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ABSTRACT

The frequency spectra of methanol in three phases liquid, crystal I and crystal II were determined by incoherent inelastic neutron scattering. The measurements were performed using a Beryllium Filter Time-of-Flight Spectrometer. Neutron inelastic scattering spectra and frequency spectra allowed assignments of five peaks, corresponding to frequencies: 420 cm^{-1} attributed to vibrational modes of crystalline lattice, 240 and 160 cm^{-1} associated to stretching of hydrogen bonds, 82 and 50 cm^{-1} interpreted as vibrational and torsional modes of CH_3OH units in dimers, trimers, tetramers and pentames. The results suggest crystal I phase as an intermediate phase between liquid and crystal II, concerning the structural and dynamical properties of molecules and their correlation. The plastic character of crystal I is discussed.

I – INTRODUCTION

Methanol, CH_3OH, has been classified as a globular compound[34]. These compounds display peculiar physical properties, for instance small entropy of melting and a phase transition in solid state with large entropy change, due to different degree of orientation of their molecules as a function of temperature. The phase transition is from a low-temperature crystalline phase (crystal II) with low symmetry to a crystalline phase (crystal I), stable between phase transition (II → I) and melting temperatures, with high symmetry and a certain degree of plasticity. For this reason they are called plastic crystals[32,35]. The unusual properties have been attributed to almost spherical symmetry of molecules about the center of mass as a result either of the geometrical distribution of the atoms or of rotation of the molecule about its center.

In particular, methanol has high triple point, at 175.59 K[4] and shows a first order transition at 157.34 K[4]. From X-ray studies on methanol, it was established crystal II as monoclinic and crystal I as orthohombic[33] or hexagonal[16].

Based on its small entropy of melting (4.38 cal/mol K)[4], methanol was classified as a plastic crystal according to Timmermans'[34] empirical definition of a plastic crystal as a substance which has an entropy of melting less than 5 cal/mol K. However the plastic feature of crystal I is questionable[4] because of the small entropy of transition (0.966 cal/mol K) and the decrease in heat capacity across the crystal II → crystal I transition, atypical for plastic crystals.

Although the structure and atomic dynamics of methanol have been investigated by a variety of spectral methods, infrared[15,19], Raman[17,18,21], NMR[5], neutron inelastic scattering[1,23,24,25,26,27,29], many problems are still of interest.

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It is well established that neutron-inelastic scattering is a powerful tool to investigated the dynamical behaviour of hydrogenated molecules in the solid and liquid states. In this case the neutron scattering is essentially incoherent and due to hydrogen atoms since the incoherent scattering cross section of hydrogen atom is about 20 times that for carbon and oxygen.

In order to study the molecular dynamics of methanol in the low frequency region, neutron inelastic scattering measurements in methanol were performed at the following temperatures: 140 K (crystal II), 166 K (crystal I) and 298 K (liquid state).

II – GENERALIZED FREQUENCY SPECTRUM

Van Hove[27] emphasized the separation of the differential incoherent scattering cross section, given in the first Born approximation when the neutron-nucleus interaction is described by means of the Fermi pseudopotencial[10,20], in two factors.

$$\frac{d^2\sigma_{inc}}{d\Omega\, d\omega} = A\ S_{inc}(\vec{Q},\omega)$$

where, for a given momentum and energy transfers in the scattering process, $S_{inc}(\vec{Q},\omega)$ is independent of neutron energy as well of the interation potential, depending solely on the dynamics of the scatterer, whereas A dependes only on the properties of individual particles of the scattering system. $S_{inc}(\vec{Q},\omega)$ is called "Incoherent Scattering Law".

Here, $\hbar\vec{Q}$ and $\hbar\omega$ denote the momentum and energy transfer in the colision between the neutron and the scatterer and through the relations.

$$\vec{Q} = \vec{k}_0 - \vec{k} \qquad \text{and} \qquad \omega = \frac{\hbar k_0^2}{2m} - \frac{\hbar k^2}{2m},$$

m being the neutron mass and $\hbar$ Planck's constant divided by 2π, are expressed in terms of initial and final wave vectors $\vec{k}_0$ and $\vec{k}$.

The incoherent scattering law, $S_{inc}(\vec{Q},\omega)$, is defined as the Fourier transform over space and time of the space-time self-correlation function $G_s(\vec{r},t)$.

$$S_{inc}(\vec{Q},\omega) = \frac{N}{2\pi}\int\int \exp[i(\vec{Q}\cdot\vec{r} - \omega t)]\, G_s(\vec{r},t)\, d\vec{r}\, dt$$

For a system in thermal equilibrium, the scattering law and the space-time self-correlation function mus satisfy the detailed balance condition[31].

Vineyard[37] proposed that the self-correlation function $G_s(\vec{r},t)$ could be approximated to a Gaussian function of $\vec{r}$ with the width depending on time. Egelstaff[8,9,11,12,13], using such approximation, described the scattering system in therms of "Generalized Frequency Spectrum" $Z(\omega)$, defined as a Fourier transform of the imaginary part of the velocity auto correlation function as follows.

$$\mathrm{Im}\ \langle \vec{v}(0)\cdot\vec{v}(t)\rangle = \frac{3\hbar}{2M}\int_0^\infty \omega\, Z(\omega)\, \mathrm{sen}(\omega t)\, d\omega$$

where M is the atomic mass

The generalized frequency spectrum, $Z(\omega)$, is related to the incoherent scattering law through the equation

$$Z(\omega) = \frac{4M}{\hbar\omega} \operatorname{senh}\left(\frac{\hbar\omega}{2KT}\right) \omega^2 \lim_{\hat{Q} \to 0} \frac{\tilde{S}_{inc}(\hat{Q},\omega)}{Q^2}$$

where K is the Boltzmann's constant, T the temperature of scattering system and

$$\tilde{S}_{inc}(\hat{Q},\omega) = \exp\left(-\frac{\hbar\omega}{2KT}\right) S_{inc}(\hat{Q},\omega)$$

is the symmetrical scattering law which includes the detailed balance condition.

All information about the scattering system obtained by means of neutron incoherent scattering cross section measurements, is contained in the function $Z(\omega)$. It represents the atomic and molecular movements, in the scattering system, responsable for energy and momentum transfer in terms of characteristic frequencies of the scattering system.

The limit for $\hat{Q} \to 0$ have been studied by several authors[2,3,8,7,11,12,13,14], being proposed its substitution by a generalized Debye-Waller factor:

$$2W \approx \frac{\hbar Q^2}{2M} \int_0^\infty (\hbar\omega)^{-1} Z(\omega) \coth\left(\frac{\hbar\omega}{2KT}\right) d\omega$$

III – EXPERIMENTAL

The measurements of scattered neutron distributions were carried out using a conventional cold neutron time-of-light spectrometer[2,3] at IEA-R1 research reactor. An incident beam of cold neutron, with as average energy of 3.5 meV and a full width at half-height of 2.0 meV, obtained by filtration through a blocks of polycrystalline beryllium held a liquid nitrogen temperature, hits the sample. A lead monocrystal filter is also used to reduce the gamma ray background. Neutrons scattered by the sample at a certain angle are pulsed by a curved slit slow neutron chopper operated usually at 13000 rpm and are detected by a bank of ten ^{3}He detectors arranged in one layer after an evacuated flight path of 3.15 m. The time-of-flight analysis and the data record are performed by a multi-channel analyser. The time-of-flight resolution is 1.7 % for 4 Å neutrons and 6.4% for 1 Å neutrons.

Methanol of "pro analysi" quality, purchased from J. T. Baker Co, with purity higher than 99.5% and 0.2% maximum water content, was used. The scattering sample, contained in a slab type aluminum cell, has a tickness of 0.2 mm, chosen to avoid multiple scattering. The sample container was placed in a liquid-nitrogen cooled cryostat with a 6 litre coolant reservoir, a cold finger and a nickel-chrome wire heating system. In the cryostat the sample could be held at any desired temperature between 100 and 300 K. The temperature was measured with a copper-constantan thermocouple and it was controlled within 2 K by an electro-mechanical devices which turns on or off the heating wire power supply. All measurements have been performed in transmission geometry, with the sample plane at 45° to incident neutron beam.

The energy distributions of scattered neutrons were measured at the scattering angle 40° for the methanol sample at the following temperatures: 298 K (liquid state), 166 K (crystal I) and 140 K (crystal II).

After subtraction of background and sample holder scattering, spectra were corrected for chopper transmission, detector efficiency and air scattering and absorption[2]. Figures 1, 2 and 3 shown the corrected time-of-flight spectra for three measured temperatures. Owing to the reactor schedule (7-8 h/day), each spectrum takes three weeks to be obtained.

The time-of-flight spectrum, proportional to $d^2\sigma/d\Omega dt$, after to be transform in $d^2\sigma/d\Omega d\omega$ through the relation:

$$\frac{d^2\sigma_{inc}}{d\Omega d\omega} \sim E^{-3/2} \frac{d^2\sigma_{inc}}{d\Omega dt},$$

is used to calculate the generalized frequency spectrum by means of the equations introduced in part II. Figures 4, 5 and 6 show frequency spectra obtained for different temperature conditions.

IV – RESULTS AND DISCUSSION

An analysis of scattered neutron spectra and generalized frequency spectra reveals the existence of five characteristic frequencies, shown in Table I.

Table I

Frequencies (cm^{-1}) and Assignments for Methanol

ω (cm^{-1})	420	240	160	82	50
ASSIGNMENT	Lattice vibration mode	Streching of hydrogen bonds		Vibrational and torsional modes of molecules in the globules	
PHASES AND STATES	CRYSTAL II CRYSTAL I	LIQUID CRYSTAL I CRYSTAL II		LIQUID CRYSTAL I CRYSTAL II	

The peaks observed at 420 cm^{-1} is attributed to vibrational modes of crystal lattice[15]. This peak is predominant in crystal II phase, where there is more ordering of methanol molecules. In crystal I phase the intensity of 420 cm^{-1} peak was reduced and in the measurement performed at room temperature, liquid state, it was not observed.

The peaks at 240 and 160 cm^{-1}, observed in all phases, are associated to characteristic movements of hydrogen bond stretching. Raman Spectroscopy[16,22] results are consistent with this assignment. These peaks are dominant in the frequency spectrum for the liquid state. In crystal II phase, their intensities are strongly reduced. This fact could be attributed to the restriction of individual degree of freedom of molecules, caused by their ordering in the crystalline lattice, facilitating the predominance of collective degrees of freedom, as lattice vibrations.

From neutron spectroscopy results obtained by the isotopic substitution technique[1] (CH_3OH, CD_3OH and CH_3OD), it could be concluded that the peaks at 160 cm^{-1} might be attributed to CH_3 group motions. However, Raman and infrared experiments[15,18,19] suggested that the CH_3 hindered rotation frequency changes from ca.270 cm^{-1} to ca.650 cm^{-1} at the vapour-liquid transition.

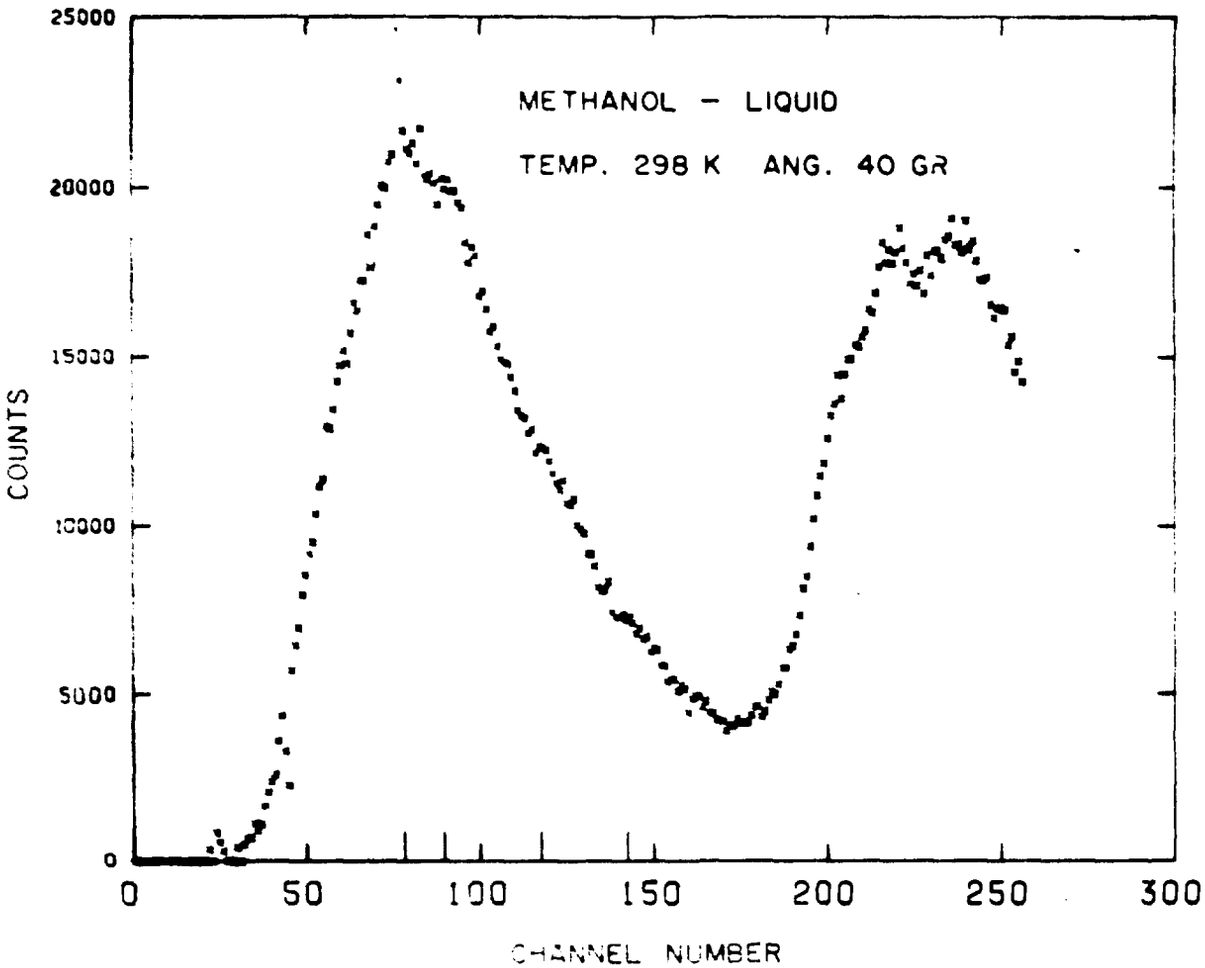

Figure 1 – Corrected Time-of-Flight Spectrum of Neutrons at an Angle of 40° by Methanol in its Liquid State as a Function of Number of 16 μsec Channels

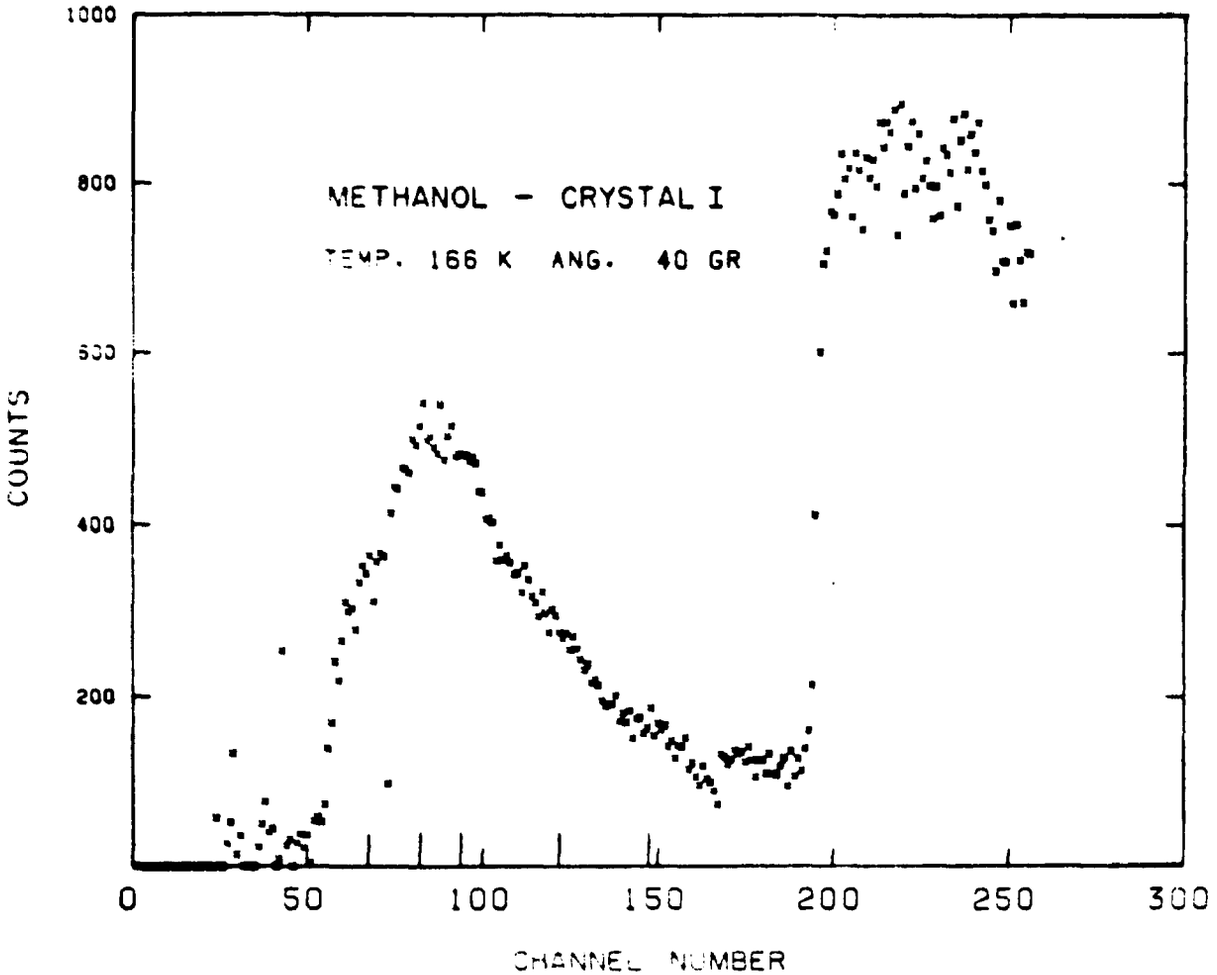

Figure 2 – Corrected Time-of-Flight Spectrum of Neutrons Scattered at an Angle of 40° by Methanol in its Crystal I Phase

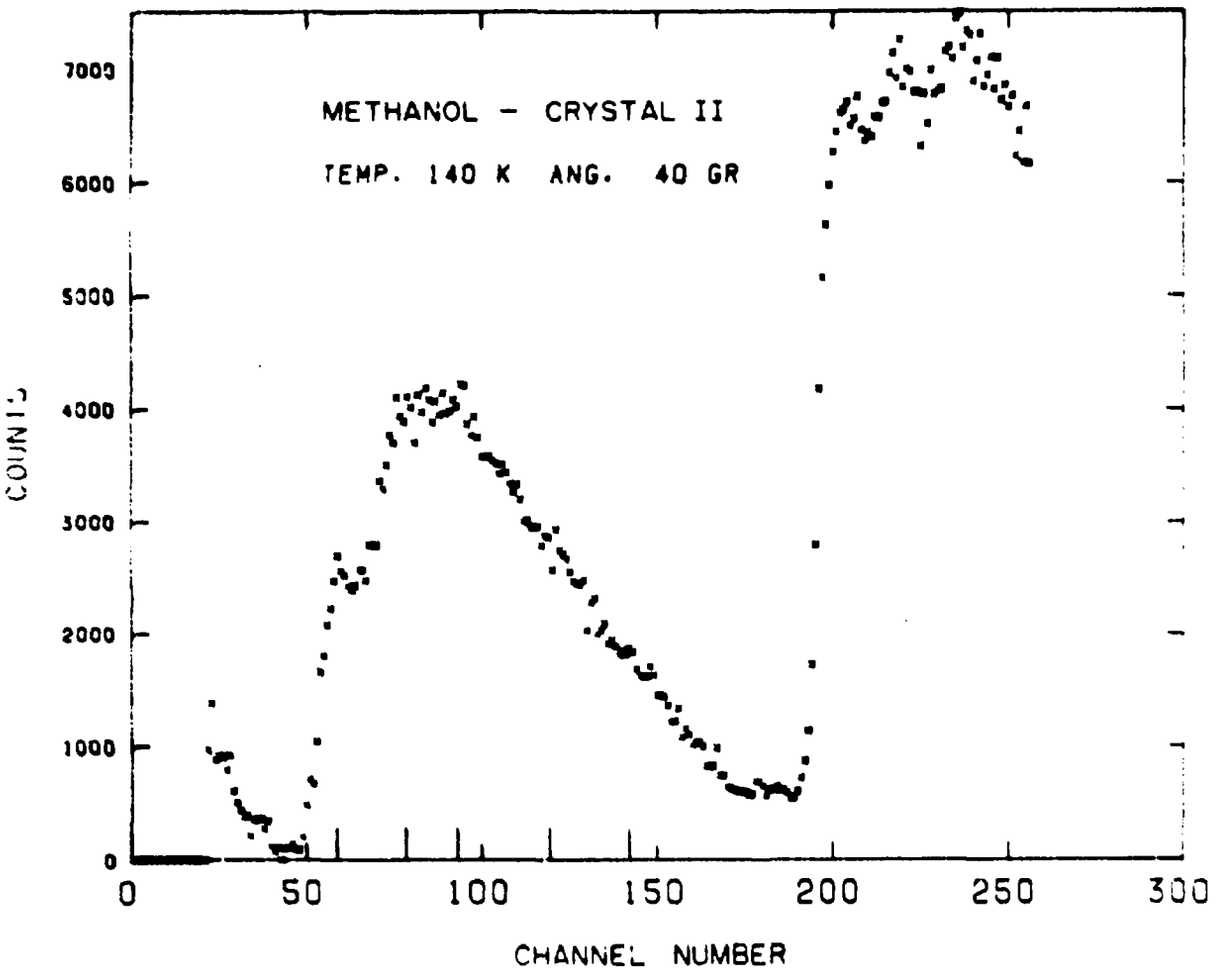

Figure 3 – Corrected Time-of-Flight Spectrum of Neutrons Scattered at an Angle of 40° by Methanol in its Crystal II Phase

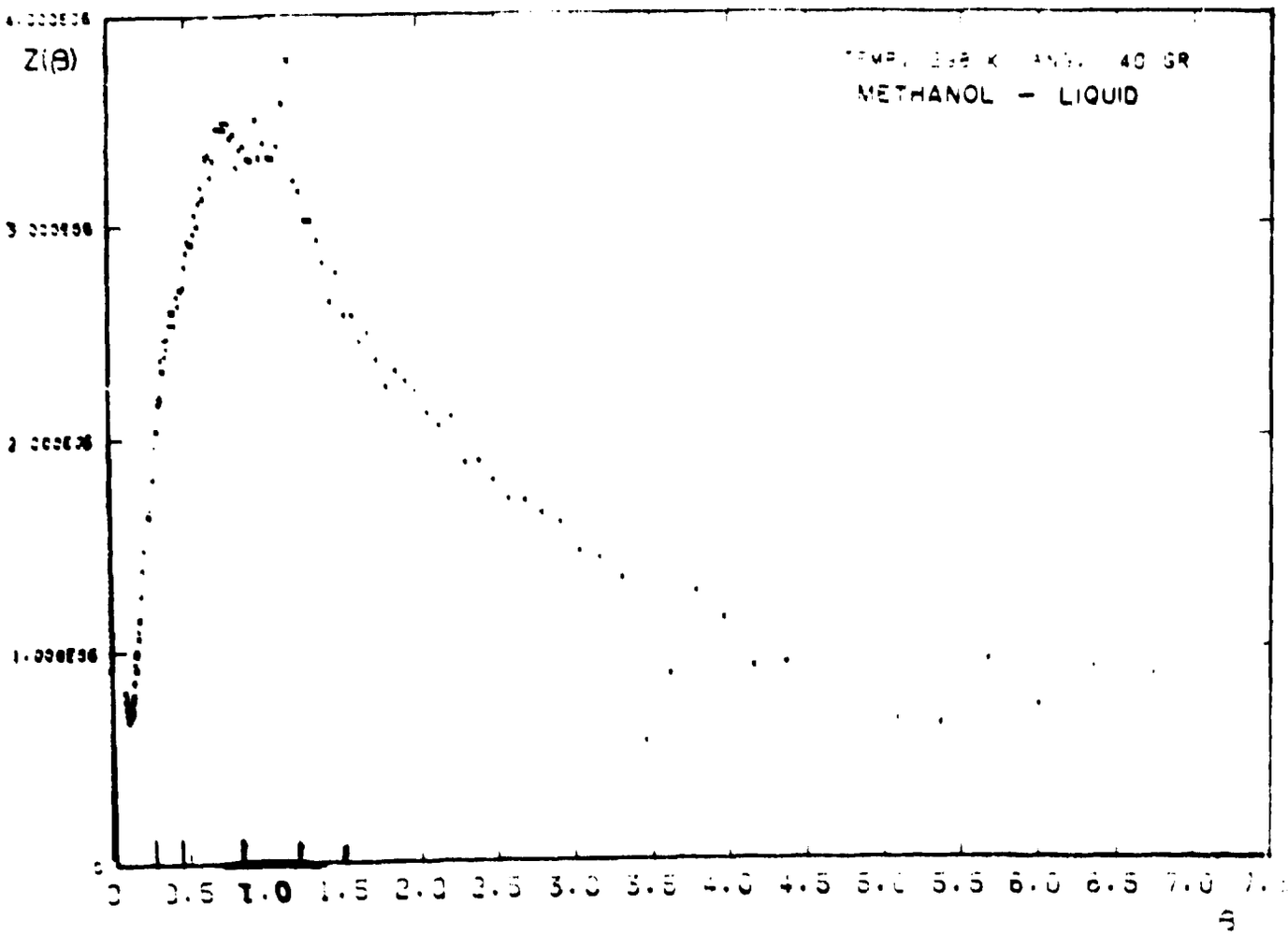

Figure 4 - Generalized Frequency Spectrum $Z(\omega)$ in Function of $\beta = h\omega/KT$ of Methanol in its Liquid State

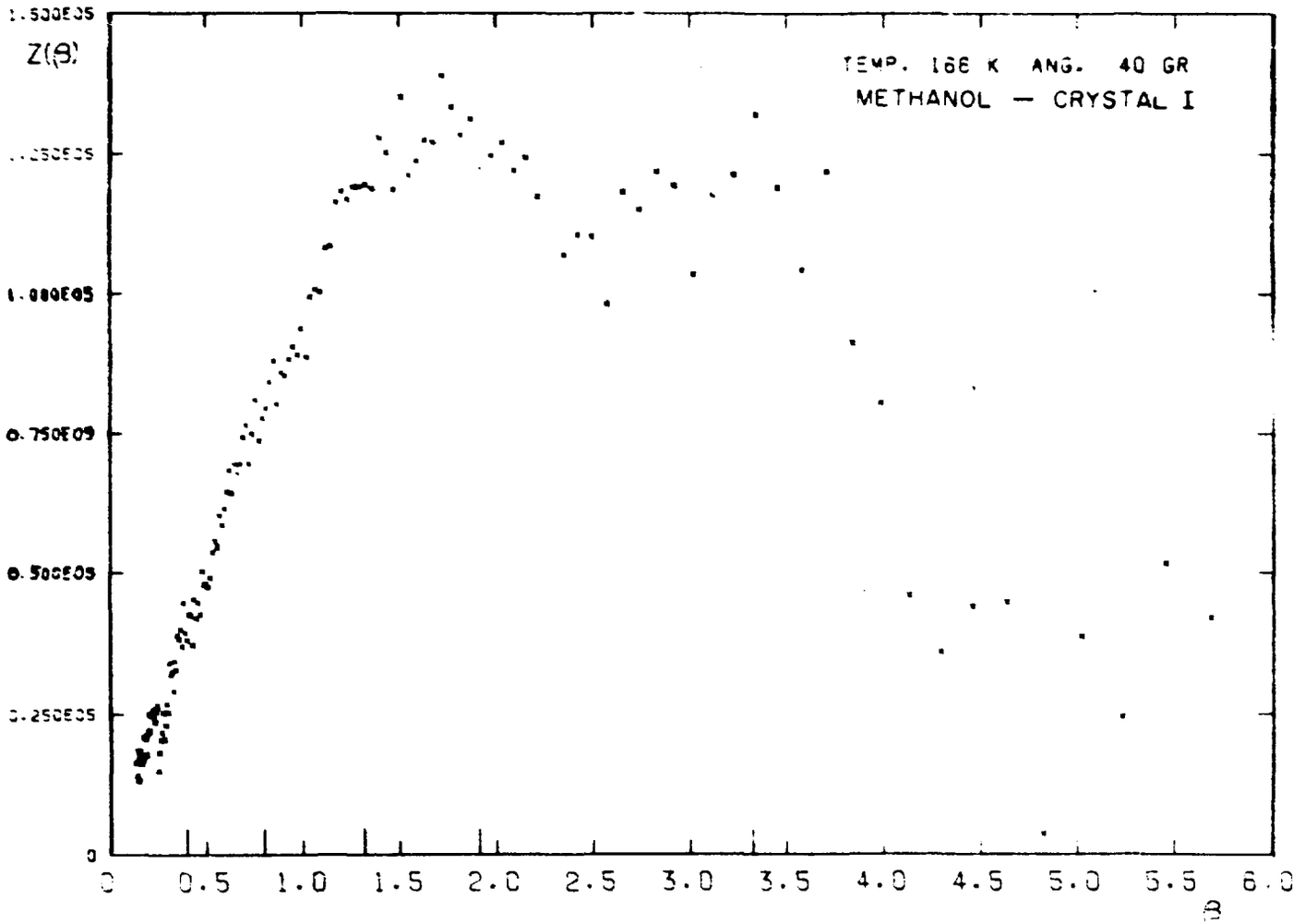

Figure 5 — Generalized Frequency Spectrum $Z(\omega)$ in Function of $\beta = \hbar\omega/KT$ of Methanol in its Crystal I Phase

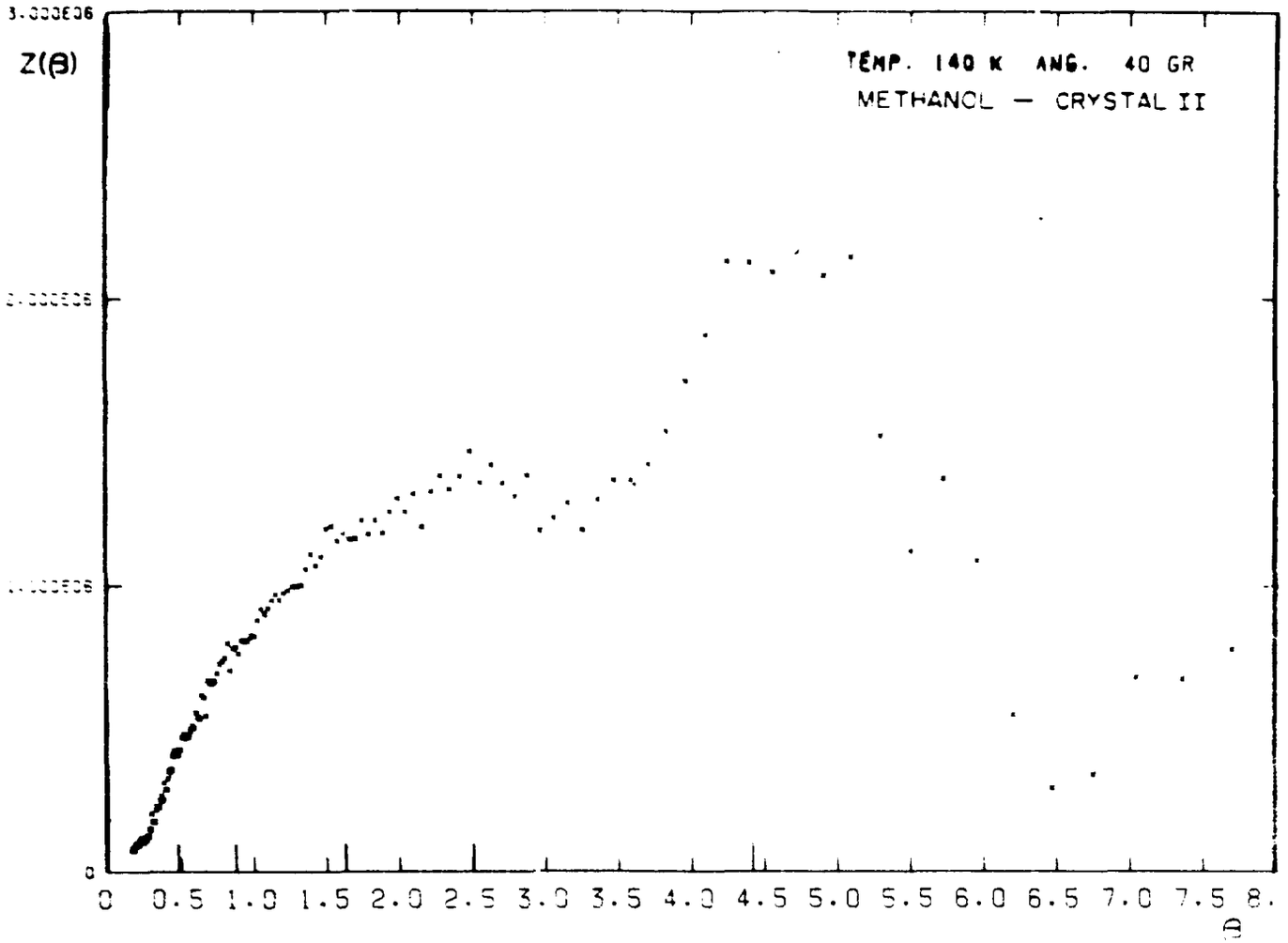

Figure 6 – Generalized Frequency Spectrum $Z(\omega)$ in Function of $\beta = h\omega/KT$ of Methanol in its Crystal II Phase

In the spectra obtained in the present work, intensities of peaks at 160 and 240 cm^{-1} are approximately equal. By analogy with the 240 cm^{-1} peak, the peak at 160 cm^{-1} was attributed to stretching of hidrogen bonds. If this peak would be originated from rotation of CH_3 group, its intensity might be larger because of the number of hydrogen envolved in this motion.

The peaks observed at 50 and 82 cm^{-1} correspond to vibrational and torsional modes of molecules associated in dimers, trimers, tetramers and pentames, by hydrogen bonds. Studies performed using several techniques[5,15,18,25,26,28] show that CH_3OH units in methanol are associated in globules containing in average 3.5 molecules. In Raman spectroscopy measurements[18], the peaks observed at frequencies below 130 cm^{-1} have been attributed to these external molecular modes.

In neutron inelastic scattering measurements, the 50 and 82 cm^{-1} peaks are better defined in the liquid state spectrum, although they have been also observed in the spectra for solid phases.

The spectrum of methanol in crystal I phase shows the same intensity for the peak attributed to the stretching of hydrogen bonds, dominant in the liquid state, and the peak correspondent to movements associated to collective degree of freedom, as lattice vibrations. It can be concluded that crystal I can be considered as an intermediate phase between liquid state and crystal II phase, concerning the structural and dynamical properties of methanol molecules and their correlation depending on temperature.

This work shows that the most important dynamical change occurs at the change of state and not at the phase transition. The low entropy of melting must be due to ordering in the liquid, maintained by hydrogen bonds as has been suggested, also, for other associated compounds, particularly tert-butanol[2,3]. The non-plastic feature of crystal I[4] is supported.

RESUMO

Determinou-se por meio do espalhamento incoerente inelástico de nêutrons, os espectros de frequência do metanol em duas fases cristalinas e no estado líquido. As medidas foram realizadas utilizando-se o dispositivo experimental Filtro de Berílio Espectrômetro de Tempo de Vôo. Nos espectros de nêutrons espalhados e nos espectros de frequência foram assinalados cinco picos correspondendo as frequências: 420 cm^{-1} atribuída a modos vibracionais da rede cristalina, 240 e 160 cm^{-1} associados ao estiramento das pontes de hidrogênio, 82 e 50 cm^{-1} interpretados como modos vibracionais e torsionais das unidades de CH_3OH associados em dimeros, trimeros, tetrameros e pentameros. Os resultados indicam a fase de cristal I como sendo intermediária entre o estado líquido e o cristal II, em termos das propriedades estruturais e dinâmicas das moléculas e sua correlação. É discutido o caráter plástico do cristal I.

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