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Observation of Piezomagnetism in a Heisenberg Paramagnet

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Piezomagnetic behaviors have been observed far above the Neel temperature in the perovskite-type layer structure compound $(C_{18}H_{37}NH_3)_2MnCl_4$ undergoing structural phase transitions. Our observations were well explained by the magnetic and the structural orders coupled together *via* a magnetostructural coupling attributable to the Dzyaloshinsky-Moriya interaction.

Key words : A. magnetically ordered materials, D. phase transitions

1. Introduction

$(C_nH_{2n+1}NH_3)_2MCl_6$ (for short CnM, M=Cd, Cu, Mn, etc...) is a perovskite-type layered system which is 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* a N-H-Cl hydrogen bonding. Each MCl_6 octahedron is more or less tilted about the direction of the normal to the layers depending on to the hydrogen bonding scheme [1].

The CnM 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 are 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 [1]. In any case, some types of chain defects occur at the transition. In the light of the Landau model, previous studies have successfully described the structural phase transitions similar to those in the liquid crystals [2], and the critical dynamics related to the structural order parameter was reported recently by the authors [3, 4].

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 [5], and the EPR (electron paramagnetic resonance) linewidth shows an angular dependence characteristic of a two-dimensional paramagnet in the paramagnetic state [6]. In particular, an angular dependence characteristic of two-dimensional magnetism was explicitly observed in the EPR signals from $(C_nH_{2n+1}NH_3)_2$-$MnCl_4$ with shorter hydrocarbon chains ($n = 2$ and 3) [7].

According to the studies of short chain compounds, the magnetic moments in the antiferromagnetic phase are aligned along the direction of the layer normal, alternately pointing in opposite directions [8]. Structurally, the $MnCl_6$ octahedra are slightly tilted from the inorganic layer as a consequence of the hydrogen bonding; hence, a spin canting can take place along the direction parallel to the layer [9].

Structural phase transitions have been studied by means of EPR in several single crystals with a perovskite structure, such as $BaTiO_3$ [10], whereas EPR studies in the CnM system have been confined to two-dimensional magnetism [6, 7]. This can be attributed to the fact that the alkylammonium chains are believed to play the main role in the phase transitions of those systems, whose lattice dynamics is sensitively reflected in ^1H or ^{13}C nuclear magnetic resonance (NMR) measurements. Thus, a study of the structural phase transitions involving the inorganic planes has been made. The Mn^{2+} EPR study will be insensitive to the nonmagnetic alkylchain motions, but sensitive to the motion or distortion of the magnetic $MnCl_6$ octahedra, as confirmed by space group studies [11], nuclear quadrupole resonance (NQR) studies [12], etc.

We recently reported EPR and NMR studies for C18Mn, in which three successive structural phase transitions were assigned [13]: a conformational transition of

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*Corresponding author: e-mail: rscel@korea.ac.kr the alkylammonium chain at 346 K (T_{c1}) accompanied by the largest thermal entrance in DSC (differential scanning calorimetry), an order-disorder transition of the alkylammonium chain at 370 K (T_{c3}) accompanied by the second largest thermal entrance, and a transition at 359 K (T_{c2}) accompanied by the smallest thermal entrance, which was associated with the magnetic inorganic layer. The structural phase transitions at T_{c1} and T_{c3} associated with the alkylammonium chain were accompanied by a ^{1}H NMR second moment reduction, unlike that at T_{c2}, and a possible magnetostructural transition is suggested by the EPR linewidth anomalies at the structural phase transitions. Here, we directly measured the magnetization in order to establish the magnetic transition accompanying a structural phase transition.

2. Experiment

The C18Mn powder was synthesized and characterized as previously reported [13]. The powder sample was packed in a nonmagnetic capsule, and the temperature- and the magnetic-field-dependent magnetization was measured using a commercial SQUID (superconducting quantum interference device) magnetometer (Quantum Design MPMS series). Because of the flexible organic layers, which makes crystal growth difficult, the structure of the system is expected to be sensitive to an applied external pressure. Thus, we measured the magnetization for loosely packed and compactly packed samples in order to investigate the effect of pressure on the magnetism of this system.

3. Results and Discussion

In Fig. 1 is shown the temperature dependence of the magnetization measured with an applied magnetic field of 2 T. An antiferromagnetic behavior is observed at low temperatures, where the broad maxima around 80 K are regarded as a precursor to antiferromagnetism. The solid line represents a fit to Curely's formula for a square lattice Heisenberg antiferromagnet [14] with an exchange integral $J/k_B \sim 8$ K. Unlike the good fit at intermediate temperatures, deviations are noticed at low and high temperatures. In this work, our attention will be focused on the high-temperature magnetic behaviors and a detailed study of the low-temperature behaviors has been discussed elsewhere [15]. The low-temperature deviation originates from a long range antiferromagnetic order whereas the high temperature deviation can be attributed to high-temperature structural phase transitions. As it is unlikely that a structural order or disorder directly affects the magnetization, a magnetostructural coupling between the structural and the magnetic order parameters appears in order to explain the high-temperature behavior. In fact, a magnetostructural coupling in the CnMn system has been reported based on neutron scattering in the antiferromagnetic phase [16]. The Dzyaloshinsky-Moriya (DM) interaction is known to be responsible for the canted antiferromagnetism observed in the CnMn system, and the neutron scattering study suggested that the DM interaction is a strong candidate for the magnetostructural coupling [16]. Thus, it can be supposed that the structural order affects the magnetization via the DM interaction.

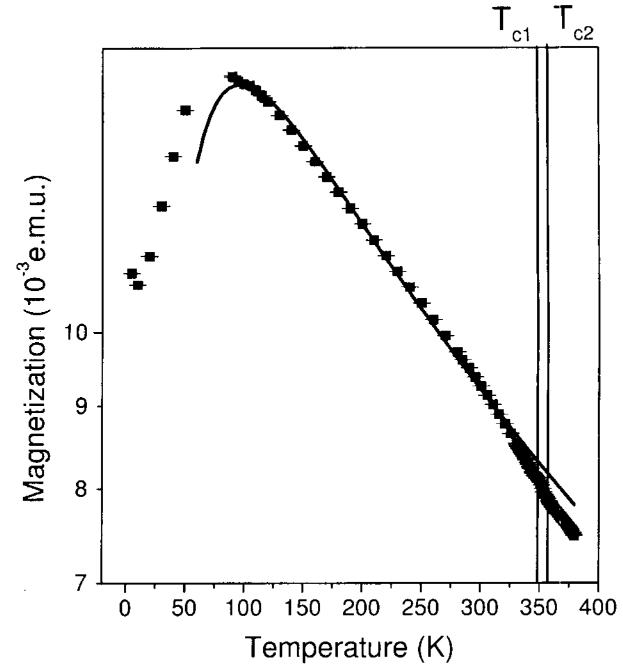

Fig. 1. Temperature dependence of the magnetization measured in an applied magnetic field of 2 T. The solid line represents a fit to Curely's formula.

Figure 2 shows the temperature-dependent magnetization for loosely packed and compactly packed samples near the structural phase transition temperatures. Whereas similar temperature dependences are observed at higher temperatures, differences are apparent at temperatures below the conformational phase transition temperature T_{c1}. This is more pronounced in Fig. 3 displaying the magnetization multiplied by temperature (MT) *vs* T, where the anomalies ascribed to the structural phase transitions are well reflected. In fact, Fig. 3 sensitively reflects the magnetic anomalies associated with the phase transition temperatures T_{c1} and T_{c2} and shows a pronounced pressure dependence of the magnetization below T_{c1}, which can readily be attributed to the presence of a type of piezomagnetic coupling in the system.

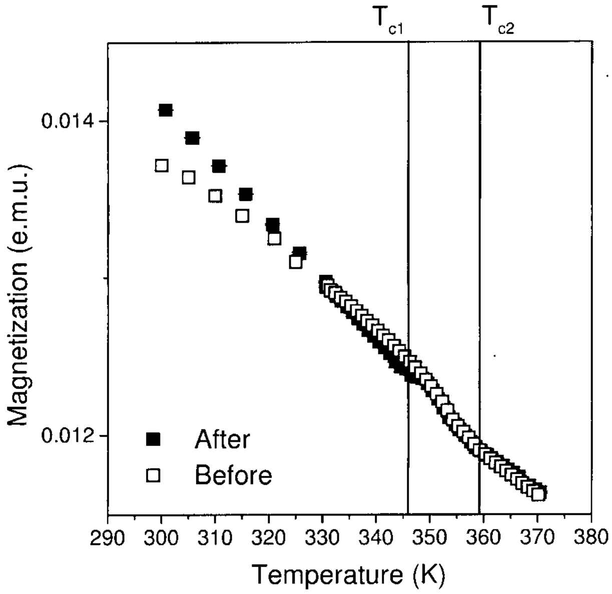

Fig. 2. Temperature dependence of the magnetization for loosely packed (solid symbols) and compactly packed (open symbols) samples measured in a magnetic field of 2 T.

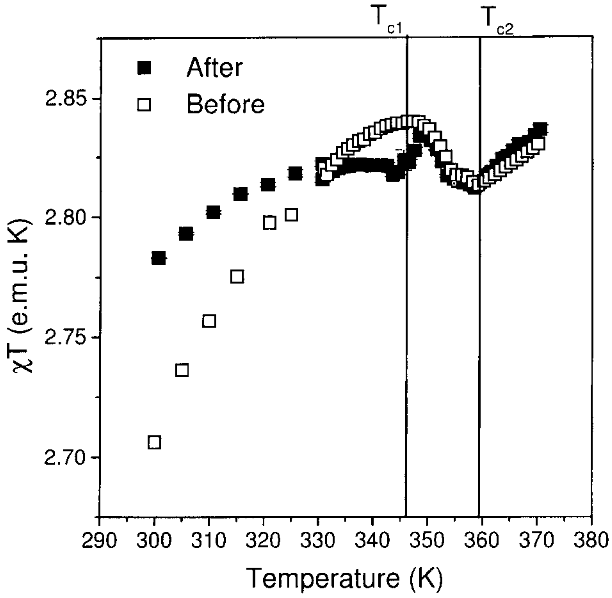

Fig. 3. Temperature dependence of the magnetization multiplied by the temperature for loosely packed (solid symbols) and compactly packed (open symbols) samples measured in a magnetic field of 2 T.

In summary, the magnetic behaviors for the perovskite-type layered-structure compound $(C_{18}H_{37}NH_3)_2MnCl_4$ were investigated by means of magnetic susceptibility measurements. As a result, a structural phase transition, as well as a low-temperature antiferromagnetic transition was well reflected in our measurements. Besides, a prominent pressure dependence, which could be attributed to a possible piezomagnetism, was observed.

Acknowledgments

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