NMR Cross-Relaxation Study of Ultraslow Motion of the Domain Wall in Channel Inclusion Compound

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We report on an NMR study of ultraslow motions in the channel thiourea-hexachloroethane inclusion compound, $[2.95(NH_2)_2CS]{\cdot}C_2Cl_6$. Temperature dependent ^{1}H NMR relaxation measurements of the powder thiourea-hexachloroethane at different resonance frequencies, from 23 to 55.5 MHz, have been carried out. Significant reduction of the spin-lattice relaxation time at 38 and 47 MHz is caused by the cross-relaxation of protons via the quadrupole chlorine nuclei. We show that the effective ^{1}H-^{35}Cl cross-relaxation observed in a powder sample is due to a slow mode process, when the molecules of the domain wall exhibit a correlated translational and rotational motion over the channel. Such propagation of the domain wall is confirmed by atom-atomic potential calculation. – Pacs: 76.60-k, 76.60.Es, 61.44.Fw, 61.66.Hq

Key words: NMR; Cross-Relaxation, Domain Wall; Ultraslow Motion; Inclusion Compounds.

1. Introduction

In thiourea inclusion compounds, the guest molecules are entrapped within the unidirectional, non-intersecting tunnels of a hydrogen-bonded thiourea network and form a quasi-one dimensional subsystem [1, 2]. In general, the host and guest periods do not coincide, which may yield incommensurate (IC) structure. The ground state of the IC chain can be viewed as a commensurate (C) chain with a sequence of equidistant discommensurations (solitons, or kinks). In channel compound with dense guest packing, such kinks cannot disappear if the ratio of the numbers of the host to guest molecules is unchanged. Kink mobility may be associated with some translational and rotational motion of the guest molecules in the channel. Our previous NQR studies and atom-atomic potential calculation have shown that the non-stoichiometric thiourea inclusion compounds exhibit a structure that differs from conventional continuum models of the incommensurate state [3 - 5]. The guest sublattice of non-stoichiometric thiourea-hexachloroethane comprises two types of commensurate or nearly commensurate finite molecular chains (domains), having different structure and separated by domain walls (Fig. 1) [4, 5]. Moreover, the calculation also predicts an almost barrierless (soliton-like) propagation of the domain walls along the channel [5]. While the structural features of thiourea-C_2Cl_6 have recently been studied [4], the motions in the guest sublattice, though having been pointed out, were not cleared up. The present work is focused on the investigation of the dynamics of the domain wall.

In this paper, we report ^{1}H NMR measurements of the powder thiourea-hexachloroethane inclusion compound, $[2.95(NH_2)_2CS]{\cdot}C_2Cl_6$, at resonance frequencies 23.0, 38.0, 47.0, and 55.46 MHz. Significant reduction of spin-lattice relaxation time at 38 and 47 MHz is caused by the cross-relaxation of protons via the quadrupole chlorine nuclei. We show that the effective ^{1}H-^{35}Cl cross-relaxation observed in the powder sample is due to a slow mode process, when the molecules of the domain wall exhibit a correlated translational and rotational motion along the channel. Such a propagation of the domain wall was predicted by atom-atomic potential calculation. We show that

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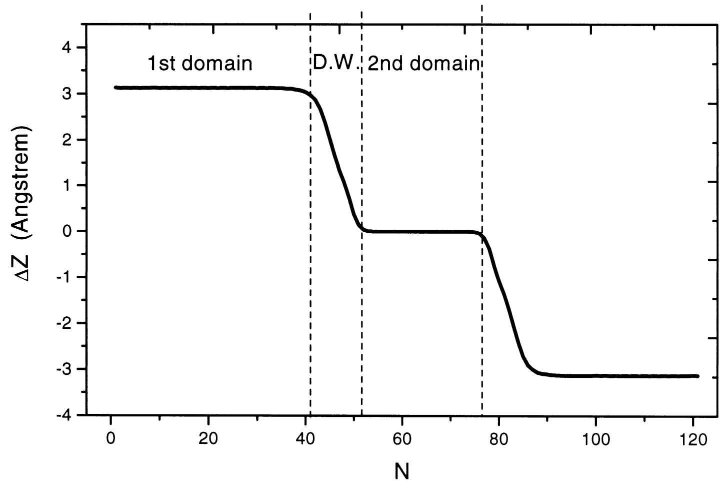

Fig. 1. Characteristic features of the positions calculated for the 121 guest molecules in the channel of thiourea-C_2Cl_6 inclusion compound [4, 5]. Ordinate ΔZ is a position relative to the origin of the half-parameter of the host sublattice. N is the number of molecule in the chain; domains of the types I and II and domain wall (D. W.) are shown.

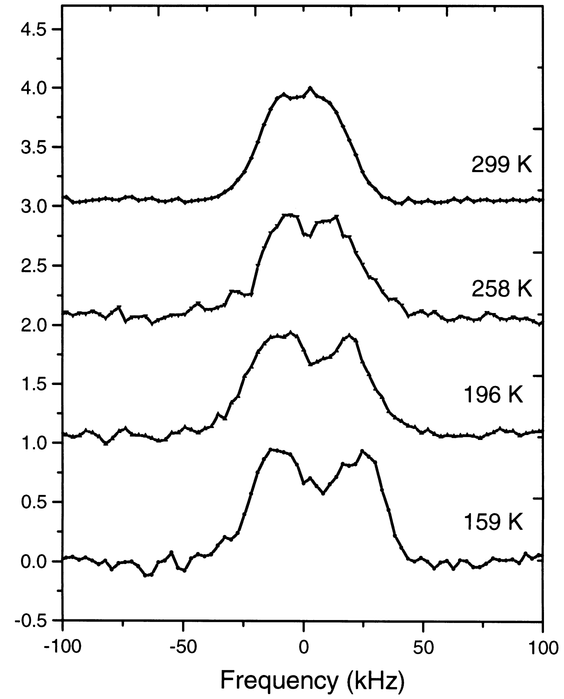

Fig. 2. ^{1}H NMR spectra of powder thiourea-C_2Cl_6 inclusion compound at different temperatures.

the NMR cross-relaxation effect is an effective tool to investigate ultraslow motions, especially in incommensurate and disordered structures.

2. Experimental

^{1}H NMR spectra and spin-lattice relaxation times of the powder thiourea-C_2Cl_6 inclusion compound have been measured using a Tecmag pulse spectrometer and Oxford Instruments cryostat in the temperature range from 95 to 355 K. The spectra have been obtained at 55.46 MHz using solid echo ($\frac{\pi}{2}$-τ-$\frac{\pi}{2}$) pulse sequence with phase cycling. The values of T_1 have been measured by means of saturation comb sequence. The duration of the $\pi/2$ pulse was 1.2 µs.

3. Results and Discussion

The ^{1}H NMR spectra of the powder thiourea-C_2Cl_6 inclusion compound are shown in Figure 2. Splitting in the spectra at low temperatures, corresponding to the "rigid" thiourea lattice, is caused by dipole-dipole interaction of protons of the NH_2-groups. At higher temperature, the fine structure is averaged by hindered rotation of the thiourea molecules around the C=S bond direction usually observed in thiourea inclusion compounds [6, 7].

Temperature dependences of the ^{1}H NMR spin-lattice relaxation time T_1 measured at different frequencies are given in Figure 3. A drop of T_1 at 250 to 350 K, correlating with the ^{1}H line narrowing in the same temperature range, is caused by the aforementioned hindered rotation of the thiourea molecule and its NH_2-groups [6, 7]. Since the thiourea molecules are bound by hydrogen bonds, they start to rotate at higher temperatures than those of the C_2Cl_6 molecules that are packed within van der Waals contact of each other.

As seen from Fig. 3, the temperature dependences of the ^{1}H NMR spin-lattice relaxation time are different at different resonance frequencies. The temperature dependences of T_1 at 23 and 55.46 MHz show a pronounced minimum at $T \sim 175$ K, which is a

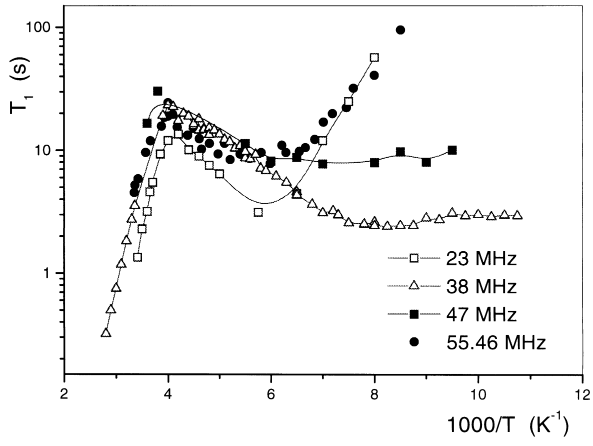

Fig. 3. Temperature dependence of the ^{1}H spin-lattice relaxation time in the thiourea-C_2Cl_6 inclusion compound at the resonance frequencies of 23.0 MHz (open squares), 38.0 MHz (triangles), 47.0 MHz (filled squares) and 55.46 MHz (circles).

typical relaxation minimum characteristic for molecular motion [8]. Since the host thiourea molecules exhibit a "rigid" lattice below ~ 250 K (Fig. 2), the observed behavior of T_1 is assigned to the rotational motion of the guest molecules or their CCl_3-groups. Activation energy of this process, calculated from the T_1 ($1/T$) curve at 23 MHz, is (13.3±0.8) kJ/mol. The main contribution to the spin-lattice relaxation in this case is caused by a modulation of the dipole-dipole interaction between protons of the host thiourea molecules and spins of the chlorine atoms of the guest molecules. Qualitative estimation of T_1 is in good agreement with this relaxation mechanism. However, in contrast to the data obtained at 23 and 55.46 MHz, T_1 measurements at 38 and 47 MHz show no temperature minimum but a plateau (with $T_1 \sim 3$ s and 9 s, respectively) in the low temperature region where, according to the BPP mechanism, fast molecular motion is frozen. Taking into account that these ^{1}H NMR frequencies are close to the ^{35}Cl NQR frequency of the guest molecules ν_Q (which is around 40.5 MHz), one can conclude that this behavior is caused by the cross-relaxation between ^{1}H and ^{35}Cl spin subsystems [9]. (For the sake of simplicity, we consider ^{35}Cl nuclei with natural abundance of 75.5%; similarly, one can consider ^{37}Cl with the abundance of 24.5%). The coupling of the spins of the quadrupole chlorine nuclei with the lattice is strong, causing them to be a fast relaxing subsystem. Interaction of the chlorine spins with protons is a part of the Hamiltonian that couples the proton spins to the lattice. When the ^{1}H NMR frequency $\nu(^1\mathrm{H})$ and the ^{35}Cl NQR frequency coincide, an effective channel for the spin-lattice relaxation of protons via quadrupole ^{35}Cl nuclei occurs. For the Cl nucleus with $I = 3/2$, the Zeeman splitting of the chlorine electric quadrupole energy levels yields four high frequency transitions which are symmetric about the pure NQR frequency ν_Q [10]:

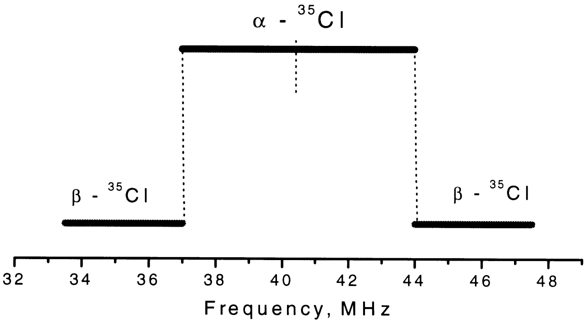

Fig. 4. The calculated ^{35}Cl NQR frequency ranges in which a chlorine transition can coincide with the proton resonance frequency in the applied magnetic field B_0 = 0.84 T. The symbols α and β refer to the transitions given in (1).

$$\begin{aligned} \alpha:\ \nu &= \nu_\mathrm{Q} \pm \left[3\cos\theta - (4 - 3\cos^2\theta)^{1/2}\right]\gamma B_0/4\pi, \\ & \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (1) \\ \beta:\ \nu &= \nu_\mathrm{Q} \pm \left[3\cos\theta + (4 - 3\cos^2\theta)^{1/2}\right]\gamma B_0/4\pi. \end{aligned}$$

Here θ is the angle that the symmetry axis of the electric field gradient (EFG) makes with the applied magnetic field B_0, and γ is the magnetogyric ratio of the nucleus. The ^{1}H NMR frequency 38 MHz corresponds to magnetic field B_0 = 0.84 T. Due to the angular dependence of ν. (Eq. 1), in this field the α-transition covers the range of ±3.5 MHz (from 37 to 44 MHz with $\nu_Q(^{35}\mathrm{Cl})$ = 40.5 MHz), and the β-transition covers the ranges from 33.5 to 37 and from 44 to 47.5 MHz (Fig. 4). We note that the inner pair of transitions is always stronger than the outer pair and that the intensities of the β-components vanish at the lowest and highest ends of the diapason [10]. For the ^{1}H NMR frequency 47 MHz (B_0 = 1.104 T), the corresponding region covered by the α- and β-transitions is 31.3 to 49.7 MHz. Therefore the coincidence of the proton frequencies of 38 and 47 MHz and the ^{35}Cl NQR frequency perturbed by applied magnetic field, obtained in our experiment, is reached for some orientations. It was demonstrated [11] that such an effect leads to the independence of T_1 with regard to temperature (flatness) at the frequency where Zeeman-quadrupole cross-relaxation occurs. (Deviation from the plateau at higher temperature is caused by molecular rotation that moves the quadrupole frequency from the corresponding range). This mechanism works in the "rigid" lattice and for slow (in the NMR scale) motion, when the lifetime of a molecule in each position is long enough to guarantee the essential energy transfer between two subsystems.

Due to the angular dependence of the Zeeman splitting of the chlorine electric quadrupole energy levels, the aforementioned cross-relaxation effect at a given proton frequency is usually observed in single crystals for a particular orientation corresponding to $\nu(^{35}\mathrm{Cl}) = \nu(^{1}\mathrm{H})$ [12]. On the other hand, the cross-relaxation is hardly obtainable in powder samples with the "rigid" lattice. In such a case, due to the angular distribution of molecular orientations, the number of nuclei for which the condition $\nu(^{35}\mathrm{Cl}) = \nu(^{1}\mathrm{H})$ is performed, is too small. An interesting way to observe the cross-relaxation effect in a powder was demonstrated in the classic paper of Woessner and Gutowsky [13], who rotated slowly the powder sample to allow nuclei to run over all orientations during the experiment. This method resulted in significant reduction of the proton T_1 in solid polycrystalline *p*-dichlorobenzene from 2×10^4 s to values as short as 2.5 s. In our experiment, however, we observe an effective cross-relaxation in a powder without sample rotation. To explain this effect, one have to suggest a slow molecular motion in the system, when a molecule slowly runs in turn through a number of positions corresponding to different NQR frequencies in the vicinity of the proton NMR frequency, yielding the energy level crossing available for most of nuclei. We argue that this effect is realized in the compound under study. As mentioned above, an atom-atom potential calculation predicts an almost barrierless propagation of the domain walls along the channel [4, 5]. The matter is that positions of the neighbor molecules in the domain wall are separated by small energy barriers. Thus the molecules can easily move from a global energy minimum to a local one, exhibiting simultaneous small turns of 40 - 60° and translations of about 0.5 Å. Due to the dense packing of the guest molecules, such translational and rotational motions are correlated and involve also the neighbor guest molecules. Mobile domain walls can move over the channel with an activation energy of around 5 kJ/mol. Such collective motion might be significantly slower than the motion of a lone molecule, and lifetimes of the corresponding states may be comparable with the spin-lattice relaxation time of ^{35}Cl nuclei, yielding an effective ^{1}H-^{35}Cl cross-relaxation. The value of the ^{35}Cl NQR spin-lattice relaxation time T_1 is $\sim$1 ms at 90 K [4]. A lifetime of the same order requires the frequency of the molecular jumps to be of $\sim$1 kHz, which readily corresponds to the aforementioned ultraslow motion. Thus, to interpret the experimentally observed cross-relaxation behavior, one can suggest the ultraslow motion of the domain walls (possibly soliton-like) to exist.

Our study shows that the NMR cross-relaxation effect is an effective tool to investigate ultraslow motions, in particular in incommensurate and disordered structures.

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