THERMAL DIFFUSE SCATTERING OF X-RAYS

G. M. BORGONOVI, R. FULFARO, K. IMAKUMA,
C. RODRIGUES and L. A. VINHAS

PUBLICAÇÃO IEA N.º 260
Fevereiro — 1972

INSTITUTO DE ENERGIA ATÔMICA
Caixa Postal 11049 (Pinheiros)
CIDADE UNIVERSITÁRIA "ARMANDO DE SALLES OLIVEIRA"
SÃO PAULO — BRASIL

THERMAL DIFFUSE SCATTERING OF X-RAYS (*)

G.M. Borgonovi, R. Fulfaro, K. Imakuma,
C. Rodrigues and L.A. Vinhas

Divisão de Física Nuclear
Instituto de Energia Atômica
São Paulo - Brasil

Publicação IEA Nº 260
Fevereiro - 1972

(*) Report written by G.M. Borgonovi on leave from Gulf Radiation Technology, San Diego, California.

Table of contents

THERMAL DIFFUSE SCATTERING OF X-RAYS

G. M. Borgonovi, R. Fulfaro, K. Imakuma,
C. Rodrigues and L. A. Vinhas

ABSTRACT

This report describes the activities in the field of thermal diffuse scattering of X-rays performed during the period from Feb 1971 to Jan 1972

The activities were both experimental and computational The experiment apparatus was modified in order to measure the diffuse scattering in a copper crystal. Therefore X-ray monochromatization and monitoration systems were constructed In the computational field several codes were prepared and tested, the main code is a program for the exact calculation of the second order diffuse scattering

1. Introduction and summary.

The purpose of this report is to summarize the activities performed during the year starting February 1971 in the field of Thermal Diffuse Scattering of X-rays from crystals.

Thermal Diffuse Scattering (TDS) of X-rays is the study of the weak intensity scattered outside the Bragg positions. This intensity is determined by the fact that the atoms in a real crystal oscillate about their equilibrium positions.

Since the TDS depends on the movement of the atoms, it follows as a consequence that the study of TDS can reveal important details about this movement and finally about the force field which are determining the characteristic modes of vibration of the atoms in a crystal[1][2].

The experimental study of TDS of X-rays is one of the available tools for the investigation of lattice dynamics. In recent years this technique has been somehow overshadowed by the more recent technique of inelastic scattering of neutrons[3], mainly used in conjunction with triple axis crystal spectrometers

While recognizing the general superiority of the neutron method for lattice dynamics studies, it should be stressed that for a number of crystals, due to the high absorption cross section, the neutron method cannot be applied.

It seems therefore important, for the determination of the dynamical properties of crystals like indium or cadmium, which are strong neutron absorbers, to be able to rely on the X-ray method. Bacause of this reason (and also bacause of the absence at the Instituto de Energia Atômica of a triple axis crystal spectrometer facility) a program of study of the TDS of X-rays was begun. The research involved experimental as well as theoretical and calculational studies. Some of the developments made under this program may be useful for parallel lines of research and it seems therefore useful to summarize the results.

The approach taken has been that of concentrating on a standard crystal for which good results are already available both with X-rays and neutrons. The crystal chosen was copper, for which good theoretical descriptions of the interatomic force fields are available[4].

The aim of the program in the past year has been to obtain reliable results from the Cu sample. Reasonable agreement of the present data with the theoretical values have been obtained, however a number of improvements in the data taking apparatus could still be made.

Preliminary measurements were performed using a pair of balanced filters to monochromatize the radiation. This situation was clearly unsatisfactory, therefore a crystal monochromating system was constructed and also monitorization of the incident beam was introduced. Additional improvements would be the adoption of a proportional counter instead of a scintillator, the evacuation of the area around the sample and the use of a curved crystal monochromator.

Section 2 describes the derivation of the zero, one and two phonon X-ray scattering in a short and compact form.

Section 3 describes the development of experimental techniques. Besides the description of the experimental details, fall into this section the preparation of computer codes for orientation of single crystals, data collection, data analysis, the description of the monochromator and of the monitoring system.

Section 4 describes the calculational methods used to compute the formulas derived in Section 2. Particular emphasis was given to the exact calculation of the two phonon term and to the comparison with approximate treatments. A large amount of computing work is necessary to calculate exactly the two phonon term. For this reason it was found convenient to store partial results from the theoretical models on magnetic tapes and also to store on a magnetic tape a number of subroutines used in the calculation.

Three appendices have been inserted for the convenience of eventual future users of the codes developed.

Appendix I contains the input instructions for some of the codes developed under the program. Appendix II contains a summary of instructions to handle magnetic tapes at the IBM 360 computer of the Institute of Physics at the University of Sao Paulo, including instructions for use of already compiled subroutines stored on a magnetic tape.

Appendix III contains a brief description (with the calling statement and arguments) of a number of routines which are presently stored on magnetic tape.

2. Theoretical background.

In this section we summarize the essential steps in the derivation of the X-ray intensity scattered by a crystal when we allow for thermal motion of the atoms The scattered intensity will be expressed in electron units. An electron unit is the quantity e^4/m^2c^4 (e = electron charge, m = electron mass, c = speed of light) and is equal to 7.935 barn. An intensity in electron units is essentially a microscopic cross section.

Given a crystal with N atoms of the same type fixed at positions $\underline{r}_n$, the total intensity in electron units, apart from a polarization factor, is given by:

$$I_{eu} = f^2 \sum_{m=1,N} \sum_{n=1,N} e^{2\pi i \underline{Q} \cdot (\underline{r}_m - \underline{r}_n)} \qquad (1)$$

where f is the atomic scattering factor and $\underline{Q}$ is the momentum transfer ($|\underline{Q}| = 2\frac{\sin\theta}{\lambda}$, θ being one half of the scattering angle and λ the X-ray wavelength).

If the atoms in the crystal are subject to thermal motion, they will be displaced from their equilibrium positions by amounts $\underline{u}_n$ which depend on time. Equation (1) then becomes:

$$I_{eu} = f^2 \sum_{\substack{m=1,N \\ n=1,N}} e^{2\pi i \underline{Q} \cdot (\underline{r}_m - \underline{r}_n)} \; e^{2\pi i \underline{Q} \cdot (\underline{u}_m - \underline{u}_n)} \qquad (2)$$

The intensity is now a time dependent function. We are interested in the average value of this intensity, or:

$$\langle I_{eu} \rangle = f^2 \sum_{\substack{m=1,N \\ n=1,N}} e^{2\pi i \underline{Q} \cdot (\underline{r}_m - \underline{r}_n)} \left\langle e^{2\pi i \underline{Q} \cdot (\underline{u}_m - \underline{u}_n)} \right\rangle \qquad (3)$$

where the brackets $\langle \cdots \rangle$ indicate a time average.

Within the limits of the harmonic approximation the displacement of an atom from its equilibrium position can be expressed as a superposition of normal modes of vibration in the following way:

$$\underline{u}_m = \sum_{qj} \underline{C}_{qj} \; e^{2\pi i \underline{q} \cdot \underline{r}_m} \; e^{i\omega_{qj} t} \qquad (4)$$

In Eq. (4) $\underline{C}_{qj}$ and ω_{qj} are the polarization vector and the circular frequency of a crystal wave of wave vector $\underline{q}$ and branch j. The sum is to be made over one Brillouin zone.

In performing the average in Eq. (3) the quantum mechanical result known as Bloch's theorem can be used. The theorem states that

$$\left\langle e^{A} \right\rangle = e^{\langle A^2 \rangle / 2} \qquad (5)$$

where the operator A is any linear combination of harmonic oscillator coordinates. Using Bloch's theorem, equation (4) and performing an average over an ensemble of harmonic oscillators in equilibrium at temperature T one obtains

$$\left\langle e^{2\pi i \underline{Q}\cdot(\underline{u}_m - \underline{u}_n)} \right\rangle = e^{-2\pi^2 \langle (\underline{Q}\cdot(\underline{u}_m - \underline{u}_n))^2 \rangle} = e^{-\sum_{\underline{q}j} G_{\underline{q}j}\{1-\cos 2\pi \underline{Q}\cdot(\underline{r}_m - \underline{r}_n)\}} \quad (6)$$

where

$$G_{\underline{q}j} = \frac{h}{2mN} \frac{(\underline{Q}\cdot\underline{e}_{\underline{q}j})^2}{\nu_{\underline{q}j}} \coth \frac{h\nu_{\underline{q}j}}{2KT} \quad (7)$$

In (7) m is the mass of the atoms in the crystal, $\nu_{\underline{q}j}$ is the frequency of the wave $\underline{q}j$, h the Planck's constant and K the Boltzmann's constant. The sum in (6) is again over one Brillouin zone.

The sum

$$\sum_{\underline{q}j} G_{\underline{q}j} = 2M \quad (8)$$

is known as Debye Waller factor.

We can now replace (6) into (3) obtaining:

$$\left\langle I_{eu} \right\rangle = f^2 \sum_{\substack{m=1,N \\ n=1,N}} e^{2\pi i \underline{Q}\cdot(\underline{r}_m - \underline{r}_n)} e^{-\sum_{\underline{q}j} G_{\underline{q}j}\{1-\cos 2\pi \underline{q}\cdot(\underline{r}_m - \underline{r}_n)\}} =$$

$$= f^2 e^{-2M} \sum_{\substack{m=1,N \\ n=1,N}} e^{2\pi i \underline{Q}\cdot(\underline{r}_m - \underline{r}_n)} e^{\sum_{\underline{q}j} G_{\underline{q}j} \cos 2\pi \underline{q}\cdot(\underline{r}_m - \underline{r}_n)} \quad (9)$$

The last exponential in (9) is now expanded obtaining:

$$\left\langle I_{eu} \right\rangle = f^2 e^{-2M} \sum_{\substack{m=1,N \\ n=1,N}} e^{2\pi i \underline{Q}\cdot(\underline{r}_m - \underline{r}_n)} \{1 + \sum_{\underline{q}j} G_{\underline{q}j} \cos 2\pi \underline{q}\cdot(\underline{r}_m - \underline{r}_n) +$$

$$+ \frac{1}{2} \sum_{\underline{q}j} \sum_{\underline{q}'j'} G_{\underline{q}j} G_{\underline{q}'j'} \cos 2\pi \underline{q}\cdot(\underline{r}_m - \underline{r}_n) \cos 2\pi \underline{q}'\cdot(\underline{r}_m - \underline{r}_n) + \cdots \} \quad (10)$$

$$= I_0 + I_1 + I_2 + \cdots$$

The above procedure is known as phonon expansion. I_0 is the zero phonon or elastic term

while I_1 and I_2 are the one phonon and two phonon contribution. The dependence on $\underline{r}_m$ and $\underline{r}_n$ can be eliminated by taking advantage of the fact that

$$\sum_{\substack{m=1,N \\ n=1,N}} e^{2\pi i \underline{Q} \cdot (\underline{r}_m - \underline{r}_n)} = N \sum_{m=1,N} \Delta(\underline{Q}) \tag{11}$$

where

$$\Delta(\underline{Q}) = \begin{cases} 0 & \text{if} \quad \underline{Q} \neq \underline{\tau} \\ 1 & \text{if} \quad \underline{Q} = \underline{\tau} \end{cases} \tag{12}$$

Equation (11) is a very good approximation for N very large. In (12) $\underline{\tau}$ is any reciprocal lattice vector.

After using (11) and (12) in (10) and after some manipulations we obtain the following expressions for the one and two phonon intensities **per atom**:

$$\frac{I_1}{N} = f^2 e^{-2M} N \sum_j G_{\underline{Q}j} \tag{13}$$

$$\frac{I_2}{N} = \frac{f^2 e^{-2M}}{2} N \sum_{jj'} \sum_{\underline{q}} G_{\underline{q}j} G_{\underline{Q}+\underline{q}-\underline{\tau},j'} \tag{14}$$

Methods used to calculate exactly (13) and (14) for a cubic crystal will be described in Section 4. Due to the simple expression of the one phonon term, if one can measure the one phonon intensity one can derive important information about the lattice dynamics of a crystal, especially from measurements performed in symmetry directions.

The measured intensity is usually a sum of one phonon, two phonon and modified or Compton intensities, higher order TDS being generally disregarded. The exact calculation of equation (14), using a model, is rather laborious, but can be performed using a digital computer. Such exact calculation has been one of the purposes of the present program.

3. Development of experimental techniques.

3.1. Orientation of single crystals.

One of the requirements in a measurement of thermal diffuse scattering is a precise positioning of the crystal with respect to the incident and scattered X-ray beams. The equipment available was a Rigaku-Denki wide angle SG-8 diffractometer with a goniostat which permits three rotations of the crystal sample about the axes ω, χ and ϕ.

The standard geometry of the diffractometer is shown in fig. 1, which illustrates the angles ω, χ, ϕ and 2θ. Two codes have been developed to facilitate single crystal work. The code LEAST permits the determination, by iterative least squares method, of the Euler angles ϵ, η, ξ which define the orientation of the crystal with respect to the laboratory system. Figure 1 shows this laboratory system OXYZ and a system Oxyz fixed with the crystal. The Euler angles are defined when the goniostat is in a fundamental position, that is with the circle normal to the X-ray beam. To use LEAST one has first to determine experimentally a minimum of three (non coplanar) Bragg reflections. After the Euler angles have been found, the code ORIENT permits to calculate the settings for bringing into reflecting position any desired lattice plane.

The code LEAST and ORIENT are presently limited to cubic crystals but could be easily modified for different symmetries.

The input description for the code LEAST and ORIENT is given in Appendix I.

3.2. **Data taking.**

Disregarding the TDS of order higher than two, the total intensity scattered from a crystal outside a Bragg direction is

$$I_{total} = I_1 + I_2 + I_3 \qquad (15)$$

where I_1 and I_2 are the first and second order TDS respectively and I_C is the Compton intensity. For lattice dynamics studies it is important the accurate determination of I_1. Since I_2 and I_C can be obtained theoretically, one can see that it is essential to measure the **absolute** total intensity, that is to measure I_{total} in electron units. Rather than try to measure the incident beam it is better to measure the scattering from an amorphous sample of known composition, like paraffin or lucite, and use this as a standard.

In measuring the scattered intensity one has to account for divergence and absorption corrections [5]. No provision was made yet for divergence correction, but absorption was taken into account. If one uses a crystal plate and the incident and scattered beams are symmetric with respect to the normal to the plate, the absorption correction is independent of the scattering angle. A code DATA was written for data taking. The code computes the position of the crystal for scattering from a desired point in reciprocal space, with the additional condition that the scattering be symmetric with respect to the crystal face. Input to the code are the Euler angles and the orientation of the normal to the crystal plate. The code is designed in such a way to be used during the data taking process, the actual number of counts being written directly on the paper output from the computer.

For accurate measurements of diffuse scattering monochromatic radiation is required. Since a monochromator before the sample was not available with the present X-ray equipment, a preliminary measurement was made using a set of Ni and Co balanced filters. The crystal used was a 10x10x5 mm copper slab, with the face parallel to the plane 220. The scattering from lucite at 145° was used as standard to put the intensity in absolute units.

It was soon clear that the balanced filter method is not accurate enough, however the experiment provided useful experience in developing parallel aspects of the technique.

Fig. 2 shows an example of experimental data already reduced, as compared with the sum of one and two phonon TDS and Compton scattering. It can be seen that in spite of the large statistical errors the order of magnitude of the intensity measured is correct.

Average counting times were about 8 minutes each, for the Cobalt as well as the Nickel filter. The X-ray generator was run at 35 KV and 20 mA.

The precision of these measurements is not high enough to permit any conclusions about the validity of the lattice dynamical model.

Input description for the code DATA, which prepares the paper output necessary for data taking, is given in Appendix I.

3.3 Data analysis

The procedure for data analysis is similar to that described in ref. (6). Briefly, the counting rate from the sample is given by:

$$(CR)_S = K \frac{1+\cos^2 2\theta_S}{2} \frac{I_{total}\ (eu)}{(\mu_m A)_S} \tag{16}$$

while the counting rate from the lucite sample ($C_5H_8O_2$) is given by

$$(CR)_L = K \frac{1+\cos^2 2\theta_L}{2} \frac{5\,[f^2 + i\,(M)]_c + 8 + 2\,[f^2 + i\,(M)]_o}{5\,(A\,\mu_m)_c + 8\,(A\,\mu_m)_H + 2\,(A\,\mu_m)_o} \tag{17}$$

In (16) and (17) the suffixes S,L,C,H,O refer to sample, lucite, carbon, hydrogen, and oxygen respectively. K is a proportionality constant, 2θ is the scattering angle, f is the atomic scattering factor, i(M) is the modified (Compton) scattering per atom, A is the atomic weight and μ_m is the mass absorption coefficient.

$(CR)_S$ and $(CR)_L$ are count rates corrected for background. A code ANALYSIS which computes the intensity in electron units on the basis of (16) and (17) has been written. The code computes the error on the absolute intensity from all the statistical errors involved and uses linear interpolation from tabulated values for the atomic scattering factors and the Compton scattering.

3.4. Monochromatization of X-rays.

After the initial trial with the pair of balanced filters a monochromating system was built and adapted to the Rigaku wide angle diffractometer. The support for the crystal monochromator allows for rotation, translation and tilting motion of the crystal. These movements were obtained using parts of standard Rigaku goniometric heads.

A pictorial drawing of the monochromator support is shown in fig. 3. The support was designed to be used with the reflection 200 of LiF and Cu K_{α} radiation. When using the monochromator the X-ray tube has to be displaced from its original position. An aluminum support, which allows for some adjustment of the tube for intensity optimization, was built.

A suggested procedure for aligning the monochromator is the following:

a) Check optically that the axis of the output collimator from the monochromator intersects the ω axis in the center of the goniostat.

b) With detector at zero degrees (no slits) orient the LiF monochromator for maximum diffracted intensity.

c) Use the fine rotation of all the diffractometer around the ω axis for further optimization.

d) Measure the angular position of the incident beam and correct the values of 2θ for the inevitable angular displacement of the beam from the zero of the diffractometer.

3.5. Monitorization of the incident beam.

Although the output from the X-ray generator is remarkably stable, the addition of a monochromator makes the stability of the monochromatic beam rather critical. Very small misalignments like those produced by an ambient temperature variation affect sensibly the incident intensity.

For this reason and because of the long counting periods imposed by the low counting rates in diffuse scattering experiments, it was thought necessary to introduce a monitoring system.

Fig. 4 shows a view of the monitoring system and associated electronics. The monitorization was implemented by a NaI (Thallium activated) scintillator, positioned in such a way to measure the part of the incident beam scattered by a thin mylar foil.

The monitoring channel was realized with modular electronics independently of the main Rigaku electronics panel. However, the low voltage supply for the monitor preamplifier was obtained from the Rigaku unit (two outputs are available from the back of the pulse forming unit located close to the SCA unit), and the timing circuit in the Rigaku electronics was used to control the gate input of the monitor scaler. The pulse from the preamplifier requires pulse shaping and therefore a differentiating amplifier (ORTEC 410) was used.

The stability of the monitor was checked by varying the tube output and comparing the measured counts in a fixed period of time to the corresponding quantity from the main detector centered on a Bragg reflection from a single crystal. The two counters appeared to be tracking each other well within the statistical errors.

3.6. Experimental results.

After introducing the monochromator and the monitorization system, the experiment with the copper crystal was repeated. The diffuse scattering along the line joining the reciprocal lattice points (3, 1, 0) and (1, 3, 0) was measured. At 35 KV and 20 mA, using a flat LiF monochromator and about one degree divergence before and after scattering, the average count rate was only about twice the background. The measurement of the background is therefore extremely important. The background can be measured in two ways. One way is to leave the sample in place and cover the collimator in front of the detector with lead. This prevents photons scattered from the sample to enter the detector, but it is a bit optimistic evaluation, since it does not take into account scattering from air. Another way to measure the background is to leave the detector open but remove the sample. This method was used in all the background corrections. It has the advantage of accounting for air scattering, although it does not account for possible background induced by the sample.

Fig. 5 shows the measured diffuse intensity in electron units/atom. The points correspond to measurements of signal and background of about half an hour each.

The use of the monochromator technique is clearly an improvement over the previous measurement with balanced filters. However there are still systematic differences with the calculated values. These differences are presumably due to the following causes:

a) Fluorescence from copper.

b) Inaccurate accounting of the scattering from air. This effect could be eliminated by evacuating the area around the sample.

c) Low ratio signal to background. Use of a proportional counter, which has an energy resolution better than scintillator, could improve the signal to background ratio.

Agreement with the central part of the diffuse peak is difficult to obtain, because of the strong variation of the curve and because of the dependence on the angular resolution.

4. Calculational methods.

A large part of the program was devoted to the developments of calculational methods to compute the thermal diffuse scattering. As a result of this effort a journal article was prepared[7].

After the decision was made to use copper as standard for measurements of thermal diffuse scattering, it became important to have an accurate calculation of the first and second order TDS, as well as of the Compton scattering. The Compton scattering can be taken directly from existing tabulations[8]. In order to calculate the first and second order TDS one has to use a theoretical model. A model with interactions up to the fourth neighbours was used with the values of the force constants as derived by Sinha[4].

The calculation of the first order TDS is quite simple once one has the dynamical matrix. However, the calculation of the second order TDS is much more difficult since it requires a sum over the Brillouin zone. It has been customary to use approximate methods to calculate the

second order term. The approximations involve the assumption that the temperature be high in comparison with the crystal frequencies and the use of a Debye model (no dispersion).

It was considered interesting to perform an exact calculation of the second order term, that is to use eq. (14) with a realistic model.

In doing so one is faced with the following difficulties:

a) The frequencies and the polarization vectors for a number of points in the irreducible part of the Brillouin zone must be stored in the computer memory. For an accurate calculation it would be desirable to use a very large number of points, as compatible with the size of the computer memory. It was found that a mesh of 795 points in the irreducible part of the Brillouin zone was satisfactory for the present calculation.

b) The sum in (14) must be carried out over the entire zone, although the standard mesh of 795 points covers only 1/48 of the zone. This requires the use of symmetry transformations to pass from one to the other of the 48 parts composing the Brillouin zone.

A computer program for the exact calculation of the two phonon scattering intensity was developed. During the development of this code it was found convenient to use magnetic tapes as storage medium both for data and for programs (subroutines).

The advantage of storing data (in this case the frequencies and polarization vectors for all the points in the mesh) is obvious. Less obvious is the advantage of storing subroutines on a tape. When the programmer is using certain subroutines very often it is convenient to have all these subroutines stored on a tape at the computer center. The routines can be already compiled.

With some instructions to enter the content of the tape in the memory, the programmer can have at his disposal a personal library of routines. A number of routines have been written on a tape (tape LIB). The instructions for writing routines on a tape and for using the tape with the IBM 360 computer of the Institute of Physics at the University of São Paulo are contained in Appendix II. A brief description with the calling statements of the subroutines presently on tape LIB is given in Appendix III.

Fig. 6 shows the frequency spectrum of copper calculated with 9500 points in the irreducible part of the Brillouin zone, after some smoothing. Fig. 7 shows the Brillouin zone with the part in the first quadrant divided in six equivalent segments. Fig. 8 shows diagrammatically the steps necessary to calculate exactly the two phonon term. As evidenced by equation (14), after having selected a wave vector $\underline{q}$ one has to calculate $G_{\underline{Q}+\underline{q}-\underline{r}j}$. This requires the knowledge of the frequencies and polarization vectors at the mesh point closest to $\underline{Q}+\underline{q}-\underline{r}$.

The transformation from one to another irreducible part of the Brillouin zone is performed by one of 48 similarity transformations. The 3x3 orthogonal matrices representing these transformations are obtained as product of two matrices belonging to subgroups of six and eight matrices respectively. One subgroup transforms within one octant, while the other

subgroup transforms from one octant to another. The subroutine SEGMNT identifies, for a given $\underline{q}$ vector in the Brillouin zone, which matrices in the two subgroups are needed to transform $\underline{q}$ into the first standard irreducible element.

The results of the exact calculation of the second order TDS have been compared to the results of parallel calculations which compute the TDS with different continuous approximations, namely the approximation of Olmer[9], calculated with a method developed by Borie[10], and the approximation of Walker[1]. The results of these calculations have been documented in ref (7).

5. Conclusions and recommendations.

The present report should give an idea of what has been done in order to develop the hardware and software necessaries to perform diffuse scattering measurements. The success of a program of study of the diffuse scattering of X-rays depends on the step by step development of a number of capabilities, both in the experimental and in the calculational fields. While one year may be a short period to develop all the necessary capabilities, a documented progress has been made in the following areas:

a) Development of computer techniques for orientation of single crystals.
b) Monochromatization of X-rays.
c) Monitorization of X-rays.
d) Development of computer programs and storage of programs on magnetic tapes.

It is hoped that the capabilities developed will not be entirely lost and that at least to some extent the investigation of diffuse scattering will be continued. Besides the inherent interest in the dynamical properties responsible for the thermal diffuse scattering, there are some good reasons why this type of investigation should be continued. The main research interest of the Crystallography Group of the Division of Nuclear Physics at the Instituto de Energia Atomica seems to be the relationship between X-ray scattering and defects produced by irradiation.

In the opinion of the writer of this report, the most powerful tool for defects investigation (in the field of X-ray scattering) is precisely the diffuse part of the scattering. This is because any deviations, either of thermal origin or radiation induced, of the atoms from their ideal lattice positions will contribute to the scattering outside the Bragg peaks, and this scattering will be due entirely to such deviations (apart of course from the modified scattering). In other words the amount of information contained in the region outside the Bragg peaks is, from the point of view of the deviations from the ideal structure, much higher than the information contained in the Bragg peaks.

For these reasons, and in view of the interests of the Crystallography Group, it would be advisable that the investigation of diffuse scattering be continued. It should be noticed that the diffuse scattering from an irradiated or otherwise damaged crystal is composed of two parts. The part due to thermal motion could be, in convenient cases, calculated by methods similar to the ones developed in the past year and mentioned in this report.

The acquisition of a doubly bent monochromator and of a proportional counters are steps recommended if the studies of diffuse scattering, either thermal or radiation induced, are to be continued

References.

1. C.B. Walker, Phys. Rev 103,547 (1956).
2. E.H. Jacobsen, Phys Rev. 97, 654 (1955).
3. B.N. Brockhouse, Inelastic Scattering of Neutrons in Solids and Liquids, IAEA, Vienna (1961), p. 113.
4. S.K. Sinha, Phys Rev. 143, 422 (1966).
5. W.A Wooster, Diffuse X-Ray reflections from Crystals, Oxford 1962, p. 44.
6. B.E. Warren, X-Ray Diffraction, Reading, Mass. 1969, p. 169.
7. G.M. Borgonovi, "An Exact Calculation of the Second Order Thermal Diffuse Scattering", submitted for publication to Acta Crystallographica, 1972.
8. International Tables for X-Ray Crystallography, Vol. III.
9. P. Olmer, Bull. Soc. Franc. Miner 71, 145 (1948).
10. B. Borie, Acta Cryst. 14, 566 (1961).

List of figures.

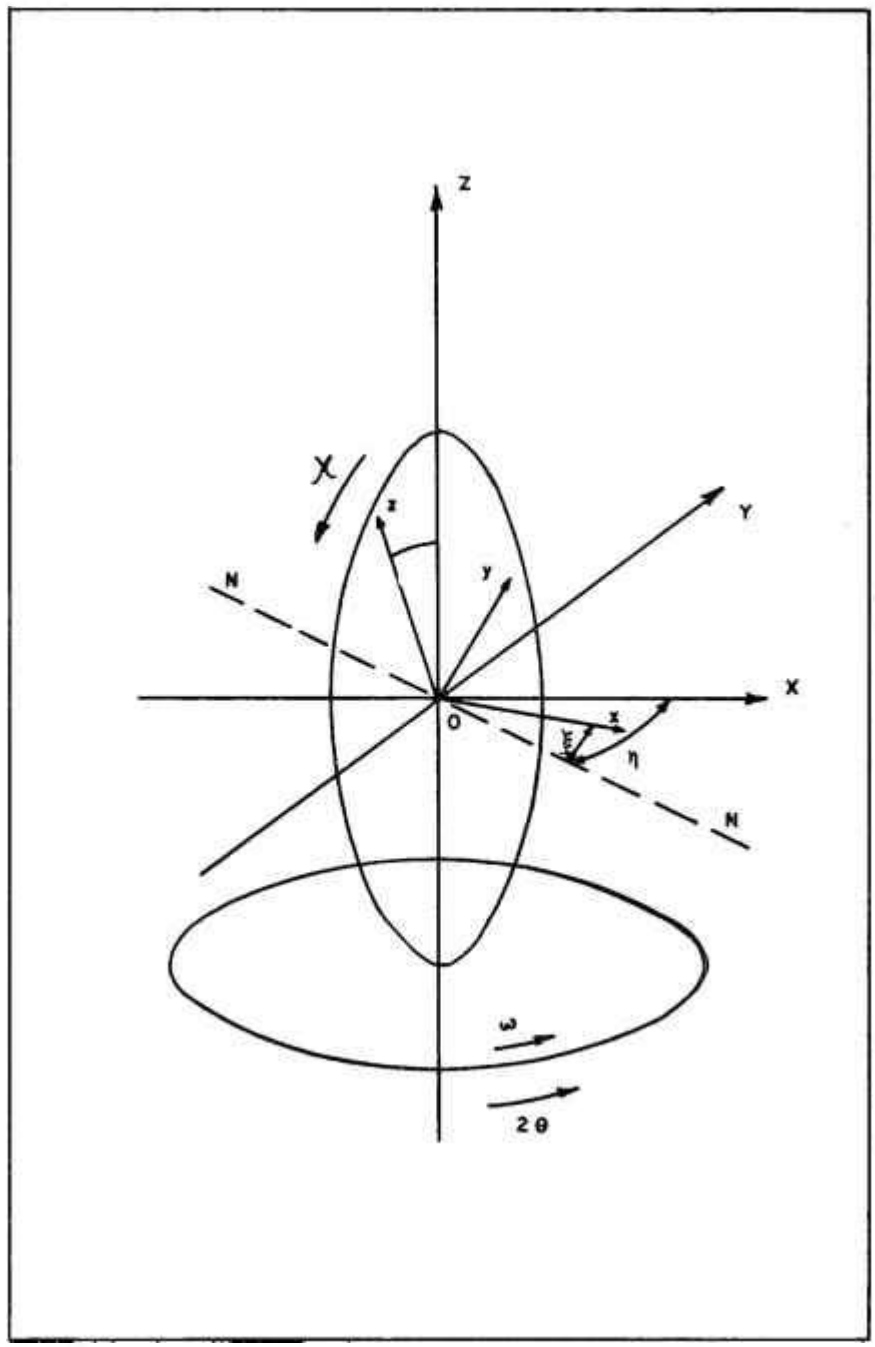

Figure 1

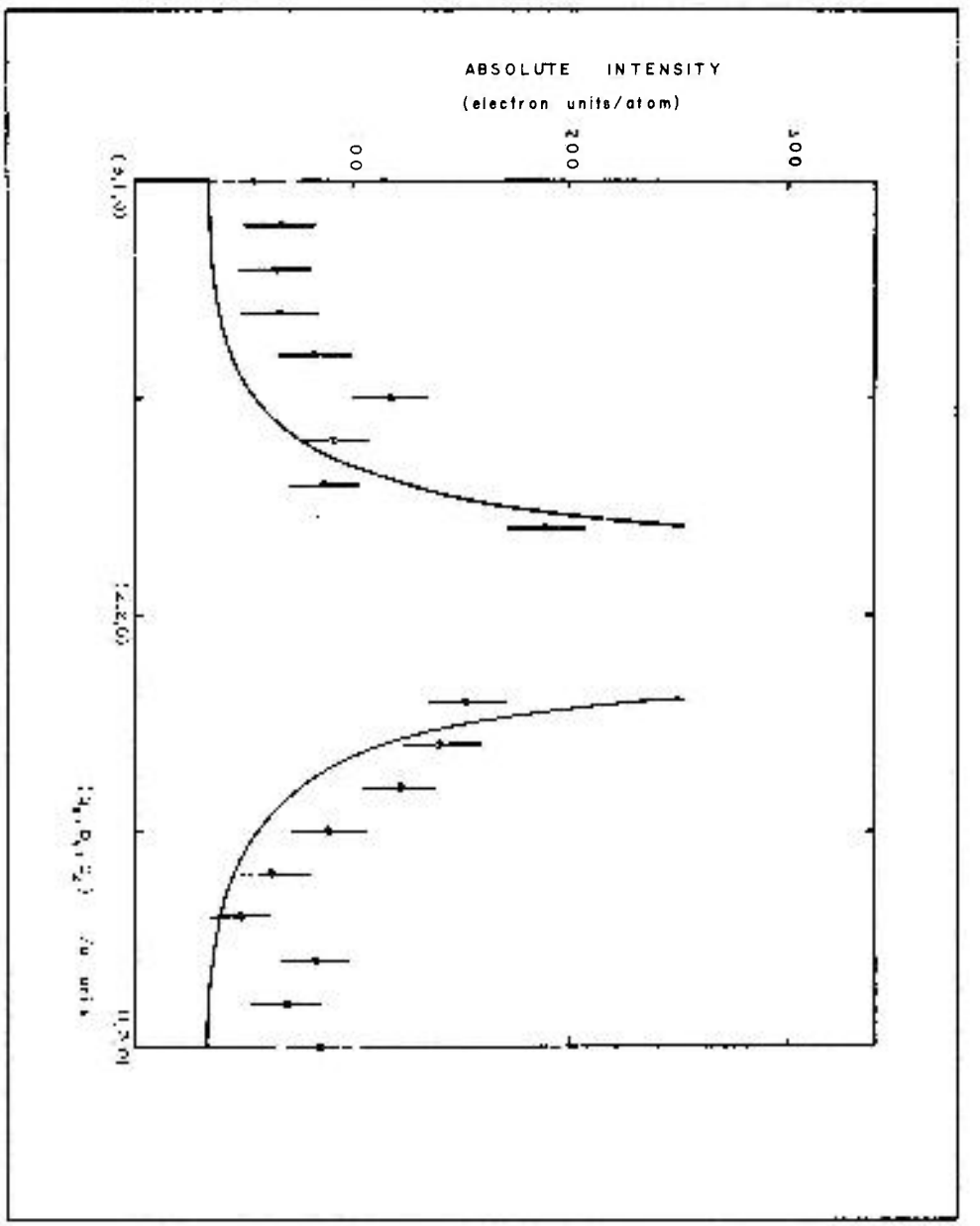

Figure 2

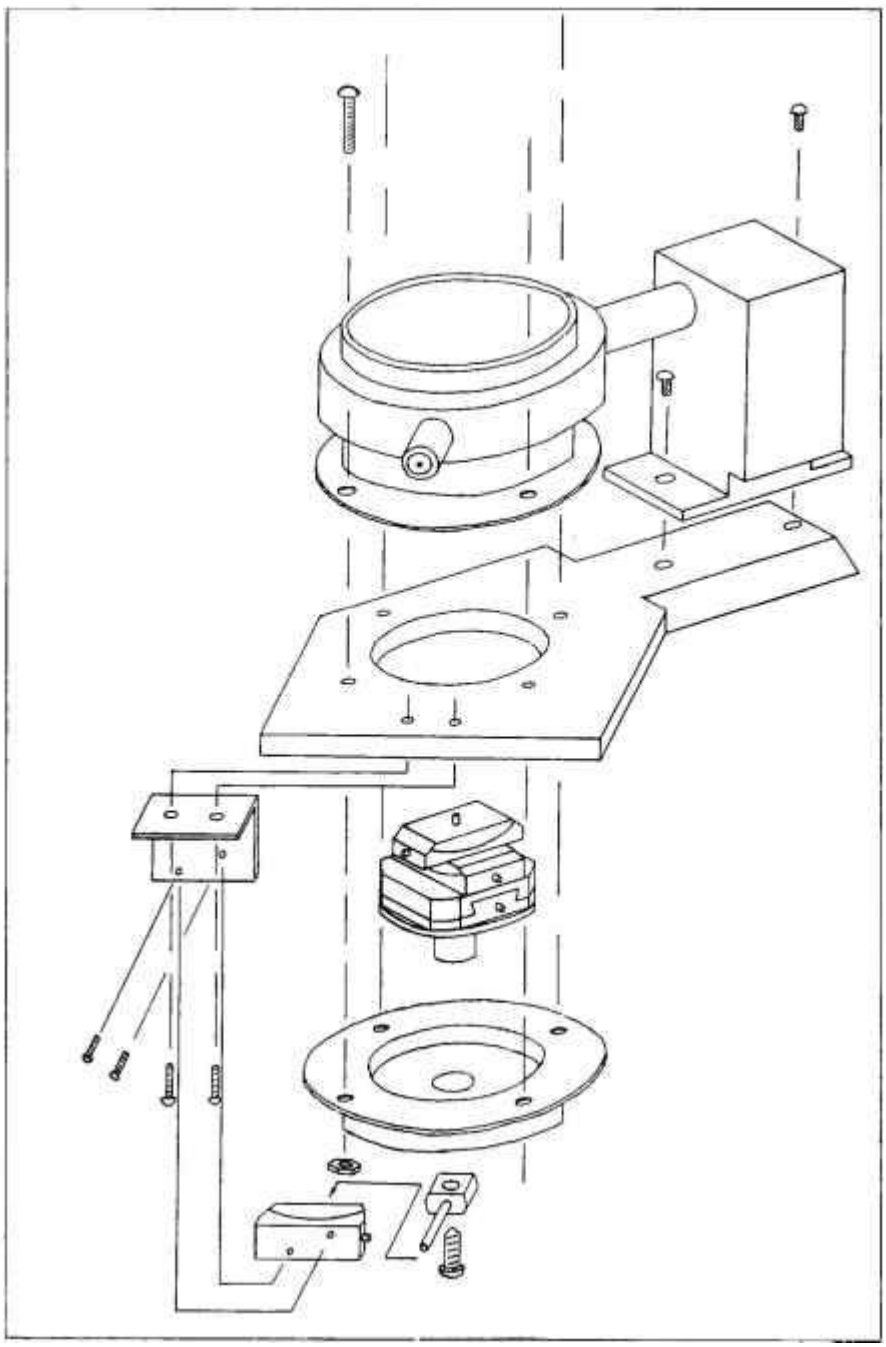

Figure 3

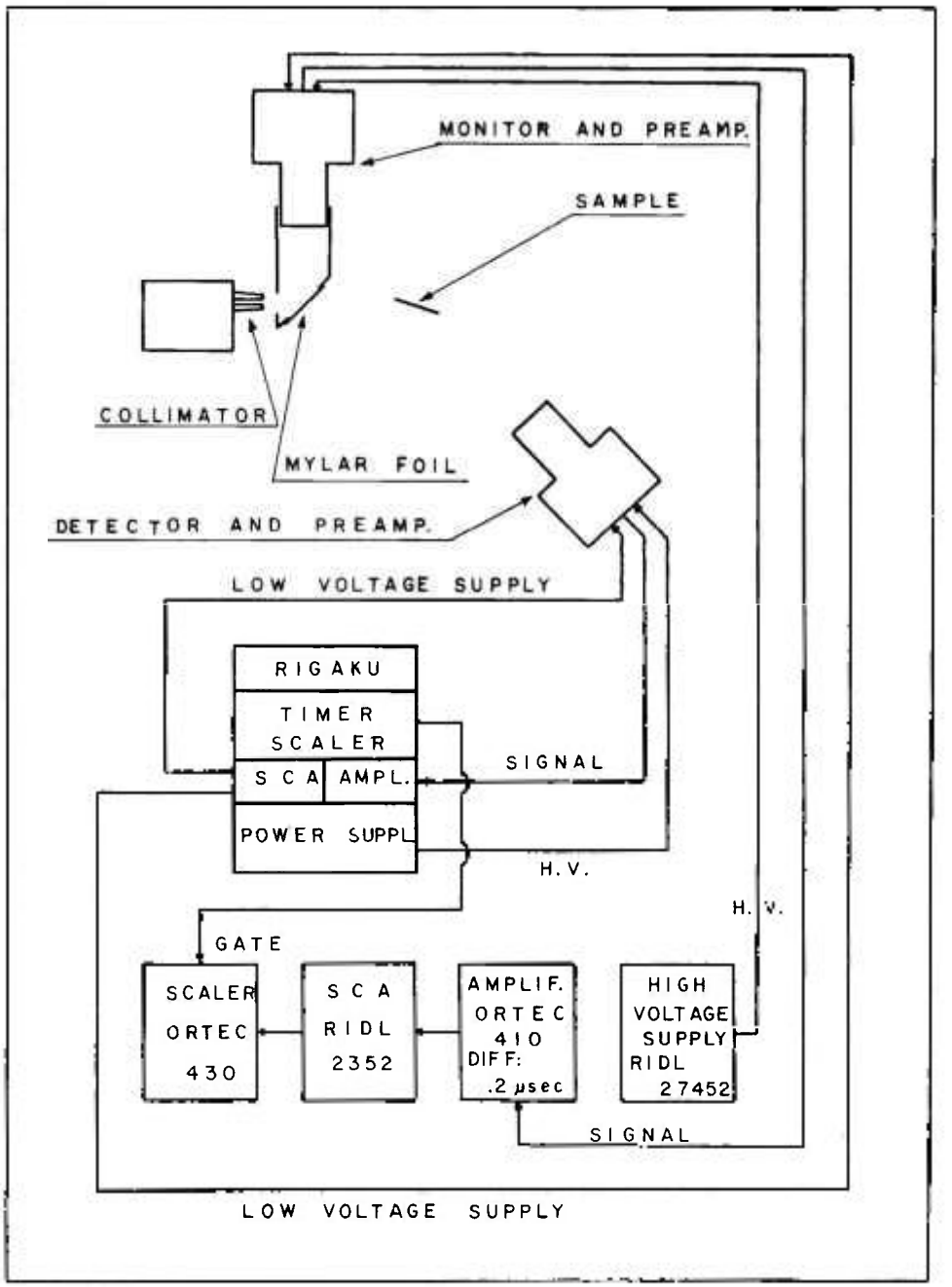
MONITOR AND PREAMP.
SAMPLE
COLLIMATOR
MYLAR FOIL
DETECTOR AND PREAMP.
LOW VOLTAGE SUPPLY
RIGAKU
TIMER SCALER
S C A
AMPL.
POWER SUPPL
SIGNAL
H. V.
H. V.
GATE
SCALER ORTEC 430
S C A RIDL 2352
AMPLIF. ORTEC 410 DIFF: .2 μsec
HIGH VOLTAGE SUPPLY RIDL 27452
SIGNAL
LOW VOLTAGE SUPPLY

Figure 4

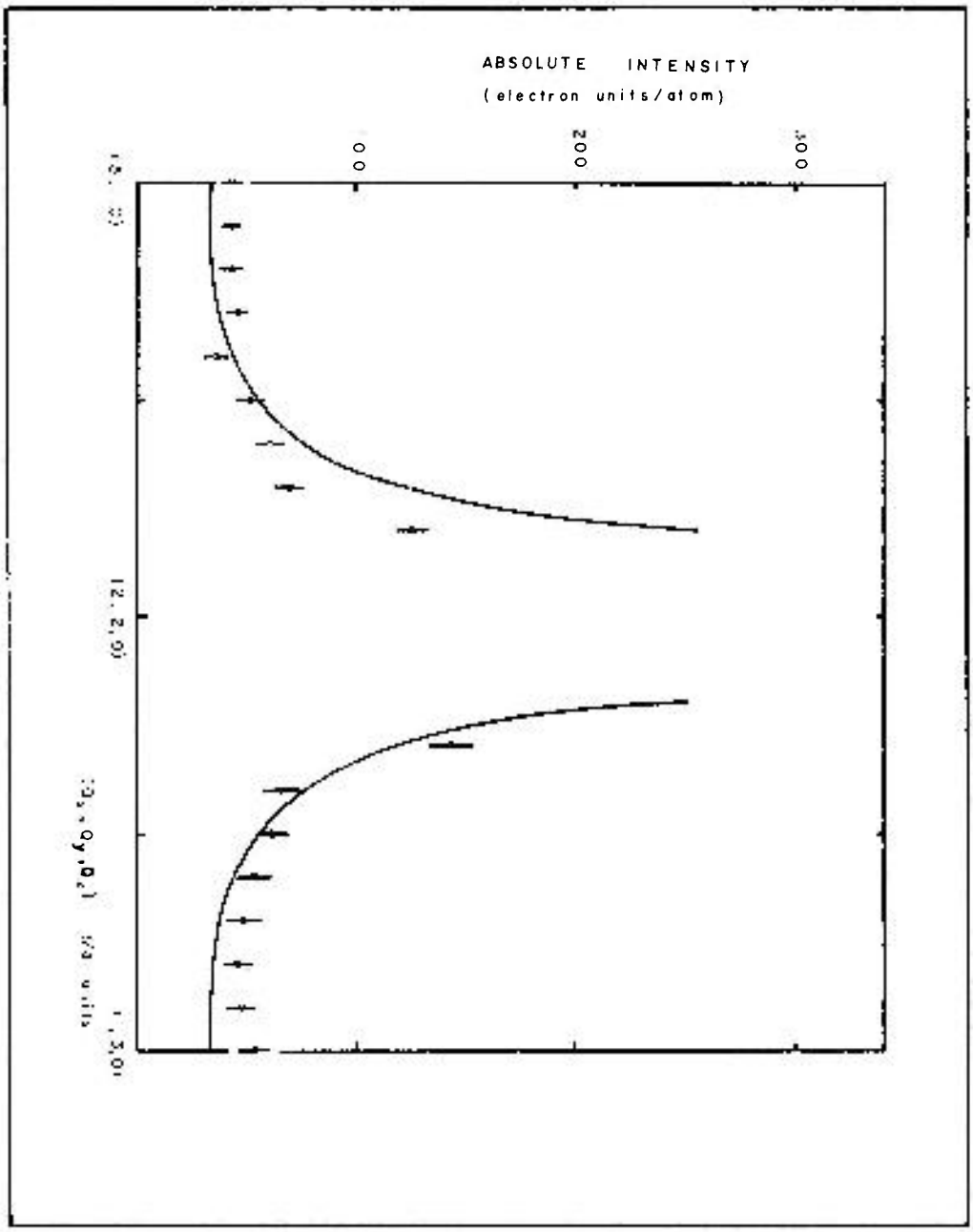

Figure 5

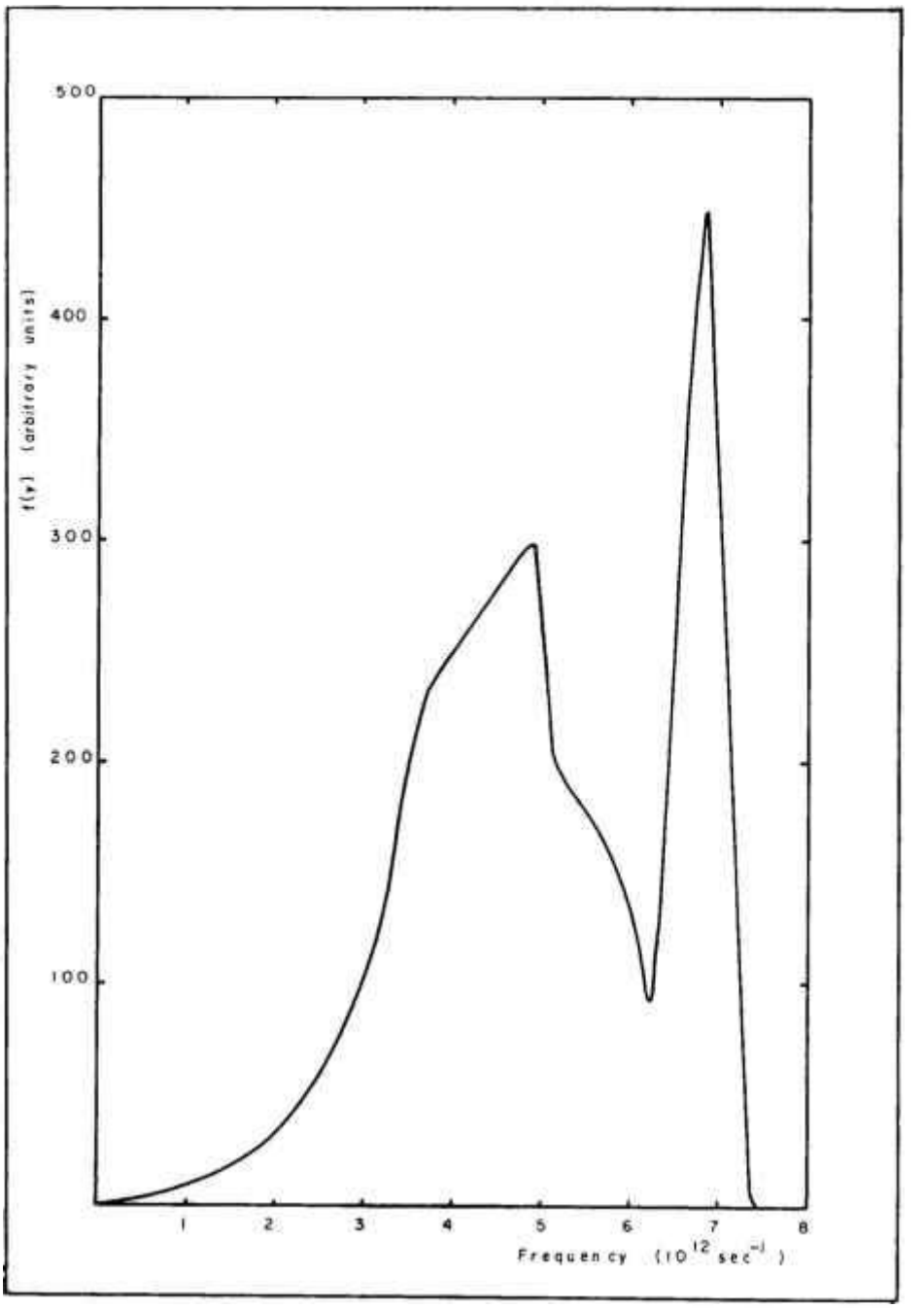
500
400
300
200
100
f(ν) (arbitrary units)
1
2
3
4
5
6
7
8
Frequency (10^12 sec^-1)

Figure 6

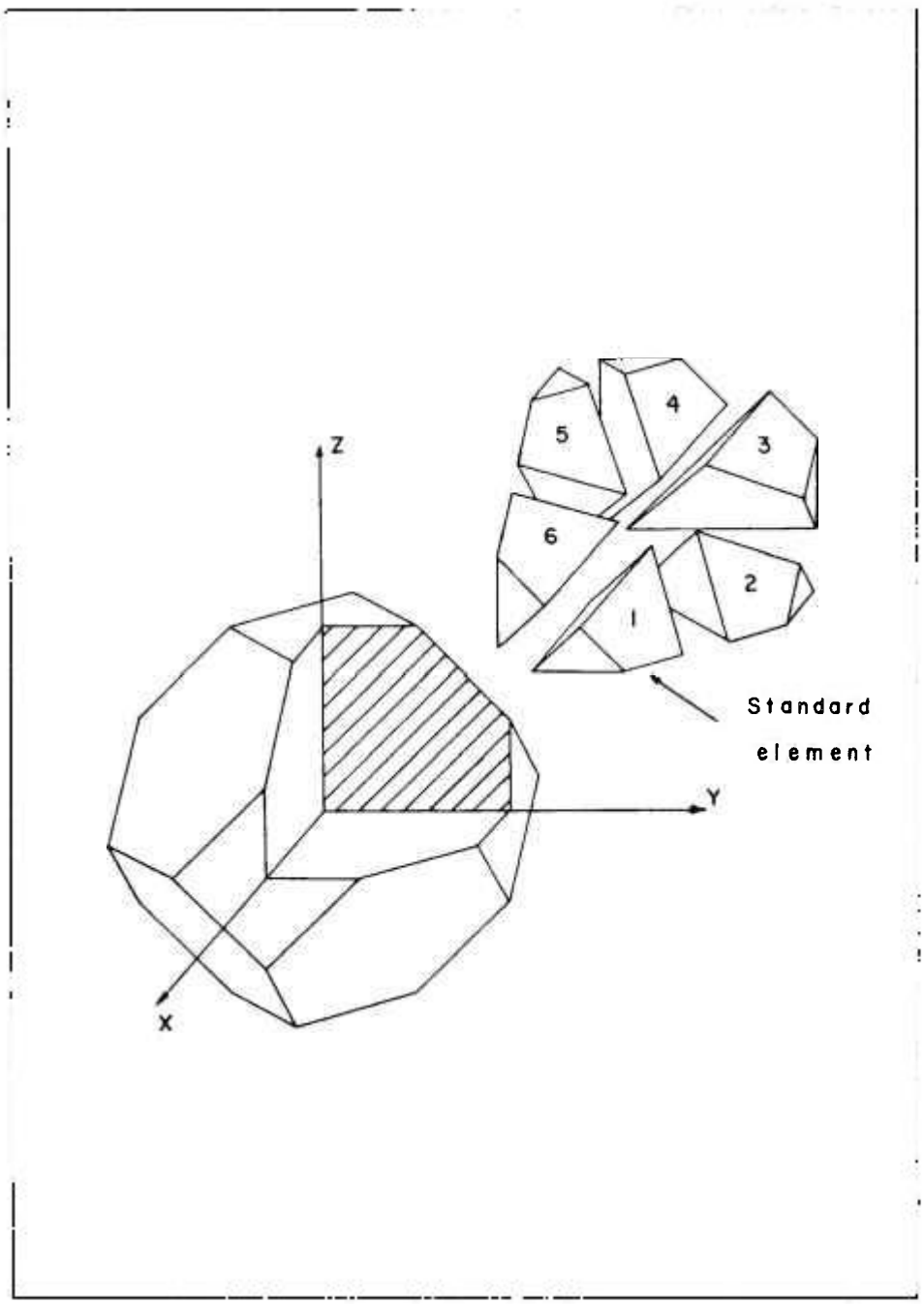

Figure 7

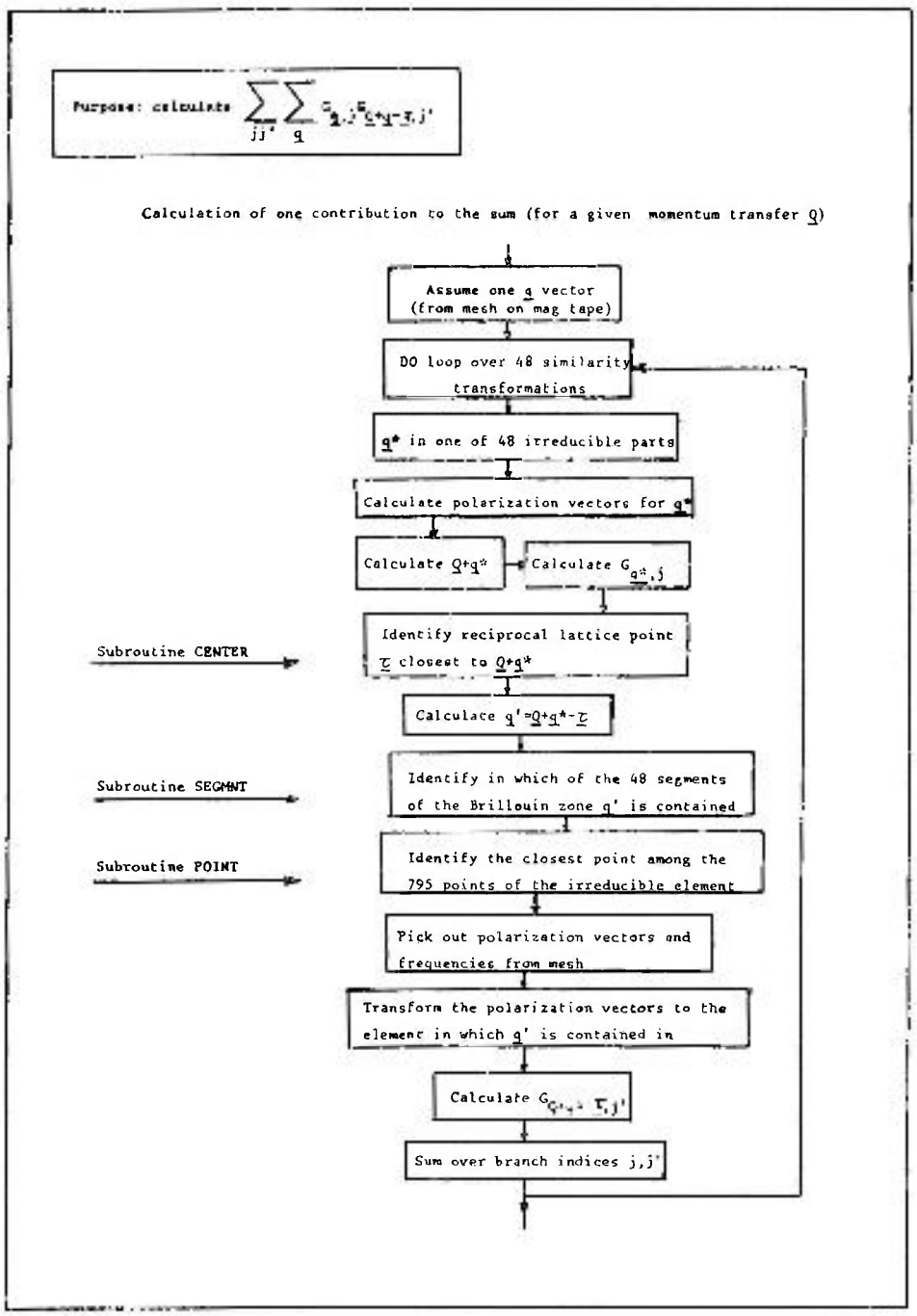
Purpose: calculate $\sum_{jj'} \sum_{q} G_{q,j} E_{Q+q-\tau,j'}$
Calculation of one contribution to the sum (for a given momentum transfer Q)
Assume one q vector (from mesh on mag tape)
DO loop over 48 similarity transformations
q* in one of 48 irreducible parts
Calculate polarization vectors for q*
Calculate Q+q*
Calculate $G_{q^*,j}$
Subroutine CENTER
Identify reciprocal lattice point τ closest to Q+q*
Calculate q'=Q+q*-τ
Subroutine SEGMNT
Identify in which of the 48 segments of the Brillouin zone q' is contained
Subroutine POINT
Identify the closest point among the 795 points of the irreducible element
Pick out polarization vectors and frequencies from mesh
Transform the polarization vectors to the element in which q' is contained in
Calculate $G_{Q+q^*-\tau,j'}$
Sum over branch indices j,j'

Figure 8

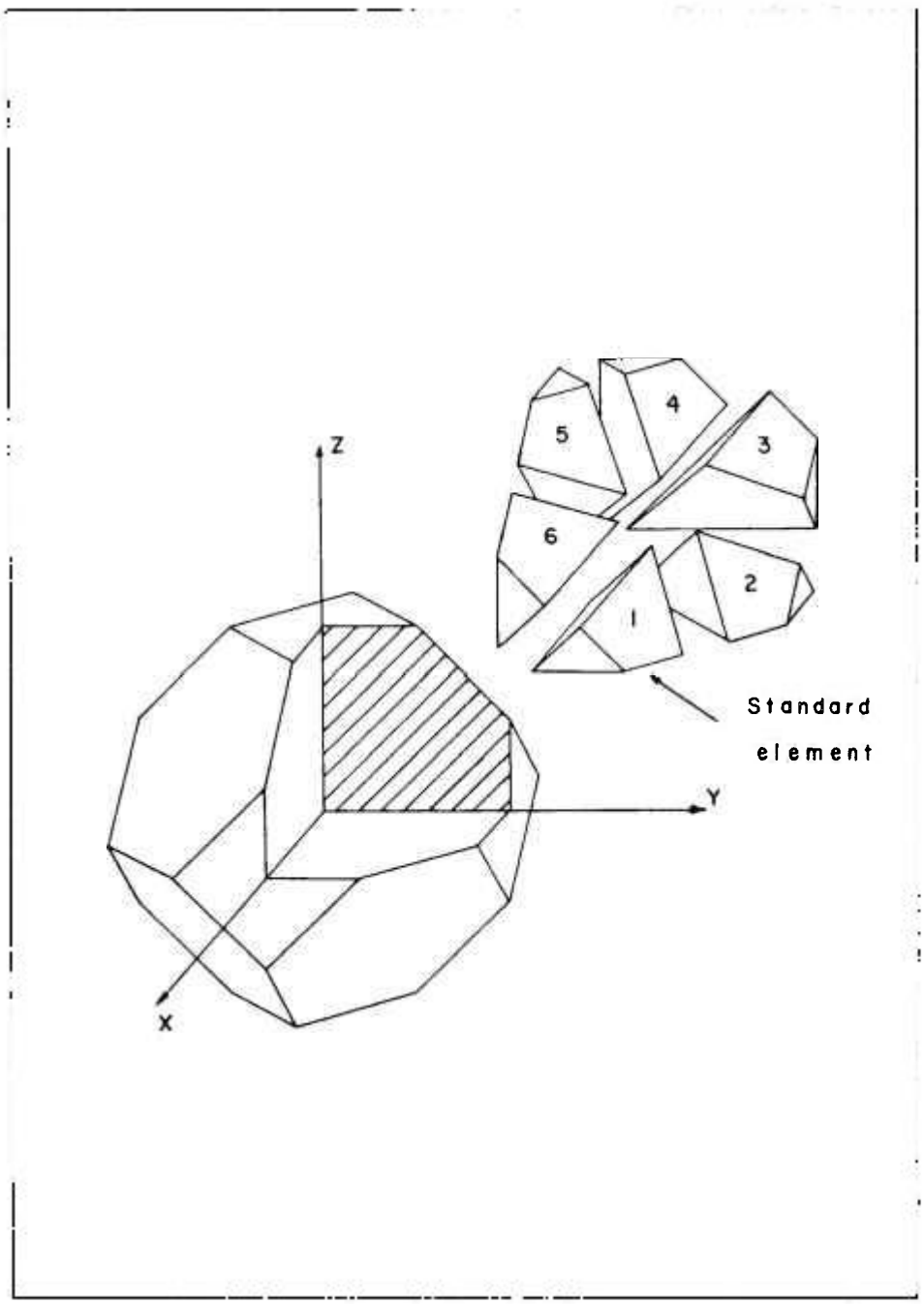

Figure 7

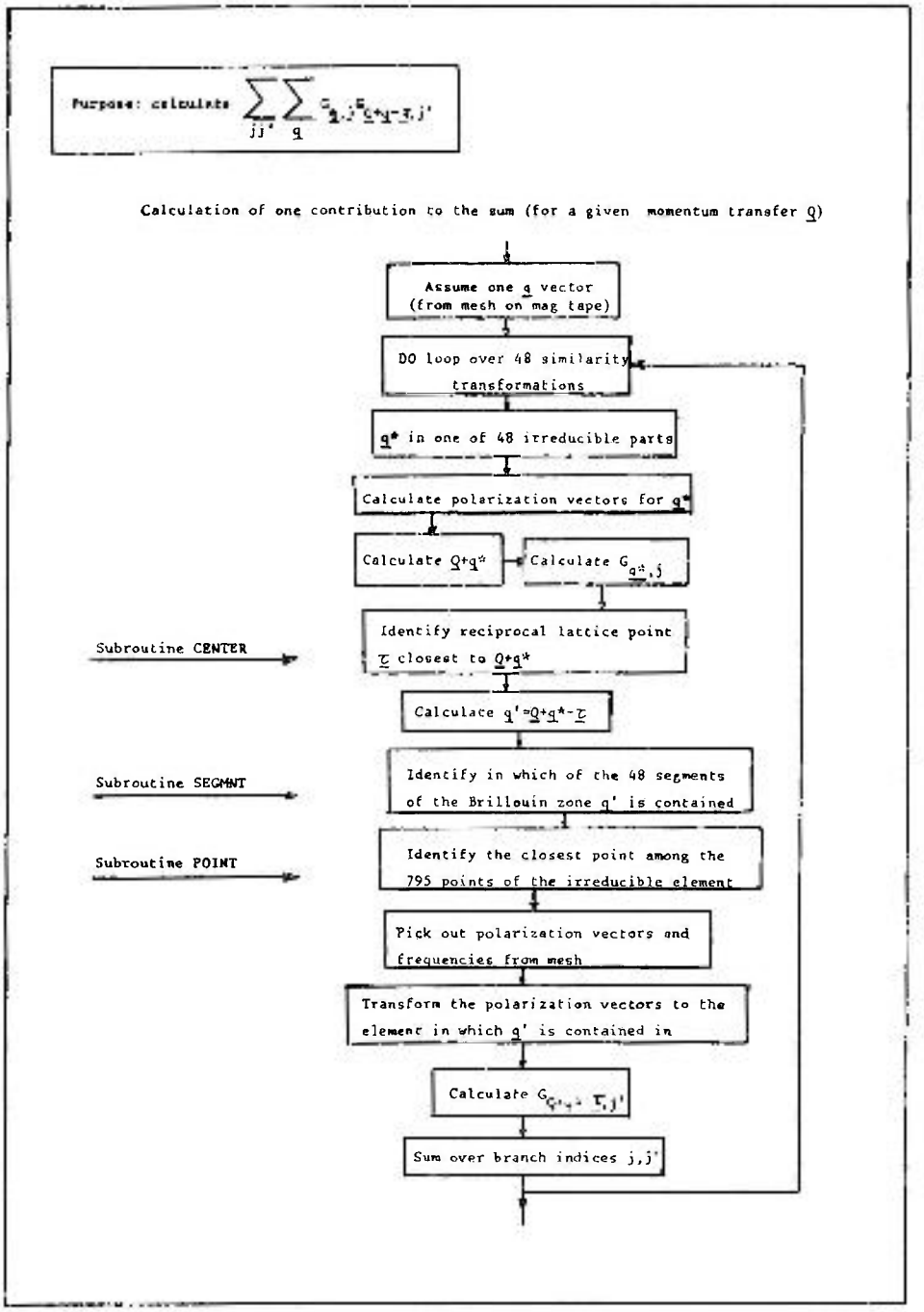
Purpose: calculate $\sum_{jj'} \sum_{q} G_{q,j,\tau,j'}$
Calculation of one contribution to the sum (for a given momentum transfer Q)
Assume one q vector (from mesh on mag tape)
DO loop over 48 similarity transformations
q* in one of 48 irreducible parts
Calculate polarization vectors for q*
Calculate Q+q*
Calculate $G_{q^*,j}$
Subroutine CENTER
Identify reciprocal lattice point τ closest to Q+q*
Calculate q'=Q+q*-τ
Subroutine SEGMNT
Identify in which of the 48 segments of the Brillouin zone q' is contained
Subroutine POINT
Identify the closest point among the 795 points of the irreducible element
Pick out polarization vectors and frequencies from mesh
Transform the polarization vectors to the element in which q' is contained in
Calculate $G_{Q+q^*,\tau,j'}$
Sum over branch indices j,j'

Figure 8

Appendix I

Input description of some computer codes developed under the program of thermal diffuse scattering.

1. Program LEAST

Card	Item	Format	Symbol	Description
1	1	20A4	COM	Comment
2	1	E10.5	A	Lattice parameter (Å)
	2	E10.5	WL	X-ray wavelength (Å)
3	1	I10	NR	Number of input reflections ($\geqslant 3$)
3+J	1	E10.5	AH	Miller's indices h,k,l of
	2	E10.5	AK	the observed reflection
	3	E10.5	AL	(positive)
	4	E10.5	OM	The observed angle ω
	5	E10.5	CHI	The observed angle χ
	6	E10.5	TRT2	The observed angle 2θ

J = 1,NR. Several problems may be run simultaneously by stacking sequentially groups of data.

2. Program ORIENT

Card	Item	Format	Symbol	Description
1	1	20A4	COM	Comment
2	1	E10.5	EPS	The angle ϵ
	2	E10.5	ETA	The angle η
	3	E10.5	CSI	The angle ξ
	4	E10.5	AO	Lattice parameter
3	1	E10.5	WL	X-ray wavelength
4	1	E10.4	AH	Miller's indices for
	2	E10.4	AK	desired reflection
	3	E10.4	AL	

Card number 4 can be repeated any desired number of times.

Appendix I

Input description of some computer codes developed under the program of thermal diffuse scattering.

1. Program LEAST

Card	Item	Format	Symbol	Description
1	1	20A4	COM	Comment
2	1	E10.5	A	Lattice parameter (Å)
	2	E10.5	WL	X-ray wavelength (Å)
3	1	I10	NR	Number of input reflections ($\geqslant 3$)
3+J	1	E10.5	AH	Miller's indices h,k,l of
	2	E10.5	AK	the observed reflection
	3	E10.5	AL	(positive)
	4	E10.5	OM	The observed angle ω
	5	E10.5	CHI	The observed angle χ
	6	E10.5	TRT2	The observed angle 2θ

J = 1,NR. Several problems may be run simultaneously by stacking sequentially groups of data.

2. Program ORIENT

Card	Item	Format	Symbol	Description
1	1	20A4	COM	Comment
2	1	E10.5	EPS	The angle ϵ
	2	E10.5	ETA	The angle η
	3	E10.5	CSI	The angle ξ
	4	E10.5	AO	Lattice parameter
3	1	E10.5	WL	X-ray wavelength
4	1	E10.4	AH	Miller's indices for
	2	E10.4	AK	desired reflection
	3	E10.4	AL	

Card number 4 can be repeated any desired number of times.

3. Program DATA

Card	Item	Format	Symbol	Description
1	1	20A4	COM	Comment
2	1	I10	NTIMES	Number of copies of output
3	1	E10.5	A	Lattice parameter
	2	E10.5	WL	X-ray wavelength
	3	E10.5	EPS	The angle ϵ
	4	E10.5	ETA	The angle η
	5	E10.5	CSI	The angle ξ
4	1	E10.5	QNX	Direction cosines of
	2	E10.5	QNY	the normal to the
	3	E10.5	QNZ	crystal face.
	4	E10.5	CMU	Absorption coeff. (barns)
5	1	I10	NP	Number of $\underline{Q}$ points.
5+J	1	E10.5	QX(J)	
	2	E10.5	QY(J)	Components of $\underline{Q}$ (in units of 1/a)
	3	E10.5	QZ(J)	

Appendix II

Use of magnetic tapes with the IBM 360 computer of the Institute of Physics at the University of Sao Paulo

1. **Use of data tapes**

Transfer of data between the memory and a magnetic tape unit is performed with FORTRAN instructions. Two control cards are needed, to be inserted preferably before the control card beginning execution. One control card is to instruct the operator to mount the tape in a physical unit, the second control card is to assign a FORTRAN logical unit to the physical unit.

Example:

```
// PAUSE COLOCAR FITA MESH (BORGONOVI,IEA) NA UNIDADE 181 PROTEGER
// SYS003 ACCESS MESHTAPE, 181 =
```

2. **Use of program tapes**

It has been convenient to use a tape which contains a number of subroutines already compiled. The subroutines are entered in the memory and form a kind of personal library. To prepare the tape one first obtains relocatable modules on cards from a compilation with the control card EXEC FORTRAN(DECK). Cards MODULE are then inserted in front of each binary deck. The group of subroutines can then be written on the tape through execution of a job similar to the example given below:

```
// Identification
// PAUSE  COLOCAR FITA LIB (BORGONOVI,IEA) NA UNIDADE 181 NAO
   PROTEGER
// SYS003 ACCESS LIBTAPE, 181 =
     COPY IGJCL, ENDIN='**'
               // EXEC LNKEDT
                  MODULE SUB1
This
part              Subroutine 1 (binary deck)
will                 MODULE SUB1
be                Subroutine 2 (binary deck)
written           ------------------------
on the         /*
tape.          // RESET SYSRDR
               **
               /*
               /&
```

It will be noticed that some control cards, namely the calling statement for the linkage editor and the statement to reset SYSRDR are written on the tape. The user may want to obtain a listing of the content of the tape produced with the execution of the previous job. This can be accomplished by execution of a job similar to the following example:

```
// Identification
// PAUSE COLOCAR FITA LIB (BORGONOVI, IEA) NA UNIDADE 181 PROTEGER
// SYS002 ACCESS LIBTAPE, 181 =
// EXEC UTILS
   PRINT LINES = 61,PAD* (20,20, '  '),NUM,SIZIN = 80,SIZOUT = 80
/*
/&
```

To use the tape with the subroutines one can execute a job similar to the following example:

```
// Identification
// EXEC FORTRAN
```

Main program (FORTRAN deck)

```
/*
// PAUSE COLOCAR FITA LIB (BORGONOVI, IEA) NA UNIDADE 181 PROTEGER
// SYSIPT ACCESS LIBTAPE, 181 =
// SYSRDR ACCESS RDRTAPE, 181 =
/*
/*
// RESET SYSIPT
/*
// EXEC
```

Eventual data

```
/*
/&
```

Appendix III.

List of subroutines on tape LIB

1. **DYMFC**

Calculates the dynamical matrix of Cu according to the model of Sinha.

CALL DYMFC(QX,QY,QZ,D)

QX,QY,QZ are the components of $\underline{Q}$ in 1/a units,D is the dynamical matrix (dimensioned 3x3). The units of the elements of D are 10^{24} sec^{-2}.

2. **SOLV**

Solves the dynamical matrix of order 3, giving eigenvalues and eigenvectors.

CALL SOV(3,D,F,E)

D is the dynamical matrix, F(J) are the eigenvalues and E(J,K) is the J-th component of the K-th eigenvector.

3. **SECEQ3**

Computes the coefficients of the secular equation corresponding to a matrix of order 3.

CALL SECEQ3(D,AO,A1,A2,A3)

D is the matrix and AO through A3 are the coefficients of the equation from order 3 to zero.

4. **CUBEQ**

Solves the algebraic equation of third order.

CALL CUBEQ(AO,A1,A2,A3,X1,X2,X3)

AO through A3 are the coefficients of the equation, X1,X2,X3 are the roots of the equation.

5. **CENTER**

Calculates the closest reciprocal lattice point to a vector $\underline{Q}$.

CALL CENTER(QX,QY,QZ,CX,CY,CZ)

QX,QY,QZ are the components of $\underline{Q}$.

CX,CY,CZ are the components of the closest reciprocal lattice point.

6. **SEGMNT**

Calculates in which of 48 parts of the Brillouin zone a vector $\underline{q}_p$ is contained.

CALL SEGMNT(QPX,QPY,QPZ,QX,QY,QZ,IND8,IND6)

QPX,QPY,QPZ are the components of $\underline{q}_p$.

QX,QY,QZ are the components of a vector $\underline{q}$, equivalent to $\underline{q}_p$, in the first irreducible segment.

IND8,IND6 are indices of two matrices whose product transforms $\underline{q}_p$ into $\underline{q}$.

7. **MAT**

Performs the product of the matrix A and a vector B.

CALL MAT(A,B,C)

C is the vector resulting from application of A to B. Order of A is 3x3.

8. **COORD**

Performs a linear transformation of coordinates as a function of the Euler angles.

CALL COORD(EPS,ETA,CSI,AH,AK,AL,X,Y,Z)

EPS,ETA,CSI are the Euler angles. The components AH,AK,AL are transformed into X,Y,Z X,Y,Z are normalized to modulus one.

9. **COINV**

This is the inverse transformation of COORD.

CALL COINV(EPS,ETA,CSI,X,Y,Z,XN,YN,ZN)

X,Y,Z are transformed into XN,YN,ZN.

10. **SYM**

Computes 48 equivalent vectors in the cubic symmetry.

CALL SYM(AH,AK,AL,BH,BK,BL)

The vector (AH,AK,AL) gives rise to the vectors (BH(J),BK(J), with J from 1 to 48.

11. **SYST**

Solves a system of linear equations

CALL SYST(NEQ,NEQ1,S,V,X)

NEQ = Number of equations

NEQ1 = NEQ + 1

S,V,X are the quantities in the matrix equation $S\underline{X} = \underline{V}$.

RESUMO

Este relatório descreve as atividades desenvolvidas no período de fev. 1971 a jan. 1972 no campo do espalhamento difuso de raios X.

As atividades desenvolvidas foram de natureza experimental e computacional. O trabalho foi concentrado na modificação dos aparelhos existentes para a medida do espalhamento difuso num cristal de cobre. Por isto, foram construídos um sistema de monocromatização e um sistema de monitoração de raios X. No campo computacional numerosos códigos foram preparados e testados, o principal deles sendo um programa para o cálculo exato do espalhamento difuso de segunda ordem.

RÉSUMÉ

Dans ce travail on expose les activités sur la diffusion thermique de rayons X developpées dans la période de fev. 1971 à jan. 1972.

Les activités sont de nature experimentale et computationnele. Le travail experimental a été concentré dans la modification des appareils existents pour la mésure de la diffusion thermique d'un crystal de cuivre. Des systèmes de monitoration et monochromatization de rayons X ont été construits et installés. Dans le champs comoutationnel plusieurs programmes ont été preparés et testés. Le programme principal sert à calculer exactement la diffusion de second ordre.