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Critical dynamics in layer-structured $(C_{18}H_{37}NH_3)_2SnCl_6$

K. W. Lee, C. H. Lee, and C. E. Lee*
Department of Physics, Korea University, Seoul 136-701, Korea

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

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Phase transitions in the layer structured $(C_{18}H_{37}NH_3)_2SnCl_6$ were studied by 200-MHz ^{1}H NMR spin-lattice relaxation measurements. An order parameter corresponding to the order-disorder motion, defined by the fraction of the longer spin-lattice relaxation time constant component, revealed its three dimensionality, which was consistent with the temperature dependence of the spin-lattice relaxation rate. [S0163-1829(96)03925-2]

I. INTRODUCTION

Solid state phase transitions have been studied in model membranes similar to the biological ones.[1–10] Among them the layer compounds containing long alkylchains have received much attention because of easy preparation and manipulation. They show a variety of structural disorders: (a) planar disorder in the inorganic layer, (b) reorientational motions of the alkylchains about their long axes along with the flipping of the polar groups (e.g., NH_3) between the potential wells, and (c) conformational changes leading to a partial melting of the alkylchain part.

Model membranes of the $(C_nH_{2n+1}NH_3)_2MX_4$ type have been intensively studied. In the compounds with $M=$ Mn, Fe, Cu, Cd, and Hg, the corner-sharing MX_6 octahedra form two-dimensional MX_4^{2-} macroanions, whose negative charge is balanced by the alkylammonium ions surrounded by eight neighboring halogen atoms. Thus the alkylammonium chains are located between the inorganic layers, forming bilayers tilted with respect to the MX_4^{2-} sheet.[5]

On the other hand, in $(C_nH_{2n+1}NH_3)_2SnCl_6$ (CnSn) the $SnCl_6$ octahedra do not form two-dimensional (2D) macroanions. The NH_3 group of the alkylammonium ion is linked to the three closest octahedra by the statistically equivalent weak hydrogen bonds with the alkylchains interdigitated between the MCl$_6$ octahedra layers. The alkylammonium groups are statistically disordered around the threefold axes with the alkylchains alternately pointing up or down.[11] Thus it is interesting to compare the dynamics in the CnSn systems with results in the CnCd systems, with different structures, and this work represents one of the first NMR measurements in the CnSn systems showing two structural phase transitions.

The first systematic studies on the layer structured intercalation compounds were made by Kind and coworkers by means of the magnetic resonance in C10Cd.[5,6] Measurements of the order parameters by the ^{35}Cl and ^{14}N nuclear quadrupole resonance (NQR) and ^{1}H and ^{13}C NMR made possible a consistent understanding of dynamics of the NH_3 group and the hydrocarbon chains and the phase transitions using a Landau theory similar to that used in the liquid crystal. In contrast, little information is available on the phase transitions in the CnSn systems.[12–14] The purpose of the present study is to characterize the phase transitions in $(C_{18}H_{37}NH_3)_2SnCl_6$ (C18Sn), with the greatest chain length to be reported, using ^{1}H NMR.

II. EXPERIMENT

The powder sample of C18Sn was synthesized as reported in the literature[15] and checked by elemental analysis, IR, and x-ray diffraction. The differential scanning calorimetry (DSC) carried out between 123 and 473 K showed two highly reversible phase transitions on heating, a minor one at $T_{c1}=347$ K attributed to an order-disorder transition, and a major one at $T_{c2}=371$ K attributed to the conformational transition of the hydrocarbon chains.

The 200 MHz pulsed ^{1}H NMR measurements were made on heating in the temperature range 125–400 K. The spin-lattice relaxation times were measured by means of the inversion recovery sequence.

III. RESULTS AND DISCUSSION

The spin-lattice relaxation could be fitted into a single-exponential form at low temperatures. However, above room temperature it was nonexponential and was well fitted into a double-exponential form with two distinct time constants T_{1L} and T_{1S} corresponding to the longer time constant and the shorter one, respectively. Figure 1 shows the spin-lattice relaxation rates as a function of temperature. It is seen that the critical fluctuations are reflected around the phase transition temperatures in a pronounced manner. Figure 2 shows the temperature dependence of the fraction A of the T_{1L} component in the spin-lattice relaxation. As the shorter spin-lattice relaxation time component accounts for most of the spin-lattice relaxation and shows the critical slowing down at the order-disorder phase transition temperature T_{c1} as shown in Figs. 1 and 2, the T_{1S} and its fraction $1-A$ are ascribed to the order-disorder chain motions. Figure 2 suggests that the fraction A serves as an order parameter in the low-temperature phase, corresponding to the order-disorder transition. Figure 3 shows that A is proportional to $(T/T_{c1})^{1/3}$ below T_{c1}, giving the exponent $\beta=0.33$ for the order parameter, which is compatible with the three-dimensional Ising

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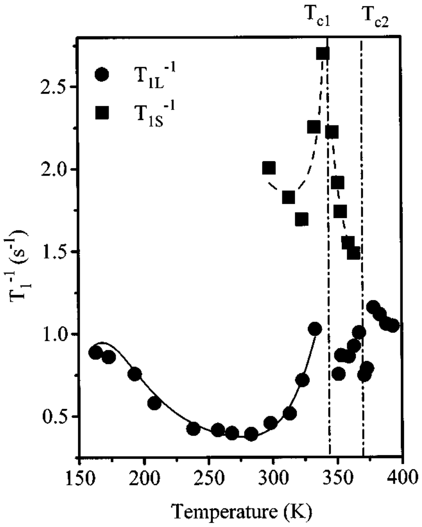

FIG. 1. Temperature dependence of the spin-lattice relaxation rate. The dashed line is fitted to Eqs. (1) and (2), and the solid line is fitted to the intramolecular dipole-dipole spin-lattice relaxation by two types of molecular motions in the low-temperature phase.

model,[16] and which also suggests that it really acts as an order parameter for the order-disorder transition.

It is known from the kinetic Ising model that the spin-lattice relaxation rate arising from the critical slowing down in order-disorder systems is given by[17]

$$T_1^{-1}\propto \tau_0|t|^{\nu d-\Delta-\gamma}, \quad T>T_c, \tag{1}$$

$$T_1^{-1}\propto \tau_0|t|^{\nu d-\Delta-\gamma}(1-|t|^{2\beta}), \quad T<T_c, \tag{2}$$

in the limit $\omega\tau(\vec{q})\ll 1$, where ν, Δ, γ, and β are the critical exponents of the correlation length, correlation time, static susceptibility, and the order parameter, and d is the dimension, with $t=(T-T_c)/T_c$. An Arrhenius temperature dependence of τ_0 is assumed.

In Fig. 1 the best fit for T_{1S}^{-1} for $T>T_{c1}$ is obtained with $\nu d-\Delta-\gamma=-0.23$ and $E=6.2\pm 0.5$ kJ. This activation energy E of the Ising variable is too small to be attributed to the rigid hydrocarbon chain and thus the Ising variable is attributed to the NH_3 polar head. Using the reported three-dimensional Ising model values of $\nu=0.63$, $\gamma=1.25$, and $d=3$, a value of $\Delta=0.87$ was obtained from the fit, which is comparable to the mean-field-approximated value of $\Delta=1$. For $T<T_{c1}$, a good fit was obtained using the values of $\nu d-\Delta-\gamma=-0.23$, $E=6.2\pm 0.5$ kJ, and $\beta=0.33$, as obtained above. The three dimensionality observed in our work is indicative of the interlayer interactions of the hydrocarbon chains in this system.

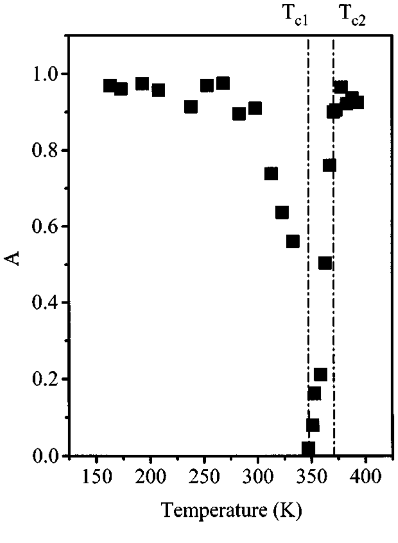

FIG. 2. The fraction A of the T_{1L} component as a function of temperature.

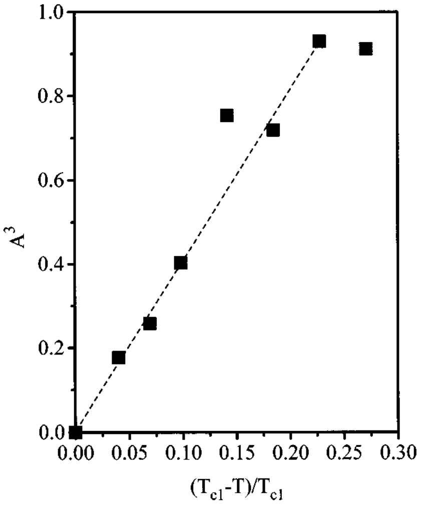

FIG. 3. The cube of the fraction A in the low-temperature phase.

While the spin-lattice relaxation had to be fitted into a double-exponential form at intermediate temperatures, it again fitted a single-exponential form well above the T_{c2}. This indicates that the spin diffusion becomes dominant enough, or that all parts of the chains become mobile enough for a single-exponential relaxation. Since the spin-lattice relaxation is dominated by the kink motion and A is nearly 1 in the high-temperature phase above T_{c2}, the gradual increase of A from 0 to 1 in the intermediate phase is indicative of the continuous kink formation in that phase.[18]

A nonexponential spin-lattice relaxation can be caused by a slight inhomogeneity of the sample, such as grain sizes and impurities. However, this can be safely ruled out in our case as our 45 MHz measurements on the same C18Sn sample showed a single-exponential spin-lattice relaxation pattern at all temperatures.[19] On the other hand, our recent rotating frame NMR measurements reflecting the ultralow-frequency dynamics showed a stretched-exponential behavior at all temperatures.[20] Thus it can be concluded that the nonexponential pattern is not caused by physically different regions in this system, but by the distinct relaxation mechanisms active in the frequency range of investigation. It may be inferred that at 200 MHz it happens that the spin-lattice relaxation is given by a single high-frequency relaxation mechanism such as the reorientational motions of the chain-end CH_3 or NH_3 groups away from the critical regimes, whereas the critical order-disorder flip-flop motion of the NH_3 polar head can make an additional contribution to the spin-lattice relaxation in the critical regimes. Then Fig. 2 can be understood as reflecting variation of the relative contributions to the spin-lattice relaxation from the two relaxation mechanisms, perhaps the normal molecular motions and the critical fluctuations, depending on the proximity to the phase transition temperatures. In fact, together with the behavior of the spin-relaxation rate T_{1S}^{-1} in Fig. 1 from the two-exponential attributed to the critical dynamics well explained by the kinetic Ising model, the behavior as an order parameter for the order-disorder transition, of the fraction A of the longer spin-lattice relaxation time component representing the normal molecular motions, shows that our two-exponential fit for the critical regimes is physically valid and plausible.

In summary, the 200 MHz ^{1}H NMR spin-lattice relaxation measurements in the long-chain layer structure compound $(C_{18}H_{37}NH_3)_2SnCl_6$ (C18Sn) sensitively reflected the phase transitions in this system. In the low-temperature phase an order parameter defined as the fraction of the longer spin-lattice relaxation time component yielded a critical exponent of 1/3, which indicates that the order-disorder transition has a three dimensional nature and that the interlayer interaction is appreciable. The temperature dependence of the spin-lattice relaxation rate was also compatible with the three-dimensional Ising model.

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*Author to whom all correspondence should be addressed.

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