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Abstract. Atom–atomic potential calculation of the channel non-stoichiometric thiourea–hexachloroethane inclusion compound shows that the structure of the guest sublattice comprises two types of finite molecular chain, having different structure and separated by domain walls. In the present paper we present results of ^{35}Cl NQR and ^{1}H NMR measurements of thiourea–hexachloroethane, $[2.95(NH_2)_2CS]C_2Cl_6$, in the temperature range from 7.5 to 90 K, which confirm this model and show the existence of such a state at least below 60 K. Two resonances in the NQR spectra were assigned to the two nearly commensurate regions, while the third resonance, showing an anomalous behaviour, was attributed to the guest molecules in the domain wall. The observed structure results from the different periodicity of the guest and host substructures and shows a difference from conventional continuum models of the incommensurate state. Propagation motion of the domain wall over the channel is discussed.

1. Introduction

In the past two decades, a large number of compounds showing incommensurate (IC) states has been studied. In IC system the periodicity q_i of at least one of the modulation waves cannot be expressed as a rational fraction of the periodicity q_L of the underlying lattice:

$$q_i/q_L \neq M/N \qquad M, N = 1, 2, 3, \ldots. \tag{1}$$

As a result, translational periodicity is lost in at least one dimension in spite of the existence of perfect long range order. The modulation waves can be either of the plane wave (sinusoidal) type or soliton-like, consisting of nearly commensurate (C) regions where the phase of the order parameter is practically constant and other regions (phase solitons) where it changes rapidly [1, 2]. It has also been shown that some of the IC phases represent in fact a sequence of long-period commensurate (LPC) phases where the superstructure wave vector varies in steps and 'locks-in' at an infinity of C phases, which may or may not be separated by an infinity of true IC phases [1–6].

One of the interesting models of the IC state was suggested by Frank and Van der Merwe [1, 7]. In this model, incommensurability is expected to result from the different periodicity of

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the guest and host sublattices. Well known examples of such a model, in the two-dimensional case, are nitrogen or krypton monolayers on a graphite substrate. These systems have been extensively studied [8, 9]. Another class of compounds where an incommensurate state resulting from different periodicity of the guest and host substructures is expected is urea $((NH_2)_2CO)$ and thiourea $((NH_2)_2CS)$ inclusion compounds. In these compounds, the guest molecules are entrapped within the unidirectional, non-intersecting tunnels of a hydrogen-bonded urea (or thiourea) network and typically pack within van der Waals contact of each other [10, 11]. In general, the host and guest periods do not coincide. Extensive theoretical studies of quasi-one-dimensional structures show that they can exhibit either commensurate or incommensurate state and also a disordered one, depending on the host–guest and guest–guest interactions and temperature [12, 13]. However, up to now only a few experimental demonstrations of incommensurate behaviour in urea/thiourea inclusion compounds are known [14–16]. For instance, an incommensurate diffraction pattern in the *n*-nonadecane/urea inclusion compound has been recently observed by neutron diffraction [16]. The sliding mode measured by Brillouin scattering has been reported for the IC urea–heptadecane inclusion compound [14]. Although such powerful tools as nuclear quadrupole resonance (NQR) and nuclear magnetic resonance (NMR) have been successfully applied to investigate inclusion compounds [17–24], incommensurability has not been extensively studied. To our knowledge, there is only one paper [25] where ^{35}Cl NQR spectrum of the thiourea-1,1,2,2-tetrachloroethane inclusion compound at liquid nitrogen temperature was attributed to the incommensurate state. Moreover, we note that the existing theories of the IC systems are mainly phenomenological; they are based on a continuum approach and hardly take into account the real atomic structure of a crystal.

Our recent atom–atom potential calculation of channel non-stoichiometric thiourea–hexachloroethane inclusion compound [26] showed that its structure is different from C and IC states mentioned above. It was found that the guest sublattice in this compound comprises two types of finite molecular chains having different structure and separated by the domain walls [26]. In the present paper we present the results of ^{35}Cl NQR and ^{1}H NMR measurements of thiourea–hexachloroethane, $[2.95(NH_2)_2CS]C_2Cl_6$, in the temperature range from 7.5 to 90 K, which confirm this model and show the existence of such a state at least below 60 K. Two resonances in the NQR spectra were assigned to the two commensurate or nearly commensurate regions, while the third resonance, showing the anomalous behaviour, was attributed to the guest molecules in the domain wall. The observed structure results from the different periodicity of the guest and host substructures and shows a difference from conventional continuum models of the incommensurate state. Motion of the domain wall over the channel is discussed. At temperatures from 73 to 90 K the resonance attributed to the molecular group in the domain wall disappears. At temperatures higher than 90 K NQR spectrum is not observed. We attribute this fact to the rotational mobility of CCl_3 groups (or C_2Cl_6 molecules) in the guest sublattice.

2. Atom–atom potential calculation and structure of the guest sublattice

X-ray diffraction has shown that, at room temperature, the host sublattice in thiourea inclusion compounds is the conventional rhombohedral thiourea tunnel structure (space group $R\bar{3}c$; $a = 10.115$ Å, $\alpha = 104.27°$, $Z = 6$; hexagonal setting of space group $R\bar{3}c$ yields $a = 15.8$ Å, $c = 12.48$ Å, $Z = 18$ [27]). The tunnel diameter varies substantially on moving along the tunnel from 5.8 to 7.1 Å [28].

Precise measurements of the composition showed that thiourea–hexachloroethane inclusion compound is a non-stoichiometric compound with the non-integer ratio of the

numbers of host to guest molecules $r = 2.95 \pm 0.01$ [29]. Thus this compound exhibits more compact packing and the chains of the guest molecules in channels are somewhat shorter than that expected for the structure in which molecules are anchored in the centres of each cavity of the host lattice. Such packing may result in incommensurability. However, the structure of the guest sublattice in this compound was unknown. Therefore, the numerical calculation of this structure by means of the atom–atom potential method has been undertaken [26]. Calculation was based on the aforementioned conventional rhombohedral thiourea tunnel structure [27] with a molecular C_3 symmetry axis lying along the channel. Details of the calculation are given elsewhere [26].

The main result of the atom–atom potential calculation of the non-stoichiometric thiourea–C_2Cl_6 inclusion compound is that the structure of the guest sublattice comprises three regions. Two of them, I and II, are ordered, finite molecular chains, corresponding to the two energetically beneficial sites of the guest molecule in the host tunnel. These domains are characterized by almost equidistant guest location with a period that is half of the period of the host lattice. The domain of type I shows the same orientation for all molecules inside it, while in the domain of type II the molecules with odd and even numbers have different orientations. Superperiods were found to be of the order of 20 to 60 host lattice periods, respectively. The third type of domain, III, is unstable and is characterized by significant difference in guest–guest distances and their mutual orientations. It was attributed to the domain wall. In principle, such a structure may be assigned to the LPC phase. The main features of such a structure are given in figure 1. Moreover, the existence of a specific possibility for a practically free molecular motion along the channel, which involves simultaneous, correlated molecular translations and rotations around its C_3 symmetry axis, was shown. Calculations show that the positions of the neighbour molecules in the domain wall are separated by small energy barriers, and molecules can exhibit both translational and reorientational motion simultaneously, involving also the neighbour guest molecules. Domain walls were shown to be mobile; they can move along the channel under applying an occasional force with an activation energy around 5 kJ mol^{-1}.

3. Experiment

^{35}Cl NQR measurements of the powder the thiourea–C_2Cl_6 inclusion compound in the temperature range from 7.5 to 90 K have been made using a Tecmag pulse spectrometer and Oxford Instruments cryostat. The NQR spectra cover a range of several hundred kHz, which is too broad to be excited by a radio-frequency (rf) $\pi/2$ pulse. Therefore the spectra were obtained using a computer-controlled point-by-point frequency sweep (with the step from 5 to 7 kHz) and acquisition of the Hahn echo amplitude at each specified frequency. These measurements have been made at reduced rf power using rather long, 'soft' pulses (the $\pi/2$ pulse was 26 μs) to excite only a small portion of the NQR line. The echo amplitude obtained represents an intensity of the actual NQR line at specified frequency. The maxima of the Fourier transform of the echoes have shown the same line shape. The number of scans usually was from 1024 to 2048, repetition time was 5 T_1. The ^{35}Cl spin–lattice relaxation time T_1 has been measured using a π–τ–$\pi/2$ inversion recovery sequence.

The ^{1}H NMR spin–lattice relaxation time has been measured using pulse NMR spectrometer in the temperature range from 96 to 350 K at three resonance frequencies, 23, 37 and 38 MHz, by means of the π–τ–$\pi/2$ inversion recovery sequence. The duration of the $\pi/2$ pulse was 1.5 μs. The magnetization decay showed exponential time dependence.
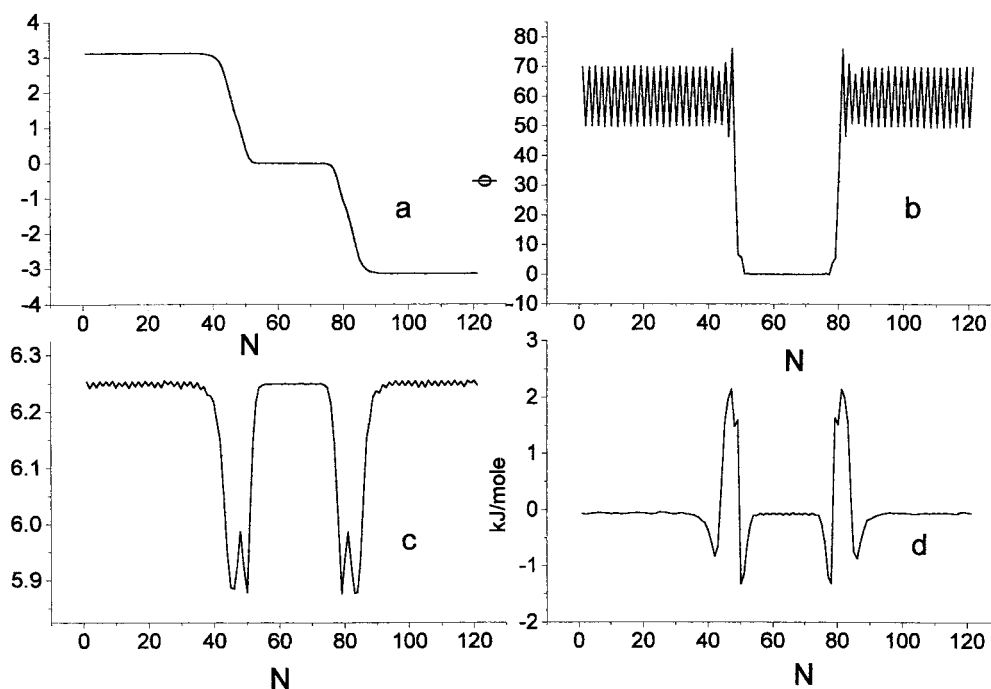
Figure 1. Characteristic features of the positions calculated for the 121 guest molecules in the channel of the thiourea–C_2Cl_6 inclusion compound: (a) position relative to the origin of the half-parameter of the host sublattice (Å); (b) angular orientation (°); (c) distance from the previous to the next guest molecule (Å); (d) deviation of the energy of interaction with the environment from the average energy over the superperiod (kJ mol^{-1}). Here N is the number of molecules in the chain; domains of the types I and II correspond to N from 55 to 75 and 95 → 121 → 1 → 35, respectively. Domain walls correspond to N from 35 to 55 and from 75 to 95, respectively.

4. Experimental results and discussion

4.1. Temperature dependent measurements of ^{35}Cl NQR spectra

^{35}Cl NQR spectra in the temperature range from 7.5 to 90 K are shown in figure 2. One can see that instead of a narrow NQR line usually observed in chlorine compounds, ^{35}Cl NQR spectra in the thiourea–C_2Cl_6 inclusion compound show a broad line with two or three maxima. Temperature dependence of the resonance frequencies, which were determined at the maxima of the resonance lines, is given in figure 3. Deconvolution of the spectra shows that they can be described as a superposition of two or three Gaussian lines, respectively.

In the low temperature region, from 7 to 60 K, the spectra exhibit three resolved maxima (figure 2); in addition to the doublet observed at 73 to 90 K, a very broad low frequency line occurs. All three lines show a characteristic temperature dependent shift caused by thermal fluctuations of the electric field gradient (EFG) due to torsional vibrations [30] (figure 3). However, while the temperature dependences of the shifts of the high and medium frequency lines are very similar, the low frequency line shows a more significant temperature dependence of the shift accompanied by the changes in the line width (figures 2, 3).

In the intermediate temperature region, from 60 to 73 K, the temperature dependent measurements show significant changes in the NQR spectra (figure 2). These transformations will be discussed below in sections 4.2 and 4.3.
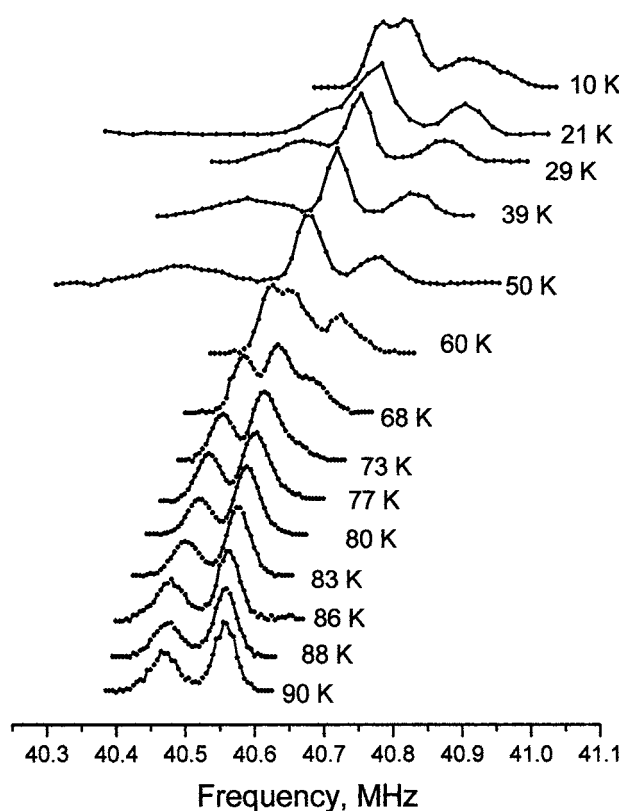
Figure 2. ^{35}Cl NQR spectra of the thiourea–C_2Cl_6 inclusion compound in the temperature range from 7.5 to 90 K. Some spectra are not shown to avoid overloading the figure.

In the high temperature region, from 73 to 90 K, the spectra show two maxima. A Gaussian fit yields the intensity ratio ∼1:1.6. At temperatures higher than T_i ∼ 90 K the NQR spectrum is not observed. We attribute this fact to the reorientational mobility of CCl_3 groups (or C_2Cl_6 molecules) in the guest sublattice. The thermally activated process of the molecular rotation starts at T ∼ 77 K, that is seen from the temperature dependence of the NQR spin–lattice relaxation time [31] (see also section 4.2). Acceleration of this process on heating decreases the lifetime of the molecule in each concrete state, making the NQR signal disappear.

4.2. Temperature dependence of ^{35}Cl NQR spin–lattice relaxation time

Temperature dependent measurements of the ^{35}Cl spin–lattice relaxation time T_1 are given in figure 4. In the high temperature region, from 60 to 90 K, the values of T_1 for two lines are close to each other and decrease sharply with increasing temperature, showing a behaviour characteristic for the thermally activated reorientation process of CCl_3 groups. The activation energy of this process, calculated from the $T_1(1/T)$ curve, is 18.7 ± 1.5 kJ mol^{-1}. In the low temperature region, from 7 to 60 K, the values of T_1 for the high and medium frequency lines are very close to each other and increase slowly with decreasing temperature. Such behaviour is usually caused by torsional vibrations [30, 32]. However, the low frequency line shows anomalously short spin–lattice relaxation time, which is shorter almost by an order of magnitude in comparison to that of the two other lines. This means that the amplitude of
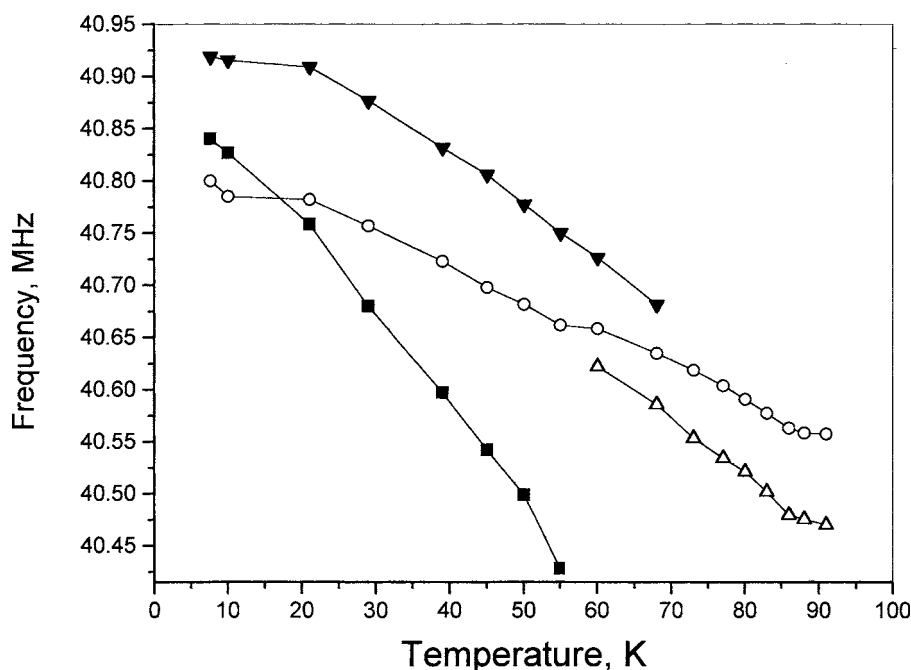
Figure 3. Temperature dependence of the ^{35}Cl NQR frequencies in the thiourea–C_2Cl_6 inclusion compound.

vibrations of the molecules assigned to the low frequency line is significantly larger than that for the other molecules; this may also be assigned to the essential molecular displacements.

As mentioned above, atom–atom potential calculations show that the guest sublattice of thiourea–C_2Cl_6 comprises two types of finite molecular chain, having different structure and separated by domain walls. This result, along with the measurements of ^{35}Cl NQR spectra and spin–lattice relaxation time, allow us to make an assignment of the resonance lines in the low temperature region. The high and medium frequency lines are assigned to the two commensurate or nearly commensurate regions (possibly of the LPC phase), while the low frequency line, showing the anomalous behaviour, is assigned to the domain wall. Peak intensities below 60 K (figure 2) qualitatively reflect the number of guest molecules in different regions shown in figure 1. In the high temperature region, from 73 to 90 K, the resonance of the third molecular group attributed to the domain wall is not obtained. One can suggest a broad distribution of EFGs over nonequivalent molecular sites which yields a broad and weak resonance invisible in the experiment. Such EFG distribution occurs after the structure transformation at $\sim$60–70 K, clearly reflected in the NQR spectra (figure 2). This transformation is probably caused by the mutual three-dimensional ordering of the domains of the guest molecules which belong to the different channels. Some details of this process can be derived from figure 3, which shows that the most intensive NQR line exhibits a continuation from the low temperature region to the high temperature region. One can assign this behaviour to the fact that the structure of one of the nearly commensurate domains of the guest molecules, which is placed in the most energetically beneficial position, does not undergo significant change in the temperature range studied. The broad transition region obtained in the experiment may mean that we deal with a state that does not exhibit complete long-range order. This is supported by no macroscopic phase transition at $\sim$60 K obtained by specific
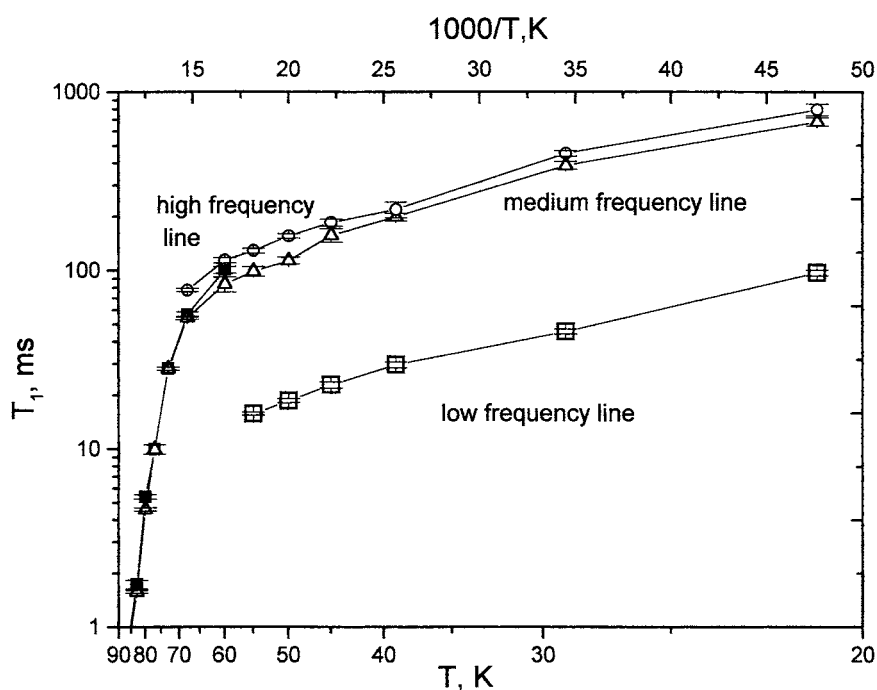
Figure 4. Temperature dependence of the ^{35}Cl NQR spin–lattice relaxation time T_1 in the thiourea–C_2Cl_6 inclusion compound.

heat measurements [33]. Such a transition is also not seen in the temperature dependence of the ^{35}Cl spin-relaxation time T_1 (figure 4).

In addition, we note that from our results, as well as from data presented in [31], one can conclude that the system under study does not show a characteristic property of the classical IC phase—a temperature-independent phason-induced spin–lattice relaxation time.

4.3. ^1H NMR relaxation and ^1H–^{35}Cl cross-relaxation

Temperature dependences of ^{1}H NMR spin–lattice relaxation time T_1 measured at frequencies 23, 37 and 38 MHz are given in figure 5. The common feature of these dependences is a sharp drop of T_1 with increasing temperature from 250 to 350 K. Such behaviour has been obtained in thiourea inclusion compounds and attributed to hindered rotation of the thiourea molecules around the C=S bond direction [17, 18]. The activation energy of this process, calculated from the $T_1(1/T)$ curve, is 41 ± 4 kJ mol^{-1}. An analogous effect was observed in urea inclusion compounds due to the molecular rotation around the C=O direction [18]; the drop of T_1 correlated with ^{1}H NMR line narrowing at the same temperature range [17].

However, as seen from figure 5, temperature dependences of the ^{1}H NMR spin–lattice relaxation time are different at different resonance frequencies. The temperature dependence of T_1 at 23 MHz shows a pronounced relaxation minimum at $T \sim 174$ K, which is a typical Bloembergen–Purcell–Pound (BPP) minimum characteristic for molecular motion [34]. We assign it to the rotational motion of the guest molecules or their CCl$_3$ groups. The activation energy of this process, calculated from the $T_1(1/T)$ curve, is 13.3 ± 0.8 kJ mol^{-1}; the correlation time is $\tau_0 = 5 \times 10^{-13}$ s ($\nu_0 = 2 \times 10^{12}$ Hz). The main contribution to the spin–lattice relaxation in such a case is caused by a modulation of dipole–dipole interaction between protons of the
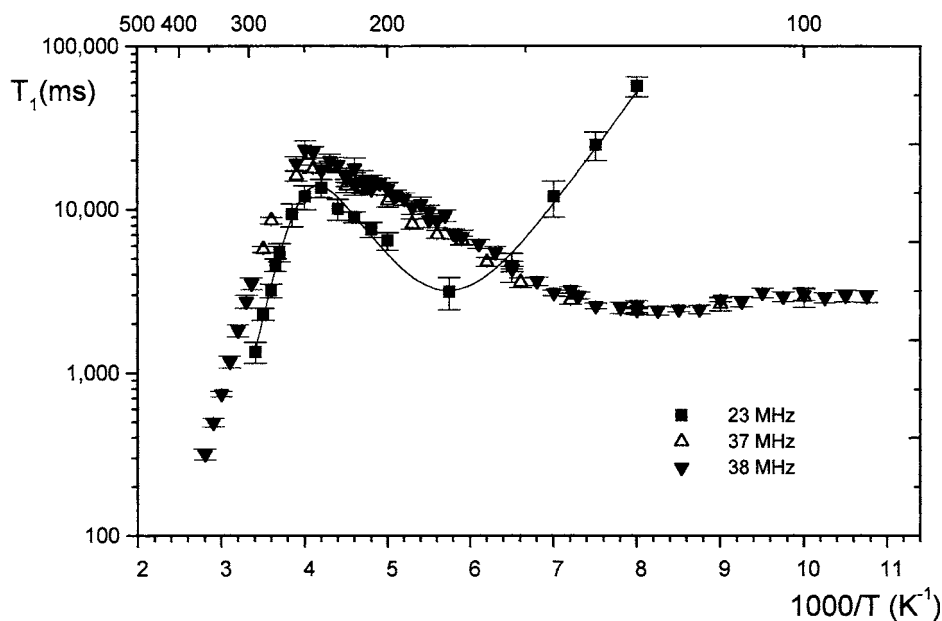
Figure 5. Temperature dependence of the ^{1}H spin–lattice relaxation time in the thiourea–C_2Cl_6 inclusion compound at the resonance frequencies of 23 (solid squares), 37 (open up triangles) and 38 (solid down triangles) MHz.

host thiourea molecules and spins of the chlorine atoms which belong to the guest molecules. The value of T_1 in the minimum is rather large. Qualitative estimation of T_1 is in agreement with the relaxation mechanism mentioned above. However, in contrast to the data obtained at 23 MHz, T_1 measurements at 37 and 38 MHz show no temperature minimum. Taking into account that these ^{1}H resonance frequencies are close to the ^{35}Cl NQR frequency of the guest molecules, one can suggest that such behaviour is caused by the cross-relaxation between ^{1}H and ^{35}Cl spin subsystems [35]. Coupling of the spins of the quadrupole ^{35}Cl nuclei with the lattice is stronger than their coupling with the spins of protons. It is therefore reasonable to consider the ^{35}Cl spins as a part of the lattice, and their coupling with the protons as a part of the Hamiltonian that couples the proton spins to the lattice. When two frequencies, namely the Zeeman NMR frequency of protons and the ^{35}Cl NQR frequency perturbed by an external magnetic field coincide, an effective channel for the spin–lattice relaxation of protons via quadrupole ^{35}Cl nuclei occurs. The ^{1}H NMR frequency 38 MHz corresponds to magnetic field $B_0 = 0.84$ T. In this field, the Zeeman splitting of the quadrupole levels of ^{35}Cl nuclei [35], which depends on the orientation of B_0 with respect to the crystalline frame, ranges within 3.5 MHz, yielding coincidence of the NMR frequency of protons and perturbed ^{35}Cl NQR frequency for some orientations. As excellently demonstrated by Stokes *et al* [36], such an effect leads to the independence of T_1 on temperature (flatness) at the frequency where Zeeman-quadrupole cross-relaxation occurs. At the same time, at the resonance frequency of 23 MHz, which is far from the ^{35}Cl NQR frequency, cross-relaxation is not effective, and a relaxation minimum is readily observed.

We note that the aforementioned cross-relaxation mechanism works in the 'rigid lattice' and for slow (in the NMR scale) motion. However, it is not effective enough in the case of the fast molecular rotation, which should yield a multiple average of EFG and thus an essential reduction of ^{35}Cl NQR frequency. In this case, the energy level crossing should not occur

at a frequency around 38 MHz. To reach agreement with the experiment, one can speculate that not all terms of the quadrupole Hamiltonian perturbed by an external magnetic field are averaged by motion. More effective cross-relaxation is expected in the case when a molecule slowly runs in turn through a number of positions corresponding to different values of EFG and thus to different quadrupole splittings. As mentioned above, atom–atom potential calculation predicts an almost barrierless propagation of the domain walls along the channel [26]. In this case, instead of the random jumps of each separate molecule, all molecules exhibit a collective, simultaneous translational and rotational (around their C_3 axes) motion. Such 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 effective ^{1}H–^{35}Cl cross-relaxation. Thus, to interpret the experimentally observed cross-relaxation behaviour, one can suggest such a slow mode process (possibly soliton-like) to exist. As seen from figure 3, the temperature dependence of the resonance frequencies in the region from 85 to 90 K is rather weak and not characteristic for the vicinity of the phase transition. One can suggest that such a behaviour may be caused by the aforementioned slow motion of the domain walls, which erodes the neighbour nearly commensurate regions involving the neighbour guest molecules from these regions into a correlated translational motion along the channel. This slow process erodes the NQR signal but does not shift the resonance.

In addition, we would like to mention a nice experiment of the authors of [37] with a urea inclusion compound. By incorporating a specific impurity (2-undecanone) into 2,10-undecanedione–urea, they made the domain reorientation spontaneously reversible when the uniaxial stress is applied and then released. This result is in a good agreement with our atom–atom potential calculations, which also show domain wall motion under applying an occasional force, as well as with the experimental data presented. We note that in our non-stoichiometric compound studied, a distortion from the rhombohedral symmetry can allow facile domain reorientation. Motion of the domain walls leads to the shortening of $T_1(^{35}$Cl$)$ of the corresponding molecular groups. A domain wall may yield a broad single-line NQR spectrum without singularities.

5. Conclusion

In conclusion, both experiment and calculation show that the guest sublattice in the channel non-stoichiometric thiourea–hexachloroethane inclusion compound comprises a structure which consists of rather long, commensurate (or nearly commensurate) regions separated by domain walls. Such structure results from the different periodicity of the guest and host substructures and shows a difference from conventional continuum models of the incommensurate state. Motion of the domain walls has been observed, and their properties can be studied in experiment.

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