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BY LOW TEMPERATURE PLASTIC PHASE  
OF t-BUTYL CHLORIDE

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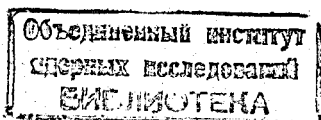
ЛАБОРАТОРИЯ НЕЙТРОННОЙ ФИЗИКИ

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**QUASIELASTIC NEUTRON SCATTERING  
BY LOW TEMPERATURE PLASTIC PHASE  
OF t-BUTYL CHLORIDE**

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## 1. Introduction

The derivatives of neopentane, having spheroidal molecules, are interesting organic compounds which exhibit rotational freedom for molecules not only in liquid, but also in the solid phase. At temperatures well below their melting point, like many other globular crystalline substances, they undergo solid-solid phase transition accompanied by a large change in entropy. For these substances it is commonly agreed that there is an abrupt decrease in molecular freedom for rotation in going from high temperature "plastic" phase to low temperature phase. Among these substances *t*-butyl chloride (TBC),  $(CH_3)_3CCl$  is of a special interest. It is known<sup>/1,2/</sup> to have three solid phases with transition temperatures at 183.1°K and 219.4°K.

This substance has been studied by different techniques. The sudden drop in dielectric constant<sup>/2,3/</sup> in going from phase I to phase II suggests the freezing of dipolar axis in the low temperature plastic phase. The structure studies<sup>/4/</sup> in this phase indicate disorder of methyl groups about C-Cl axis in agreement with evidence of molecular reorientations about this axis from spin lattice relaxation time  $T_1$  measurements<sup>/5/</sup>. These NMR studies in other phases of this compound show that molecules tumble at random in phase I, and mainly  $CH_3$  groups reorient about C-C axis in phase III. As the dynamics of molecular reorientational motion may be studied<sup>/6,7,8/</sup> by using the slow neutron scattering

technique we have performed such study for TBC. In this communication the results of neutron quasielastic scattering by polycrystalline TBC are presented. The measurements were designed for studying uniaxial reorientation of the TBC molecules in its low temperature plastic phase. The results are compared with the model and an estimation of activation energy and relaxation time was made.

## 2. Experiment

The spectra of neutrons quasielastically scattered by freshly prepared polycrystalline TBC were measured simultaneously at eight scattering angles, using inverted geometry spectrometer (KG-SOG I) at Dubna IBR-30 pulse reactor. The principle of this instrument is discussed in Ref.<sup>19</sup>. The pulses of white beam of the neutrons from the reactor hit the sample and a narrow energy band from the scattered spectrum is selected by means of a  $Be$  filter and  $Zn$  (0002) monocrystal. The primary energy of the neutrons is determined by their time of flight over the source sample distance ( $\approx 30$  m) and the position of the energy window for scattered neutrons is defined by the orientation of the monocrystals. During our measurements the crystals were set to reflect  $4.0\text{\AA}$  neutrons with the wave-length spread between 2.2% and 3.2%, depending on the experimental conditions. The shape of the resolution function was measured with the same sample at a sufficiently low temperature.

Two reasons limited the choice of scattering angles. Firstly, at higher scattering angles, the Bragg reflections from the sample or from the container appeared in quasielastic region of the spectrum and secondly, the eight arms of the spectrometer could not be moved independently. Because of these reasons, though the measurements were made at eight scattering angles, the data were analyzed only for  $33^\circ$ ,  $53^\circ$ ,  $73^\circ$ ,  $80^\circ$ ,  $93^\circ$  and  $100^\circ$ . The measurements were made for the sample

at the temperatures  $167^\circ\text{K}$ ,  $193^\circ\text{K}$  and  $208^\circ\text{K}$ , respectively. The temperature was measured with an accuracy of  $\pm 1^\circ\text{K}$ .

The spectra of incoherently scattered neutrons by TBC in all measurements consisted of a broad inelastic component and a well separated intense peak centred at about  $4.0\text{\AA}$ . The shape of the latter changed significantly in going from crystalline to plastic phase, while the former did not alter much. The data were corrected for room background and for the contribution from the empty sample holder. As the full spectrum of neutrons from the moderator hit the sample, the necessary intensity corrections were made. No corrections for multiple scattering have been made.

Figure 1 shows typical examples of the spectra (after the above-mentioned corrections) observed at  $167^\circ\text{K}$  and  $193^\circ\text{K}$ . It may be noticed that while there is a sharp elastic peak at the lower temperature broad wings appear on its both sides at  $193^\circ\text{K}$ . This broad quasielastic component becomes more prominent with increase in temperature or the scattering angle.

## 3. Analysis and Discussions of Results

The neutron scattering by TBC is predominantly that by protons and it is incoherent. Inelastic scattering in these measurements is caused by various vibrational motions of  $H$  atoms and is of no interest to us. We confined ourselves to quasielastic region. At the temperatures for which measurements were performed, the inelastic contribution in this region was very small. It was therefore subtracted by the usual extrapolation method. The development of a broad intensity component under the elastic peak in going from phase III to phase II, is believed to be because of the onset of rapid molecular reorientation at the higher temperature phase. The contribution to quasielastic scattering from methyl group reorientations about  $C-C$  axis is negligible. The potential barrier ( $4.5$  kcal/mol <sup>10/</sup>) and the frequency of oscillation ( $8.7 \times 10^{12}$  sec<sup>-1</sup> <sup>10/</sup>) for the  $CH_3$  group give

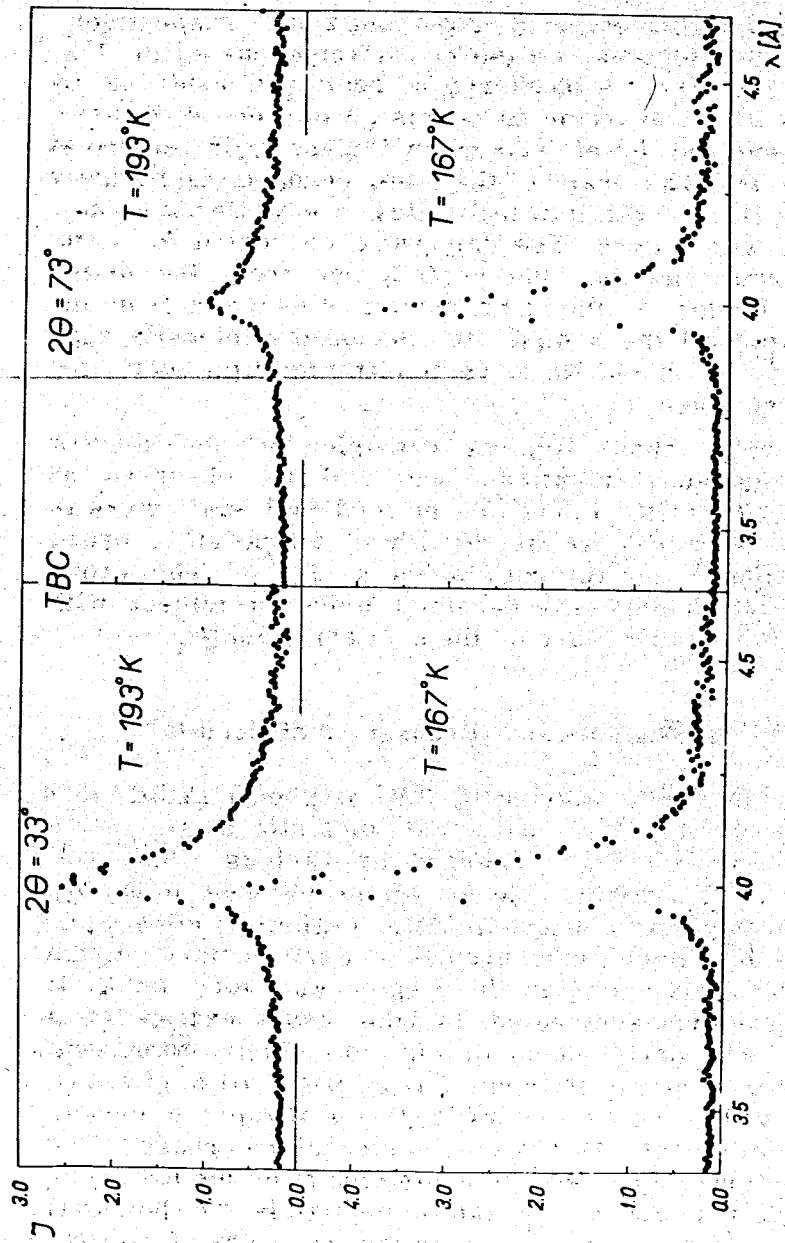


Fig. 1. Scattered neutron intensity for two temperatures ( $T$ ) and two scattering angles ( $2\theta$ ) as a function of incident neutron wavelength.

a jump rate of  $1.7 \times 10^8 \text{ sec}^{-1}$  at  $208^\circ\text{K}$ . Thus, under the conditions of this experiment it behaves as a single rigid unit. The translational diffusion may also be ignored without any error. Both X-ray and dielectric constant measurements confirm that the C-Cl axis is fixed in phase II. Therefore the quasielastic scattering in these measurements is mainly caused by uniaxial molecular reorientations about C-Cl axis.

The neutron scattering cross-section can be calculated, depending on the model for reorientations<sup>6,7</sup>. We analysed data in terms of the jump diffusion model. This assumes that the molecule oscillates about its equilibrium position for an average time  $\tau$  and then instantaneously jumps to another equilibrium position. Sköld<sup>7</sup> has derived the expression for the incoherent scattering cross-section from a tetrahedral unit reorienting by  $120^\circ$  with equal probability about its various threefold axis. Using a similar procedure, it can be shown that when the reorientation is restricted to a single axis then the scattering law in the quasielastic region is given by the formula:

$$S(K, \epsilon) = \pi \left( 1 + \frac{2 \sin KR}{KR} \right) \delta(\epsilon) + 2 \left( 1 - \frac{\sin KR}{KR} \right) \frac{\Gamma}{\epsilon^2 + \Gamma^2},$$

where  $\hbar K$  and  $\epsilon$  are the momentum and energy transfers during scattering and  $\Gamma = \frac{3}{2\tau} \hbar \cdot R$  is the distance

between two equivalent sites of the tetrahedral molecule. The first term gives the elastic scattering connected with the long time behaviour of molecules, while the second corresponds to quasielastic scattering. This formula can be used for TBC molecules reorienting about C-Cl axis only if the methyl group is treated as a rigid unit. This assumption is reasonable in the present case.  $R = 3.13 \text{ \AA}$  was used as the distance between the centres of gravity of protons in two methyl groups. The only unknown quantity in the above formulation is  $\tau$ , the average time between successive reorientations. The above expression for scattering law was folded with the instrumental resolution function and the calculated spectra were then

compared with the experimental ones. Because of the peculiar shape of the resolution function we preferred to compare the shapes of full spectra rather than the widths of spectra. The area of calculated spectrum was normalized to that of the experimental one. It is possible to choose proper value of  $\tau$ , which gives a good agreement between experimental and theoretical spectra at a particular scattering angle. This parameter was, however, so chosen as to achieve a reasonable agreement simultaneously in the whole  $K$  range of interest. The typical examples of comparison at 208°K are shown in Fig. 2, where theoretical spectra correspond to  $\tau = 10 \times 10^{-12}$  sec. Here the bars on experimental points are the statistical errors.

The agreement seems to be satisfactory for angles from 33° to 100°. However, there are some discrepancies and we should admit that in order to explain the results by this model fully, one value of  $\tau$  is insufficient. Spectra at smaller angles suggest larger relaxation time. These differences are perhaps due to the model, which assumes instantaneous jumps. The resolution of the instrument was not good enough to check the validity of more complicated models<sup>16)</sup>. Measurements with high resolution instruments should further clarify the situation.

The data at 193°K demand a value of  $14 \times 10^{-12}$  sec for  $\tau$ . The relaxation times so obtained at two temperatures give a potential barrier of 1.5 kcal/mol. The potential barrier and the relaxation times are expected to have an error of 20%.

Concluding we may say that these measurements show that in low temperature plastic phase of TBC, the molecules reorient about the dipolar axis rapidly enough to be seen by the neutrons. The present results could roughly be explained by Sköld's model with the relaxation times of  $10 \times 10^{-12}$  and  $14 \times 10^{-12}$  sec for 208°K and 193°K, respectively.

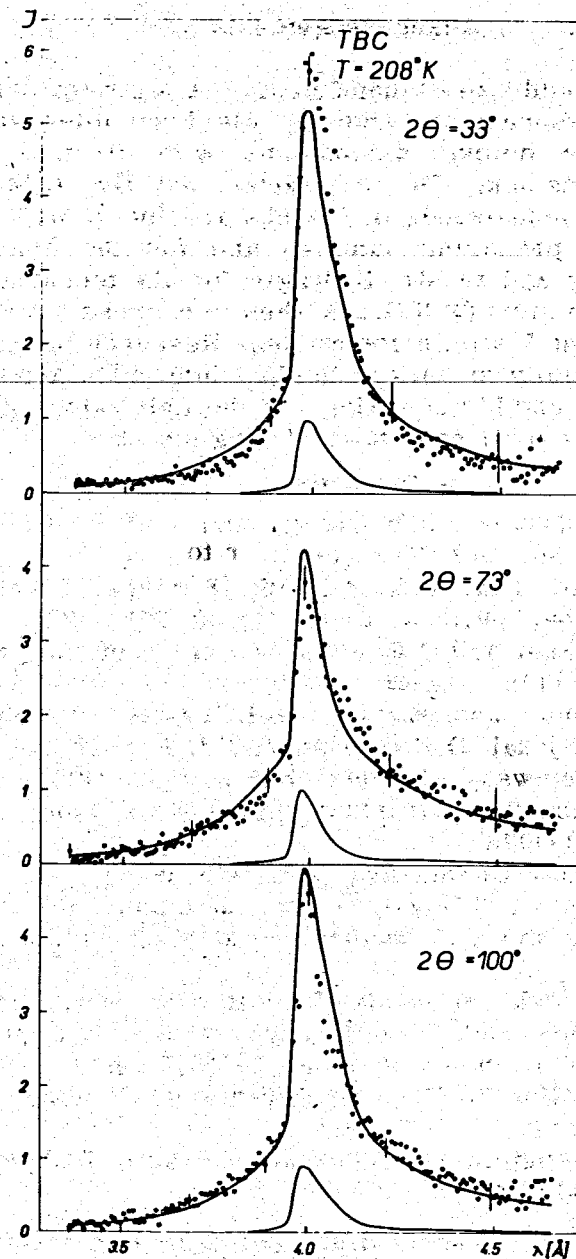


Fig. 2. Comparison of experimental (·) and calculated (—) spectra. Inserts in figure show the resolution function. The bars on experimental points are the statistical errors.

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