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ЛАБОРАТОРИЯ НЕЙТРОННОЙ ФИЗИКИ

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MOLECULAR DYNAMICS STUDY  
THE NEUTRON INELASTIC  
SCATTERING METHOD . V. SC (NH<sub>2</sub>)<sub>2</sub> .

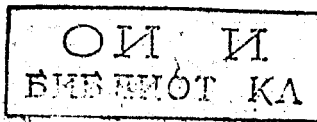
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Subm. to Physica



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## 1. Introduction

Thiourea has been for several years the subject of many theoretical and experimental studies. The enormous interest in this compound is due to its exceptional position among crystals displaying ferroelectric properties; it is a simple molecular crystal in the ferroelectric properties are not associated with the presence of hydrogen bonds.

Measurements of the dielectric constant of  $\text{SC}(\text{NH}_2)_2$  as a function of temperature, conducted by Solomon<sup>/1/</sup>, Goldsmith and White<sup>/2/</sup>, and Freyman et al.<sup>/3/</sup>, have revealed the existence of four anomalies in separating five crystallographic phases:

- 1 - below  $-150^\circ\text{C}$  - ferroelectric phase,
- 2 - between  $-105^\circ\text{C}$  and  $-97^\circ\text{C}$  - non-polar crystal,
- 3 - between  $-97^\circ\text{C}$  and  $-94^\circ\text{C}$  - ferroelectric phase,
- 4 - between  $-94^\circ\text{C}$  and  $-71^\circ\text{C}$  - non-polar crystal, and
- 5 - over  $-71^\circ\text{C}$  - paraelectric phase.

The phase transition at the temperature  $-105^\circ\text{C}$  is, as revealed by measurements of heat capacity<sup>/4/</sup>, a transition of the first kind. The nature of the remaining phase transitions is unknown.

The structure of the compound is known only for the phases 1 and 2 from roentgenographic measurements<sup>/3,5-8/</sup>. At low temperatures the compound crystallizes in the orthorhombic system ( $C_{2v}^2$  space group) with four plane molecules in the elementary cell. The molecules are arranged in two sublattices rotated at a certain angle with respect to each other about the c axis so that there arises an unbalanced electric moment parallel to the b axis. At room temperature the structure is also orthorhombical ( $D_{2h}$  space group). In the elementary cell there are four molecules arranged in two polar sublattices (with the direction on polarity parallel to the b axis) set antiparallely so that their polarities become balanced.

The maps of the distribution of electric charge densities, determined by X-ray methods, evince considerable anisotropy of the thermal motions of the molecules; the rotational vibrations of molecules about the c axis of the crystallographic system are much more hindered than for the other directions.

The dynamics of the atoms of  $\text{SC}(\text{NH}_2)_2$  in solid state have been investigated by the nuclear resonance method by Emsley and Smith<sup>/9/</sup>, by the methods of optical spectroscopy, both Raman<sup>/10/</sup> and absorption in the infra-red<sup>/11,12/</sup>, and by the dielectric method<sup>/3/</sup>.

Nuclear magnetic resonance (NMR) measurements imply that in the vicinity of  $-63^\circ\text{C}$  there appear molecular motions which cause a change in the width of the absorption line. On the basis of measurements with a thiourea single crystal, Emsley and Smith conjectured that motions are torsional vibrations of the rigid molecules performed about the C-S bond (twin axis of the molecule).

Measurements of the optical spectra of the compound have been performed only for the paraelectric phase (stable in temperatures over  $-71^\circ\text{C}$ ) for wave numbers greater than  $250\text{ cm}^{-1}$ . There are no data, however, for the region of smaller wave numbers in which there are lines linked with vibrations of the crystal lattice comprising, among other things the rotational and translational vibrations of entire molecules.

Measurements of dielectric losses as a function of frequency, conducted by Freyman et al.<sup>/3/</sup>, reveal the existence of a broad band of resonance absorption in phase 1 corresponding to a potential barrier of the order 0.11 eV.

The physico-chemical properties of the substance indicate that the phase transitions should be due to the state of the rotation motions of the rigid molecules. Two theoretical models explaining the electric properties of thiourea have been given so far.

According to the model proposed by Calvo<sup>/13/</sup>, the appearance of several phases is associated with a gradual change in the degree of alignment of the molecules in the crystal and transition to phase 5 (paraelectric) is due to a change in the degree of freedom of torsional vibrations about an axis parallel to the c axis of the rigid molecule.

On the other hand, Hideo Futama<sup>4/</sup> suggests that this transition consists in the appearance of additional potential wells, while the degree of freedom of torsional vibrations of rigid molecules remains unchanged. As no experiment has been thus far performed which would permit direct confirmation of the conclusions stemming these models, it was resolved to perform measurements inelastic scattering of neutrons by  $SC(NH_2)_2$  in the phases of ferro- and paraelectric properties. Owing to the large value of the inelastic neutron scattering cross-section of protons, and the lack of selection rules, the neutron method is particularly well suited for investigating the crystal lattice vibrations comprising vibrations of protons.

## 2. Experimental results and discussion

The measurements of inelastic scattering of neutrons by  $SC(NH_2)_2$  were performed with the time of flight spectrometer with Be-filter and Zn monochromator in front of the detector installed at the I.B.R. pulsed reactor of the Joint Institute for Nuclear Research at Dubna<sup>14,15/</sup>. The studied substance in crystalline form (degree of purity: analytical reagent) was placed in thin-walled aluminium vessels which was put into vacuum cryostat<sup>16/</sup>.

The experimental results are presented in Fig. 1-3. When comparing the distributions obtained for samples at  $-160^\circ C$  and room temperature, we are struck by their remarkable similarity. In both cases there are distinctly two groups of peaks (maxima):

- a) the group of peaks in the energy region from 50 to 140 meV, and
- b) the group of peaks at energies less than 25 meV.

The energies of the peaks and the frequencies corresponding to them are assembled in Table 1 which, for comparison, also includes the transitions observed in the optical spectra of thiourea at room temperature. The interpretation of the optical results (taken from paper<sup>11/</sup> is based on the acceptance of the  $C_{2v}$  site symmetry, i.e., the same as the case of urea, instead of the actual  $C_s$  symmetry.

As is seen from Table I, the frequencies of transitions determined by the neutron method are in good agreement with the results of optical research. The position of the peaks of the first group, interpreted as being due to intramolecular vibrations comparing the motions of the  $\text{NH}_2$  groups, varies only very slightly with temperature. This shows that there is weak interaction between the intramolecular motions and lattice vibrations.

The second set of peaks appears in the frequency region in which one should expect the appearance of lattice vibrations comprising both the rotational and translational vibrations of whole molecules. It is impossible to give a unique interpretation of these peaks without solving the questions of motion of the atoms in the crystal lattice. It follows from general deliberations, however, that motions like torsional vibrations of whole molecules should appear at frequencies higher than those of the translational motions. On this basis the three peaks appearing at the energies of 23, 17, and 12 meV have been assigned to torsional vibrations of rigid  $\text{SC}(\text{NH}_2)_2$  molecules, performed about the molecular axes 1 (parallel to the N-N atoms), 3 (perpendicular to the molecular plane), and 2 (answering to the S-C bond). The results of paper<sup>5/</sup> support this interpretation to a certain extent and, moreover, these peaks are in the frequency region in which lines arising from vibration motions appear in such molecular crystals as benzene or naphthalene<sup>14/</sup>.

The two peaks appearing at the lowest energies (7 and 4.5 meV) have been assigned to the translational vibrations of the thiourea molecules.

Attention should be paid to the fact the positions of the peaks assigned to the lattice vibrations do not change with temperature. We believe that this fact corroborates the correctness of the Hideo Futama model, since a change in the degree of freedom of rotational motions of molecular groups usually appears distinctly in neutron spectra.

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Table I  
Frequencies of thiourea

| Infrared study / 12/<br>room temp.<br>cm <sup>-1</sup> |       | Raman study / 10/<br>room temp.<br>cm <sup>-1</sup> |      | Neutron present study |      |                  |      | Assignment            |
|--|-------|---|------|-----------------------|------|------------------|------|-----------------------|
|  |       |   |      | -160°C                |      | room temp.       |      |                       |
| cm <sup>-1</sup>                                       | meV   | cm <sup>-1</sup>                                    | meV  | cm <sup>-1</sup>      | meV  | cm <sup>-1</sup> | meV  |                       |
| -  | -     | -   | -    | 48.4                  | 6    | 47.6             | 5.9  | transl.               |
| -  | -     | -   | -    | 66.1                  | 8.2  | 65.3             | 8.1  | transl.               |
| -  | -     | -   | -    | 96.8                  | 12   | 94.4             | 11.7 | rot.                  |
| -  | -     | -   | -    | 139.5                 | 17.3 | 138.7            | 17.2 | rot.                  |
| -  | -     | -   | -    | 186.3                 | 23.1 | 184.7            | 22.9 | rot.                  |
| 411  | 50.9  | 438   | 54.2 | 443.6                 | 55   | 427.4            | 53   | NH <sub>2</sub> tors. |
| 463  | 57.3  | -   | -    | -                     | -    | -                | -    | skeletal def.         |
| 486  | 60.2  | 483   | 59   | -                     | -    | -                | -    | CN                    |
| -  | -     | 505   | 62.5 | 521                   | 64.7 | 515              | 63.9 | NH <sub>2</sub> tors. |
| -  | -     | 577   | 71.5 | -                     | -    | -                | -    | NH <sub>2</sub> wagg. |
| 629  | 77.9  | 635   | 78.3 | 637                   | 79   | 629              | 78   | SCNN                  |
| 730  | 90.4  | 735   | 91.2 | -                     | -    | -                | -    | CN                    |
| 769  | 95.3  | 8-  | -    | 790                   | 98   | 778              | 96.5 | NH <sub>2</sub> wagg. |
| 1086   | 134.5 | 1094  | 136  | 136                   | 137  | 1089             | 135  | NH <sub>2</sub> rock. |

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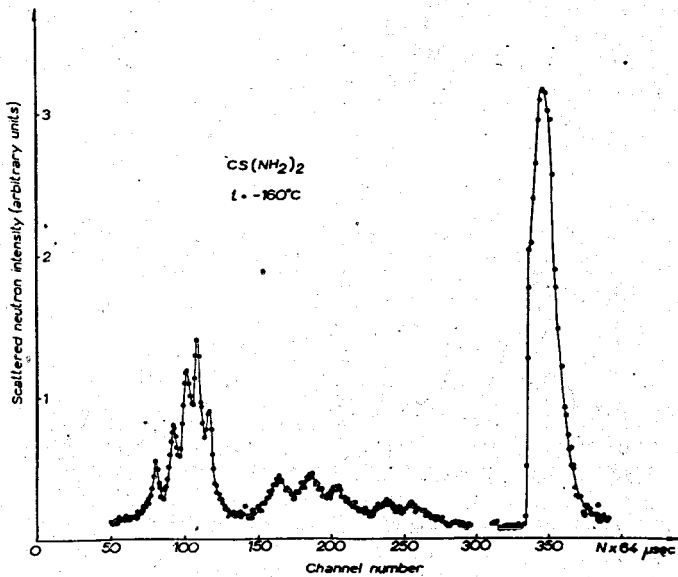


Fig. 1. The intensity of neutrons scattered from crystalline  $\text{CS}(\text{NH}_2)_2$  at temperature  $-160^\circ\text{C}$ , as a function of the analyser channel number. Channel width 64  $\mu\text{sec}$ .

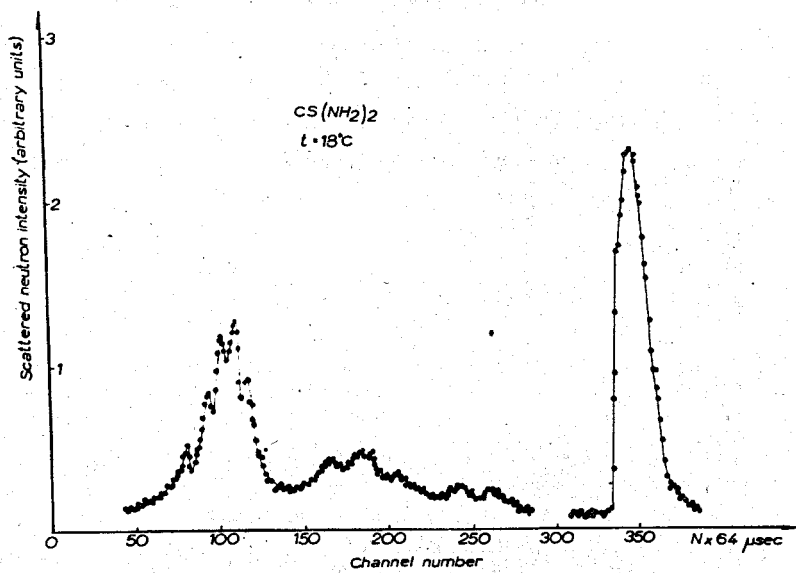


Fig. 2. The intensity of neutrons scattered from crystalline SC NH<sub>2</sub> 2 at room temperature, as a function of the analyser channel number. Channel width 64 sec.

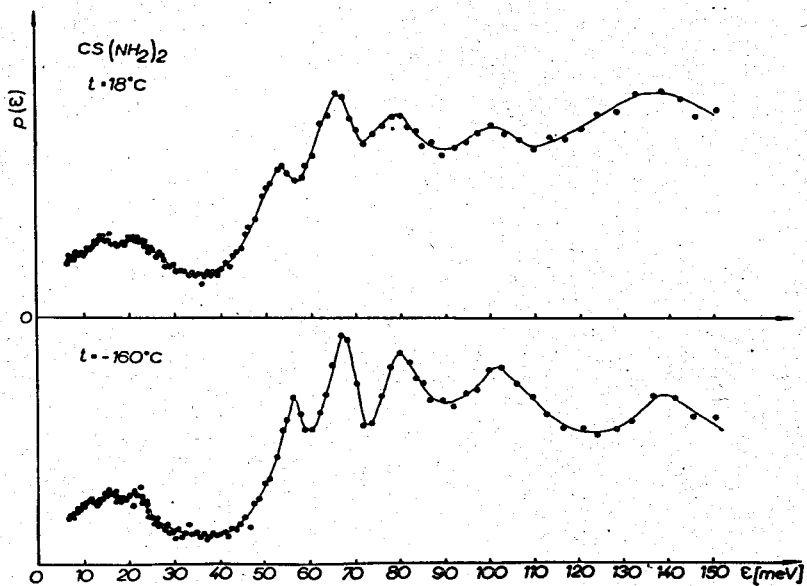


Fig. 3. The  $p(\epsilon)$  functions for  $CS(NH_2)_2$  at two temperatures ( $-160^\circ C$  and  $+18^\circ C$ ), obtained on the basis of data of Figs. 1 and 2.