^{1}H NMR study of the dimensional crossover in $C_{10}H_{21}NH_3Cl$

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^{1}H NMR was employed to study the irreversible phase transition in $C_{10}H_{21}NH_3Cl$ accompanied by an interdigitated-noninterdigitated structural change. The phase transitions were manifest in the second moment as well as in the spin-lattice relaxation rate measurements with a hysteresis upon heating and cooling. In this work, the dimensionality and its crossover were explicitly confirmed in similar systems. [S0163-1829(96)06721-5]

I. INTRODUCTION

Model membranes such as the intercalated layer structured compounds are expected to show a variety of dimensional effects, and indeed have shown two-dimensionality in magnetic transitions.[1] On the other hand, in the structural phase transitions the dimensionalities have never been explicitly confirmed either experimentally or theoretically. The n-decylammonium chloride compound $C_{10}H_{21}NH_3Cl$ (C10Cl for short) shows a structural phase transition from an interdigitated to a noninterdigitated chain configuration, and is believed to be ideal for the study of dimensionality of the phase transitions in an appropriate model.

C10Cl crystallizes at room temperature in a perfectly ordered structure consisting of layers of chlorine atoms linked to the adjacent decylammonium chains by the NH-Cl hydrogen bonding.[2] Upon heating and cooling it undergoes several solid-solid phase transitions. A study employing differential scanning calorimetry (DSC), x-ray diffraction, infrared absorption, and Raman scattering elucidated the phase transition sequences upon the first heating and cooling as[3]

$$\begin{array}{ccccc} & 322\text{ K} & & 328\text{ K} & \\ i & \rightarrow & \delta & \rightarrow & \alpha \\ \epsilon & \leftarrow & \delta & \leftarrow & \alpha \\ & 307\text{ K} & & 325\text{ K} & \end{array}$$

In the i phase, the hydrocarbon chains are in an interdigitated and all-trans conformation. Through the irreversible $i \rightarrow \delta$ transition, the hydrocarbon chains become noninterdigitated. The chain configuration in each phase is illustrated in Fig. 1 as obtained by the infrared and Raman spectroscopies and the incoherent quasielastic neutron scattering (IQNS) study.[3–5] Blinc and co-workers have explained the transition sequence and predicted the behavior of the order parameters using a Landau theory similar to that used in the liquid crystals.[6] ^{13}C NMR and ^{14}N and ^{35}Cl nuclear quadrupole resonance (NQR) studies showed that the behavior of the order parameters was consistent with their Landau theory.[7,8] However, they attributed the irreversibility to the interdigitation of the hydrocarbon chains as the irreversibility of the $i \rightarrow \delta$ transition is not explained by the Landau theory itself. Since the hydrocarbon chains are not interdigitated in the ϵ phase, the reversibility of the transitions $\epsilon \leftrightarrow \delta \leftrightarrow \alpha$ upon further heating or cooling is understood from the suggestions of Blinc and co-workers. However, the interdigitation of the hydrocarbon chains only cannot fully account for the reversibility or irreversibility of the phase transitions. It is the purpose of this paper to investigate the change of the dimensionality and the behavior of the order parameters accompanied by the irreversible structural phase transitions in this system.

II. EXPERIMENT

A C10Cl sample was prepared as reported in the literature,[9] and checked by DSC and IR measurements. The 45 MHz ^{1}H NMR second moment and spin-lattice relaxation time measurements were made by a home-built pulsed NMR spectrometer in the temperature range 300–350 K as raising and then lowering the temperature.

III. RESULTS AND DISCUSSION

The second-moment measurements manifest the phase transitions with a hysteresis upon heating and cooling as shown in Fig. 2.[6,10] The rapid decrease of the second moment near the $i \rightarrow \delta$ transition indicates the reorientation of the hydrocarbon chains and further diminution near the $\delta \rightarrow \alpha$ transition is believed to arise from the conformational disorder.[6,10] The smaller second moment in the ϵ phase than

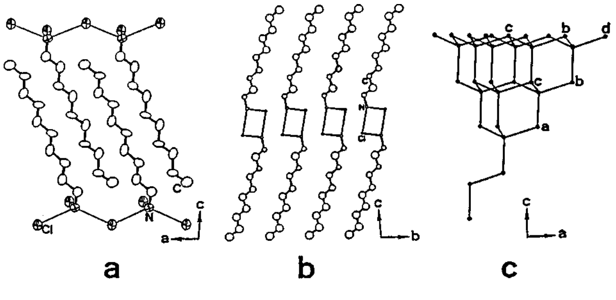

FIG. 1. Chain structure for C10Cl i<n the phase i (a) in the phases δ and ϵ (b) and in the phase α (c) (from Ref. 2).

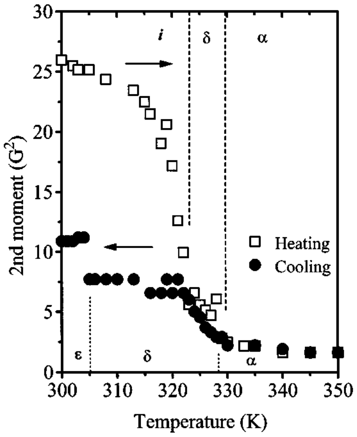

FIG. 2. The second moment measured as heating and then cooling the sample.

that in the *i* phase indicates that the hydrocarbon chains are not completely ordered, undergoing reorientational motions.

Figure 3 shows the spin-lattice relaxation rate measurements upon heating and then cooling the sample, in which a remarkable hysteresis is displayed. Together with the abrupt decrease of the second moment and of the order parameter obtained by ^{13}C NMR around 308 K (Ref. 8) and the behavior of the spin-lattice relaxation rate incompatible with the thermally activated motion, the observed temperature dependence of the spin-lattice relaxation rate indicates that the $i \rightarrow \delta$ transition is dominated by the critical dynamics. In the δ phase, the NH$_3$ polar group spends its time between two favorable sites,[8] whose critical dynamics can be described by the spin-1/2 kinetic Ising model.

Following the derivation of Mognaschi *et al.*, the spin-lattice relaxation rate below the transition temperature is expressed as[11,12]

$$T_1^{-1} = A[(T_c - T)/T_c]^{\Delta-\gamma}(1 - \langle s \rangle^2) \tag{1}$$

$$= A[(T_c - T)/T_c]^{\Delta-\gamma}\{1 - [(T_c - T)/T_c]^{2\beta}\}, \tag{2}$$

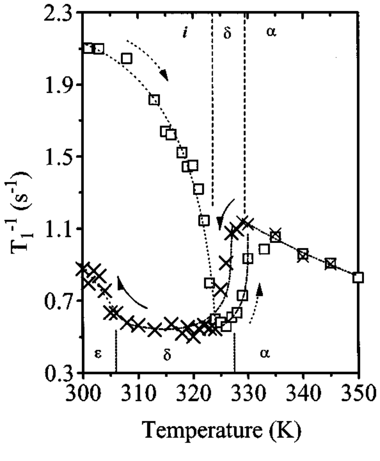

FIG. 3. The spin-lattice relaxation rate ($1/T_1$) as heating and then cooling the sample: □, heating cycle; × cooling cycle; dotted lines, fitted to Eq. (2); dot-dashed lines, fitted to Eqs. (3) and (4); double-dot-dashed line, fitted to Eq. (4).

in the limit $\omega\tau(\vec{q}) \gg 1$, where $\langle s \rangle$ is the order parameter, and Δ, γ, and β are the critical exponents of the correlation time, static susceptibility, and the order parameter, and where the proportional constant A is a quantity related to the correlation function and includes the Larmor frequency (see Ref. 12 for more details). The spin-lattice relaxation rate in the *i* phase is well fitted to Eq. (2), giving $\beta = 0.33 \pm 0.03$, $\Delta - \gamma = 0.4 \pm 0.05$, and $A = 8.8 \pm 0.5$ s^{-1}. The value of $\beta = 0.33$ is in complete agreement with the three-dimensional case. Then using the reported three-dimensional (3D) kinetic Ising model value of $\gamma = 1.25$, we get $\Delta = 1.6$. While the value of Δ is not exactly calculable in the 3D Ising model, this value of Δ is quite reasonable since the critical exponent in a universality class is a monotonous function of the dimensionality, and the 4D and 2D values are known to be 1 and 2, respectively.[13] In the *i* phase, the chains are interdigitated and thus their reorientations should be gearlike collective motions. The three-dimensionality of the collective critical dynamics indicates that the interlayer interactions are appreciable in the order-disorder transition of the hydrocarbon chains.

Since the chains are not interdigitated in the δ phase, the gearlike collective motions are not effective and no critical slowing down will be associated. Thus, the spin-lattice relaxation rate due to the order parameter can be expressed as

$$T_1^{-1} = A\{1 - [(T_c - T)/T_c]^{2\beta}\}. \tag{3}$$

In the limit $\omega\tau_c \ll 1$, the spin-lattice relaxation rate due to the thermally activated motion follows the Arrhenius-type temperature dependence[14]

$$T_1^{-1} = Be^{E/RT}, \tag{4}$$

where $B = 2/3\gamma^2\langle \Delta H^2 \rangle \tau_0$, and γ, $\langle \Delta H^2 \rangle$, and τ_0 are the protonic gyromagnetic ratio, the second moment, and the motional correlational time at infinite temperature, respectively, and R is the universal gas constant. The activation energy E in the C10Cl compound was measured by IQNS to be 18 kJ/mol in the δ phase.[5] Combining Eqs. (3) and (4) in the δ phase, the best fit was obtained with $A = 2.5 \pm 0.5$ s^{-1}, $B = 0.0003 \pm 0.0001$ s^{-1}, and with the critical exponent $\beta = 0.13 \pm 0.03$, which is compatible with that of $\beta = 0.125$ in the two-dimensional Ising model. The two-dimensional nature is readily expected, since the noninterdigitated chain configurations makes the structure of the compound quasi-two-dimensional. In the α phase, the spin-lattice relaxation rate is well fitted to Eq. (4) with the activation energy 16 kJ/mol, which is consistent with the IQNS study.[5]

At the $\epsilon \leftrightarrow \delta$ phase transition, the spin-lattice relaxation rate shows a behavior similar to that of the $i \rightarrow \delta$ phase transition although the variation of the spin-lattice relaxation rate is much smaller. The difference represents a smaller variation of the order parameter at the $\epsilon \leftrightarrow \delta$ transition than that at the $i \rightarrow \delta$ transition. The smaller spin-lattice relaxation rate in the ϵ phase than that in the *i* phase arises from a less effective collective motion of the hydrocarbon chains.

In the ϵ phase, the spin-lattice relaxation rate is well fitted to Eq. (2) with a background relaxation in the form of Eq. (4) using the kinetic Ising model values of $\beta = 0.125$ and $\Delta - \gamma = 0.25$, where $A = 0.6 \pm 0.1$ s^{-1} and $B = 0.0004 \pm 0.0001$ s^{-1} are obtained for the best fit. The activation

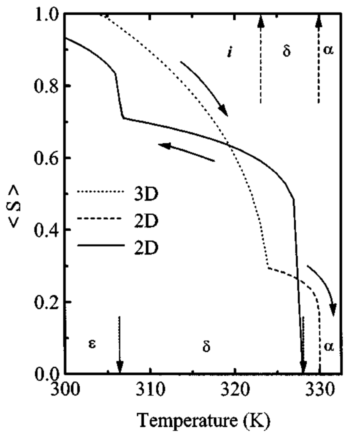

FIG. 4. The temperature dependence of the order parameter $\langle s \rangle$ as heating and then cooling the sample.

energy given by the background relaxation in the ϵ phase is close to that in the δ phase. Then, in the ϵ phase the hydrocarbon chains are expected to undergo thermal motions comparable to that in the phase δ at least around the $\epsilon \leftrightarrow \delta$ transition temperature although the ϵ phase is much more ordered.

The overall behavior of the order parameter $\langle s \rangle$ obtained from Eqs. (2) and (3) is shown in Fig. 4. Through the $i \rightarrow \delta$ transition where a three- to two-dimensional crossover takes place, it is shown that the order parameter $\langle s \rangle$ decreases monotonously, also reflecting the structural and dimensional transition at the $i \rightarrow \delta$ transition temperature, and then vanishing at the $\delta \rightarrow \alpha$ transition temperature upon heating. Upon cooling, the two-dimensional order parameter is shown to abruptly increase through the $\alpha \rightarrow \delta$ transition and also to reflect the $\delta \rightarrow \epsilon$ transition.

In summary, the irreversible structural and dimensional phase transitions in layer structure compound C10Cl involving the chain configuration changes were investigated in this paper by means of ^{1}H NMR. It was shown that the dimensionality of the chain motions in this system is directly given by the chain configurations, and a coherent behavior of the order parameter for the reorientational motions was also observed. Besides, the dimensionality of the chain motions in each phase was explicitly calculated.

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