inelastic spectrum can be represented by an effective bilinear exchange term alone.

II. THE CLASSICAL HEISENBERG CHAIN

Fisher[6] solved exactly for the static behavior of the one-dimensional Heisenberg system with nearest-neighbor exchange. The susceptibility is given by

$$\chi = g^2 \mu_B^2 N (S(S+1)/3kT)(1+u)/(1-u) \ , \tag{3}$$

where

$$u = \coth(1/x) - x \tag{4}$$

and

$$x = kT/2JS(S+1) \ ,$$

with $g=2$ for a spin-only system, μ_B is the Bohr magneton, k Boltzmann's constant, and T the temperature.

$kT\chi/N$ depends only on the ratio kT/J for given S and we have plotted this in Fig. 1 for an antiferromagnet ($J<0$) with $S=\frac{5}{2}$. This is compared with the experimentally determined susceptibilities of the quasi-one-dimensional materials $CsMnBr_3$,[7,8] $(CH_3)_4NMnCl_3$ (TMMC),[9,10] and $CH_3NH_3MnCl \cdot 2H_2O$ (MMC).[11] It is immediately apparent that the values for MMC lie consistently below those for $CsMnBr_3$ and TMMC, which are relatively well described by Fisher's expression.

The authors of the MMC analysis claim that the discrepancies can be accounted for by an approximate correction[12] to the classical expression which recognizes the finite (hence quantum-mechanical) nature of S. However, as all three of the systems considered have $S=\frac{5}{2}$, this correction should apply equally in all cases. We are led to the conclusion that the discrepancies are not due principally to quantum effects, but rather to small deficiencies in the Hamiltonian itself.

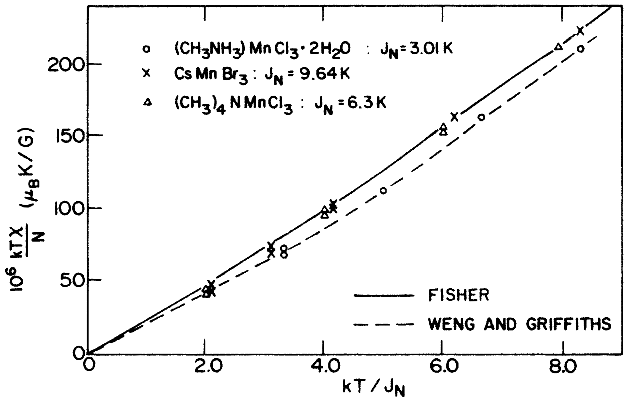

FIG. 1. Experimental susceptibility of three $S=\frac{5}{2}$ Heisenberg chain compounds. Fisher's exact solution for limitingly large S is also plotted, as is the solution with approximate corrections for finite S due to Weng and Griffiths. These corrections describe only one compound adequately, leading us to believe that deficiencies in the Hamiltonian are principally responsible for discrepancies between theory and experiment.

III. THE CLASSICAL HEISENBERG CHAIN WITH BOTH BILINEAR AND BIQUADRATIC EXCHANGE

Biquadratic exchange as well as bilinear Heisenberg exchange can be included in the analysis by considering a Hamiltonian

$$H = -2JS(S+1)\sum_j [\hat{\mathbf{S}}_j \cdot \hat{\mathbf{S}}_{j-1} + \alpha(\hat{\mathbf{S}}_j \cdot \hat{\mathbf{S}}_{j-1})^2] \ , \tag{5}$$

where the sum is over nearest neighbors along the chain and the vectors $\hat{\mathbf{S}}_i$ are classical unit vectors which can take on any orientation in space.

This model Hamiltonian has been considered by several authors;[13–15] in addition, an equivalent form

$$H = -2J\sum_i (\mathbf{S}_i \cdot \mathbf{S}_{i-1}) - 4K\sum_i (\mathbf{S}_i \cdot \mathbf{S}_{i-1})^2 \tag{6}$$

also occurs frequently in the literature. The relation between the biquadratic exchange strengths, K and α, used in these Hamiltonians, is

$$K = J\alpha/2S(S+1) \ .$$

We should point out that inclusion of a biquadratic exchange term, which reinforces the antiferromagnetic bilinear term, is a physically appealing way of producing agreement between the calculated and measured susceptibilities. In all three cases the theoretical expression with bilinear exchange alone describes the measured χ at high temperatures $[kT > JS(S+1)]$, where the spin correlations are small, but overestimates the χ at low temperatures, where spin correlations are high. Because it goes as $(\mathbf{S}_i \cdot \mathbf{S}_{i-1})^2$ rather than $\mathbf{S}_i \cdot \mathbf{S}_{i-1}$, the biquadratic term is most important at lower temperatures and reinforces the antiferromagnetic interactions, thus reducing χ and bringing theory and experiment into agreement.

Liu and Joseph[13] have solved exactly the Hamiltonian with biquadratic exchange included, as well as the more general model Hamiltonian[14]

$$H = \sum_i f(\mathbf{S}_i \cdot \mathbf{S}_{i+1}) \ ,$$

where $f(\mathbf{S}_i \cdot \mathbf{S}_{i+1})$ is a well-behaved function of the isotropic product $\mathbf{S}_i \cdot \mathbf{S}_{i+1}$, thus including interactions of higher order in the spins as well.

The solution of the Hamiltonian with biquadratic exchange included [Eq. (5)] for the susceptibility is of the same form as Eq. (3) with

$$u = \frac{\sqrt{x}\,\sinh(1/x)\exp(1/4\alpha x + \alpha/x)}{\sqrt{\alpha}\int_b^a \exp(z^2)dz} - 1/2\alpha \ , \tag{7}$$

where

$$a = (\alpha x)^{-0.5}(1-2\alpha)/2, \quad b = (\alpha x)^{-0.5}(1+2\alpha)/2 \ .$$

The results of fitting this expression to the experimentally determined single-crystal susceptibility of $CsMnBr_3$, TMMC, and MMC are shown in Fig. 2 and in the top panel of Fig. 3. Also shown for comparison in all three cases is the best fit to the experiment of Fisher's expression [Eqs. (3) and (4)].

In all three cases, the fit is clearly superior when the ex-

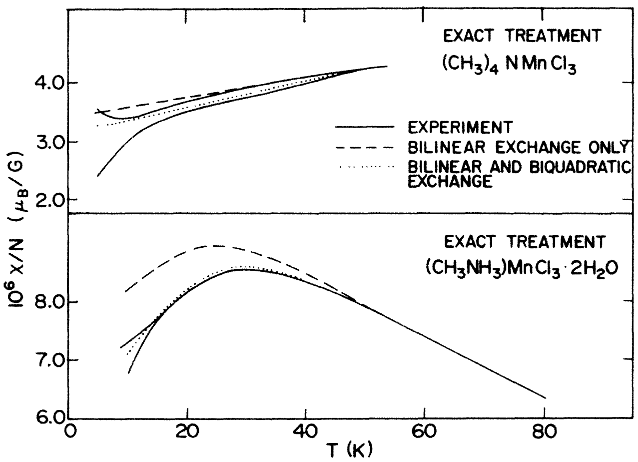

FIG. 2. Best fit of the calculated susceptibility per site for a system with both biquadratic and bilinear exchange, compared with experimental data. Also plotted for comparison is the best fit to the data of Fisher's calculation. At low temperatures the experimental susceptibilities split with $\chi(\mathbf{H}\|\mathbf{c})>\chi(\mathbf{H}\perp\mathbf{c})$ due to weak dipolar interactions.

pression with biquadratic exchange is used. This is especially pronounced for MMC and CsMnBr$_3$, as the exact expression for the classical system with bilinear exchange alone does not describe the susceptibilities well for temperatures such that $JS(S+1)>kT$; that is, below where the susceptibility "turns over." The best fit with bilinear exchange alone is better for TMMC; however, a better fit still can be achieved using the expression with biquadratic exchange.

The bilinear and biquadratic exchange values taken from the best fits are, with J and K in meV,

$$J=-0.785,\ K=0.0040,\ \alpha=-0.089 \text{ for CsMnBr}_3\ ,$$

$$J=-0.2535,\ K=0.0019,\ \alpha=-0.13 \text{ for MMC}\ ,$$

$$J=-0.55,\ K=0.0016,\ \alpha=-0.05 \text{ for TMMC}\ .$$

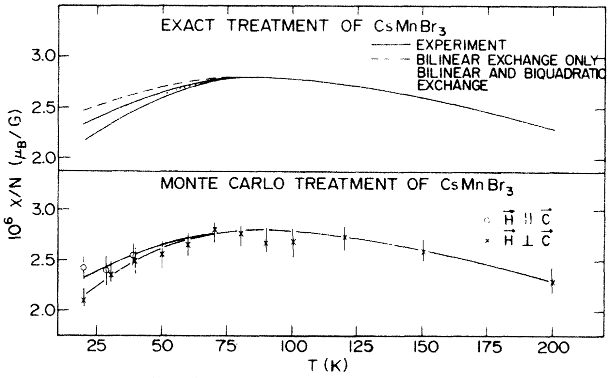

FIG. 3. Best fit of the calculated susceptibility per site for a system with biquadratic and bilinear exchange, as well as for Fisher's calculation with bilinear exchange alone, compared to experiment for CsMnBr$_3$. At low temperatures the experimental susceptibilities split with $\chi(\mathbf{H}\|\mathbf{c})>\chi(\mathbf{H}\perp\mathbf{c})$ due to weak dipolar interactions. The bottom panel shows the results of our Monte Carlo simulation of CsMnBr$_3$, which includes weak dipolar-induced anisotropy.

Biquadratic exchange makes the largest relative contribution in MMC and the smallest in TMMC; however, the magnitude of the biquadratic exchange energy is largest, by a factor of 2, in CsMnBr$_3$.

The inclusion of higher-order exchange effects, particularly bicubic, as calculated by Liu and Joseph, could alleviate the slight discrepancy between experiment and theory which treats biquadratic interactions in MMC. A bicubic term in the Hamiltonian of the form $K^1(\mathbf{S}_i\cdot\mathbf{S}_{i+1})^3$ with $K^1>0$ would be necessary to again reinforce the antiferromagnetic interactions and further lower the theoretical susceptibility values. However, these interactions would be expected to be most important at low temperatures, where weak anisotropic dipolar and single-ion interactions become dominant.

At low temperatures the measured susceptibilities display anisotropy with $\chi(\mathbf{H}\|\mathbf{c})>\chi(\mathbf{H}\perp\mathbf{c})$, where $\mathbf{c}$ is the chain axis. This is due to weak dipolar and single-ion anisotropic interactions which tend to make the plane perpendicular to $\mathbf{c}$ an easy plane. The Hamiltonian that we have considered thus far contains no such terms and hence we expect our results to lie somewhere between the two χ values at these temperatures, which they do. Approximate theories to deal with this anisotropy have been developed both for the bilinear Hamiltonian[10] and the Hamiltonian with both bilinear and biquadratic interactions.[16] However, it was found that for the cases we considered a more favorable comparison to experiment was afforded by a Monte Carlo calculation of χ for CsMnBr$_3$, which treats all the interactions exactly. This is discussed in detail in the next section.

Also present at sufficiently low temperatures is a phase transition to a three-dimensionally ordered state. This is due to the weak interchain interactions, as a truly one-dimensional system with short-range interactions displays no phase transition for $T>0$. Hence all our analysis is restricted to temperatures at which the interchain correlations are believed to be negligible, and these weak three-dimensional interactions average out.

IV. MONTE CARLO TREATMENT

In real systems the Hamiltonian also contains dipolar interactions and single-ion anisotropy terms. In this case we have no exact solution for the susceptibility and we have used the Monte Carlo method.[17]

CsMnBr$_3$ alone was treated in this way, because the anisotropy is stronger[18] than in TMMC,[19] and, more importantly, because detailed spectroscopic information regarding the strength of the biquadratic exchange term is available for CsMn$_x$Mg$_{1-x}$Br$_3$ only.[4,5]

The Hamiltonian

$$\begin{aligned} H = & -2J\sum_i \mathbf{S}_i\cdot\mathbf{S}_{i+1} - 4K\sum_i(\mathbf{S}_i\cdot\mathbf{S}_{i+1})^2 \\ & -\delta\sum_i S_i^z S_{i+1}^z + 2\mu_B H^\alpha \sum_i S_i^\alpha\ , \end{aligned} \tag{8}$$

with $J=-0.785$ meV, $K=0.0040$ meV, and $\delta=0.03$ meV. H^α is an applied magnetic field along the α direction.

The Monte Carlo calculation proceeded by the Metropolis algorithm.[20] A chain of classical spin vectors is started off in some initial configuration and a particular site spin vector is chosen at random. This vector is replaced by one of the same magnitude, but in a random direction, and the energy difference Δ_1 between the old configuration and that with the new spin is calculated on the basis of Eq. (8). This new spin is then kept or discarded according to whether another random number between 0 and 1 is greater than or lesser than $\exp(-\Delta_1/kT)$. If the new configuration is of lower energy than the old one, the new spin is kept. If it results in a higher-energy configuration, the new spin may still be kept; however, the probability of this occurring is weighted by the Boltzmann factor $\exp(-\Delta_1/kT)$. This process is referred to as a Monte Carlo step (MCS). After each such step the observable is recalculated (the induced moment in some direction) and the process is repeated such that many configurations contribute to the thermodynamic average.

In making these calculations two constraints must be taken into account. Firstly, the results of calculating any intensive observable must be independent of the size of the system. Secondly, the simulation must run through a sufficient number of MCS per spin such that equilibrium has been achieved. Both of these considerations should be most important at 20 K, as the correlation length along the chain is greatest, while the probability of replacing a spin is least.

The results shown in Figs. 3 and 5 and used in our analysis are for a system of 1000 spins, where we have executed 4000 MCS/spin. The first 1000 MCS/spin were performed without using the configurations in determining the average value of the induced moment, thus allowing for equilibration.

Finite-site effects are not expected to be important for this length of chain. This is because measurements of the correlation length[8] of $CsMnBr_3$ at 20 K showed that this value was about 10 Mn-Mn spacings. Thus our system represents 100 correlation lengths at 20 K and, of course, more at higher temperatures. Just the same, we experimented with doubling and tripling the size of the system for selected values of temperature and field, and no change in the determinations of χ was found.

Equilibration can be checked at low temperatures by looking for dependences in the observables on drastically different starting conditions. Toward this end we examined systems started off completely at random, as well as those started off in a completely ordered state. The ordered state corresponds to all spins lying within the easy plane and exactly antiparallel to both of their nearest neighbors. No difference was found in the determination of $\chi(T)$ between either starting configuration. In addition, some experimentation was carried out on the number of MCS per spin performed, as well as the number executed before configurations were included in the thermodynamic averaging.

The uncertainty associated with the calculation of an observable is more difficult to handle. Values of the induced moment per spin were calculated after each spin (on average) had undergone one MCS. The configurations then would probably not be completely statistically independent, although it is probably a reasonable approximation to treat them as if they were. The uncertainty associated with the average value of N such observables is

$$\Delta A = \left\{ N \left[\sum_i A_i^2 - \left[\sum_i A_i \right]^2 \right] \Big/ N^2(N-1) \right\}^{1/2} .$$

The average induced moment was calculated for a particular direction in the presence of three different field strengths: 10, 17.5, and 25 kG (and from three different random starting configurations). These were then plotted with their associated uncertainties and the best-fit straight line was fitted to them subject to the constraint that they must go through the origin. A typical plot is shown in Fig. 4. In all cases the straight-line fit was very good, indicating that the fields chosen were not so high as to induce nonlinear field dependences on χ.

With all our information taken into account, we estimate that our determination of χ is accurate to within $\sim 1.5\times10^{-7}$ μ_B/G spin, almost independent of temperature over the range considered.

The results of the Monte Carlo calculation for $CsMnBr_3$ are plotted along with the experimentally measured $\chi(T)$ in the lower panel of Fig. 3. Clearly, the description of the experiment by the calculation is very good. The splitting between the susceptibilities measured with **H** along the chain axis and perpendicular to it are in agreement with the calculation to within the quoted accuracy.

Figure 5 shows the two measured susceptibilities (in the two symmetry directions) at 20 K only. We have plotted the results of the Monte Carlo simulation with bilinear exchange of 0.775 meV (very close to the value of 0.785 meV used in Fig. 3) and dipolar interactions as in Fig. 3,

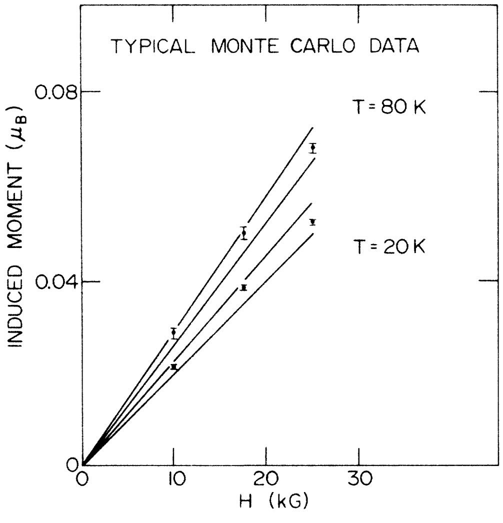

FIG. 4. Typical data from the Monte Carlo simulation are shown for two different temperatures and trial parameters in simulating $CsMnBr_3$. The error bars originate from the approximate expression given in the text and the divergence in the high- and low-slope line fits to the data give the quoted uncertainty of $\sim 1.5\times10^{-7}$ μ_B/G for the susceptibility. It is seen that no nonlinearities in the induced moment with applied field could be detected over the field range considered.

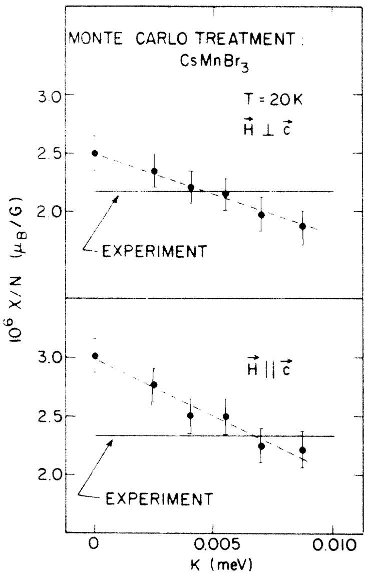

FIG. 5. Susceptibility per site in the two symmetry directions, as determined from the Monte Carlo simulation, compared to experiment for CsMnBr$_3$ at $T = 20$ K for different values of the biquadratic exchange. For $J = 0.775$ meV and a dipolar interaction strength of $\delta = 0.03$ meV, the biquadratic exchange interaction lies in the range $0.0035 < K < 0.006$ meV.

but we gradually "turn on" the biquadratic exchange interactions. Clearly, the calculation is not in agreement with the experiment in the absence of the biquadratic interactions. Agreement with experiment can only occur for $0.003 < K < 0.006$ meV for **H** perpendicular to **c** and $0.0035 < K < 0.0085$ meV for **H** along **c**. These values are consistent with the value of $K = 0.004$ meV obtained from the best fit to the full temperature dependence of χ obtained in the preceding section, which ignored anisotropic interactions.

V. DISCUSSION

Our discussion focuses on two points. Firstly, how can we reconcile the Hamiltonian parameters known from neutron scattering measurements of the spin waves in these compounds to those determined by analyzing the susceptibilities? To the best of our knowledge, no detailed spin-wave measurements have been made on MMC and, hence, discussion will concern only CsMnBr$_3$ and TMMC. Secondly, how does our determination of the biquadratic exchange energy in CsMnBr$_3$ compare with the direct spectroscopic neutron measurements made on CsMn$_x$Mg$_{1-x}$Br$_3$ by Falk *et al.*?

The determination of the nearest-neighbor exchange constant is complicated by one factor, namely that the Néel state is not the quantum-mechanical ground state, so that zero-point motion exists even at $T = 0$. This has been investigated by several authors[21,22] and it results in the spin-wave dispersion relation being written (for nearest-neighbor bilinear exchange alone) as

$$\hbar\omega = -4JSR \sin(q_c \pi) , \qquad (9)$$

with $R \simeq 1.07$ for $S = \frac{5}{2}$.

Classically, the Néel state is the ground state (all spins antiparallel to nearest neighbors) and $R = 1$. These results for the correlation factor R assume an ordered state which actually does not exist for our case.

There is only rough agreement between the bilinear exchange constant found in either TMMC or CsMnBr$_3$ taken from the best fit to Fisher's classical expression for the susceptibility using bilinear exchange alone, and the value taken from the neutron measurement of the spin-wave dispersion. These values are $-0.569 \pm .005$ and $-0.82 \pm .01$ meV for TMMC and CsMnBr$_3$, respectively. However, the main point we have made is that this expression for the susceptibility does not fit the experiment for $JS(S+1) > kT$ for the two compounds, with the effect more pronounced for CsMnBr$_3$ than for TMMC.

The spin-wave dispersion relation for a system with both nearest-neighbor bilinear and biquadratic exchange has been calculated by Falk *et al.* They get the same expression as given by Eq. (9), except that $-J$ is replaced by $|J - 4KS^2|$. The exchange parameters are consistent between the two methods (susceptibility and spin-wave dispersion). However, now we have the considerable advantage of the calculated susceptibility describing the measured susceptibility at all temperatures considered.

The second point is how does our analysis of biquadratic exchange in CsMnBr$_3$ compare with the spectroscopic measurements of Falk *et al.* Their initial measurements were made by examining the exchange splittings of Mn^{2+} pairs in CsMn$_{0.28}$Mg$_{0.72}$Br$_3$. As CsMnBr$_3$ and CsMgBr$_3$ are isostructural with essentially the same unit-cell dimensions, the comparison of our work on CsMnBr$_3$ to their work on CsMn$_{0.28}$Mg$_{0.72}$Br$_3$ is relevant.

On the basis of four observed transitions, they obtained a very good fit for the bilinear and biquadratic exchange constants. They obtained

$$J = -0.838 \pm 0.005 \text{ meV} ,$$

$$K = 0.0022 \pm 0.0002 \text{ meV} .$$

This gives biquadratic exchange which is roughly half that determined by us.

Subsequent work by this same group examined transitions between Mn^{2+} triads in the same crystal. They obtained three measured transitions which they then fitted to three exchange parameters, now including a next-nearest-neighbor bilinear exchange. Although a unique determination of the exchange parameters could have been achieved, Falk *et al.* chose to retain the biquadratic exchange constant identical to that determined in their Mn^{2+}-pair work. They obtained a reasonable description, although small discrepancies are present, with

$$J = -0.816 \pm 0.002 \text{ meV} ,$$

$$J' = -0.010 \pm 0.003 \text{ meV} ,$$

$$K = 0.0022 \pm 0.0002 \text{ meV} ,$$

as before, where J' is the next-nearest-neighbor exchange constant. As before, this biquadratic exchange value is a factor of 2 smaller than the one we determined.

However, if the unique determination of the three exchange parameters is made from the three Mn^{2+} triad transitions observed, then we obtain

$$J = -0.771 \pm 0.002 \text{ meV} ,$$

$$K = 0.0042 \pm 0.0002 \text{ meV} ,$$

$$J' = -0.013 \pm 0.003 \text{ meV} ,$$

which is in agreement with our analysis of $CsMnBr_3$.

Although we do not understand why the strength of the biquadratic exchange should be greater in triads and pure $CsMnBr_3$ than for Mn^{2+} pairs, it is not unreasonable that both the bilinear exchange gradient near the equilibrium atom separation, $\partial J / \partial a$, and the stiffness constant of a Hookes's-law—type interaction between nearest-neighbor atoms, change as Mg^{2+} ions are replaced by Mn^{2+} ions.

VI. CONCLUSIONS

We have examined the single-crystal susceptibilities of TMMC, MMC, and $CsMnBr_3$ for temperatures above at least twice their three-dimensional ordering temperatures and have found that the exact solution of the susceptibility of a classical Heisenberg antiferromagnetic chain does not describe the measured susceptibility for any of the three compounds at temperatures such that $JS(S+1) > kT$.

We do not believe these discrepancies can be argued away on the basis of quantum-mechanical corrections to the calculations, as such corrections have been shown to describe only one of the systems, MMC, adequately. Instead we assert that these discrepancies are due to small terms in the Hamiltonian, principally biquadratic exchange, which is different in all three cases. A classical treatment of the Heisenberg antiferromagnetic chain which includes both bilinear and biquadratic exchange interactions was applied to this problem. The expression obtained for the susceptibility describes all three systems very well for the temperatures considered and is a marked improvement over the expression which included bilinear exchange alone for the cases of $CsMnBr_3$ and MMC.

The analysis of $CsMnBr_3$ was extended to include the weak dipolar and single-ion terms in the Hamiltonian which produce an anisotropic susceptibility at low temperatures. We have done this via a classical Monte Carlo calculation which treats all the interactions exactly. To within the quoted uncertainty, we describe the measured single-crystal susceptibility completely, and the final Hamiltonian parameters are in agreement with previous spin-wave neutron measurements of $CsMnBr_3$.

Our final parameters are not in agreement with measurements by Falk *et al.* on transition energies between states of Mn^{2+} pairs. However, they are in agreement with their measurements dealing with transitions in Mn^{2+} triads.

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