Specific Heat and Nuclear Quadrupole Resonance Study of Thiourea-Hexachloroethane Inclusion Compound

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Z. Naturforsch. **55 a,** 335–338 (2000); received August 23, 1999

Presented at the XVth International Symposium on Nuclear Quadrupole Interactions, Leipzig, Germany, July 25 - 30, 1999.

Specific heat and ^{35}Cl nuclear quadrupole resonance (NQR) measurements of the channel thiourea-hexachloroethane inclusion compound are presented. Experimental NQR data confirm the results of atom-atom potential calculations that the guest sublattice comprises two types of nearly commensurate finite molecular chains, having different structure and separated by domain walls. Specific heat measurements show phase transition near 96 K.

Key words: NQR; Specific Heat; Inclusion Compound; Thiourea; Hexachloroethane.

1. Introduction

Thiourea-C_2Cl_6 is a non-stoichiometric inclusion compound with the non-integer ratio of the numbers of host to guest molecules $r = 2.95 \pm 0.01$, in which guest molecules are entrapped within the unidirectional, non-intersecting channels of a hydrogen-bonded network. Generally, periods of the host and guest sublattices in such systems do not coincide. Theoretical studies show that such quasi-one dimensional structures can exhibit either a commensurate or an incommensurate state and also a disordered one, depending on the host-guest and guest-guest interactions and temperature [1, 2]. 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 commensurate (C) phases, which may or may not be separated by an infinity of true IC phases [3, 4].

Recent atom-atom potential calculations of thiourea-C_2Cl_6 show that the guest sublattice comprises two types of nearly commensurate finite molecular chains, having different structure and being separated by domain walls [5]. In this paper, we present the results of ^{35}Cl nuclear quadrupole resonance (NQR) measurements of the channel thiourea-hexachloroethane inclusion compound at 7.5 to 90 K, which confirm the aforementioned model. Specific heat measurements show a phase transition near ~ 96 K.

2. Experimental

The ^{35}Cl NQR measurements of the powder thiourea-C_2Cl_6 inclusion compound at 7.5 to 90 K were made using a Tecmag pulse spectrometer and an Oxford Instruments cryostat. The NQR spectrum covers 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 steps from 5 to 7 kHz) and acquisition of the Hahn echo amplitude at each specified frequency. The measurements were done at reduced *rf* power using rather long, "soft" pulses ($\pi/2$ pulse was 26 μs) to excite only a small portion of the NQR line. The echo amplitude obtained represents the intensity of the actual NQR

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line shape at a specified frequency. The spin-lattice relaxation time T_1 was measured using the π-τ-$\pi/2$ inversion recovery sequence.

The specific heat (C_p) of thiourea-C_2Cl_6 at 80 to 300 K was measured using a home-built adiabatic calorimeter. The method employed here was a method of continuous heating at constant power at adiabatic conditions. The specific heat was calculated from the experimentally measured derivative dT/dt (here T is temperature and t is time).

3. Results and Discussion

The specific heat measurements show that the $C_p(T)$ curve exhibits an anomaly near ~ 96 K (Figure 1). The location of the peak depends slightly on the measurement rate. The phase transition also exhibits a very pronounced relaxation time.

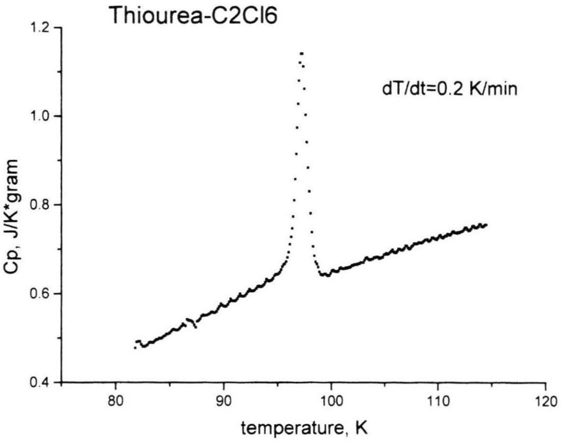

Fig. 1. Specific heat of the thiourea-C_2Cl_6 inclusion compound at in the temperature range 80 to 115 K.

Typical ^{35}Cl NQR spectra in the temperature range from 7.5 to 90 K are shown in Figure 2. Instead of a narrow NQR line usually observed in chlorine compounds, the ^{35}Cl NQR spectra of the thiourea-C_2Cl_6 inclusion compound show a broad line with two or three maxima. The temperature dependence of the resonance frequencies at the maximums of the resonance lines is given in Figure 3.

In the high temperature range, from 77 to 90 K, the spectrum shows two maxima. These maxima have been assigned to the edge singularities of the NQR lineshape of incommensurate (IC) phase [6], suggesting that the incommensurability results from the different periodicity of the guest and host sublattices. At temperatures higher than T_i ~ 90 K no NQR spectrum is observed. We attribute this to the reorientational mobility of the CCl_3-groups (or C_2Cl_6 molecules) in the guest sublattice, accompanied by the order-disorder phase transition found by heat capacity measurements. Fast molecular motion should yield a multiple average of quadrupole interactions preventing a signal in the studied frequency range.

In the low temperature range, from 60 to 7.5 K, the spectrum exhibits three resolved maxima (Fig. 2); in addition to the doublet, a 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 (Figure 3). However, while the shifts of the high and medium frequency lines are almost identical, the low frequency line shows a more significant temperature dependence, accompanied by changes in the line width.

In the intermediate temperature range, from 73 to 60 K, the measurements show significant changes in the NQR spectra (Figures 2, 3). These changes may be attributed to a structural phase transition accompanied by mutual 3D ordering of guest molecules that belong to the different channels. Such a transition is observed in most inclusion compounds [7].

In the low temperature phase, from 7 to 60 K, the spin-lattice relaxation rates T_1 for the high and medium frequency lines are very close to each other and increase slowly with decreasing temperature (Figure 4). This is usually caused by torsional vibrations. However, the low frequency line shows an anomalously fast spin-lattice relaxation rate, which is faster by almost an order of magnitude in comparison to that of the two other lines (Figure 4). This means that the amplitude of vibrations of the molecules assigned to the low frequency line are significantly larger than for the other molecules.

As mentioned above, atom-atom potential calculations show that the guest sublattice comprises two types of finite molecular chains, having different structures and being separated by domain walls. This, along with the measurements of the ^{35}Cl NQR spectra and the spin-lattice relaxation time, allows us to make an assignment of the resonance lines in the low temperature phase. 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

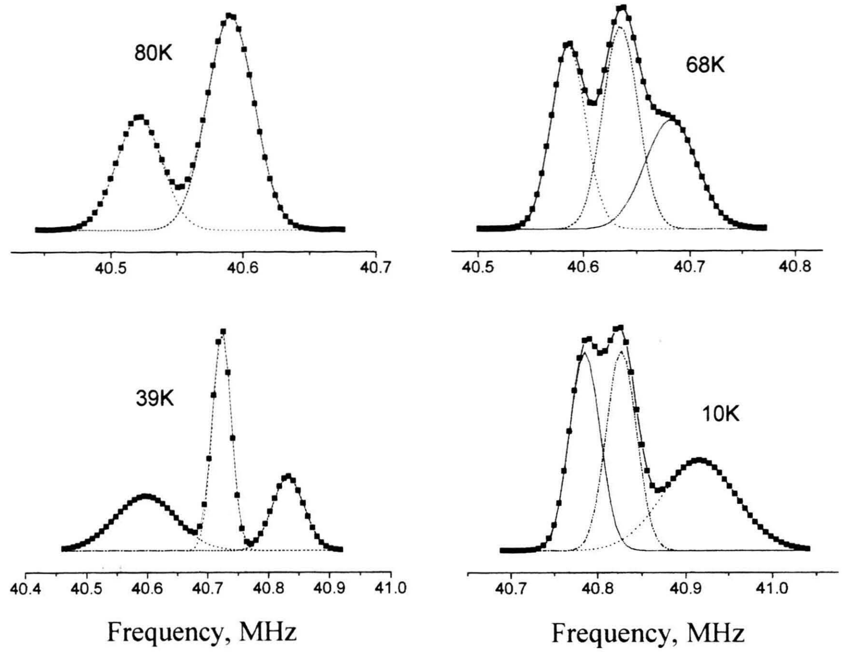

Fig. 2. Typical ^{35}Cl NQR spectra of the thiourea-C_2Cl_6 inclusion compound at 7.5 to 90 K. The dotted and thin lines are the result of deconvolution of the broad features.

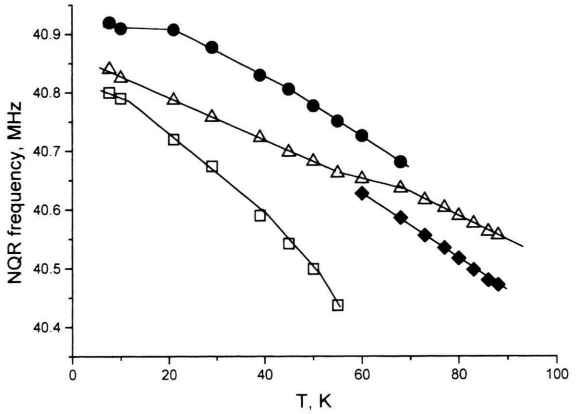

Fig. 3. Temperature dependence of the NQR frequencies in the thiourea-C_2Cl_6 inclusion compound. The resonance frequencies at 7.5 to 10 K are given assuming that the lines do not replace each other with variation of temperature.

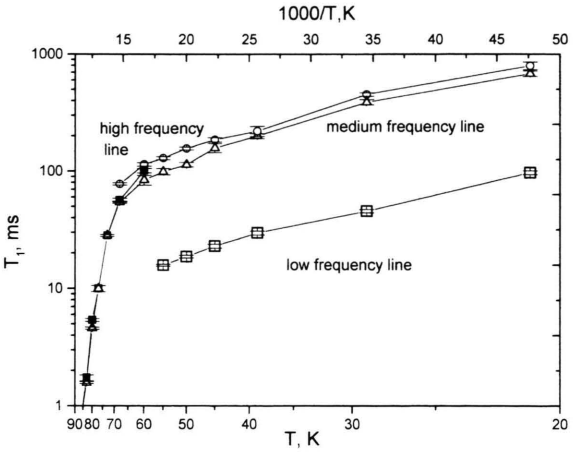

Fig. 4. Temperature dependence of the ^{35}Cl NQR spin-lattice relaxation time T_1 in thiourea-C_2Cl_6 inclusion compound.

behavior, is assigned to the domain walls. However, in the high temperature phase, from 73 to 90 K, the third molecular group, attributed to the domain walls is not obtained. One can suggest this is due to the molecular motion inside the domain walls, where each molecule runs in turn over all possible positions characterized by different EFG values and thus by different NQR frequencies, making the resonance broad and undetectable. One can also suggest that this motion corresponds to a soliton-like longitudinal propagation of the domain wall along the channel predicted by atom-atom potential calculations [5].

The obtained structure of the guest sublattice results from the different periodicity of the guest and host substructures and differs from the conventional continuum models of the incommensurate state.

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