

Two-dimensional Antiferromagnetism in the Perovskite-type Layered Compounds $(C_nH_{2n+1}NH_3)_2MnCl_4$

Kyu Won Lee¹, Chang Hoon Lee¹ and Cheol Eui Lee¹ and J. K. Kang²

¹Department of Physics, Korea University, Seoul 136-701, Korea

²Department of Chemistry, Jeonju University, Jeonju 560-759, Korea

(Received 30 December 1999)

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 for the transition temperatures and the exchange energies for long chain compounds are in marked contrast to previous expectations.

1. Introduction

The perovskite-type layered structure compounds $(C_nH_{2n+1}NH_3)_2MCl_4$ (C_nM for short), with $M=Cd, Cu, Mn, \text{etc.}$, are constituted of alternating organic and inorganic layers. The inorganic layer consists of corner-sharing MCl_6 octahedra, and the organic one consists of alkylammonium chains attached to the inorganic layer via 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 [1].

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 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 [2]. In either 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 liquid crystals [3] and critical dynamics related to the structural order parameter were reported [4, 5].

When M is Cu or Mn , the magnetic behavior of C_nM exhibits a two-dimensional character. The magnetic susceptibility shows a large anisotropy at the magnetic phase transition [6] and the EPR (electron paramagnetic resonance) linewidth shows an angular dependence characteristic of a two-dimensional paramagnet in the paramagnetic state [7]. In particular, angular dependence of EPR signals characteristic of two-dimensional magnetism was explicitly observed in $(C_nH_{2n+1}NH_3)_2MnCl_4$ with shorter hydrocarbon chains (n

$=2$ and 3) [8].

According to studies of short chain compounds, the magnetic moments in the antiferromagnetic phase are aligned along the layer-normal direction, alternately pointing in opposite directions. Accordingly, the C_nMn system has the layer-normal direction as an easy axis and so an Ising type of anisotropy [9]. 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 [1, 9].

The C_nMn system has been known as a representative quasi-two-dimensional Heisenberg antiferromagnet [6]. Although 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 C_nMn system has been regarded as a testing ground for the assumption that a longer alkylammonium chain length gives rise to a lower antiferromagnetic ordering temperature, because a longer chain length, or a greater interlayer distance, would result in a weaker interlayer interaction [6]. 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 [6]. However, the tendency has not been tested in much longer chain compounds, and it is the purpose of this work to report and discuss the antiferromagnetic transition in those compounds.

2. Experiment

Samples of C_nMn were synthesized and characterized as previously reported [10]. Powder samples with chain lengths $n=2, 3, 4, 6,$ and 12 were packed in a nonmagnetic

*Corresponding author: E-mail: rscel@kucncx.korea.ac.kr

capsule, and the temperature dependent magnetization was measured using a commercial SQUID (superconducting quantum interference device) magnetometer (Quantum Design MPMS series).

3. Results and Discussion

Figure 1 shows the magnetization of C_4Mn measured in a magnetic field of 0.3 T, in which typical antiferromagnetic behavior is observed and a broad maximum near 80 K is indicative of short range antiferromagnetic correlation. According to Curely's work for the square lattice two-dimensional Heisenberg antiferromagnet [11], the magnetic susceptibility is given by

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

where L , G , J , and β are the Langevin function, the Landé factor, the exchange energy, and $1/kT$ (k is the Boltzman constant), respectively. The experimental data can be fairly well fitted to Eq. (1), as shown in Fig. 1, where the solid line represents the fit. Curely also developed a relation [11] between the exchange energy and the temperature at which the susceptibility has a maximum value as:

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

where $T(\chi_{max})$ is the temperature of the maximum susceptibility, and $S=5/2$ is the spin of Mn^{++} . Thus, the exchange energy can be obtained both from Eqs. (1) and (2) for compounds with various chain lengths n .

Figure 2 shows that the exchange energy found from Eqs. (1) and (2) for various chain lengths n are consistent within the error limits, and are nearly chain length independent for

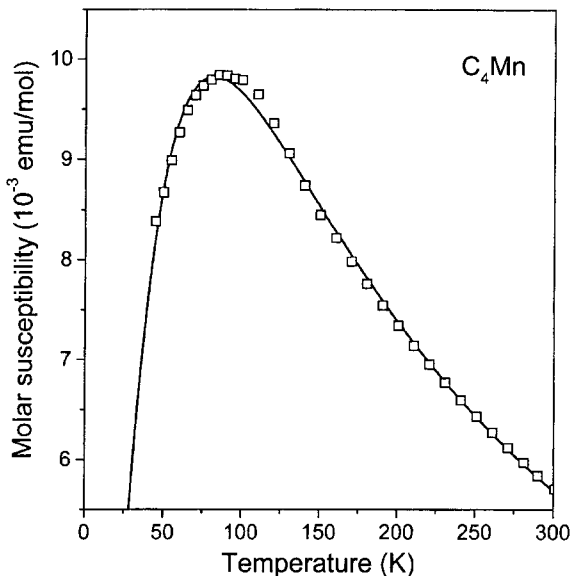


Fig. 1. The temperature dependence of the molar susceptibility of C_4Mn measured in an applied magnetic field of 0.3 T.

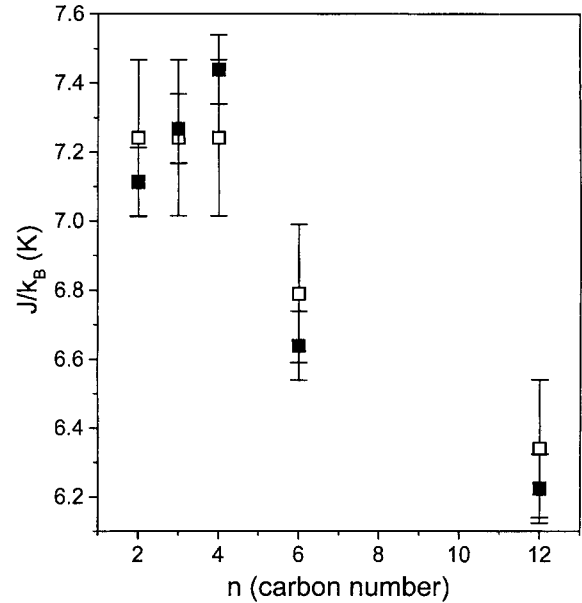


Fig. 2. Exchange energy divided by K_B vs the carbon number n . The solid symbols were obtained by fitting to Curely's work (Eq. (1)), and the open symbols from the magnetization maximum temperatures (Eq. (2)).

$n < 4$. On the other hand, for $n > 4$, the exchange energy decreases with increasing n . The interlayer exchange interaction is known to be smaller than the intralayer exchange by a factor of 10^4 [6]. Thus, the exchange energies obtained can safely be regarded as the intralayer ones. The decrease of the intralayer exchange interaction may be due to the structural distortions (including a change in the bond distance between 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.

Figure 3 shows the low field magnetization measured in 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 K for C_3Mn in Fig. 3, which is consistent with the literature [12]. However, for n equal to or greater than 4, it was found to be $43 K \pm 1 K$. These observations are in marked contrast to the previous expectation that the transition temperature would decrease with increasing interlayer distance in layer structured compounds. In spite of the nearly constant transition temperatures for chain lengths n equal to or greater than 4, in Fig. 2 the intralayer exchange interaction was found to decrease with increasing chain length n . 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. A variety of interactions such as the Ising anisotropy and the Dzyaloshinsky-Moriya (DM) inter-

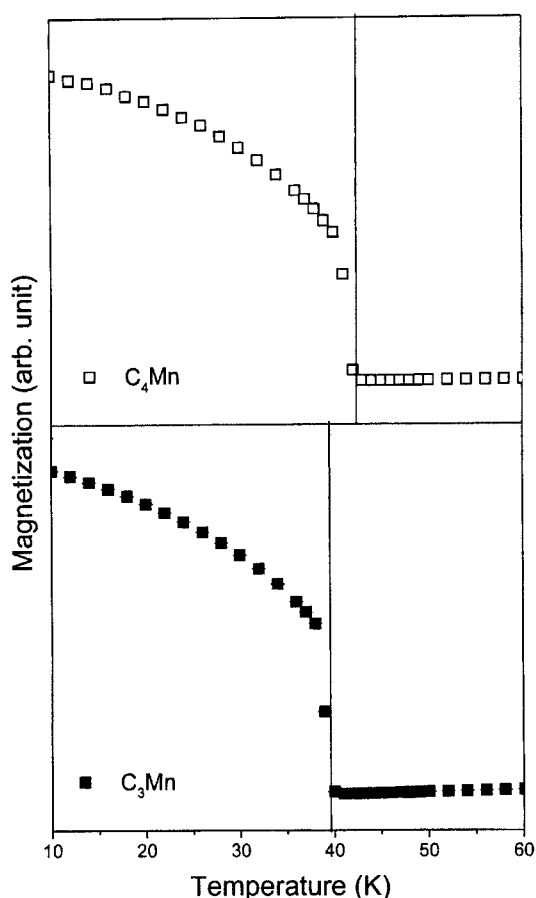


Fig. 3. The temperature dependence of the magnetization measured in 1 mT for C_3Mn and C_4Mn .

action [6, 13] are known to play a role in the antiferromagnetic transition, although they are much smaller than the exchange interaction. In fact, they are known to play a certain role in the transitional behavior, i.e., the Ising anisotropy determines the easy axis and the DM interaction induces spin canting. For the long chain compounds it is expected that the interlayer exchange interaction, which dictates the magnetic transition temperature for short chain compounds, becomes smaller than the aforementioned interactions. In that case, the finite magnetic ordering temperature in the Heisenberg antiferromagnet can be dictated by the Ising anisotropy interaction, which is usually much stronger than other interactions such as the DM interaction. In fact, the Ising anisotropy does not depend on the chain length and in the two-dimensional Ising system where a

finite ordering temperature is allowed, an ordering temperature independent of chain length can be explained.

In summary, we have studied the antiferromagnetic transitions in the well known quasi-two-dimensional Heisenberg antiferromagnetic system $(C_nH_{2n+1}NH_3)_2MnCl_4$ with various chain lengths. The antiferromagnetic transition temperatures are independent of the chain length for long chain compounds, in contrast to the common expectation. We conjecture that the Ising anisotropy, which does not depend on the chain length, is responsible for the finite ordering temperature, and that the structural distortion modifies the exchange interactions.

Acknowledgments

This work was supported by the Korea Science and Engineering Foundation through the Center for Electro- and Photo-Responsive Molecules, and by the Korea Research Foundation (BK21).

References

- [1] E. R. Peterson and R. D. Willet, *J. Chem. Phys.*, **56**, 1879 (1972).
- [2] R. Kind, S. Plesko, H. Arend, R. Blinc, B. Zeks, J. Seliger, B. Lozar, J. Slak, A. Levstik, C. Filipic, V. Zagar, G. Lahajnar, F. Milia and G. Chapuis, *J. Chem. Phys.*, **71**, 2118 (1979).
- [3] R. Blinc, M. I. Brugar, V. Rutar, B. Zeks, R. Kind, H. Arend and G. Chapuis, *Phys. Rev. Lett.*, **22**, 1679 (1979).
- [4] K. W. Lee, C. H. Lee, C. E. Lee and J. K. Kang, *Phys. Rev., B* **54**, 8989 (1996).
- [5] K. W. Lee, C. H. Lee, C. E. Lee and J. K. Kang, *Phys. Rev., B* **53**, 13993 (1996).
- [6] J. de Jongh, *Magnetic Properties of Layered Transition Metal Compounds* (Kluwer Academic Publishers, 1986).
- [7] H. Benner, *Phys. Rev., B* **18**, 319 (1978).
- [8] H. R. Boesch, U. Schmocker, F. Waldner, K. Emerson and J. E. Drumheller, *Phys. Lett.*, **36A**, 461 (1971).
- [9] D. B. Losee, K. T. McGregor, W. E. Estes, and W. E. Hatfield, *Phys. Rev., B* **14**, 4100 (1976).
- [10] C. H. Lee, K. W. Lee, C. E. Lee and J. K. Kang, *J. Korean Phys. Soc.*, **34**, L485 (1999)
- [11] J. Curely and J. Routh, *Physica B* **254**, 298 (1998).
- [12] H. A. Groenendijk, A. J. Duijneveldt and R. D. Willet, *Physica B* **98**, 53 (1979); *ibid.* **101**, 320 (1980).
- [13] T. Morya, *Phys. Rev.*, **120**, 91 (1960).