A Proton NMR Study of n-Decylammonium Chain Dynamics in the Perovskite-type Layered Compound $(C_{10}H_{21}NH_3)_2CdCl_4$

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Dedicated to Professor H. W. Spiess on the occasion of his 50th birthday

A detailed proton second moment and spin-lattice relaxation time investigation of the bilayered compound $(C_{10}H_{21}NH_3)_2CdCl_4$ is reported. In the low temperature phase the methyl group executes a classical threefold reorientation, while the NH_3 group is involved in a similar reorientation in an asymmetric potential well. Evidence for defect chain motions in this phase has been found, and infomation regarding the potential wells associated with these motions has been extracted from the data. In the high temperature phase, slow chain defect motions and fast fourfold reorientations of chains about their long axes, parallel to the normal to the bilayer, have been observed.

Key words: Bilayered compounds; Phase transition; Spin-lattice relaxation; Molecular motions; Defect motions.

1. Introduction

Extensive studies of the perovskite-type layer compounds with general formula $(C_nH_{2n+1}NH_3)_2MCl_4$ (henceforth referred to as C_nM) [1, 2], have contributed to a better understanding of phase transitions in layered structures, including two-dimensional lipid layers occurring in biomembranes [3]. The inorganic sheets, consisting of corner-sharing MCl_6 octahedra, with $M = Cd^{2+}$, Mn^{2+}, Cu^{2+}, etc., form a two-dimensional solid matrix. The cavities between the octahedra are occupied by NH_3 polar heads of *n*-alkylammonium groups which form $N-H \cdots Cl$ hydrogen bonds. Thus the hydrocarbon chains are sandwiched between inorganic layers.

These compounds exhibit a variety of structural phase transitions which are governed by the dynamics of the alkylammonium chains. The base transitions can be divided into two classes, viz. order-disorder transitions of the rigid all-*trans* chains and conformational transitions which lead to a partial "melting" of the hydrocarbon part of the chains. The latter type of transition occurs only if $n > 3$.

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Of the compounds which show these phase transitions, $C_{10}Cd$ is the one most thoroughly studied one. The results of calorimetric, X-ray diffraction, NMR [2], vibrational spectroscopy [4] and incoherent neutron diffraction [5] investigations have shown that it undergoes two first-order phase transitions at 308 K and 312 K. In the low temperature (LT) ordered phase ($T < 308$ K), the hydrocarbon chains are tilted at $\sim 40°$ with respect to the normal to the inorganic layers. However, the chains of adjacent layers form a zig-zag arrangement along the normal to the inorganic layers, resulting in two nonequivalent chains (X and Y) which are packed in an ..XYX.. sequence. The X chains exhibit a single gauche defect between the first and second carbon atoms, while the Y chains have a similar defect between the second and third carbon atoms [2].

In the narrow intermediate temperature (IT) phase between 308 K and 312 K the chains are still tilted with respect to the normal, but a conformational disorder between the X and Y orientations is present [2].

At the transition to the high temperature (HT) phase (312 K) a dramatic change in the molecular ordering, and therefore the crystal structure, takes place. A significant increase in the interlayer spacing is associated with the chains being oriented parallel to the normal to the inorganic layers in this phase. It has

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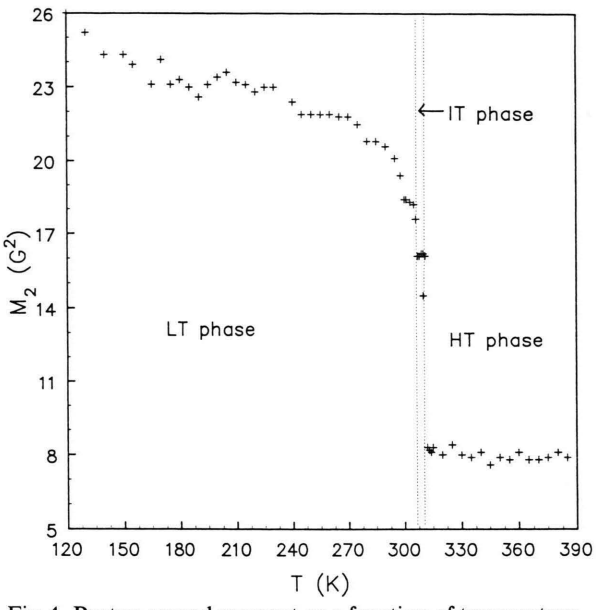

Fig. 1. Proton second moment as a function of temperature.

been suggested that chain defects diffuse along the chain axes [2], resulting in a so-called "chain melting".

In this paper a detailed proton NMR study of polycrystalline $C_{10}Cd$ is reported with the aim to identify the chain and segmental dynamics and to relate the revealed motions with the phase transitions occurring in this system.

2. Experimental

Polycrystalline $C_{10}Cd$, deuterated at the sixth carbon position, was prepared according to the method described by Kind and Roos [6]. The mixing of decylammonium chloride, prepared as described previously [7], and cadmium chloride in ethanol led to the formation and precipitation of the compound. After separation it was recrystallized several times from methanol. Deuteration was required for other experiments on the same sample.

Experimental proton second moments, M_2, were obtained as a function of temperature by using a Spin Lock continuous wave spectrometer operating at 19 MHz. Signal averaging and corrections for finite modulation amplitudes were made on a personal computer interfaced to the spectrometer. The average of up to five spectra was obtained at each temperature.

Proton spin-lattice relaxation times in the laboratory frame, T_1, were made at 200 MHz and 75 MHz on a Bruker CXP 200 pulse spectrometer and a homemade pulse spectrometer, respectively, by applying a train of sixteen closely spaced 90° saturating pulses, followed at a variable time interval τ by a single 90° measuring pulse. The train of pulses destroys all residual magnetization in a relatively short time, thereby eliminating the need for waiting several T_1's between measurements. The decay of the magnetization was exponential at all temperatures.

The same saturation method was used in measuring the proton spin-lattice relaxation time in the rotating frame, $T_{1\varrho}$, as a function of temperature. In this case the saturating pulse train was followed after about $T_1/2$ by a 90° rf pulse. This pulse was then followed immediately by a second rf pulse which was 90° phase shifted with respect to the first pulse. $T_{1\varrho}$ values were obtained from the slopes of semi-log plots of magnetization versus τ graphs, where τ was the length of the 90° phase shifted pulse.

3. Results and Discussion

3.1 Second Moments

The temperature dependence of M_2 in the LT, IT and HT phases is displayed in Figure 1. A plateau of 22 ± 2 G^2* is observed between 270 K and 150 K. Below this temperature the second moment increases slowly without reaching a rigid lattice value in the temperature range covered. Above 270 K M_2 starts to decrease, reaching a value of ~ 16 G^2 in the IT phase. Increasing the temperature further results in a sudden drop to a plateau value of ~ 8 G^2 in the HT phase.

The total rigid lattice proton second moment of a polycrystalline *n*-alkane is given by [8]

$$M_2 = 26.3 + 19.1/(n+1), \tag{1}$$

where n is the number of carbon atoms per chain. Using this equation, good estimates can be obtained for the second moments of the $C_{10}Cd$ sample. For example, since the $C_{10}H_{21}NH_3$ chain is fully deuterated at the sixth carbon atom, it can be approximated as *n*-C_{10}. The rigid lattice second moment, including the larger contribution due to the replacement of one methyl group ($r_{H-H} = 1.78$ Å) by an NH_3 group ($r_{H-H} = 1.68$ Å), is then estimated to be ~ 30 G^2. Other calculated second moments are 16 G^2 and 8 G^2 for chains executing twofold and fourfold reorientations,

* $1\,G^2 = 10^{-2}\,mT^2$.

respectively, 27 G^2 for rigid chains with methyl groups executing threefold reorientations and 23.7 G^2 if, in addition to the methyl group reorientations, the NH_3 groups also execute threefold reorientations.

The plateau of 22 ± 2 G^2 between 270 K and 150 K is in agreement with a model in which the chains are stationary, but with threefold reorientations of methyl and NH_3 groups. A single defect motion should produce a relatively small second moment reduction, which would be difficult to observe in second moment experiments.

Above 270 K the second moment decreases sharply as a function of increasing temperature, implying that reorientations of chains are taking place. The M_2 values in the IT phase is approximately 16 G^2, the calculated value for a twofold motion of the chains, but this phase is too narrow (~ 4 K) to identify a plateau unambigiously. It is also possible that the chains are in an asymmetric fourfold potential and that jumps through 90° between two adjacent minima occur with the other two orientations having relatively low populations. Evidence for such a motion has been found in a deuteron study of this compound [9].

The plateau of 8 G^2 in the HT phase is due to fast fourfold reorientations of chains about their long axes in a symmetrical potential well. In this phase the chain axes are parallel to the normal to the bilayer [2]. Vibrational results [4], as well as unpublished deuteron results [9], revealed that chain defect motions are superimposed on the fourfold reorientations of the chains. However, since the proton second moment is not reduced to a value lower than 8 G^2, it is clear that chain melting does not occur in this compound. In $C_{10}Zn$ [10] chain melting reduces the proton second moment to ~ 1 G^2 in the high temperature phase.

3.2 Spin-Lattice Relaxation Times

3.2.1. Low Temperature Phase

The spin-lattice relaxation times in the laboratory and rotating frames are displayed in Figs. 2 and 3, respectively, as a function of $1000/T$ ($=\beta$). T_1 shows a broad asymmetrical minimum of ~ 450 ms at a Larmor frequency of 200 MHz. The corresponding minimum at a Larmor frequency of 75 MHz is 200 ms and exhibits a similar asymmetrical behaviour. $T_{1\varrho}$ at $H_1 = 10$ G decreases with lowering temperature. However, the nonlinear dependence of $\ln T_{1\varrho}$ on β suggests that an overlapping of several relaxation mechanisms

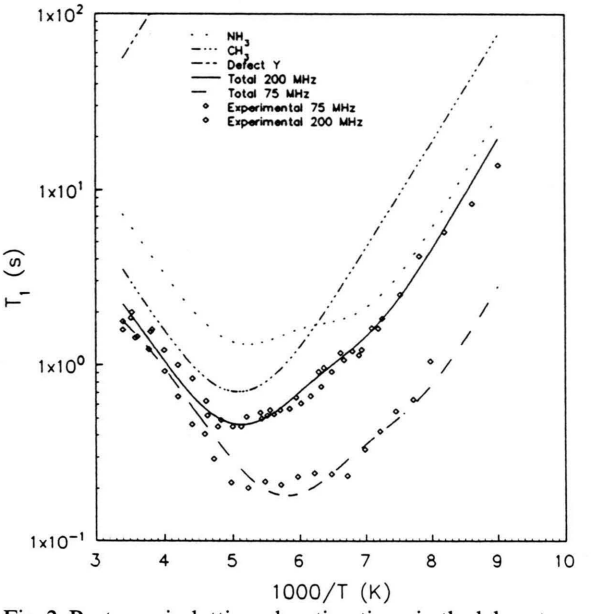

Fig. 2. Proton spin-lattice relaxation times in the laboratory frame as functions of inverse temperature in the LT phase. Contributions of the different motions to the relaxation rate are also shown.

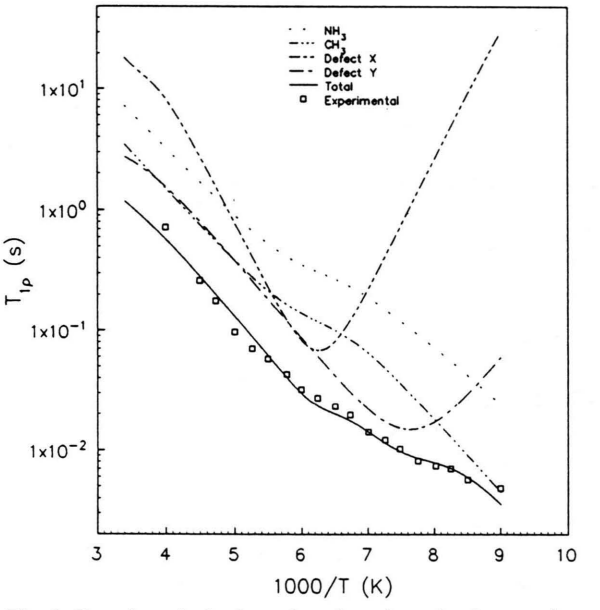

Fig. 3. Protein spin-lattice relaxation times in the rotating frame as functions of inverse temperature in the LT phase. Contributions of the different motions to the relaxation rate are also shown. The solid line represents the best fit to the data. $H_1 = 10$ G.

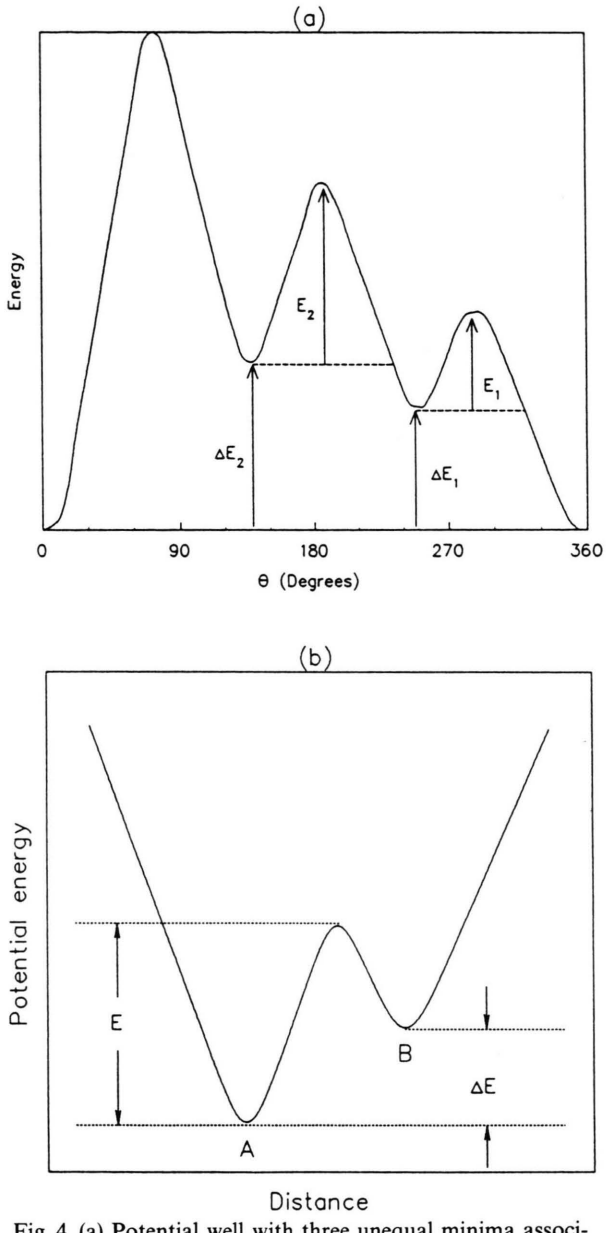

Fig. 4. (a) Potential well with three unequal minima associated with the motion of the NH_3 groups. (b) Potential well for defect chain motions in the LT phase.

might be present. Two unresolved minima seem to be present at $\beta \simeq 6.3\ K^{-1}$ and $\beta \simeq 8.3\ K^{-1}$.

Since the lowest barriers to reorientation are expected to be for threefold reorientations of methyl and NH_3 groups, it is assumed that the asymmetry of the T_1 minima is due to overlapping of the relaxation rates of these reorientations. Substituting the calculated intramolecular proton second reductions of 2.5 G^2 and 3.5 G^2 for CH_3 and NH_3 groups, respectively, into the standard expressions for the relaxation rates due to these motions [11]

$$1/T_1 = 2/3\,\Delta M_{2i}\,\gamma_H^2\,\{\tau_{ci}/(1+\tau_{ci}^2\,\omega_0^2) + 4\,\tau_{ci}/(1+4\,\omega_0^2\,\tau_{ci}^2)\} \tag{2}$$

and

$$1/T_{1\varrho} = \Delta M_{2i}\,\gamma_H^2\,\{5/3\,\tau_{ci}/(1+\tau_{ci}^2\,\omega_0^2) + 2/3\,\tau_{ci}/(1+4\,\omega_0^2\,\tau_{ci}^2) + \tau_{ci}/(1+4\,\omega_0^2\,\tau_{ci}^2)\}, \tag{3}$$

where

$$\tau_{ci} = \tau_{0i}\exp(E_i/RT), \tag{4}$$

a satisfactory simultaneous fit could not be obtained with any set of parameters τ_{0i} and E_i $(i=1,2)$. It was clear that the calculated laboratory frame relaxation times were always much shorter than the measured ones. On the other hand, if the contribution from NH_3 groups was excluded, the calculated relaxation times were much longer than the measured ones. Therefore, it was concluded that both these motions contribute to the relaxation rate, but that one is not fully effective. In a recent investigation of $C_{10}H_{21}NH_3Cl$ [12], it was shown convincingly that the NH_3 group in that compound reorients among three unequal potential minima, as illustrated in Figure 4. Since the hydrogen atoms of this group are hydrogen bonded to the neighbouring chlorine atoms, different bonding distances and a slight distortion of the NH_3 group make such a potential well likely. A threefold reorientation of an NH_3 group in this well is a less effective relaxation mechnism than a reorientation in a symmetrical threefold well.

Pollak and Ailion [13] and Latanowicz and Pajak [14] derived expressions for the relaxation rates due to reorientations among three unequal potential wells. These relaxation rates can be approximated as

$$1/T_1 \simeq \gamma_H^2\,\Delta M_{2i}\,[3\,a_{1i}/(a_{1i}+2)^2\,\{\tau_{1i}/(1+\omega_0^2\,\tau_{1i}^2) + 4\,\tau_{1i}/(1+4\,\omega_0^2\,\tau_{1i}^2)\} + 1/(a_{2i}+2)\,\{\tau_{2i}/(1+\omega_0^2\,\tau_{2i}^2) + 4\,\tau_{2i}/(1+4\,\omega_0^2\,\tau_{2i}^2)\}] \tag{5}$$

and

$$1/T_{1\varrho} \simeq 3/2\,\gamma_H^2\,\Delta M_{2i}\,[3\,a_{1i}/(a_{1i}+2)^2\,\{\tau_{1i}(1+4\,\omega_{1i}^2\,\tau_{1i}^2)\} + 1/(a_{2i}+2)\,\{\tau_{2i}(1+4\,\omega_1^2\,\tau_{2i}^2)\}], \tag{6}$$

where

$$\tau_{ji} = t_{0ji}\exp(E_{ji}/RT) \tag{7}$$

Table 1. Motional parameters obtained from a simultaneous fit of the relaxation model to all the relaxation data.

Motion	Parameter	
NH_3	E_1 (kJ/mol)	12.5 ± 1.0
(Threefold)	E_2 (kJ/mol)	11.3 ± 1.0
	ΔE_1 (kJ/mol)	3.3 ± 0.5
	ΔE_2 (kJ/mol)	1.7 ± 0.3
	τ_{01} (s)	$(2 \pm 1) \times 10^{-13}$
	τ_{02} (s)	$(5 \pm 2) \times 10^{-14}$
	ΔM_2 (G^2)	3.2 ± 0.2
CH_3	E (kJ/mol)	11.7 ± 1.0
(Threefold)	τ_0 (s)	$(4 \pm 1) \times 10^{-13}$
	ΔM_2 (G^2)	2.6 ± 0.2
Defect (X)	E (kJ/mol)	12.5 ± 1.0
	τ_0 (s)	$(2.0 \pm 2.0) \times 10^{-11}$
	ΔM_2 (G^2)	0.10 ± 0.05
	ΔE (kJ/mol)	4 ± 1
Defect (Y)	E (kJ/mol)	21.0 ± 2.0
	τ_0 (s)	$(3.0 \pm 1.0) \times 10^{-13}$
	ΔM_2 (G^2)	0.022 ± 0.005
	ΔE (kJ/mol)	6 ± 2

and

$$a_{ji} = \exp(\Delta E_{ji}/RT), \quad (j = 1, 2). \tag{8}$$

The energies E_j and ΔE_j for the NH_3 reorientation are shown in Figure 4. If $\Delta E_1 = \Delta E_2 = 0$ and $E_1 = E_2$, these expressions reduce to the standard relaxation rates for wells with equal depths (2) and (3).

Using a model in which the methyl groups execute threefold reorientations among three equal potential minima ($i = 1$) and NH_3 groups execute a similar reorientation, but among three unequal potential minima ($i = 2$), a good fit to the T_1 data was obtained. However, the discrepancy between the calculated and measured $T_{1\varrho}$ values was still severe. Adjustment of the ten available parameters failed to yield a better fit to the rotating frame results. Since the number of variable parameters is already large, one is rather reluctant to introduce another motion. However, the systematic analysis of the results which has been presented, strongly suggests that the dynamics of the system is not limited to threefold reorientations of CH_3 and NH_3 groups.

The relatively fast decrease of the second moment in the high temperature region of the LT phase (Fig. 1) has already been assigned to a chain reorientation. However, such a motion results in a second moment reduction of several gauss^2, while the discrepancy between calculated and measured $T_{1\varrho}$ values corresponds to a second moment reduction of less than 1 G^2. Therefore, it is concluded that the reorientation of entire chains cannot account for the observed discrepancy.

Although X-ray [2] and vibrational [4] studies of the LT phase are, apart from the two defects close to the NH_3 polar heads (X and Y molecules), in agreement with an ordered solid, jumps between kink conformations could contribute to the relaxation rates. It has been shown that in the low temperature orthorhombic phase of *n*-alkanes defect orientations are present [15, 16], although other studies, including infrared investigations [4], could not identify these orientations. The $T_{1\varrho}$ experiment is very sensitive to slow jumps between an all-*trans* and a defect orientation and it was possible to identify these motions, although the population of the defect orientations was of the order of 1%. $T_{1\varrho}$ minima corresponding to these motions occur when the jump rates are approximately equal to H_1, but since the defect orientations have relatively low populations, the minima are shallower than those calculated for these motions if the all-*trans* and defect orientations were equally populated.

If the dipolar interactions are modulated by molecular jumps between two equilibrium positions A and B with different energies, the reduction in second moment, ΔM_2^*, is given by [17]

$$\Delta M_2^* = 4 \Delta M_2 a/(a+1)^2, \tag{9}$$

where ΔM_2 is the calculated reduction if the two orientations are equally populated (high temperatures). Here

$$a = P_A/P_B = \exp(\Delta E/RT) \tag{10}$$

is the relative probability of occupation of orientations A and B, where ΔE is the energy difference between the minima. The height of the barrier between the minima, E, is the activation energy of a jump between the two orientations, as shown in Figure 4.

Keeping in mind that there are two nonequivalent chains X and Y in the LT unit cell of $C_{10}Cd$, it is assumed that two defect motions ($i = 3, 4$) contribute to the total relaxation rate. This model involves four different motions (threefold reorientations of CH_3 and NH_3 groups and two defect motions) and sixteen adjustable parameters. An acceptable fit, shown in Figs. 2 and 3, was obtained with the parameters listed in Table 1. The second moment reductions associated with the two defect motions are relatively small (0.022 G^2 and 0.10 G^2), but compatible with second moment reductions for chain defect motions observed in *n*-alkanes [15, 16]. Also shown in Figs. 3 and 4 are

the individual contributions of the four motions to the relaxation rates in the laboratory frame at 200 MHz and the rotating frame, respectively. Although the contributions of the defect motions to the total relaxation rate in the laboratory frame is negligible, they are indeed sizeable in the rotating frame. Unfortunately, unlike in the case of *n*-alkanes where the $T_{1\varrho}$ minima due to defect motions and threefold reorientations of methyl groups are well-resolved, the minima due to the defect motions are largely obscured by the other motions in $C_{10}Cd$. It is emphasized that it is not possible to obtain an acceptable fit to the data if these defect motions are neglected.

According to a vibrational study of selectively deuterated *n*-decylammonium chains in $C_{10}Cd$ [4], the following kink conformations may be present in the high temperature phase: two gt_5g' forms ($gt_5g't$ and tgt_5g', denoted P_1 and P_2 respectively); four gt_3g' forms ($gt_3g't_3$, $tgt_3g't_2$, $t_2gt_3g't$ and t_3gt_3g', denoted P_3, P_4, P_5, and P_6 respectively); six gtg' forms ($gtg't_5$, $tgtg't_4$, $t_2gtg't_3$, $t_3gtg't_2$, $t_4gtg't$ and t_5gtg', denoted P_7, P_8, P_9, P_{10}, P_{11}, and P_{12}, respectively). In this notation g and g′ denote rotations about the relevant C–C bond through $+120°$ and $-120°$ respectively and the numbering starts from the carbon atom adjacent to the NH_3 group. P_4 is greatly favoured in the HT phase of $C_{10}Cd$ [4]. Although the chains are in the gt_7 (X) abd tgt_6 (Y) configurations in the LT phase, transformations to one or more of the abovementioned kink conformations cannot be ruled out in any of the phases. It is not possible to identify the specific intermethylene bonds about which rotations to gauche positions take place in the LT phase. However, in the simplest situation where chains X and Y jump between their crystallographically determined orientations and defect orientations P_1 and P_2 respectively, second moment reductions of 0.6 G^2 and 1.5 G^2, respectively, would results at infinitely high temperatures. The discrepancy between the calculated and observed second moment reductions is attributed to the fact that the two possible orientations of a specific chain have different populations in the temperature range under consideration. If it is assumed that the lowest activation energy is associated with the P_1 defect orientation, a comparison of the calculated second moment reductions and those obtained from the best fit to the relaxation data, using equation (9), yields a rough estimate of the values of the parameter a at the temperatures at which the $T_{1\varrho}$ minima associated with the defect motions occur. ΔE values for these

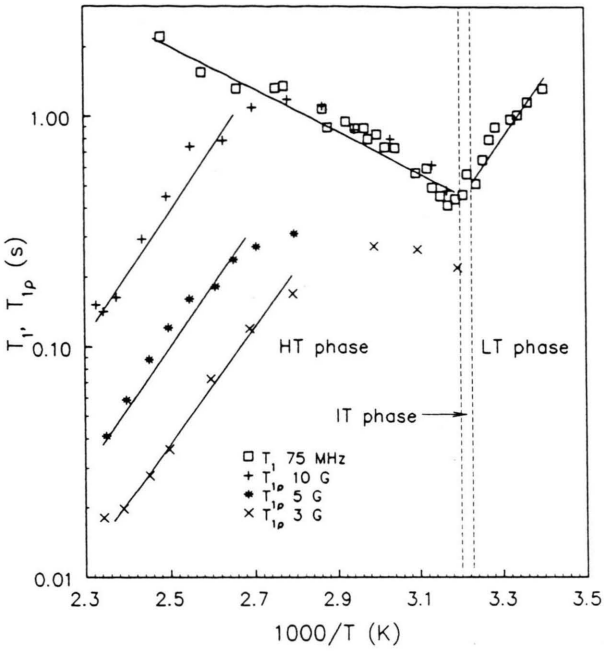

Fig. 5. Proton spin-lattice relaxation times in the laboratory and rotating frames as functions of inverse temperature in the HT phase. The lines only serve as a guide to the eye.

defect motions were obtained from (3) and are listed in Table 1. It follows that the defect orientations of the X and Y chains have relative populations of ~10% and ~20%, respectively, at room temperature. It is obvious that relatively large errors must be associated with these values.

Let us point out that the same T_1 dependences as those observed in the LT phase may be due to quantum effects, however, this mechanism is ruled out because the activation energies for CH_3 and NH_3 reorientations are rather high [18].

3.2.2 High Temperature Phase

Vibrational [4] and incoherent neutron scattering experiments [5] show that in the HT phase the dynamical disorder increases in going from the NH_3 polar heads to the methyl groups. The increase in T_1 and decrease in $T_{1\varrho}$ ($H_1 = 10$, 5, and 3 G) with increasing temperature in the HT phase, shown in Fig. 5, reveals fast and slow molecular motions, respectively. The β dependance of T_1 yields an activation energy of ~21 kJ/mol for fourfold reorientations of entire chains. The decrease of $T_{1\varrho}$ with increasing tempera-

ture is caused by another slow motion with a relatively high activation energy of ~ 46 kJ/mol. Since $T_{1\varrho}$ is proportional to H_1^2 in this phase, it is unlikely that this mechanism is the previously suggested diffusion of kinks along the chains [3]. This type of translational displacement of a kink requires that $T_{1\varrho} \propto H_1^{0.75}$ [18]. Therefore, it is believed that the temperature dependence of $T_{1\varrho}$ in this phase is due to an additional chain defect motion or motions.

4. Conclusions

In the low temperature phase methyl and NH_3 groups execute threefold reorientations in symmetric and asymmetric potential wells, respectively. Two defect motions of chain ends, with the defect orientations having populations of less than 20% at room temperature, have been identified in this phase. Just before the transition to the high temperature phases, evidence of reorientations of entire chains has been found. In the intermediate phase the asymmetric shape of the fourfold potential well favours jumps through 90° between two adjacent equilibrium positions. In the high temperature phase fast fourfold reorientations of the chains in a symmetric fourfold potential takes place. An additional slow motion of the chains, most probably an additional defect motion, has been identified in this phase.

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[1] K. J. Schenk and G. Chapuis, J. Phys. Chem. **92,** 7141 (1988).
[2] R. Kind, S. Plesko, H. Arend, R. Blinc, B. Zeks, J. Seliger, V. Lozar, G. Lahajnar, F. Milia, and G. Chapuis, J. Chem. Phys. **71,** 2118 (1979).
[3] G. F. Needham, R. D. Willet, and H. F. Franzen, J. Phys. Chem. **88,** 674 (1984).
[4] L. Ricard, M. Rey-Lafon, and C. Biran, J. Phys. Chem. **88,** 5614 (1984).
[5] F. Guilaume, G. Coddens, A. J. Dianoux, W. Petrys, M. Rey-Lafon, and C. Sourisseau, Mol. Phys. **67,** 665 (1989).
[6] R. Kind and J. Roos, Phys. Rev. B: Solid State **13,** 45 (1976).
[7] S. Jurga, V. Macho, B. Hüser, and H. W. Spiess, Z. Phys. B Condensed Matter **84,** 43 (1991).
[8] E. R. Andrew, J. Chem. Phys. **18,** 607 (1950).
[9] S. Jurga, H. W. Spiess, and B. Hüser, to be published.
[10] J. Fenrych, E. C. Reynhardt, S. Jurga, and K. Jurga, Mol. Phys. (accepted for publication).
[11] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9,** 888 (1954).
[12] E. C. Reynhardt, S. Jurga, and K. Jurga, Mol. Phys. In the press.
[13] M. Pollak and D. C. Ailion, J. Chem. Phys. **67,** 3029 (1977).
[14] L. Latanowicz and Z. Pajak, Ber. Bunsenges. Phys. Chem. **93,** 1440 (1989).
[15] I. Basson and E. C. Reynhardt, J. Chem. Phys. **93,** 3604 (1990).
[16] I. Basson and E. C. Reynhardt, J. Chem. Phys. **95,** 1215 (1991)
[17] E. R. Andrew and L. Latanowicz, J. Magn. Reson. **68,** 232 (1986).
[18] W. Mueller-Warmuth, R. Schueler, M. Prager, and A. Kollmar, J. Magn. Reson. **34,** 89 (1979).
[19] W. Nusser, R. Kimmich, and F. Winter, J. Phys. Chem. **92,** 6808 (1988).