

## Magnetism in the Layered Structure Compound (C<sub>18</sub>H<sub>37</sub>NH<sub>3</sub>)<sub>2</sub>MnCl<sub>4</sub>

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We have studied magnetostructural phase transitions in the perovskite-type layered structure compound (C<sub>18</sub>H<sub>37</sub>NH<sub>3</sub>)<sub>2</sub>MnCl<sub>4</sub> by means of electron paramagnetic resonance (EPR) and superconducting quantum interference device (SQUID) measurements. Distinct slopes were observed in the linear temperature dependences of the Mn<sup>2+</sup> EPR linewidth in the low and high temperature phases. Besides, linewidth anomalies at the transition temperatures sensitively reflect the magnetic changes arising from the MnCl<sub>6</sub> octahedra.

### 1. Introduction

Perovskite-type layered compounds of general formula (C<sub>n</sub>H<sub>2n+1</sub>NH<sub>3</sub>)<sub>2</sub>MCl<sub>4</sub> (C<sub>n</sub>M for short) show a variety of structural phase transitions, believed to be governed by the dynamics of the alkylammonium groups and by the rotational motions of the MCl<sub>4</sub> macroanions about their crystallographic axes. For M=Cd, Cu, and Mn, the mineral layers are constituted of more or less distorted corner-sharing MCl<sub>6</sub> octahedra forming a two-dimensional matrix and are sandwiched between hydrocarbon layers as shown in Fig. 1 [1]. For (C<sub>10</sub>H<sub>21</sub>NH<sub>3</sub>)<sub>2</sub>CdCl<sub>4</sub> (C10Cd), which shows two structural phase transitions, Blinc et al. have shown that order parameters used in the liquid crystals, pertinent to the alkylammonium chains, properly describe the phase transition sequence, while the inorganic layers play an indirect role [2, 3].

When M is Cu or Mn, the magnetic behavior of C<sub>n</sub>M exhibits a two-dimensional character. The magnetic susceptibility shows a large anisotropy at the magnetic phase transition [4] and the EPR linewidth shows an angular dependence characteristic of the two-dimensional paramagnet in the paramagnetic state [5]. In particular, the angular dependence of

EPR signals, which is characteristic of two-dimensional magnetism, has been explicitly observed in (C<sub>n</sub>H<sub>2n+1</sub>NH<sub>3</sub>)<sub>2</sub>MnCl<sub>4</sub> with shorter hydrocarbon chains ( $n=2$  and 3). Thus, our sample with  $n=18$  and greater interplanar distance (and presumably greater two-dimensionality) is readily expected to show a similar angular dependence. A study on K<sub>2</sub>MnF<sub>4</sub> shows that two-dimensional spin diffusion gives rise to the linear temperature dependence and the characteristic angular dependence of the EPR linewidth [7].

C<sub>n</sub>Mn has been intensively studied for the cases of  $n=1, 2,$  and 3 [5, 8]. However, for  $n$  greater than 10, most studies have been confined to DSC (differential scanning calorimetry) measurements. As a result of such measurements, two successive phase transitions have been found for  $n=10, 12,$  and 14 [4, 9]. Structural phase transitions have been studied by means of EPR in the perovskite structured single crystals like BaTiO<sub>3</sub> [10]. On the other hand, EPR studies of in the C<sub>n</sub>M systems have been confined to the two-dimensional magnetism [4], and have not been attracting much attention regarding the structural phase transitions. In fact, it has been believed that the alkylammonium chains play the main role in the phase transitions of those systems. The Mn<sup>2+</sup> EPR study will be insensitive to the non-

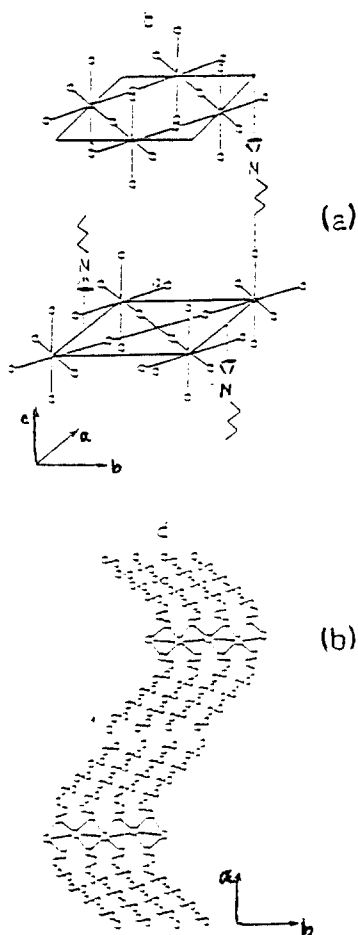
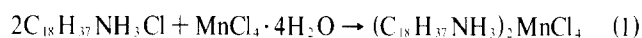


Fig. 1. (a) The overall structure of  $(C_nH_{2n+1}NH_3)_2MnCl_4$ . (b) Projection of the  $(C_nH_{2n+1}NH_3)_2MnCl_4$  ( $n=10$ ) structure on the  $bc$  plane.

magnetic alkylchain motions but sensitive to the motion or distortion of the magnetic  $MnCl_6$  octahedra, as confirmed by the space group studies [11] and nuclear quadrupole resonance (NQR) studies [12], etc. Thus, it is the purpose of the present work employing EPR and SQUID to investigate magnetic changes associated with the structural phase transitions in the layered structure compound C18Mn containing the magnetic  $Mn^{2+}$  ions.

## 2. Experiment

The  $(C_{18}H_{37}NH_3)_2MnCl_4$  (C<sub>18</sub>Mn) powder sample was made according to the reaction



The powder was twice recrystallized and then vacuum dried. The DSC measurements were made to identify the phase transition temperatures (Fig. 2) and the SQUID data were taken for magnetic susceptibilities. For  $Mn^{2+}$  EPR

measurements, a Bruker ESP 300 spectrometer was employed in the X-band frequency range (9.4 GHz). The magnetic susceptibility was measured by SQUID (Quantum Design) at 4.7 T.

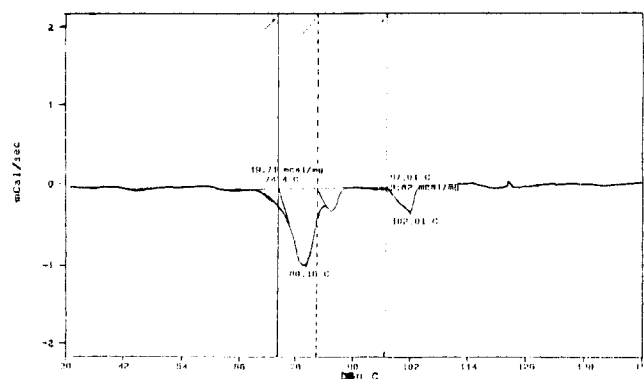


Fig. 2. The DSC pattern of C18Mn.

## 3. Results and Discussion

The DSC measurements show three structural phase transitions. The onset temperatures of the DSC anomalies correspond to a major transition at about 346 K ( $T_{C1}$ ), a minor one at about 359 K ( $T_{C2}$ ), and an intermediate one at about 370 K ( $T_{C3}$ ). In analogy to the layered structure compounds of similar type, the major transition can be attributed to a conformational transition, and one of the other two transitions can be assigned to an order-disorder phase transition of the hydrocarbon chain [2, 3]. In fact, <sup>1</sup>H NMR (nuclear magnetic resonance) second moment measurements showed an abrupt change at  $T_{C1}$  and smaller but noticeable change at  $T_{C3}$ . On the other hand, no noticeable change in the second moment was observed at  $T_{C2}$ . Since <sup>1</sup>H NMR probes only the hydrocarbon chain and not the magnetic inorganic plane, this indicates that the transitions at  $T_{C1}$  and  $T_{C3}$  arise from the organic chain, whereas that at  $T_{C2}$  has to do with changes in the inorganic plane. Of the two transitions at  $T_{C1}$  and  $T_{C3}$ , the major transition is supposed to correspond to the conformational transition involving kink formation on the hydrocarbon chains. Then, the transition at  $T_{C3}$  can be attributed to the order-disorder transition of the hydrocarbon chain involving smaller changes in the DSC pattern and in the second moment.

The magnetic susceptibility multiplied by temperature ( $\chi T$ ) vs  $T$  in Fig. 3 shows phase transitional behaviors around the transition temperatures  $T_{C1}$  and  $T_{C2}$ . On the other hand, no anomaly is found around  $T_{C3}$  which is presumably associated with the order-disorder transition of the hydrocarbon chain. Thus it is observed that the phase transition at  $T_{C3}$  involves no magnetic transition.

While the magnetic transitional behavior at  $T_{C2}$  can be uniquely attributed to the distortion of the magnetic  $MnCl_4$  octahedra on the inorganic plane, the magnetic transitional behavior at the conformational transition temperature  $T_{C1}$

deserves special attention. In other words, the changes in the nonmagnetic hydrocarbon chains would normally involve no magnetic changes. Thus, the magnetic transitional behavior at  $T_{c2}$  should indicate that the conformational or structural transition of the hydrocarbon chain induces a change in the magnetic plane. In fact, the  $\text{NH}_3$  group connecting the hydrocarbon chain to the magnetic  $\text{MnCl}_4$  octahedra is believed to be able to couple the two structures. In this sense, the phase transition at  $T_{c1}$  can be regarded as a magnetostructural transition where the structural change in the hydrocarbon chain induces a change in the magnetic planes. Indeed, a discontinuity in the EPR resonance field, a first-order behavior was observed only at  $T_{c2}$ , which is indicative of a purely magnetic transition. Of course, our system of  $\text{C18Mn}$  is supposed to be a Heisenberg paramagnet in the whole temperature range investigated, but structural changes in the magnetic plane ascribed to the distortion of the  $\text{MnCl}_4$  octahedra are observed in this work.

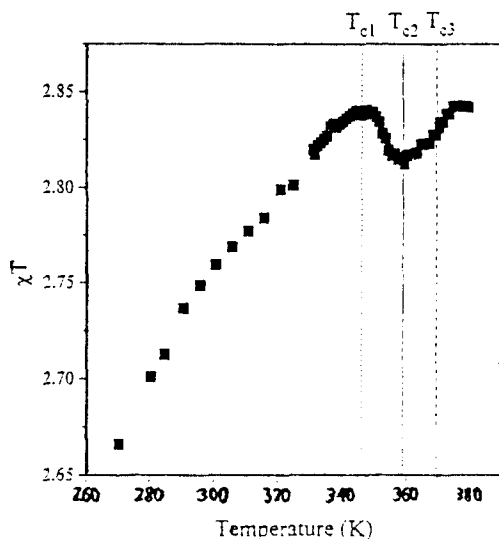


Fig. 3. SQUID magnetic susceptibility multiplied by temperature ( $\chi T$ ) vs temperature.

The magnetic susceptibility of a Heisenberg paramagnet can be approximated by [4, 13]

$$\chi T = C \exp(2J/k_B T) \quad (2)$$

where  $J$  is the exchange integral. In the low temperature structurally ordered phase in Fig. 3, the susceptibility has the temperature dependence of a Heisenberg paramagnet with an exchange integral  $J/k_B \cong -50$  K.

Figure 4 shows the temperature dependence of the EPR FWHM (full width at half maximum) linewidth of our sample. It is considered to be quite similar to that of  $\chi T$ , which is characteristic of two-dimensional magnetism [7]. As was discussed earlier, linear temperature dependence of the linewidth can arise from two-dimensional spin diffusion [7]. Together

with pronounced fluctuations around the intermediate phase, it exhibits a linear temperature dependence well below  $T_{c1}$  and well above  $T_{c2}$ , distinct slopes reflecting distinct magnetic structures in different phases. The negative slope between the transition temperatures  $T_{c1}$  and  $T_{c2}$  is attributed to a transitional behavior due to the magnetostructural phase transitions involving the coupling between the hydrocarbon chains and the magnetic  $\text{MnCl}_4$  octahedra.

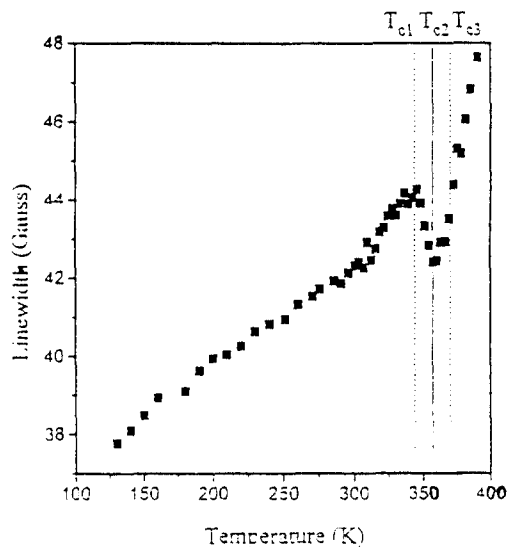


Fig. 4. EPR linewidth vs temperature.

In summary, layer structured  $(\text{C}_{18}\text{H}_{37}\text{NH}_3)_2\text{MnCl}_4$  was investigated by means of EPR and SQUID measurements. As a result, two-dimensional magnetism characteristic of the structure was well reflected in the temperature dependences of the magnetic susceptibility and the EPR linewidth, as well as transitional behaviors around the magnetostructural phase transitions.

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