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Magnetic ordering in two-dimensional Heisenberg antiferromagnets with variable interlayer distances

Kyu Won Lee, Chang Hoon Lee, and Cheol Eui Lee*
Department of Physics, Korea University, 136-701 Seoul, Korea

J. K. Kang
Department of Chemistry, Jeonju University, 560-759 Jeonju, Korea

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We have investigated the finite temperature magnetic ordering in the quasi-two-dimensional Heisenberg antiferromagnetic system $(C_nH_{2n+1}NH_3)_2MnCl_4$ with various chain lengths n. Our results indicate that in long-chain compounds with large interlayer distances, secondary interactions in magnitude besides the exchange interaction, such as the Ising anisotropy and the Dzyaloshinsky-Moriya interaction, play an important role in the magnetic phase transitions.

I. INTRODUCTION

Stimulated by the discovery of the high T_c superconductivity and antiferromagnetic superconductivity in two-dimensional Heisenberg systems, intense studies are being carried out on the two-dimensional Heisenberg magnetism, resulting in a better understaning of both the two-dimensional magnetism itself and the interrelationship between the magnetism and the conductivity.[1,2] In an ideal two-dimensional Heisenberg magnet no finite temperature magnetic ordering is theoretically allowed.[3] However, because of the inevitable interlayer exchange interaction in real magnetic systems, the theoretical proposition can hardly be verified. Despite notable progress in the understanding of two-dimensional magnetism aforementioned, this problem remains far from being resolved.

The perovskite-type layered structure compounds $(C_nH_{2n+1}NH_3)_2MnCl_4$ (CnM for short), with M=Cd, Cu, Mn, etc., have been known as representative quasi-two-dimensional Heisenberg antiferromagnets.[3] Although theoretically an ideal two-dimensional Heisenberg system cannot have a finite ordering temperature, a weak interlayer exchange interaction in the system can lead to a finite temperature antiferromagnetic ordering, and the interaction can be controlled by changing the alkylammonium chain length. Thus the CnMn system has been regarded as a testing ground of the assumption that a longer alkylammonium chain length gives rise to a lower antiferromagnetic ordering temperature, because the longer the chain length, or greater the interlayer distance, the weaker the interlayer interaction.[3] Indeed, for short chain compounds with $n<4$, it was observed that the antiferromagnetic transition temperature shifts toward a lower temperature for a longer interlayer distance.[3] However, the tendency has not been tested in much longer chain compounds, and it is the purpose of this paper to report and discuss the antiferromagnetic transition in those compounds.

The CnM systems are constituted of alternating organic and inorganic layers. The inorganic layer consists of a corner-sharing MCl_6 octahedra, and the organic one consists of the alkylammonium chains attached to the inorganic layer via a N-H-Cl hydrogen bonding. Each MCl_6 octahedron is more or less tilted about the layer-normal direction according to the hydrogen bonding scheme.[4]

The system shows a variety of structural phase transitions, believed to be governed by the dynamics of the alkylammonium groups. Typically two successive structural phase transitions associated with the organic chains have been observed: One is the conformational transition leading to the partial chain melting and the other is the order-disorder transition of the NH_3 polar group accompanied by the reorientational motion of the alkylammonium chain.[5] In any case some types of chain defects occur at the transition. Previous studies have successfully described the structural phase transitions in the light of the Landau model similar to those in the liquid crystals,[6] and the critical dynamics related to the structural order parameter has recently been reported by the authors.[7,8]

When M is Cu or Mn, the magnetic behavior of CnM exhibits a two-dimensional character. The magnetic susceptibility shows a large anisotropy at the magnetic phase transition[3] and the EPR (electron paramagnetic resonance) linewidth shows an angular dependence characteristic of the two-dimensional paramagnet in the paramagnetic state.[9] In particular, an angular dependence of EPR signals characteristic of two-dimensional magnetism was explicitly observed in CnMn with shorter hydrocarbon chains ($n=2$ and 3).[10]

According to the studies for short-chain compounds, the magnetic moments in the antiferromagnetic phase are aligned along the layer-normal direction alternately pointing in opposite directions. Accordingly, the CnMn system has the layer-normal direction as an easy axis and so an Ising type of anisotropy.[11] Structurally, the $MnCl_6$ octahedra are slightly tilted from the inorganic layer as a consequence of the hydrogen bonding, and hence a spin canting can take place along the layer-parallel direction.[4,11]

II. EXPERIMENT

The $(C_nH_{2n+1}NH_3)_2MnCl_4$ powder sample was made according to the reaction[12]

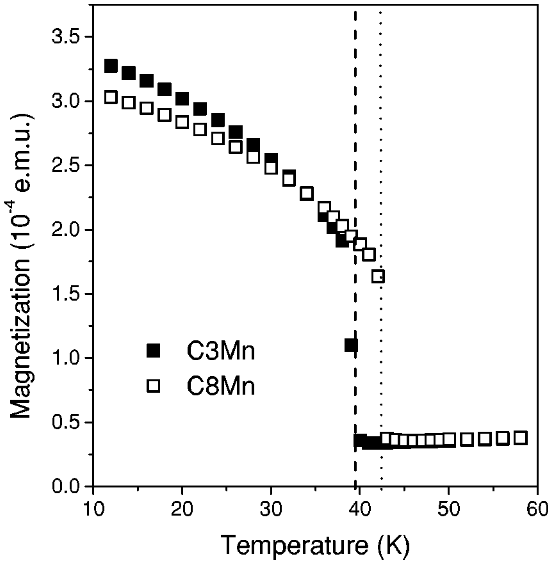

FIG. 1. The temperature dependence of the magnetization measured in an applied magnetic field of 1 mT for C3Mn and C8Mn, from which the magnetic transition temperatures were found.

$$2\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_3\mathrm{Cl}+\mathrm{MnCl}_2 4\mathrm{H}_2\mathrm{O}\rightarrow(\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_3)_2\mathrm{MnCl}_4 +4\mathrm{H}_2\mathrm{O}.$$

The powder was twice recrystallized and then vacuum dried. The stoichmetry and the structure were checked by elemental analysis and x-ray diffraction.

The powder samples with the chain lengths $n=2$ to 12 were packed in a nonmagnetic capsule (weakly diamagnetic with no temperature dependence and easily corrected for measurements) and the temperature dependent magnetization was measured using a commercial SQUID (superconducting quantum interference device) magnetometer (Quantum Design MPMS Series). The remanent magnetic field in the SQUID susceptometer, estimated to be within ± 10 μT using a paladium standard sample, was corrected for. The samples were zero-field cooled to 5 K, and the magnetization was measured as increasing temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the low-field magnetization measured in an applied magnetic field of 1 mT. Although we cannot directly measure the sublattice magnetization, fortunately, the canted spin component gives rise to a ferromagnetic transition in a weak field. As a consequence, the antiferromagnetic transition temperature can be determined from the weak-field magnetization. The antiferromagnetic transition temperature is found to be 39.5 K ± 0.5 K for C3Mn in Fig. 1, which is consistent with the literature.[13] However, for n $\geqslant 3$, the transition temperature increases gradually with increasing n before becoming nearly saturated around 43 K± 1 K as shown in Fig. 2.

In Fig. 2, previously reported transition temperatures[14] for $n=1$ and 2 and those for $n\geqslant 3$ measured by us, were plotted as a function of the chain length. As previously supposed the transition temperature for $n\leqslant 3$ is shown to decrease with increasing interlayer distance and can readily be attributed to the weakening of the interlayer interaction. However, the increase of the transition temperature for $n\geqslant 4$ in spite of the increasing interlayer distance is in marked contrast to the previous expectation that the transition temperature would decrease with increasing interlayer distance in the layer structured compounds. In order to check the possibility that the increase of the transition temperature for $n\geqslant 4$ indeed arises from an increase of the exchange energy, we have calculated the exchange energy from the high-field magnetization below the spin-flop field (about 2.3 T), which shows the antiferromagnetic behavior.

Figure 3 shows the magnetization for C3Mn measured in a magnetic field of 0.3 T, in which a typical antiferromagnetic behavior is observed and a broad maximum near 80 K is indicative of the short-range antiferromagnetic correlation. The exchange energy obtained from the susceptibility may

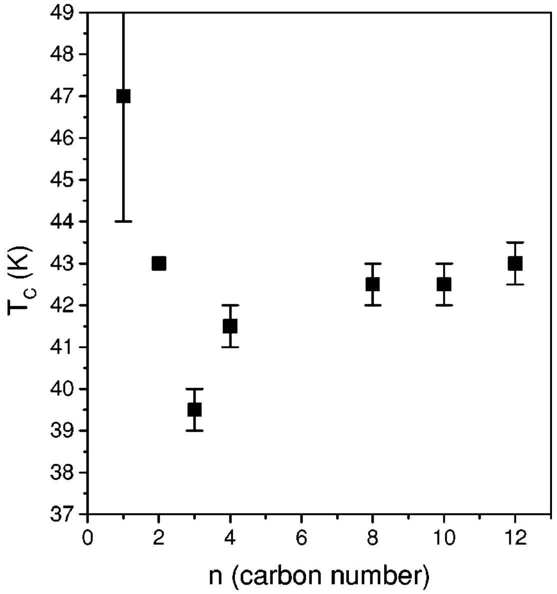

FIG. 2. The transition temperature vs carbon number n. The values for C1Mn and C2Mn were taken from Ref. 14.

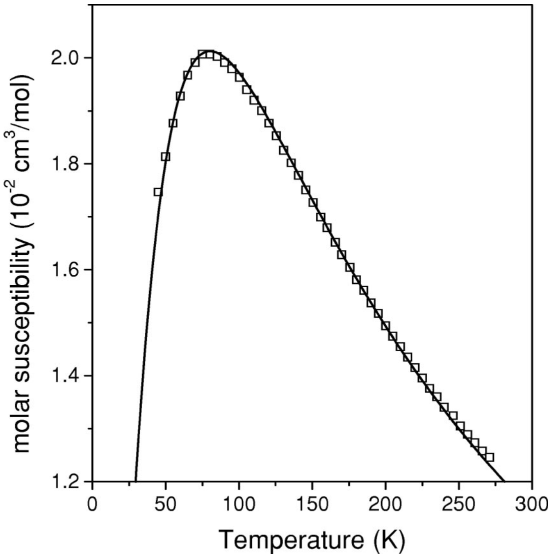

FIG. 3. The temperature dependence of the magnetic susceptibility for C3Mn measured in an applied magnetic field of 0.3 T. The solid line represents a fit to Curely's work.

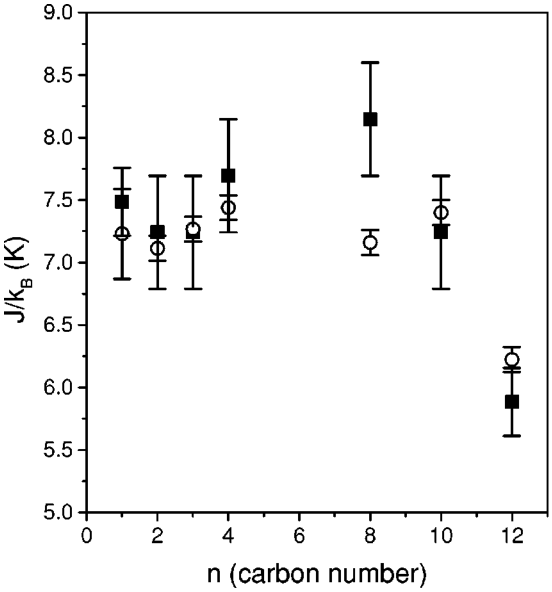

FIG. 4. Exchange energies vs the carbon number n. The solid symbols were obtained from the magnetization maximum temperature [Eq. (2)], and the open symbols by fitting to the Curely's work [Eq. (1)]. The values for C1Mn were taken from Ref. 15.

differ slightly depending on the formalism. We have analyzed the magnetization data consistently using Curely's work, which is reported to be particularly accurate for the Mn^{++} ions.[15] According to Curely's work for the square lattice two-dimensional Heisenberg antiferromagnet,[15] the temperature dependent magnetic susceptibility is given by

$$\chi=\frac{\beta G^2}{3}\left(\frac{1+L(-\beta J)}{1-L(-\beta J)}\right)^2, \tag{1}$$

where L, G, and J are the Langevin function, the Lande factor, and the exchange energy, respectively, and $\beta=1/kT$ (k is the Boltzmann constant). The experimental data were quite well fitted to Eq. (1) as shown in Fig. 3, where the solid line represents the fit. In addition, Curely also developed a relation between the exchange energy and the temperature at which the susceptibility has a maximum value as[15]

$$\frac{kT(\chi_{max})}{JS(S+1)}=1.2625, \tag{2}$$

where $T(\chi_{max})$ is the temperature of maximum susceptibility, and $S=5/2$ is the spin of Mn^{++}. A linear relationship between the susceptibility maximum temperature and the exchange energy is predicted in other formalisms as well. Therefore, although the absolute value of the exchange energy obtained from the susceptibility maximum temperature can vary slightly depending on the formalism, the overall correlation can be taken to be valid.

Figure 4 shows that the exchange energies found from Eqs. (1) and (2) for various chain lengths n are consistent within errors, and are nearly chain-length independent for $n \leqslant 4$. The apparent decrease of the intralayer exchange interaction for $n \geqslant 8$ may be due to the structural distortions (including a change in the bond distance between the Mn^{++} ions) with increasing chain length. In order to identify a possible structural change near the antiferromagnetic transition, further structural studies are now under way. The difference between the exchange energies obtained from Eqs. (1) and (2) is, if any, a measure of the validity of Curely's work for the CnMn systems.[15] A possible origin of the discrepancy is the crystalline anisotropy or the single-ion anisotropy. Because the magnetic spin in the CnMn system is located in the symmetric s orbital, the single-ion anisotropy must be very small, and indeed our measured EPR g-value anisotropy for C3Mn is below 10^{-3}. Thus the deviation from the perfect square lattice would be the main origin of the discrepancy. The interlayer exchange interaction is usually much smaller than the intralayer one by at least a factor of 10^4.[3] Thus, the exchange energies obtained can safely be attributed to the intralayer interactions.

As can be seen from Figs. 2 and 4, the chain-length independent exchange energies for $n \leqslant 3$ are not incompatible with the chain-length dependence of transition temperature, which indicates that the transition temperature is not dictated by the intralayer exchange energy, but by the interlayer interaction. In other words, the interlayer exchange energy decreasing with increasing chain length n results in lower transition energy for $n \leqslant 3$ as observed in Fig. 2. On the other hand, the behavior of the transition temperature for $n \geqslant 4$ cannot be accounted for either by the chain-length dependence of the intralayer exchange energy in Fig. 4, or by the decreasing interlayer exchange energy with increasing interlayer distance. Thus, for chain lengths $n \geqslant 4$, the transition temperature is obviously not dictated by the exchange energies.

For large chain lengths ($n \geqslant 8$) the interlayer interaction would be weak enough for us to regard the CnMn system as an ideal two-dimensional system, but the finite temperature magnetic ordering is seen to be still taking place, and the transition temperature is independent of both the intralayer and the interlayer exchange interaction. This indicates that the canted antiferromagnetic transition temperature is determined by an additional interaction other than the antiferromagnetic exchange interaction, at least in the long-chain compounds. Besides the exchange interactions, the next greatest interactions in magnitude, the Ising anisotropy[6] and the Dzyaloshinsky-Moriya (DM) interaction,[16] are known to play a role in the antiferromagnetic transition, even though they are very small in comparison to the exchange interactions, the Ising anisotropy determining the easy axis and the DM interaction inducing the spin canting. In a recent Monte Carlo study for the classical Heisenberg antiferromagnet on a triangular lattice, it was shown that the easy-plane anisotropy strongly affects the transition temperature.[17] Furthermore, because a finite temperature magnetic ordering is allowed in the two-dimensional Ising system and the Ising anisotropy will be independent of the chain length, i.e., interlayer distance, the finite temperature magnetic ordering independent of the interlayer distance can be explained in terms of the Ising anisotropy. In fact, the deviation from the isotropic Heisenberg system due to the Ising anisotropy would enable a magnetic ordering at a finite temperature,[3] just as a deviation from the perfect two-dimensional lattice would enable a magnetic ordering. The Ising anisotropy energy is about 10^{-3} J,[18] which is compatible with the g-value anisotropy.

The magnitude of the other possible origin of the transition temperature for the long-chain compounds, the DM interaction, is of the order of $(\Delta g/g)J$, where Δg is the deviation from the free-electron g-value,[16] and was determined to be of the order of 10^{-3} J from our EPR measurements. Thus, the two interactions, the Ising anisotropy and the DM interaction, turn out to be of the same order of magnitude, and the DM interaction will also be independent of the chain length. Therefore, the role of the DM interaction in the finite temperature magnetic ordering cannot be completely excluded, either.

In summary, we have studied the antiferromagnetic transitions in the well-known quasi-two-dimensional Heisenberg antiferromagnetic systems $(C_nH_{2n+1}NH_3)_2MnCl_4$ with various chain lengths. As a result, the antiferromagnetic transition temperature was shown to be independent of the chain length for long-chain compounds contrasting to the previous assumptions, for which the Ising anisotropy was suggested to be responsible.

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*Author to whom correspondence should be addressed. Electronic address: rscel@kuccnx.korea.ac.kr

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