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TITLE

Studies of molecular dynamics with neutron scattering techniques (part of a coordinated programme on neutron scattering techniques)

FINAL REPORT FOR THE PERIOD

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AUTHOR(S)

Laercio A. Vinhas

INSTITUTE

Instituto de Energia Atomica
Nuclear Physics Department
Sao Paulo, Brazil

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FINAL REPORT OF THE RESEARCH PROJECT RC/1755-BRA(1755/R2/RB)

"NEUTRON INELASTIC SCATTERING DYNAMICS OF SOLIDS AND LIQUIDS AND OF HYDROGEN IMPURITIES IN TRANSITION METAL"

INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES* (IPEN), SÃO PAULO, BRASIL

CHIEF SCIENTIFIC INVESTIGATOR: LAERCIO ANTONIO VINHAS

PERIOD: MAY-1976 - DECEMBER-1979

The activities developed under the Research Project RC/1755-BRA can be divided in the following main topics.

I) IPEN Triple-Axis Neutron Spectrometer: construction, automation and performance on lattice dynamics studies.

II) Study of the dynamics of hydrogenous compounds by neutron inelastic scattering.

III) Metal/Hydrogen Systems studied by neutron inelastic scattering.

## I) IPEN Triple-Axis Neutron Spectrometer

At the beginning of the period covered by the Research Contract we intensified our efforts to conclude the construction and assembly of a Triple-Axis Spectrometer whose design and construction had been started previously. In the design, the following characteristics have been considered: mechanical simplicity, facility of construction and flexibility of operation, without loosing the accuracy of the equipment. In the construction, components for industrial applications were adapted in order to minimize the construction cost and to become the assembly easier.

A sketch of IPEN triple-axis spectrometer is given in figure 1. Monochromatic neutrons with a wavelength 1.435Å were selected from the collimated Maxwellian reactor beam by Bragg scattering from the (111) plane of a Copper single crystal($x_1$). These neutrons, were allowed to strike the scattering

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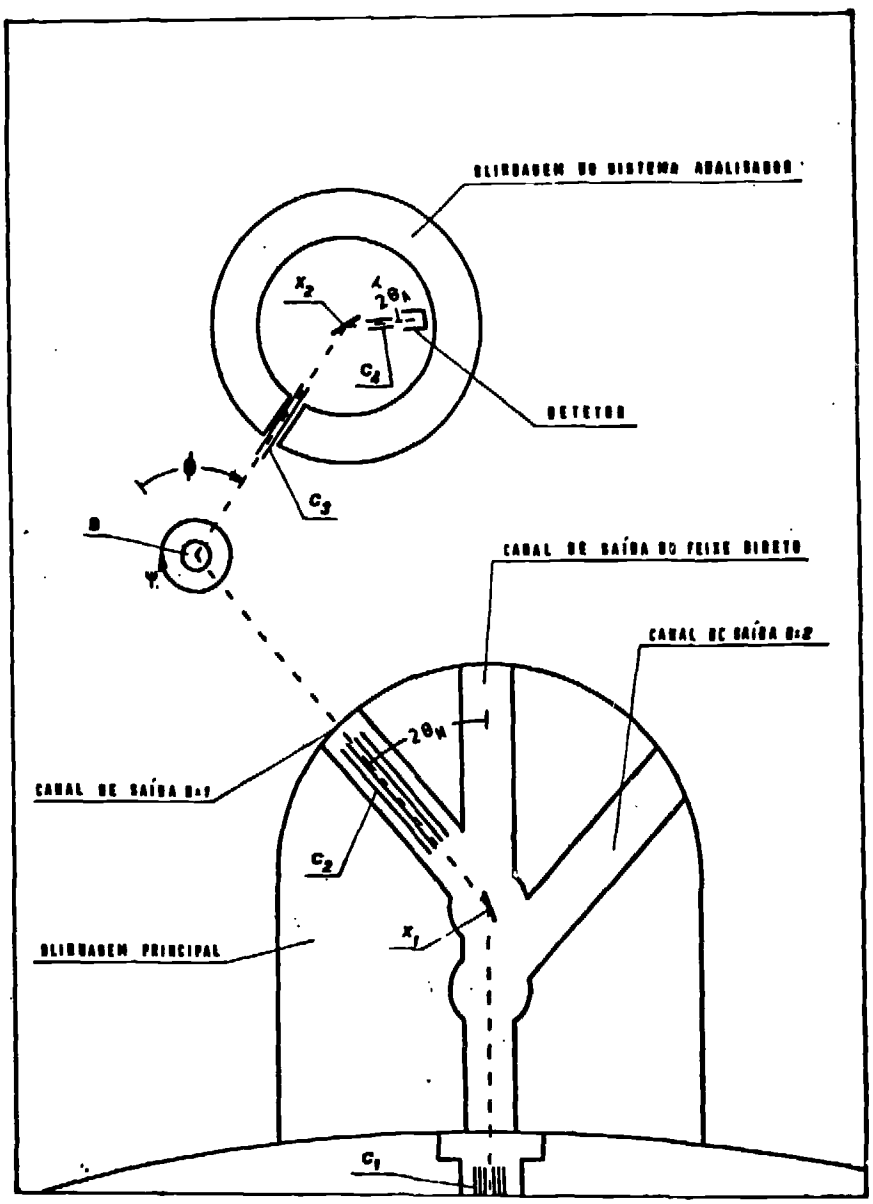
* New designation of Instituto de Energia Atômica(IEA).




– Diagrama Esquemático do Espectrômetro de Cristal de Três Eixos para Nêutrons do IEA

FIGURE 1

sample placed on a goniometer located in S. The neutrons scattered by the sample at an angle $\phi$ are analyzed in energy by means of an analyzer crystal spectrometer(pyrolitic graphite(002) single crystal and $^3He$ detector).

Details about the IEA(IPEN) Triple-Axis Spectrometer can be seen in the paper "Design, Construction and characteristics of IEA Triple-Axis Spectrometer" published in the IEA Technical Report Series under the number 477 (1977) (copy of this paper is the annex I of this report).

The incident wavelength determination and angular scales calibration were performed measuring diffraction patterns of nickel. The energy resolution of the spectrometer were determined through measurements on a vanadium sample.

After the calibration and resolution determination, we have performed the first coherent inelastic neutron scattering measurements with IEA Triple--Axis Spectrometer: Dispersion relation for copper along the three major symmetry directions (00$\xi$), (0$\xi\xi$) and ($\xi\xi\xi$). The purpose of these measurements was to check the performance of IEA Triple-Axis Spectrometer on phonon studies. Usually copper is used as a standard for this kind of study. The measurements were carried out operating the Triple-Axis Spectrometer in the "Constant Q" mode at neutron energy loss(phonon creation). Two typical neutron groups, obtained for (00$\xi$) transversal branch, are shown in figure 2. The line through the points are drawn by hand and does not represent any fitting procedure. The normal-mode frequencies $\omega$ and reduced wave vectors $\xi$ determined for the symmetry directions are given in Table I. This table shows also the results obtained by Svensson at alii(Physical Review 155(1967)619) e Nicklow at alii (Physical Review 164 (1967)922) for comparison. The results of Table I are plotted in Figure 3 to give the dispersion relation for copper in the major symmetry directions. An excellent agreement can be observed between the results obtained in the present experiment and the data for copper presented in the litterature. This comparison indicates that the IEA Triple-Axis Spectrometer is in good

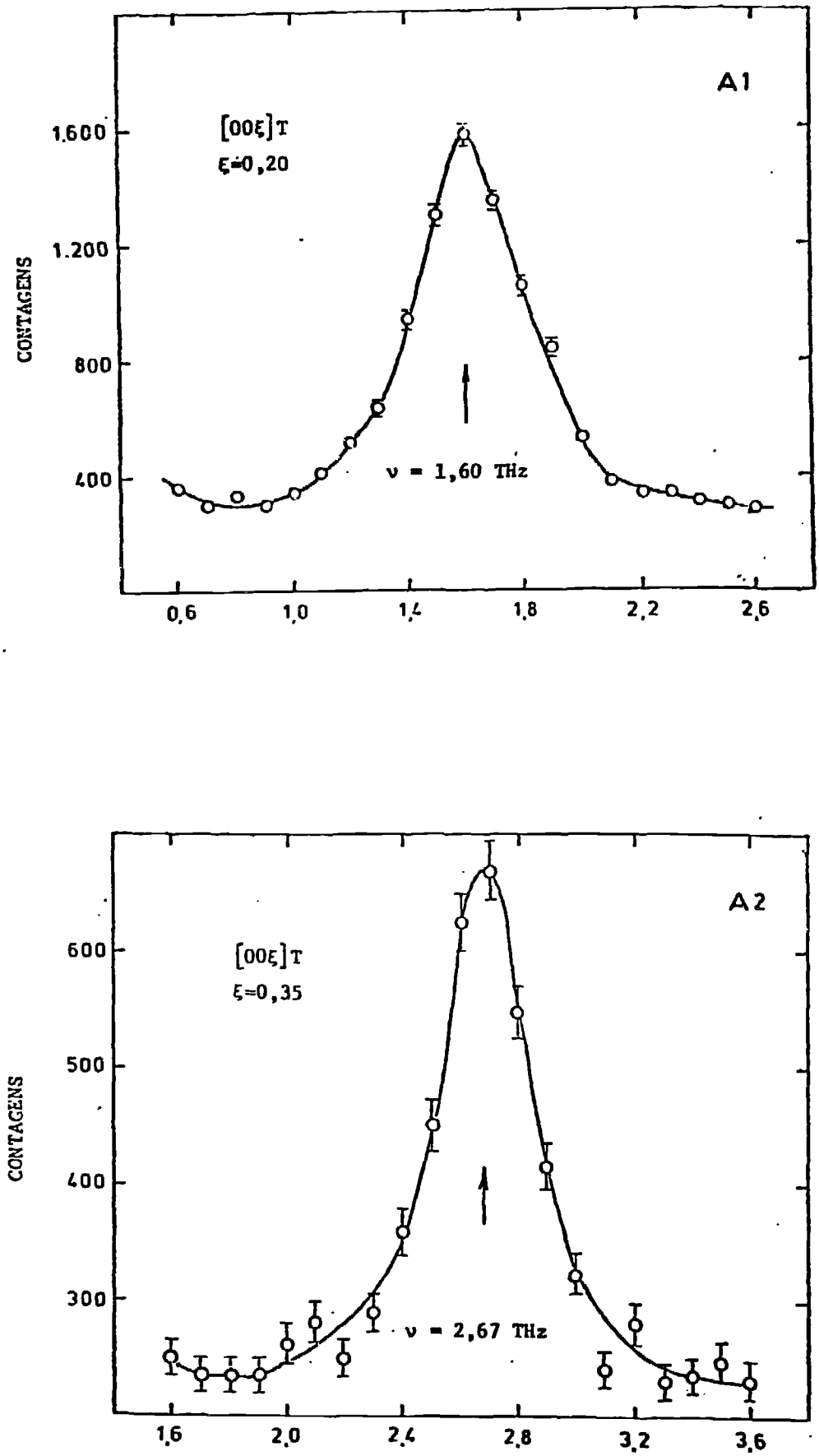
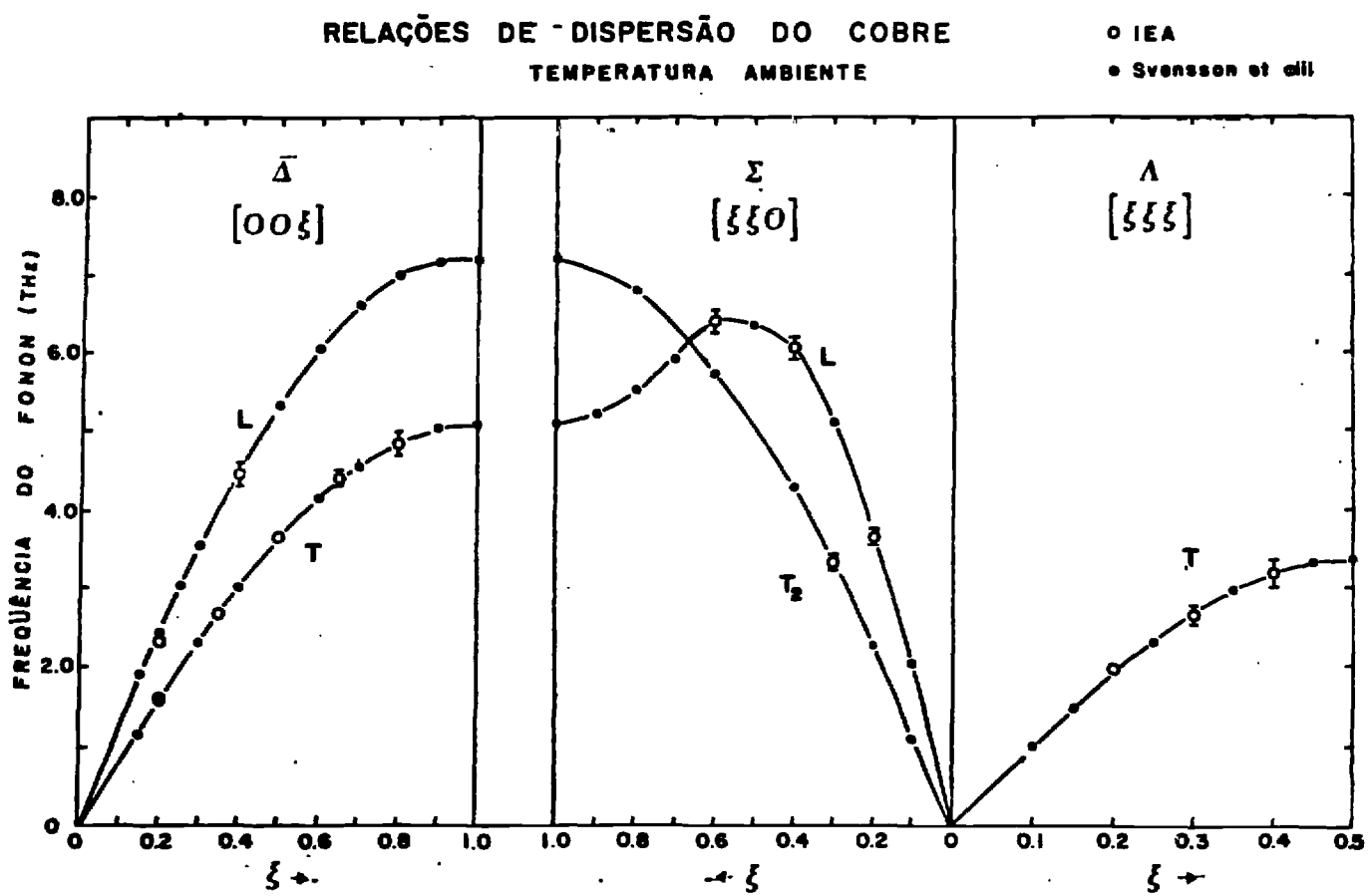

A1
[00ξ]T
ξ=0,20
1.600
1.200
800
400
CONTAGENS
ν = 1,60 THz
0,6
1,0
1,4
1,8
2,2
2,6
A2
[00ξ]T
ξ=0,35
600
500
400
300
CONTAGENS
ν = 2,67 THz
1,6
2,0
2,4
2,8
3,2
3,6
FREQÜÊNCIA ν(THz)

FIGURE 2

TABLE I

Frequências Obtidas Neste Trabalho, Comparadas com as Encontradas na Literatura

| | | ξ | Presente Trabalho ν(THz) | SVENSONN et alii ν(THz) | NICKLOW et alii ν(THz) |
|---|---|---|---|---|---|
| DIREÇÃO Δ | | | [00ξ] T | | |
| | A1 | 0,20 | 1,60 ± 0,04 | 1,56 ± 0,04 | 1,60 ± 0,02 |
| | A2 | 0,35 | 2,67 ± 0,05 | 2,64 ± 0,04 | ± |
| | A3 | 0,50 | 3,66 ± 0,06 | 3,62 ± 0,04 | 3,67 ± 0,03 |
| | A4 | 0,65 | 4,40 ± 0,10 | 4,34 ± 0,05 | ± |
| | A5 | 0,80 | 4,84 ± 0,14 | 4,86 ± 0,07 | 4,88 ± 0,10 |
| | | | [00ξ] L | | |
| | B1 | 0,20 | 2,30 ± 0,06 | 2,42 ± 0,07 | 2,44 ± 0,04 |
| | B2 | 0,40 | 4,45 ± 0,15 | 4,47 ± 0,07 | 4,50 ± 0,05 |
| DIREÇÃO Σ | | | [ξξ0] $T_2$ | | |
| | C1 | 0,30 | 3,34 ± 0,10 | 3,37 ± 0,04 | 3,41 ± 0,03 |
| | | | [ξξ0] L | | |
| | D1 | 0,20 | 3,68 ± 0,08 | 3,70 ± 0,08 | 3,67 ± 0,03 |
| | D2 | 0,40 | 6,05 ± 0,15 | 5,97 ± 0,08 | 6,00 ± 0,10 |
| | D3 | 0,60 | 6,40 ± 0,15 | 6,38 ± 0,12 | 6,35 ± 0,15 |
| DIREÇÃO Λ | | | [ξξξ] T | | |
| | E1 | 0,20 | 1,96 ± 0,06 | 1,87 ± 0,06 | 1,89 ± 0,06 |
| | E2 | 0,30 | 2,65 ± 0,12 | 2,66 ± 0,06 | 2,69 ± 0,05 |
| | E3 | 0,40 | 3,20 ± 0,18 | 3,17 ± 0,07 | 3,21 ± 0,07 |




– Relações de Dispersão do Cobre à Temperatura Ambiente para as Três Direções de maior Simetria. Os Resultados Experimentais Obtidos Neste Trabalho (círculos brancos) são Comparados com os Obtidos por Svensson et alii (círculos negros). A Curva Cheia Representa o Cálculo Teórico Apresentado Nessa Referência

FIGURE 3

operational conditions and it is able to perform original measurements. A paper showing these results and details about experimental procedures was published in the IEA Technical Report Series("Performance of IEA Triple--Axis Crystal Spectrometer: measurements of dispersion relation of Copper" IEA Technical Report nº 504(1978)) (Annex II).

The informations and data contained in the two mentioned papers are included in the Master Thesis of C.Fuhrmann, researcher of our Group. This thesis was submitted in partial fulfillment of the requirements for the degree of Master of Science to Instituto de Energia Atômica, associated to University of São Paulo, in June 1978. The supervisors were Dr. R. Fulfaro and Dr. L.A.Vinhas.

In order to obtain better results in coherent inelastic neutron scattering experiments using the IPEN triple-axis spectrometer, the focusing conditions for this spectrometer were studied. For the instrument focusing conditions attainment, expressions were deduced taking in account the finite collimation, incident and scattered wave vectors, and interplanar spacing of monochromator and analyser crystals. The focusing conditions were graphically represented with the scope to establish an practical and adequate routine procedure for focusing the spectrometer. An experimental test of the method was made by measuring accustic phonon peaks propagating in the (00ξ) direction of a copper crystal. The measurements were performed in several focusing conditions, such as: optimum, good and defocused. The results shown in figure 4 evidentiate the usefulness of the focusing conditions.

Concerning the devices for the automatic control of IEA Triple-Axis Spectrometer, Dr. Jan Kulka, expert of International Atomic Energy Agency, in collaboration with the local staff, has designed it. The devices were designed to control automatically the three main axes of the Triple-axis spectrometer, named $\psi$, $\phi$ and $2\theta_A$(see figure 1), and other three axes refering to the sample goniometer installed on the spectrometer. The

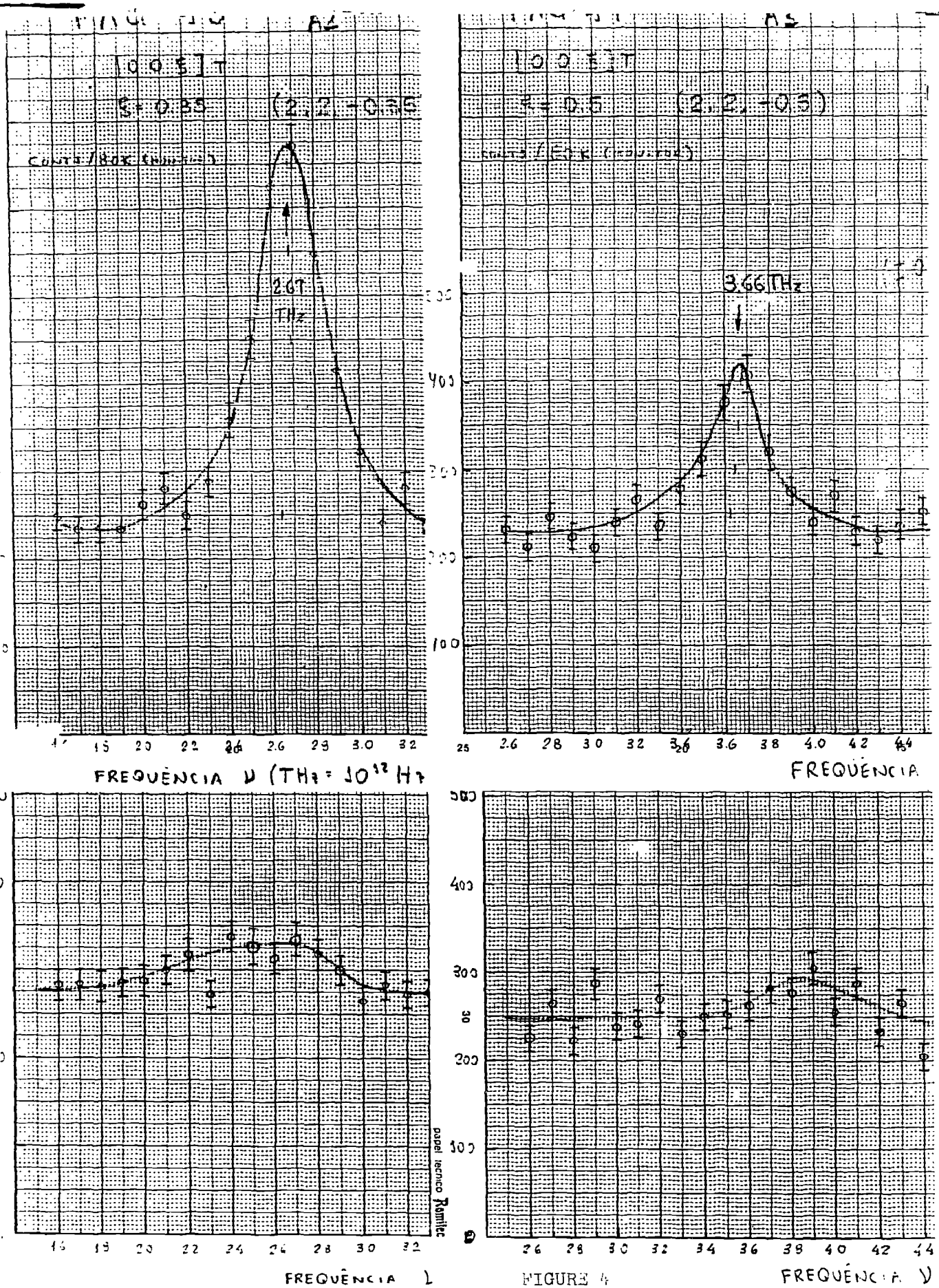

100 K
S = 0.85 (2.2, -0.35)
2.6 THz
FREQUÊNCIA ν (THz = 10^12 Hz)
100 K
S = 0.5 (2.2, -0.3)
3.66 THz
FREQUÊNCIA
FREQUÊNCIA
papel técnico Ramilec
FREQUÊNCIA ν

FIGURE 4

system does not use a computer, the movements and the angular setting are performed by stepping motors controlled by an electronic circuit. The number of revolution that each axes turns, is counted by a pick-up. The input/output of data performed through a Teletype.

The assembly of the electronic part of logic control system was completed, the cabinet including front panel with switches and indicators, and rear panel with connectors, was constructed. The motors were choosen and purchased. The pulse generator circuit and the power supply for the motors were designed and constructed. The assembly containing logic control unit, pulse generator, stepping motors, motor power supply, Teletype and pick up, were checked with success.

The gears and mechanical components had already been designed and their construction are almost finished at IEA(IPEN) mechanical workshop.

## II) Study of the Dynamics of Hydrogenous Compounds by Neutron Inelastic Scattering

Concerning the dynamics of hydrogenous compounds, we have studied some organic globular compounds as tert-butanol, cyclohexanol and methanol, and the dynamics behaviour of water present in DNA.

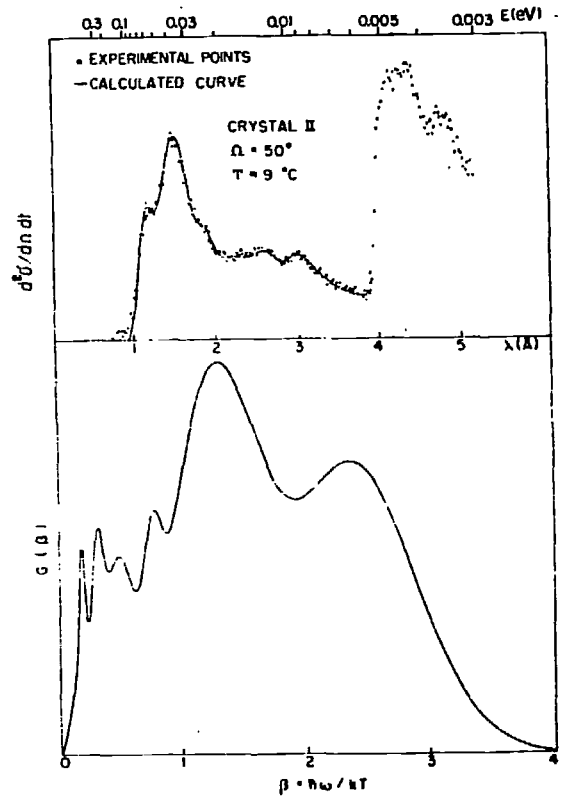
There is a large interest in the study of globular compounds because of their peculiar physical properties, attributed to the almost spherical symmetry of their molecules. The globular compounds show high triple point, small entropy of melting and a phase transition, in solid state, with large entropy change. This phase transition occurs from a low symmetry crystalline phase, stable at low temperatures between the transition point and the melting point. The high symmetry is called plastic crystal or rotational phase due to display a certain degree of plasticity and an un hindered rotation of molecules around their lattice positions.

Molecular dynamics of tert-butanol, cyclohexanol and methanol in at least two phases in the solid state and in the liquid state was investigated by cold neutron inelastic scattering. Measurements were taken with a conventional

cold neutron(beryllium filter) time-of-flight spectrometer at the IEA-R1 reactor. Energy gain spectra were collected at scattering angles between $20^{o}$ and $90^{o}$. After subtraction of background and sample holder. scatter ing, spectra were corrected for chopper transmission, air scattering and detector efficiency. Generalized frequency spectra were obtained from the corrected time-of-flight distribution using the procedures introduced by Egelstaff (Nuclear Science Engineering 12(1962)250,260).

The self-diffusion of these compounds were studied by quasi-elastic neutron scattering. For tert-butanol and cyclohexanol the measurements were per formed using the Beryllium Filter Time-of-flight spectrometer and for methanol the Triple-axis Spectrometer.

Molecular dynamics of tert-butanol, in the temperature interval $8-35^{o}C$, in two crystalline phases and in the liquid state was investigated. In elastic spectra remained essentially the same, indicating short range order in liquid state. Frequency spectra (Figure 5) allowed the following assignment of peak positions: The peak at 33 meV, very well pronounced and dominant in the neutron spectrum, must be associated to the $1 \leftrightarrow 0$ transition of $CH_3$ torsional motions; the peak at 50 meV corresponds to the $2 \rightarrow 0$ transition superposed to skeletal molecular movements; the peak at 20 meV corresponds to the stretching of hydrogen bonds between molecules; the valley at 14 meV probably separates the regions of internal and external modes. The peaks at 6 and 9 meV may be of translatory or librational origin. A barrier $V_1 = (4.0 \pm 0.2)$kcal/mol for $CH_3$ internal rotation was obtained. Quasi-elastic broadening and Debye-Waller factors were analysed in terms of models for molecular diffusion and the results compared with NMR data.To explain the results, it is proposed the existence of two different motions: individual molecular librations superposed to a co operative rotational diffusion involving groups of molecules associated by H bonding. It was concluded that cooperative rotational diffusion occur in both solid and liquid states. A paper presenting the main results of this research was published in Journal of Chemical Physics 68(1978) 5636-42(Annex III of the present report).




– Measured Spectrum $d^2\sigma/d\Omega dt$ for Crystal II and Calculated Curve as a Function of Neutron Wavelength, With Corresponding Neutron Energy. The Lower Figure Shows $G(\beta)$ Function (Sum of Seven Gaussian Functions) from Which the Calculated Spectrum in the Upper Figure Was Obtained

FIGURE 5

The frequency spectra of cyclohexanol in three crystalline phases (at temperatures 287K-crystal I, 253K-crystal III and 183K-crystal II) and in the liquid state were determined by incoherent inelastic neutron scattering. Neutron inelastic spectra (figures 6 and 7) and frequency spectra (figures 8 and 9) fitted to a sum of Gaussian functions show evidences for events around 36-44, 62-79, 120-148, 216-250 and 384-509 $cm^{-1}$ assigned as hindered rotation of molecules, lattice vibrations, hydrogen bond stretching, out-of-plane and in-plane ring bending modes respectively. These results are contained in the paper "Atomic motions in liquid and solid cyclohexanol studied by incoherent inelastic neutron scattering" published in the IPEN Technical Report Series* with the number 001(1979) (Annex IV).

Neutron quasi-elastic scattering measurements on solid and liquid cyclohexanol over the range of temperatures between 100 and 300K were used to investigate different models for molecular diffusion. The line width of quasi-elastic peak determined from the observed broadening of incident line as a function of the square of momentum transfer ($Q^2$), for several temperatures, are given in figure 10. Diffusion coefficients were determined from the slope of these curves. The variation of diffusion coefficients with temperature allowed us to determine the activation energy for diffusion in solid and liquid states. The values obtained were $(0.49 \pm 0.01)$kcal/mol and $(6.40 \pm 0.26)$kcal/mol. These results evidenced the large rotational diffusion in this globular compounds. These results are included in the Master Thesis of V.S.Walder, researcher of our Group. This thesis was submitted in partial fulfillment of the requirements for the degree of Master of Science in the Institute of Physics, University of São Paulo (September 1977). The supervisor was Dr. L.A.Vinhas.

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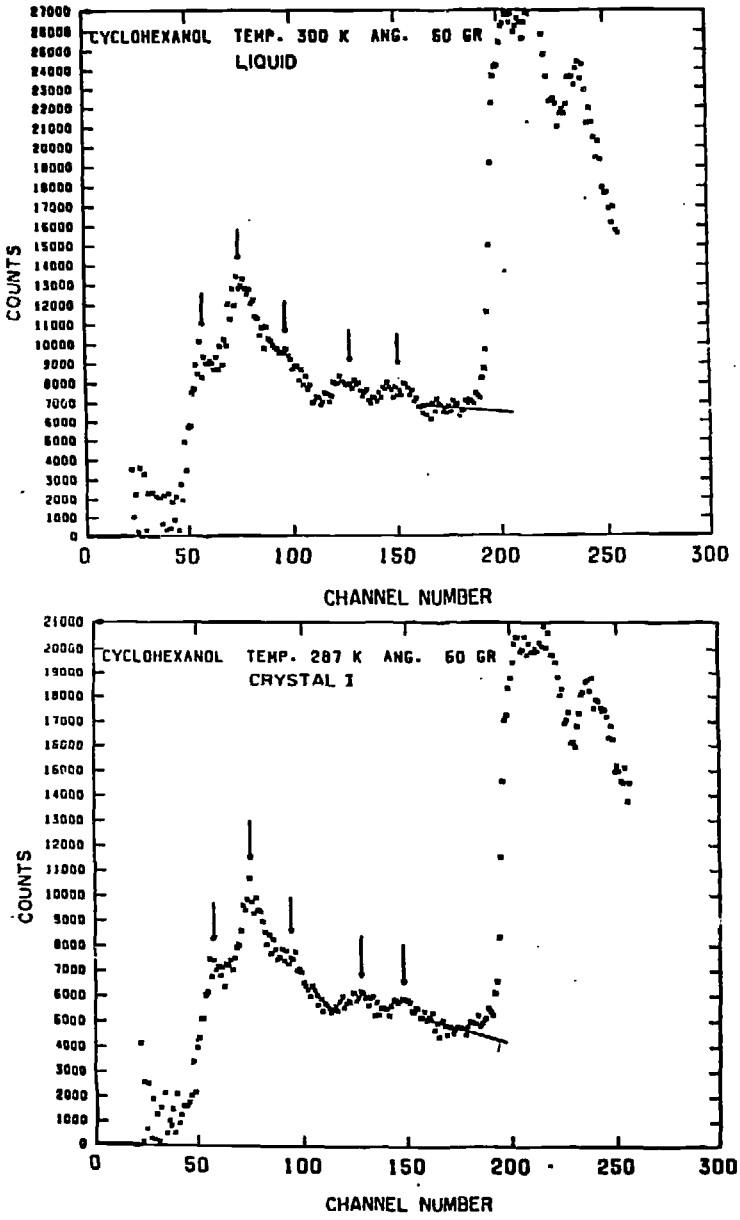
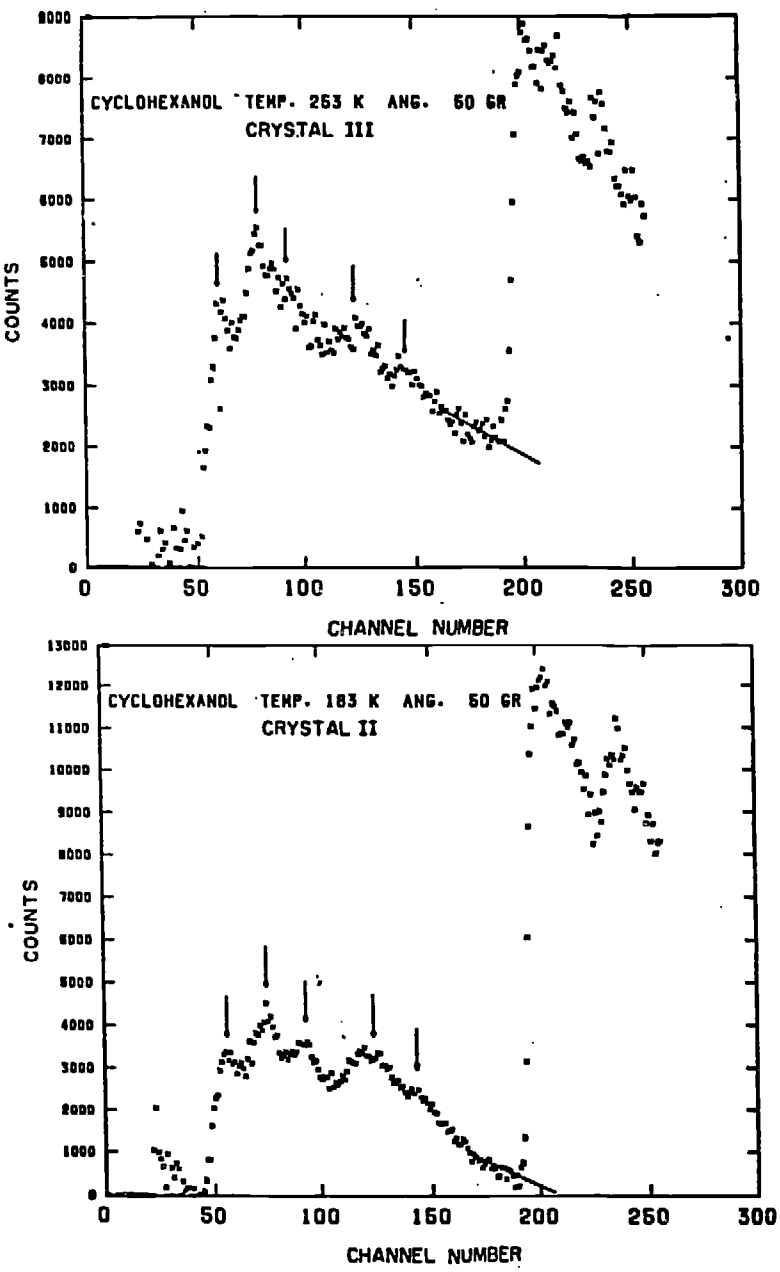
* IPEN Technical Report Series is the continuation of the IEA Technical Report Series.




– Corrected Time-of-Flight Spectra of Neutrons Scattered at an Angle of 50° by Cyclohexanol in its Liquid and Solid (Crystal I) Phases.

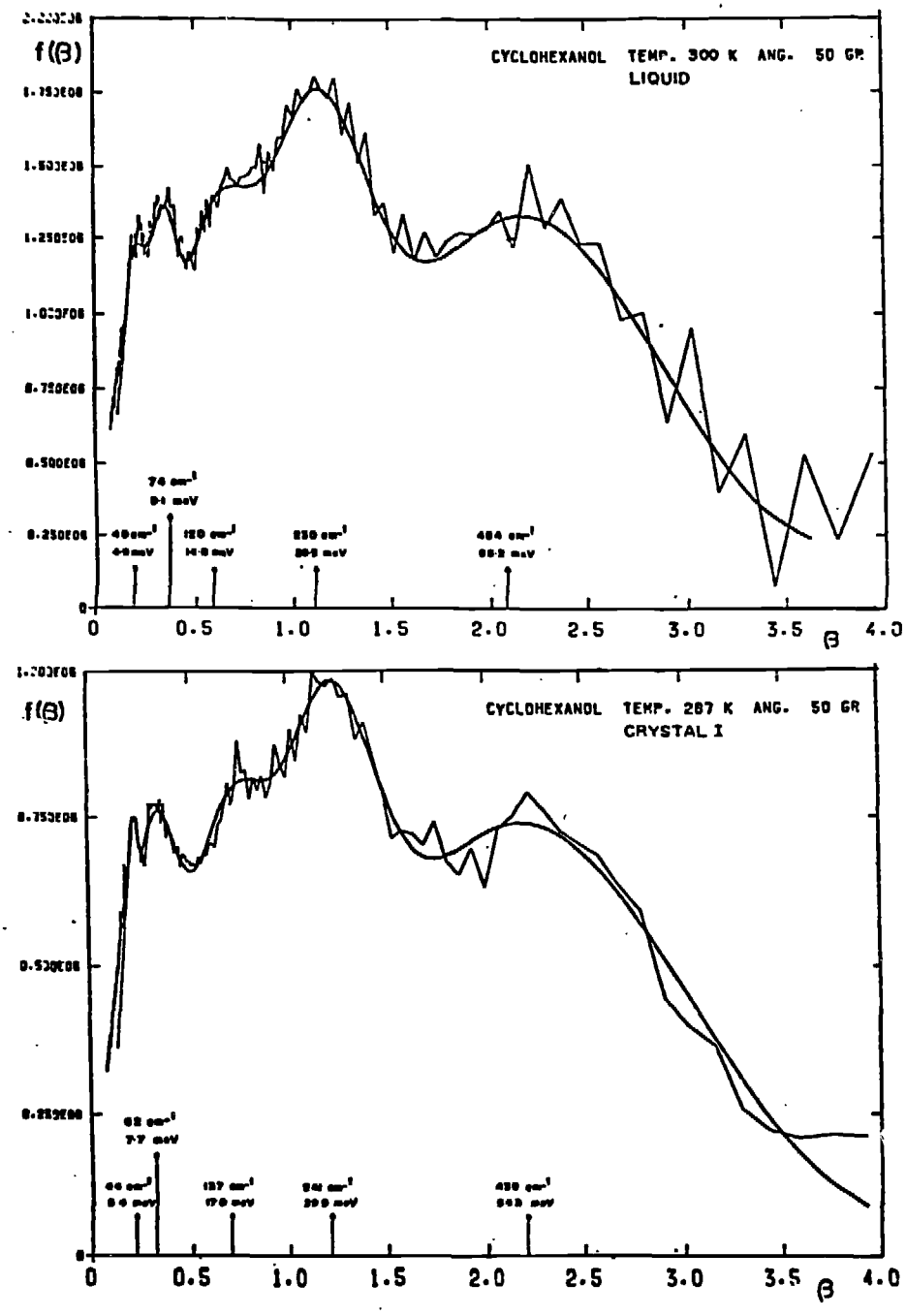
FIGURE 6




– Corrected Time-of-Flight Spectra of Neutrons Scattered at an Angle of 50° by Cyclohexanol in its Crystall III and Crystal II Phases.

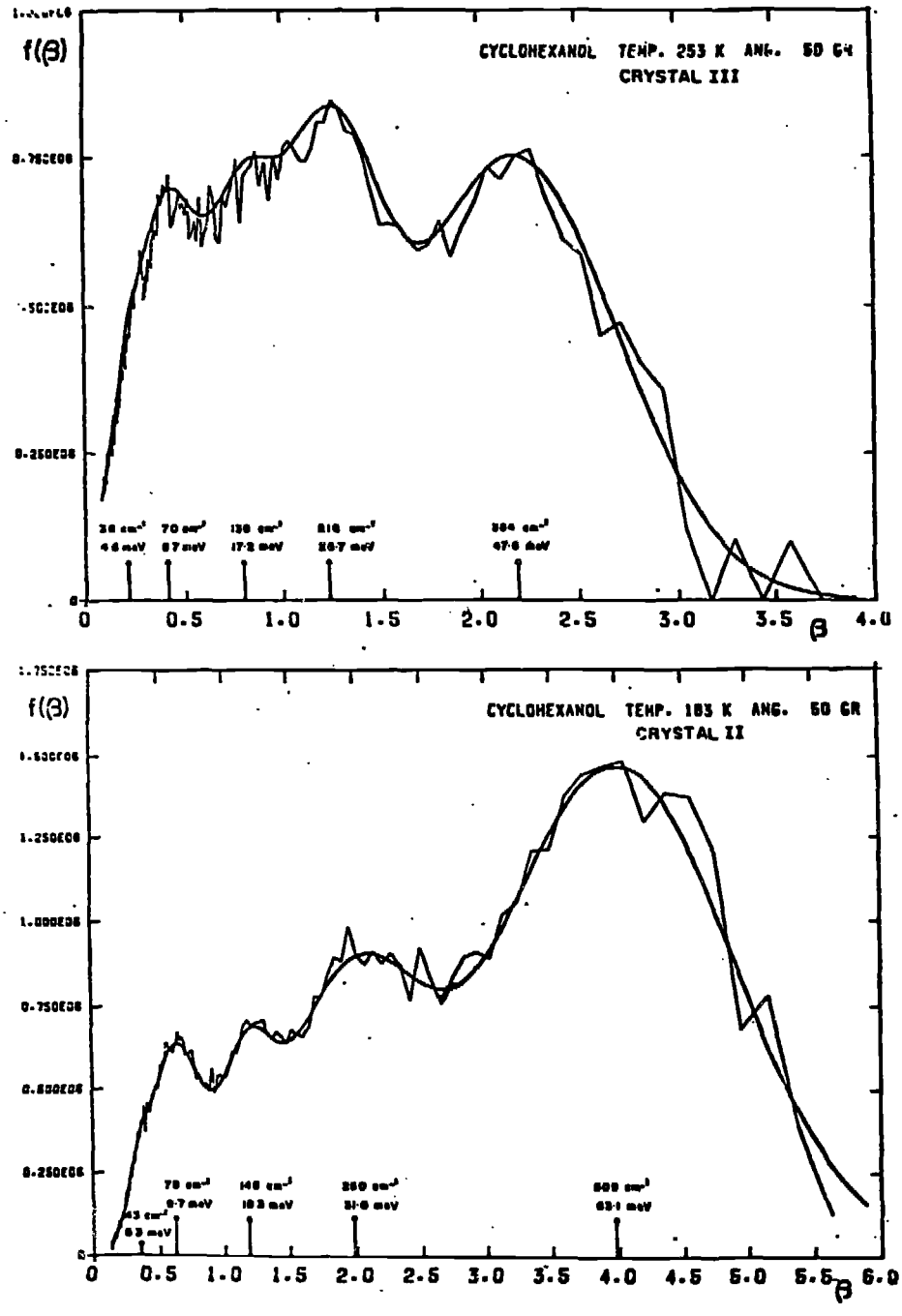
FIGURE 7

* New designation of Instituto de Energia Atômica(IEA).




- Generalized Frequency Spectra as a Function of $\beta = \hbar w/KT$. Smooth curve denotes the Best Fitted Spectrum, Calculated as Sum of Five Gaussian Functions. The arrows Mark the Positions of Peaks.

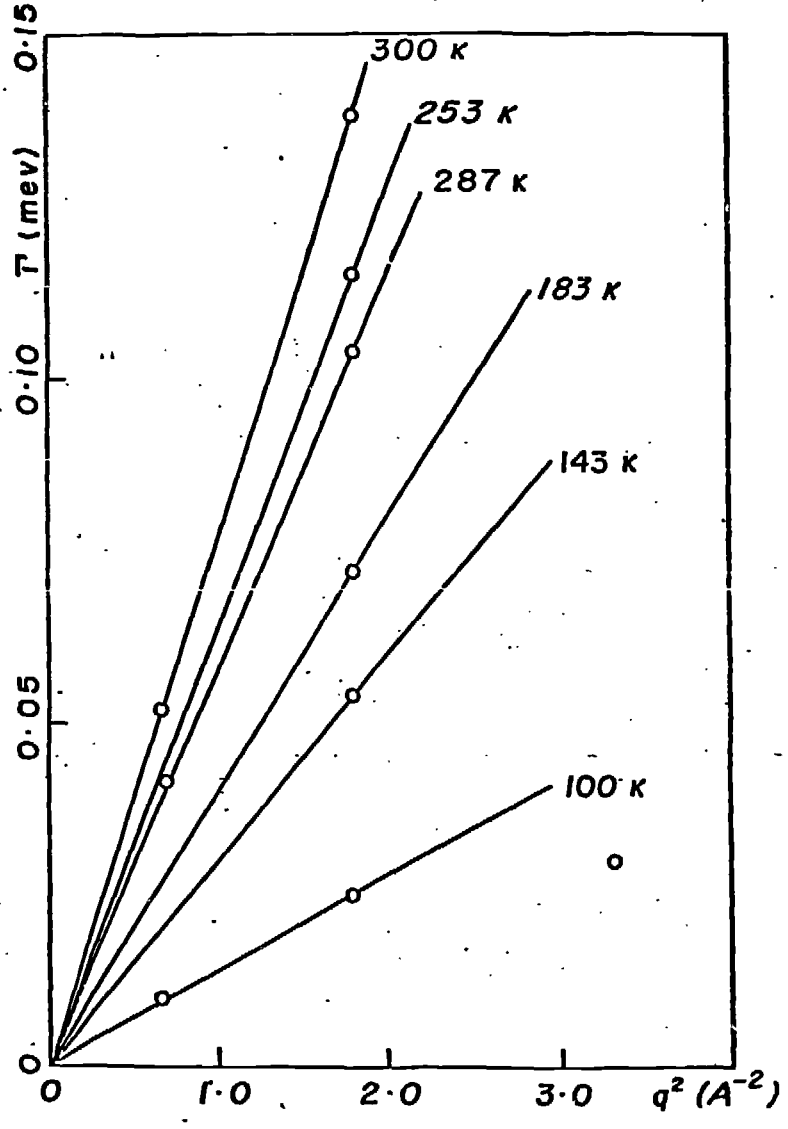
FIGURE 8




— Generalized Frequency Spectra as a Function of $\beta = \hbar w/KT$. Smooth curve denotes the Best Fitted Spectrum, Calculated as Sum of Five Gaussian Function. The arrows Mark the Positions of Peaks.

FIGURE 9

This comparison indicates that the IEA Triple-Axis Spectrometer is in good




– Comportamento do Alargamento do Pico quase Elástico com o Quadrado da Transferência da Quantidade de Movimento, para Várias Temperaturas.

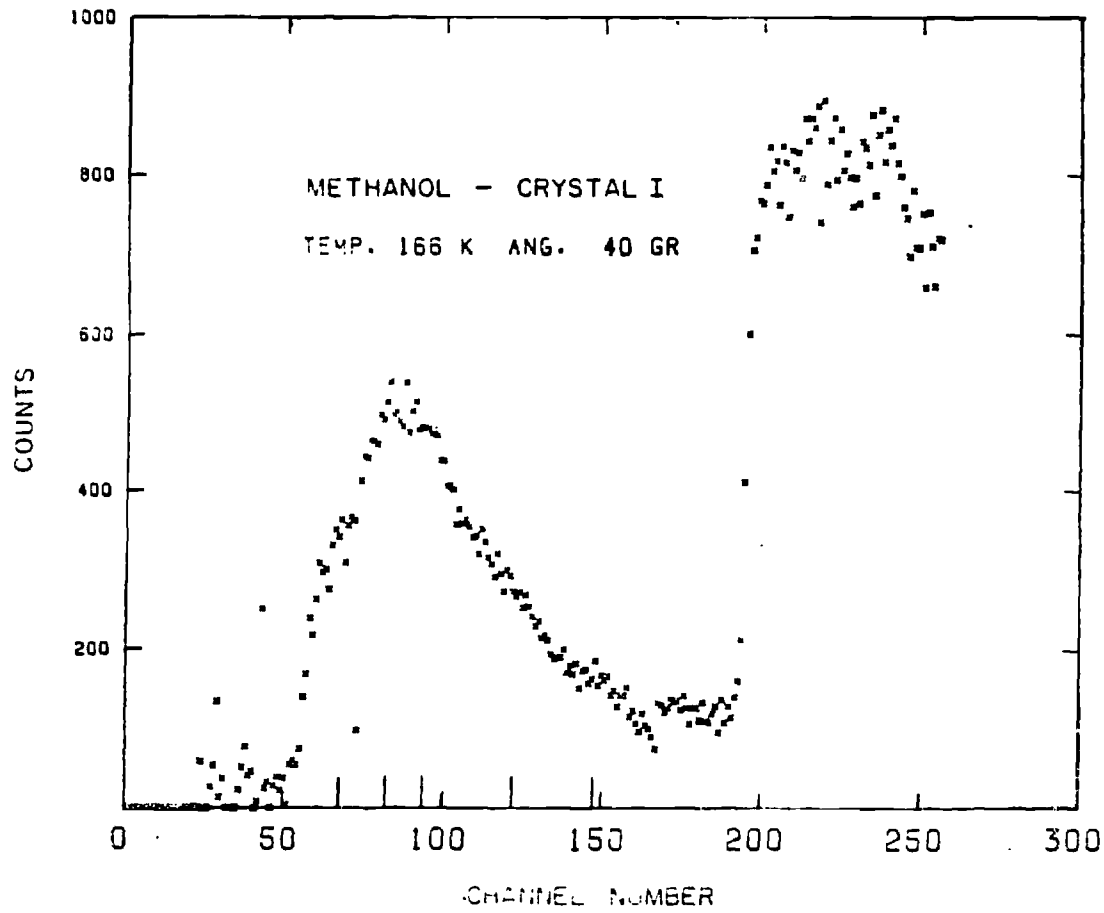
FIGURE 10

FREQUÊNCIA ν(THz) FIGURE 2



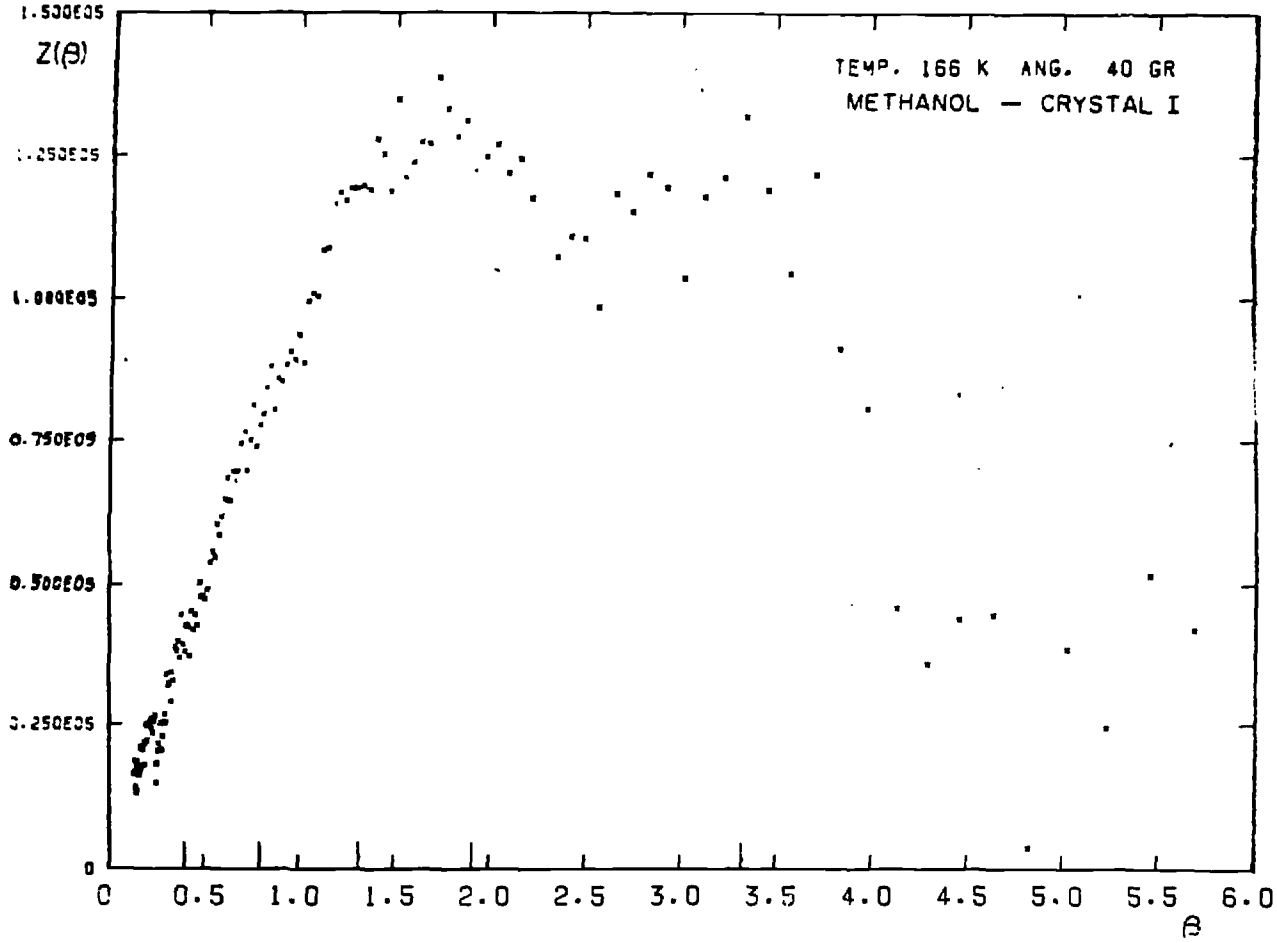
The molecular dynamics of methanol, in the liquid state and two crystalline phases was investigated by cold neutron incoherent inelastic scattering. Neutron scattered spectra were collected at the scattering angle $40^{o}$ for the sample at several temperatures: 298K(liquid), 166K(crystal I) and 140K(crystal II). Neutron inelastic scattering spectra(figure 11) and frequency spectra(figure 12) allowed the assignment 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 suggested crystal I phase as an intermediate phase between liquid and crystal II, concerning the structural and dynamical properties of molecules and their correlation. This work shows that the most important dynamical change occurs at the change of state and not at phase transition. The low entropy of melting must be due to ordering in the liquid, maintained by hydrogen bonds. The non-plastic feature of crystal-I is supported. The paper "Atomic motions in solid and liquid methanol by neutron inelastic scattering" was published in the IPEN Technical Report Series, with the number 002(1979) (Annex V).

Translational and rotational diffusion in methanol in the liquid state, were studied by quasi-elastic neutron scattering. The measurements were performed using the Triple-axis Spectrometer. The broadening and the integrated intensity of elastic line were determined for several scattering angles or momentum transfer(Q). The study of the broadening of elastic line were performed admitting that the cross section is a Lorentzian function of energy. The Lorentzian half-width $\Delta E$ was determined fitting the measured spectra with a double convolution of a Lorentzian function with the incident spectrum and spectrometer resolution. A typical experimental result and fitting are shown in figure 13. Figure 14 shows the results obtained for $\Delta E$ as a function of $Q^2$. These results were analysed in terms of globular models. The best fit is shown in



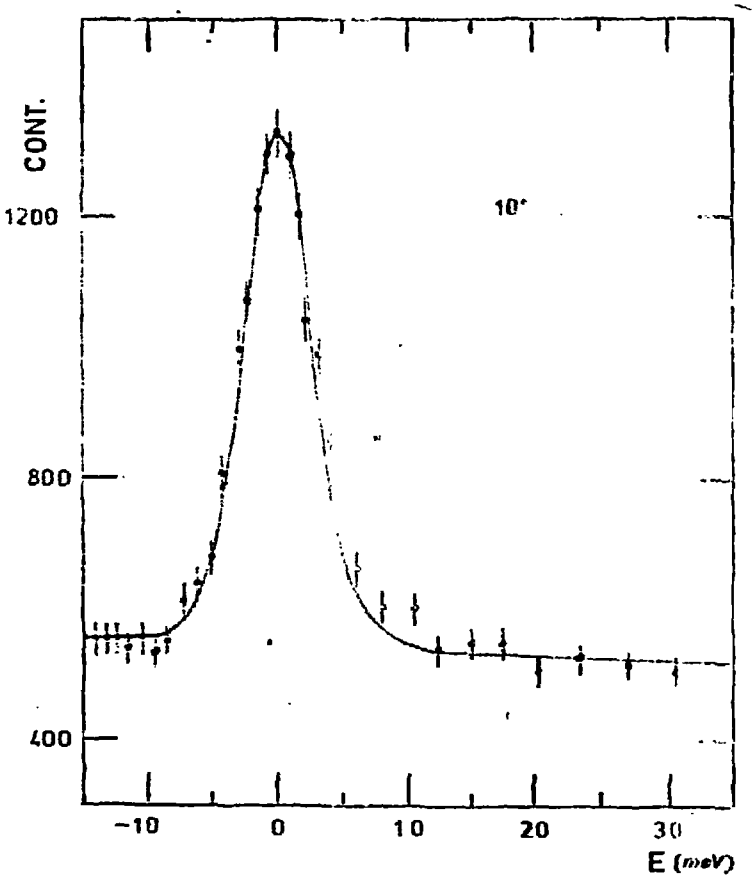

– Corrected Time-of-Flight Spectrum of Neutrons Scattered at an Angle of 40° by Methanol in its Crystal I Ph

FIGURE 11



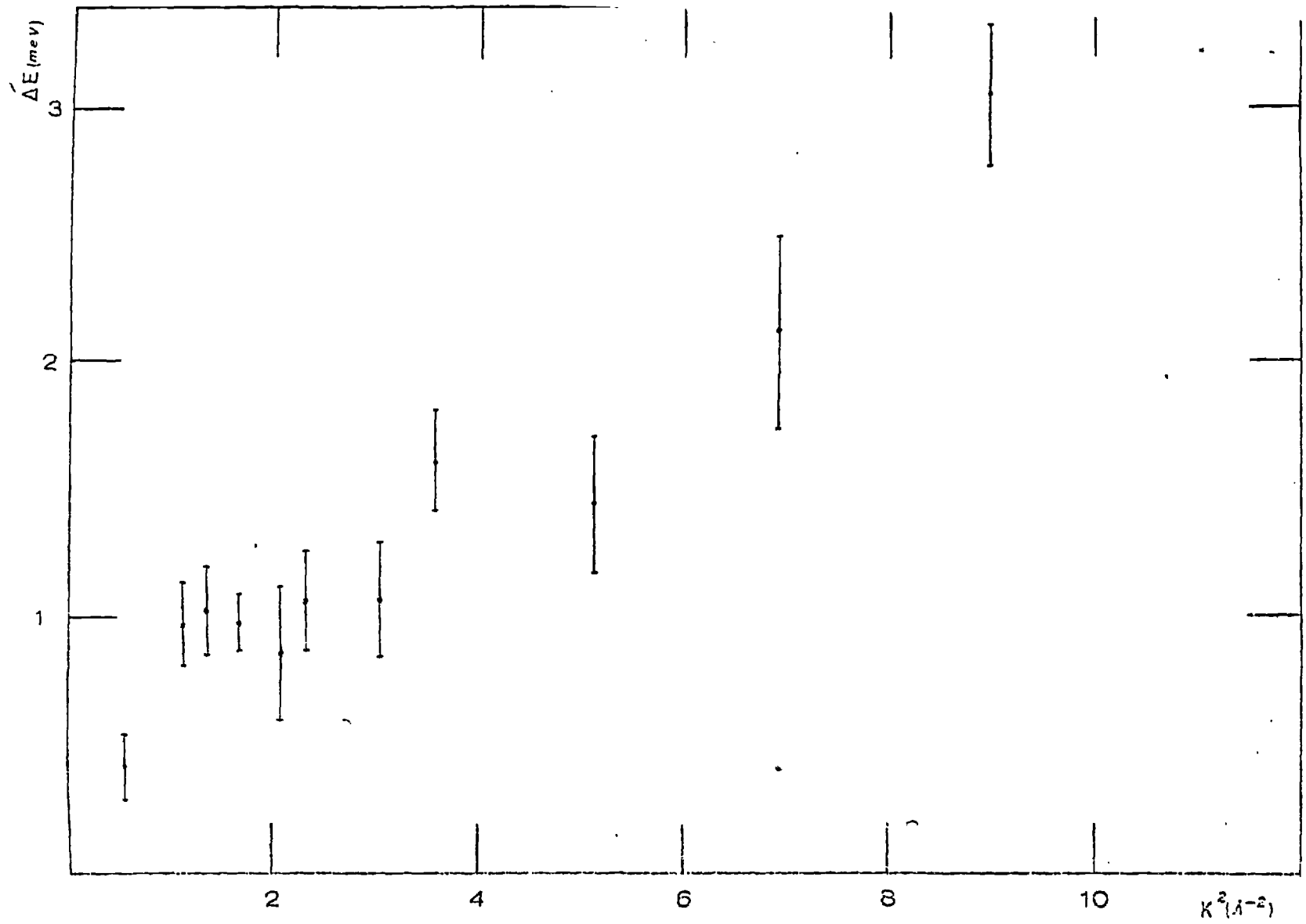

— Generalized Frequency Spectrum $Z(\omega)$ in Function of $\beta = \hbar\omega/KT$ of Methanol in its Crystal I Phase

FIGURE 12




ESPECTRO QUASE-ELÁSTICO

FIGURE 13




- ALARGAMENTO DA LINHA QUASE-ELÁSTICA
FIGURE 14

FREQUÊNCIA L

FIGURE 4

FREQUÊNCIA V

figure 15. This analysis indicates the existence of globules with the distance of proton position to the center of gravity of the globule 3.9Å. It indicates that polymers with small number of molecules are the principal components of the globules. Also it indicates that the globules execute rotational and translational diffusive motions. These results are included in the Master Thesis of A.M.Figueiredo Neto. This thesis was submitted in partial fulfillment of the requirements for the degree of Master of Science to Instituto de Energia Atômica, associated to University of São Paulo (February 1978). The supervisor was Dr. L.A.Vinhas.

Neutron inelastic scattering measurements were performed on natural and dehydrated DNA samples, using a cold neutron time-of-flight spectrometer, in order to study the dynamics of water present in this biological molecule. The water frequency spectrum (figure 16) obtained from a subtraction between natural and dehydrated DNA spectra, was compared with those for liquid water and ice. The results indicate that water molecule motions in the helicoidal DNA structure are quite similar to those in liquid water.

More details about this experiment can be seen in the paper "Dynamics of water in Deoxyribonucleic acid studied by neutron inelastic scattering" submitted for publication in the IPEN Technical Report Series and a copy is the annex VI of this report.

On the other hand, following the scientific visit of L.A.Vinhas to Chalk River Nuclear Laboratories, Ontario, Canada, supported by International Atomic Energy Agency, in September 1976, a paper describing details about the research performed, during the scientific visit, on the lattice dynamics of 1 methylthymine and cytosine monohydrate was presented in the International Conference on Lattice Dynamics held in Paris, September 5-9, 1977. A copy of the paper published in the Proceedings of the Conference, edited by M.Balkanski on page 494, is the Annex VII.

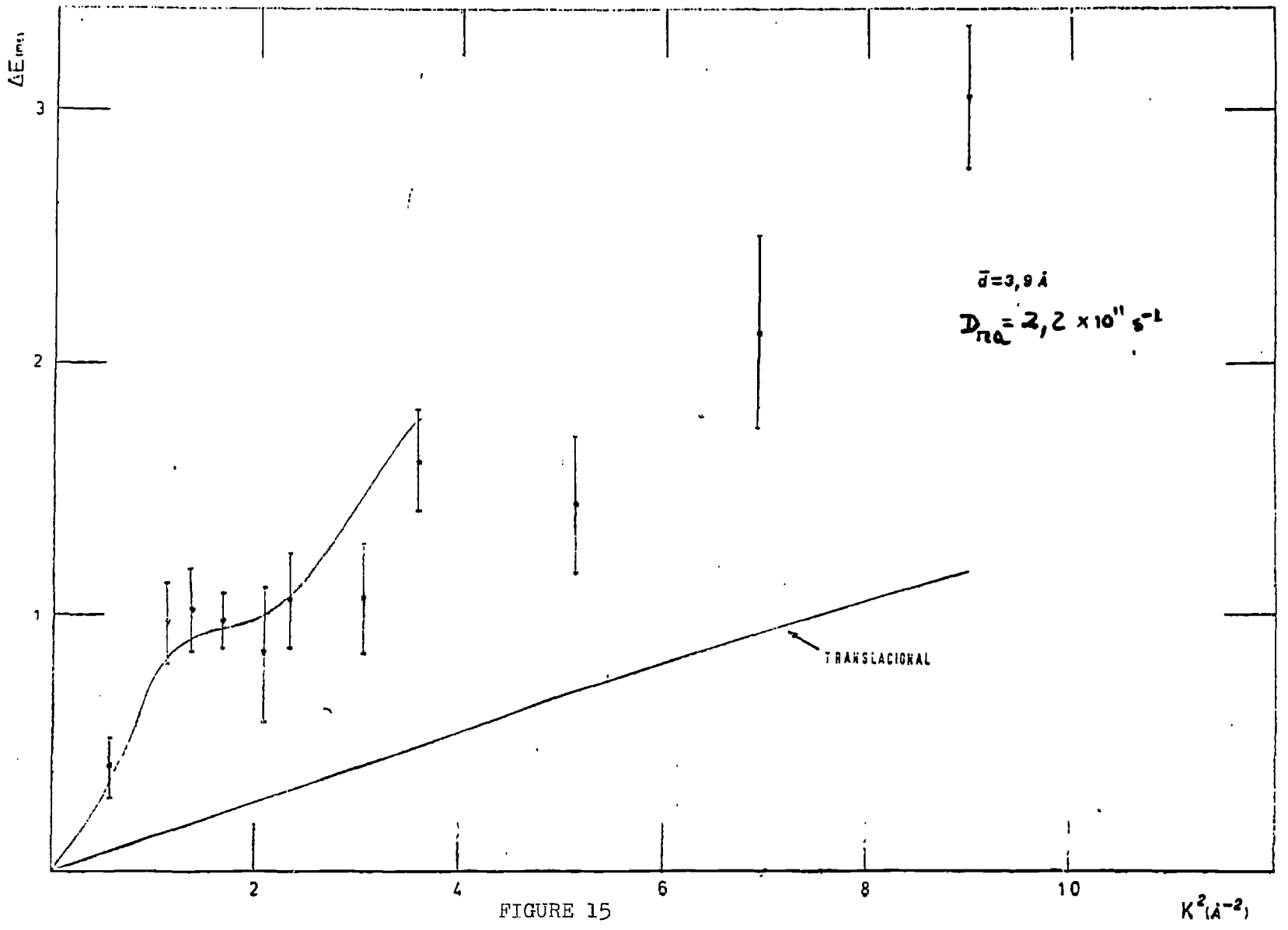
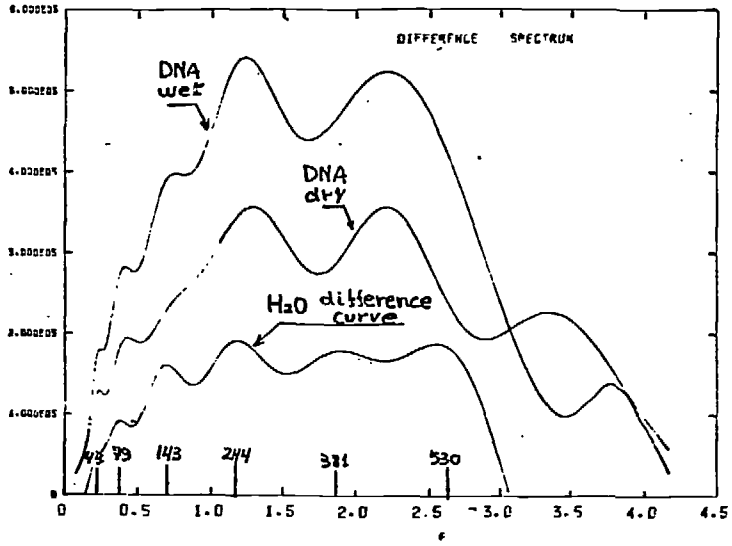



FIGURE 15




- Frequency spectra of "wet" and "dry" DNA. The difference spectrum is due to water in DNA. The assigned frequencies are indicated by the vertical lines in the lower part of the figure.

FIGURE 16

## III) Metal/Hydrogen Systems Studied by Neutron Inelastic Scattering

In a number of metals, hydrogen can be dissolved with very high concentration, where the hydrogen atoms occupy sites of an interstitial lattice. In certain regions of the phase diagrams of these systems, these hydrogen are extremely mobile, and jump rates as high as $10^{12}$ per second have been observed.

The quasi-elastic neutron scattering measurements are useful to study details of hydrogen diffusion in metals on an atomic scale. In principle neutron scattering results contain complete information about the motion of diffusing hydrogen. In practice, however, the data are always analysed in terms of phenomenological models. This means that the amount of information actually obtained depends on the existence of an adequate model for diffusion. So far the half-width of quasi-elastic line for several metal/hydrogen systems has been determined dependent on momentum transfer in the scattering process and compared with theoretical predictions based on a simple jump diffusion theory. Only for the system PdHx in its alpha phase a quantitative agreement of the experimental results with this theory could be observed. In all other cases either no fit was possible or further assumptions must be considered. It is necessary to perform more measurements in order to increase the knowledge about the problem.

The first procedures to start a research program on metal/hydrogen systems using neutron inelastic scattering are:

a) to design and to assemble a system for sample preparation;

b) to do a compilation of the specific bibliography;

c) to choose the samples.

The system to dope metal samples with hydrogen has been designed and assembled. The inconel retort was connected to a common vacuum system. A precision manometer was installed to monitor the quantity of hydrogen absorbed by the metal, measuring the pressure of the remaining hydrogen gas. It is necessary to use a manometer of mechanical pressure gauge type to avoid sparks in the hydrogen atmosphere. The furnance was assembled

over wheels in order to be rolled away for faster cooldown of the retort. In such way, it is possible to dope metal samples in a better controlled manner.

The performance of the system as a whole has been verified by the preparation of polycrystalline metal samples. The samples consisted of niobium plates (2x5x0.2cm) which were degassed at a temperature of 1000°C. Afterwards, they were loaded at 550°C from a gas atmosphere of hydrogen. The hydrogen contents were determined by the weight increase. After studies of several conditions of temperature and gas pressure, the precision to obtain a preselect value for hydrogen concentration has been reached 10%.

On other hand, we have done a almost complete compilation of the bibliography on the following areas:

a) dynamics of hydrogen in metals studied by neutron scattering;

b) theory of hydrogen diffusion in metals;

c) techniques for sample preparation.

About 300 paper were listed. A study program about the most relevant papers in this literature was carried out. This allowed us to choose the kind of problems of interest.

Single crystals of niobium, molibdenium, tantalum, palladium, titanium and zinc have been purchased. These crystals were oriented using the triple axis spectrometer as neutron diffractometer. The single crystals having cylindrical form and the direction < 110> parallel to cylinder axes within 3° were choosen to be used as samples. These conditions are necessary in order to obtain the principal symmetry directions of crystals by a simple rotation, without change the geometry.

Due to several problems only now we are in condition to begin the experimental part of this research.

The present research contract, contributes significantly to the development of our neutron scattering group allowing an enlargement of our research field and an improvement on the level of research.

Concerning the triple-axis Spectrometer and lattice dynamics studies, providing some essential equipment, as large monochromator crystals and electronic modules and components, it made possible the end of the construction and the assembly of the triple-axis Spectrometer. Supporting a scientific visit of L.A.Vinhas at Chalk River Nuclear Laboratories, it allowed for this researcher to acquire solid and theoretical background in the study of lattice dynamics using triple-axis Spectrometer.

Concerning the metal/hydrogen systems, it provided the system for sample preparation which is essential to begin a research program in this area.

On the other hand, several experiments performed under the present contract were used by three members of the group to elaborate their Master Thesis. This represents a large contribution in the formation of especialized researchers.

As a result of the research contract, the neutron scattering Group of IPEN is now in condition to perform experiments on hydrogen in metals and lattice dynamics in an international level.

## PAPERS PUBLISHED ON WORK DONE UNDER THE CONTRACT

### Publications

1) "Design, construction and characteristic of IEA Triple-Axis Spectrometer" R.Fulfaro, L.A. Vinhas, C.Fuhrmann, R.Liguori and C. Parente, IEA Technical Report N) 477 (1977).

2) "Performance of IEA Triple-Axis Crystal Spectrometer: measurements of dispersion relation of copper" C. Fuhrmann, R.Fulfaro and L. A.Vinhas, IEA Technical Report Nº 504 (1978).

3) "Molecular dynamics of tert-butanol studied by neutron inelastic scattering" L.Q.Amaral and L.A.Vinhas, Journal of Chemical Physics 68, 5636-42 (1978).

4) "Atomic motions in liquid and solid cyclohexanol studied by incoherent inelastic neutron scattering" V.S. Walder and L.A.Vinhas, IPEN Technical Report Nº 001 (1979).

5) "Atomic motions in solid and liquid methanol by neutron inelastic scattering" A.M.Figueiredo Neto and L.A.Vinhas, IPEN Technical Report N) 002 (1979).

6) "Dynamics of water in Deoxyribonucleic acid studied by neutron inelastic scattering" V.S. Walder, L.A.Vinhas and R.Fulfaro, submitted for a publication in IPEN Technical Report Series.

7) "The lattice dynamics of crystalline DNA pyrimines" P.Martel, B. M. Powell and L.A. Vinhas.

### Master Thesis

1) "Aspects of molecular dynamics of cyclohexanol studied by neutron inelastic scattering" V.S.Walder, thesis to obtain the degree of Master of Science, submitted to Institute of Physics, University of São Paulo (September 1977).

2) "Molecular dynamics of methanol studied by neutron inelastic scattering" A.M.Figueiredo Neto, yhesis to obtain the degree of Master of Science, submitted to Instituto de Energia Atômica, University of São Paulo (February 1978).

3) "Design and construction of a Triple-axis Crystal Spectrometer. Evaluation of its performance by measuring copper dispersion relations" C. Fuhrmann, thesis to obtain the degree of Master of Science, submitted to Instituto de Energia Atômica, University of São Paulo (June 1978).

Papers presented at Conferences

- "V Iberomarican Meeting on Crystallography" (V Congresso Iberoamericano de Cristalografia), held in Madrid, Spain, December 10-17/1976.
  - "Movements of hydrogen in transition metals studied by means of slow neutron scattering" L.A.Vinhas, R.Liguori Neto and R. Fulfaro.
- "VI Iberoamerican Meeting on Crystallography" (VI Congresso Iberoamericano de Cristalografia), held in Santiago, Chile, January 8-13/1979.
  - "Performance of IEA-Triple-Axis Spectrometer: measurements of dispersion relation of copper" C. Fuhrmann, E. Fulfaro and L.A. Vinhas.
  - "Phase transitions on methanol studied by slow neutron inelastic scattering" A.M.Figueiredo Neto, L.A. Vinhas and V.S.Walder.
  - "Study of translational and rotational diffusion in methanol by neutron scattering" A.M.Figueiredo Neto and L.A.Vinhas.
  - "Dynamics of water in DNA, ex-Thymus" V.S.Walder, L.A. Vinhas and R. Fulfaro.

TITLE: NEUTRON INELASTIC SCATTERING: DYNAMICS OF SOLIDS AND LIQUIDS AND OF HYDROGEN IMPURITIES IN TRANSITION METAL

RESEARCH INSTITUTE: INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES (ex-INSTITUTO DE ENERGIA ATÔMICA), SÃO PAULO, SP-BRASIL

CHIEF SCIENTIFIC INVESTIGATOR: LAERCIO ANTONIO VINHAS

PERIOD OF CONTRACT: MAY-1976 - DECEMBER-1979

SCIENTIFIC BACKGROUND AND SCOPE OF PROJECT:

The main objective of the project is to study the dynamics properties of the condensed states of matter employing slow neutron inelastic scattering techniques. The following is a brief description of the research scopes:

a) IPEN Triple-axis Neutron Spectrometer: construction, automation and performance on lattice dynamics studied;

b) study of the dynamics of hydrogenous compounds, in particular globular compounds. There is a large interest in the study of these compounds because of their peculiar physical properties, as small entropy of melting and a phase transition in solid state with large entropy change;

c) study of metal/hydrogen system, in particular the diffusion of hydrogen in transition metals. In principle, neutron inelastic scattering results contain complete information about the motions of diffusing hydrogen on an atomic scale. In practice, however, the data are always analysed in terms of phenomenological models. Thus, it is necessary measurements on several systems in order to increase the knowledge about the problem.

Experimental Method

The Triple-axis Neutron Spectrometer was used to perform neutron coherent inelastic scattering on crystals in order to determine dispersion relations and to study lattice dynamics. The molecular dynamics of hydrogenous compounds have been investigated by cold neutron incoherent inelastic scattering. The measurements have been performed using the "Beryllium Filter Time-of-Flight Spectrometer". The Triple-axis Spectrometer have also been used to perform quasi-elastic scattering in order to study auto-diffusion on hydrogenous compounds and diffusion of hydrogen in metals.

Results Obtained and Conclusions

a) The construction and assembly of a Triple-axis Spectrometer have been concluded. In the construction, components for industrial applications were adapted in order to minimize the construction cost and to become the assembly easier. Dispersion relation for copper along the three major symmetry direction was performed to check the performance of the spectrometer on phonon studies. The excellent agreement observed between the results obtained in the present experiment and the data for copper presented in the literature indicates that the IPEN Triple-axis Spectrometer is in good operational conditions.

b) Molecular dynamics of tert-butanol, cyclohexanol and methanol, in at least two phases in the solid state and in the liquid state was investigated. Neutron inelastic spectra and frequency spectra fitted to a sum of Gaussian functions allowed the assignment of several peaks for each compound in each phase. These peaks are interpreted as characteristic atomic or molecular motions. Translational and rotational diffusion in these compounds have been studied by quasi-elastic scattering and the results analyzed in terms of models for molecular diffusion. The general conclusion is: while cooperative rotational diffusion exists even in crystal phases, the solidlike behavior is evidenced by the inelastic spectra of the liquid state. The low entropy of melting must be due to ordening in the liquid, maintained by H bonds.

c) A research program on metal/hydrogen systems using neutron inelastic scattering was started. A system to dope metal samples with hydrogen in a controlled manner has been designed, constructed and assembled. The performance of the system as a whole has been verified by preparation of polycrystalline metal samples. At the moment we are in conditions to begin the experimental part of this research.

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