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Magnetic correlations in the $S=\frac{5}{2}$ quadratic lattice Heisenberg antiferromagnet Mn(HCOO)$_2$·2(ND$_2$)$_2$CO

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The magnetic correlations in the quadratic lattice $S=5/2$ Heisenberg antiferromagnet Mn(HCOO)$_2$·2(ND$_2$)$_2$CO ($T_N=3.77$ K) have been studied by means of specific heat and neutron-scattering experiments. With a universal temperature scale, the temperature behavior of both the magnetic heat capacity and spin correlations are quantitatively accounted for by the pure quantum self-consistent harmonic approximation by Cuccoli *et al.* for $S=5/2$.

In recent years much interest has been focused on the low-dimensional quantum Heisenberg antiferromagnets (QHA's), such as one-dimensional systems and two-dimensional high-T_c superconductors, in connection with gap and gapless excitations. The Hamiltonian of such a system can be written as

$$\mathcal{H}=J\sum_{\langle i,j\rangle} S_i\cdot S_j, \qquad (1)$$

where $\langle ij\rangle$ runs over all pairs of nearest-neighbor spins. Numerous theoretical and computational approaches have been applied to QHA's for a variety of one-dimensional systems. The method utilizing a mapping of the low-energy spectrum of Eq. (1) onto the quantum nonlinear sigma model (QNLσM) has played a significant role in a sense that it considers crucial dependence of massive (gap) and massless (gapless) excitations on the spin-quantum number S through the topological term.[1] The application of QNLσM to the two-dimensional QHA system has been performed by Chakravarty, Halperin, and Nelson (CHN),[2] and the results compared with those for spin correlations in the $S=1/2$ high-T_c family systems such as La$_2$CuO$_4$.[3] The method has subsequently been extended by Hasenfratz and Niedermayer (HN).[4] As can be expected from the mapping procedure of the lattice Hamiltonian onto the continuous Hamiltonian, this theory should be more applicable for a larger value of S. This intuitive prediction has motivated some experiments and theories thereafter. The theory of CHN-HN qualitatively explains the temperature dependence of the spin correlation length of real systems in the form

$$\xi=\frac{e}{8}\frac{c}{2\pi\rho_s}\exp\left(\frac{2\pi\rho_s}{T}\right)\times\left[1-\frac{T}{4\pi\rho_s}+O\left(\frac{T}{2\pi\rho_s}\right)^2\right], \quad (2)$$

where ρ_s is the spin stiffness constant, dependent on S and J. Recently, however, some theories and experiments have pointed out that QNLσM might well be applicable even for the case of $S=1/2$.[3,5,6] But the number of experimental reports is limited for $S>1/2$.[7–11]

In this paper, we investigate the magnetic correlations in the $S=5/2$ Heisenberg antiferromagnet Mn(HCOO)$_2$·2(ND$_2$)$_2$CO (MF2U) with a simple quadratic lattice, which has the low magnetic ordering temperature $T_N=3.77$ K and the exchange constant $J/k_B=0.68$ K.[12] We will show that both the magnetic heat capacity and the spin-correlation length of MF2U are better described by these developed theories rather than QNLσM.

The series of compounds M(HCOO)$_2$·2(NH$_2$)$_2$CO (M =Mn, Fe, Co, Ni, Cd, Zn, and Mg) were studied by one of the present authors (K. Yamagata) from the crystallographical or magnetic structural point of view.[13] Mn^{2+} ions of the manganese compound, with its space group $P4_12_12$ (a =12.178 Å, c=25.909 Å), are coupled antiferromagnetically via formate radicals, forming the simple quadratic magnetic layers perpendicular to the c axis, which are separated from each other by the intervening urea molecules. The magnetism of this layered compound quite resembles the two-dimensional Heisenberg-like behavior of the well-studied parent compound Mn(HCOO)$_2$·2H$_2$O, as can be anticipated from their transition temperatures T_N (3.77±0.02 K for the former and 3.69±0.04 K for the latter case) and J/k_B (0.68±0.04 K, and 0.70±0.04 K, respectively).[14]

In the present study, the magnetic heat capacity was measured by the heat pulse method for the nondeuterated urea
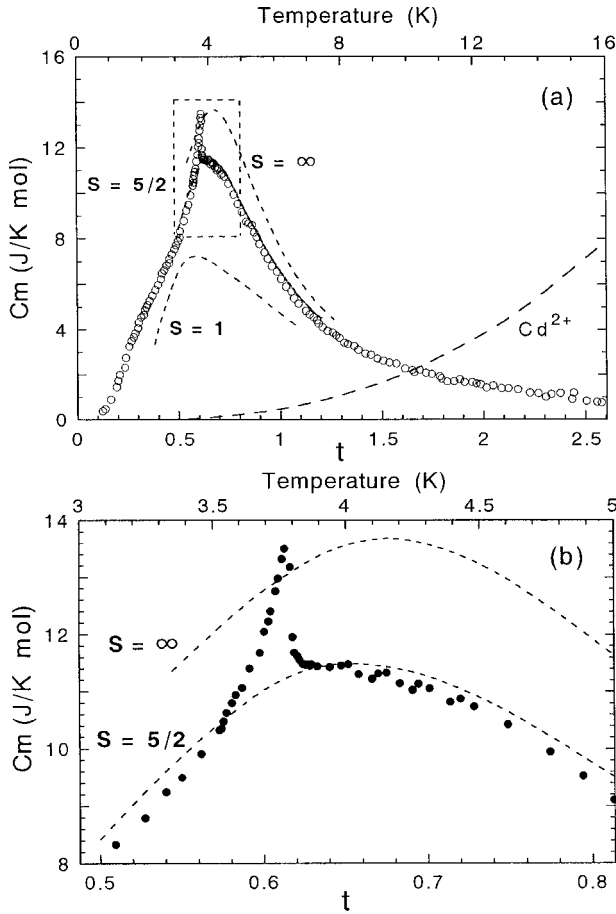
FIG. 1. Magnetic heat capacity of MF2U. The heat capacity of the isostructural Cd^{2+} compound is approximated with a dashed curve to see the lattice contribution. The results above T_N agree with the theoretical results of HTSE (Ref. 15) for the $S=5/2$ two-dimensional Heisenberg antiferromagnet with the exchange constant $J/k_B=0.68\pm0.04$ K (Ref. 12). The results of PQSCHA for $S=1$, $5/2$ and the classical limit (Ref. 17) are indicated. (b) shows the details of the broad specific heat maximum located at around 4 K [enclosed part in (a)].

FIG. 2. Temperature variation of the peak intensity at the magnetic Bragg position (1,1,0) of MF2U. The solid curve presents a fit to $I\propto(T_N-T)^{2\beta}$, with $T_N=3.795$ K and $\beta=0.20\pm0.02$.

MF2U. The lattice contribution to the heat capacity was subtracted by the use of the isostructural Cd^{2+} compound. Figure 1 shows the experimental results of the magnetic heat capacity measurement of MF2U. Above T_N the results agree with the high-temperature series expansions (HTSE)[15] with $S=5/2$ and $J/k_B=0.68$ K±0.04 K. The value of J is consistent with those estimated for the magnetic susceptibility[12] and from the exchange field.[16] A small peak is seen at T_N besides the characteristic broad maximum of two-dimensional magnetic system as shown in Fig. 1. In the recent theory of the pure quantum self-consistent harmonic approximation (PQSCHA),[17] both the magnetic heat capacity and the spin-correlation length are given versus the reduced temperature $t=T/2J\tilde{S}^2$, where $\tilde{S}$ is the effective spin length. When we introduce the reduced temperature $t=T/2J\tilde{S}^2$ and $2J\tilde{S}^2=6.15$, the PQSCHA result not only nicely reproduces the experimental results including the maximum value at 4 K, but also overlaps smoothly with the HTSE results at high
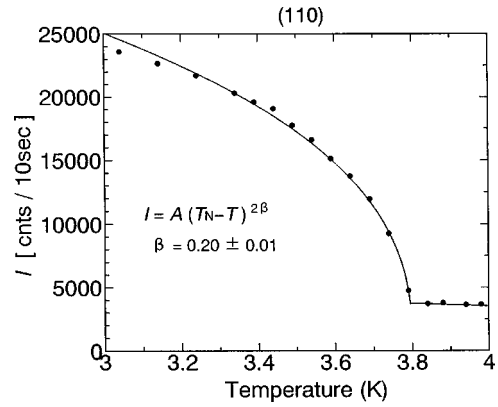
temperatures, as shown in Fig. 1. This scaling gives $\tilde{S}=2.14$, which is rather close to $S=5/2$, when we consider the spin reduction of 0.19 given by the spin-wave theory for a simple quadratic lattice. These results indicate that the PQSCHA well reproduces the magnetic heat capacity data with a reasonable reduced temperature scale, being consistent with the HTSE.

For the neutron-scattering experiment, a single crystal of the deuterated urea compound MF2U of the averaged size of $(0.7$ cm$)^3$ was prepared. The neutron-scattering experiments were performed on the spectrometer ISSP-PONTA, installed at JRR-3M in the Tokai Establishment of JAERI. The (002) reflection of pyrolytic graphite (PG) was used as a monochromator. A PG filter was employed to eliminate the higher-order reflections from the monochromator. The spectrometer was operated in the two-axis mode without an analyzer. The incident neutron energy E_i was fixed at $E_i=14.8$ meV. The crystal was set into an *Orange*-type ^{4}He cryostat with its [110]- and [001]-directions in the scattering plane. Prior to the experiments on the spin-correlation length of the deuterated single crystal of MF2U, we measured the temperature dependence of the magnetic Bragg intensity I for the reflection (1,1,0) around T_N. By subtracting the temperature independent background, we could fit the data by a single power law, $I=A(T_N-T)^{2\beta}$, with $T_N=3.795$ K and $\beta=0.20\pm0.02$, as shown in Fig. 2. This value of T_N is almost identical to $T_N=3.77\pm0.02$ K of the nondeuterated system, showing that the magnetism of the deuterated and nondeuterated urea MF2U are essentially the same. The value of β agrees with those of several other layered magnets including $Mn(HCOO)_2\cdot2H_2O$ (Ref. 18) and La_2NiO_4.[8]

With this single crystal of MF2U, the two-dimensional (2D) correlation length ξ and the structure factor S_0 were measured by two-axis scans. Scans were performed keeping the final neutron wave vector parallel to the 2D magnetic ridge (1,1,l) in order to integrate the 2D magnetic fluctuations rorrectly for constant 2D wave vector q_{2D} (q_{2D} is the momentum transfer from the 2D antiferromagnetic ridge) in the energy range from $-k_BT$ to E_i.[8] Depending on the intensity and the temperature, ranging $T_N<T<8.52$ K($=2.5$ T_N), two sets of collimator sequence for the spec-

FIG. 4. The theoretical magnetic correlation length ξ plotted against the reduced temperature $t = T/2J\tilde{S}^2$ (Ref. 17) and the experimental results for MF2U. The curves correspond to the values for $S = 1/2$, 1, 5/2 and the classical limit, respectively, from the left side.
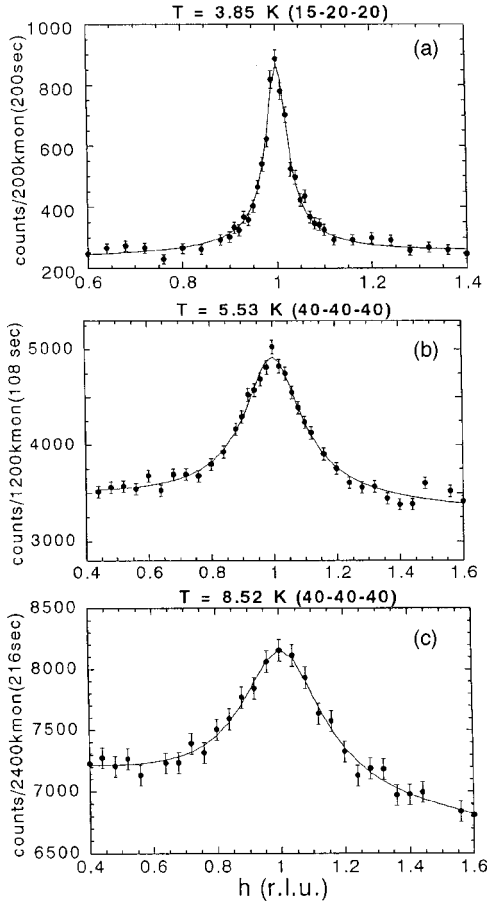
FIG. 3. Representative profiles of the two-axis scans along the direction $(h, -h, 0)$ for the two-dimensional plane of MF2U. The solid lines represent the Lorenzian scattering function convoluted with the instrumental resolution.

trometer, $15'$-$20'$-$20'$ and $40'$-$40'$-$40'$ were employed. Representative scattering profiles from the two-axis scans are given in Fig. 3. The magnetic scattering intensity $I(\boldsymbol{q}_{2D})$ from the two-axis scans is fitted to the following simple Lorentzian line shape,

$$I(\boldsymbol{q}_{2D}) \propto S_0 / (1 + \boldsymbol{q}_{2D}^2 \xi^2). \tag{3}$$

We convoluted with the spectrometer resolution function including a slightly sloping background to deduce ξ and S_0 for each T.

In the quantitative description of the thermal development of ξ or S_0 for a general value of S,[2,4,17,19] the choice of the temperature scales, such as T/ρ_s, T/J, $T/JS(S+1)$ or T/S^2, becomes essential. Here we use the same reduced temperature $t = T/2J\tilde{S}^2$ introduced above for the interpretation of magnetic specific heat in the frame of PQSCHA. The results are summarized in Fig. 4. It is clear that our present data for MF2U are approaching the $S=5/2$ theoretical curve at lower temperatures $t < 0.8$. For $t > 0.8$, however, the experimental results rather approach the curve for the classical limit. It is pointed out theoretically[20] and experimentally[11] that the $S=5/2$ QHA should cross over from classical scaling to renormalized classical behavior near the upper bound of spin en-
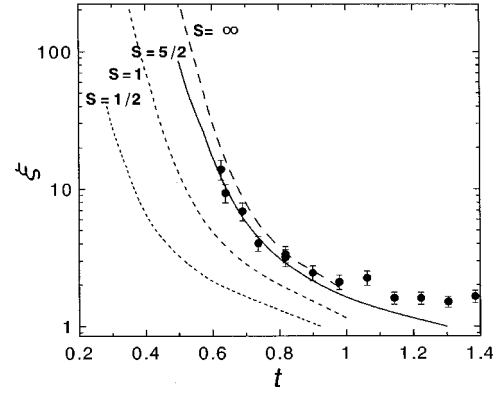
ergy spectrum, which is expected around $T = JS(S+1)/1.1$, giving 5.7 K in the present system. This value corresponds to $t = t_c = 0.93$, being relevant for the above experimental behavior. Looking at other experimental results being referred to in this paper, we notice that ξ seems to cross over to ξ for the higher S around t_c of the individual systems (as can be seen in Refs. 17 and 19). For comparison the PQSCHA predictions for other S values are indicated in Fig. 4. The experimental values for $S=1/2$ substances, such as La_2CuO_4,[3] $Sr_2CuO_2Cl_2$,[5] and $Cu(DCOO)_2 \cdot 4D_2O$,[6] are reported as falling almost on the $S=1/2$ theoretical curve. The results for La_2NiO_4 (Ref. 8) and K_2NiF_4 (Ref. 7) are fitted to the theory for $S=1$. We mention that the structure factor of MF2U, or S_O/ξ^2, also shows almost the same behavior as ξ, both above and below $t=0.8$. When we take the temperature scale $T/JS(S+1)$, as employed in the recent report on Rb_2MnF_4,[11] we have $JS(S+1)=5.95$ with $S=5/2$ and $J/k_B=0.68$ K, i.e., a value comparable with $2J\tilde{S}^2 = 6.15$ in the present scale $t = T/2J\tilde{S}^2$.

Another comprehensive expression for the thermal development of spin correlations for a general value of S is given in the high-temperature series expansion theory by Elstner et al., in which $S\xi$ vs T/JS^2 plots only slightly depend on S.[19] Our experimental results seem to agree in this case as well, except for higher temperatures where ξ also indicates the cross over, as shown in Fig. 4. Here we only mention the validity of ξ_{CHN-NH} derived from QNLσM for the general value of S. One would expect this theory to fit much better for larger S. It is a surprise that this theory gives rather better agreement with the results for real $S=1/2$ compounds than for the systems with $S>1/2$. The same tendency is found in comparison with other theories, e.g., the ratio of ξ evaluated by Elstner et al.[19] to ξ_{CHN-NH} is about 0.8 for $S=1/2$, but it becomes 0.25–0.6 for $S=5/2$ in the corresponding temperature region.

Now we comment on the anisotropy in MF2U. The magnetic susceptibilities χ_c for the perpendicular direction (c axis) to the magnetic plane, and χ_a and χ_b for the two axes in the plane were measured by a superconducting quantum in-

terference device system in the temperature range 1.8–50 K. The observed differences between them were within 1% above T_N, and they were well reproduced by HTSE (Ref. 15) for $S = 5/2$, $g = 2.00$, and $J/k_B = 0.68 \pm 0.04$ K,[12] giving a characteristic broad maximum around 6 K. Just in the vicinity of T_N, χ_c exceeded χ_a and χ_b by about 3%, and even below T_N they showed nearly the same decreasing behavior. Moreover the magnetization for the three axes at 1.8 K showed the same linear increase up to 5 kOe (limit of the present apparatus). Only a minute deviation from the linearity was seen at $H = H_A = 1.7$ kOe, if any. This linearity is shown to continue up to the exchange field of $H_e = 106$ kOe.[16] These facts imply that the magnetic easy and hard axes are not easily identified for a bulk single crystal of MF2U. Considering the existence of a 4_1 screw axis along the c axis, we might expect some long period spin structure along the perpendicular direction to the magnetic plane below T_N. Our neutron-scattering experiment, however, did not show any sign of satellite peak. The determination of the spin structure below T_N and the T-H phase diagram has been studied experimentally[21] and theoretically.[22] In the case of Rb_2MnF_4, the isotropic limit of the Heisenberg spin symmetry can be obtained by applying the external field along the effective anisotropy axis.[10] The above experiments on MF2U, however, indicate that above T_N the system can be regarded as being isotropic. Even if we take the anisotropy field $H_A = 1.7$ kOe tentatively, we have $H_A/H_e = 1.7\%$, which might cause a spin crossover from the Heisenberg to a lower symmetry only just above T_N.

In summary the magnetic correlations in the quadratic lattice $S = 5/2$ Heisenberg antiferromagnet $Mn(HCOO)_2 \cdot 2(ND_2)_2CO$ ($T_N = 3.77$ K) have been studied by means of specific heat and neutron-scattering experiments. With the use of the common reduced temperature scale, both the magnetic heat capacity and the thermal development of the spin correlations are well described by the theory of PQSCHA for $S = 5/2$, without any indication of approaching the results predicted by QNLσM. This is an experimental work, where the magnetic correlations reflected in the heat capacity and neutron-scattering experiments are quantitatively interpreted within the same theoretical frame work.

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