

THE STRUCTURE OF
LIQUID SEMICONDUCTORS

by

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ABSTRACT

By using the method of elastic neutron scattering, structure factors were measured for the chalcogens tellurium, selenium and sulphur in the liquid state. Partial structure factors were also obtained for the liquid semiconductors Cu_2Te , CuTe and Ag_2Te . By Fourier transforming these structure factors radial distribution functions (R.D.F's) were found.

Structural models consisting of ionic bonding, covalent bonding and clusters were compared with the experimental data, and the interpretation was aided by the construction of computer models by a 'Monte-Carlo' method. It was concluded that the liquid semiconductors investigated have a complex structure with mainly covalent bonding; also that liquid selenium consists of chains of atoms and liquid tellurium has a network structure similar to that outlined by Cabane and Friedel (1971).

INTRODUCTION

There exists a group of liquid conductors whose electronic properties are different from those of metals and are similar to those of semiconductors. Such liquids are usually referred to as liquid semiconductors. (These should not be confused with liquids formed by melting solid semiconductors. These liquids are frequently metallic in nature.) A review of the electrical properties of liquid semiconductors has been given by Enderby (1974).

There are two main types of liquid semiconductors. There are those based on the chalcogens (e.g. pure liquid selenium or liquid Ag_2Te), and those formed when metals of very different electronegativities are alloyed together in a certain proportion (e.g. Mg_3Bi_2). Our understanding of liquid semiconductors is very limited. Explanation of the electrical and thermodynamic properties is hampered by a lack of knowledge of the atomic order. The work here is an attempt to fill this gap by obtaining structural information about these liquids through the method of neutron diffraction.

Experimental data, using neutron diffraction techniques is given

- (i) for the liquid chalcogens Te, Se and S,
- (ii) for liquid Te-Se mixtures.
- (iii) for the liquid semiconductors Cu_2Te and Ag_2Te and
- (iv) for the equi-atomic system liquid CuTe .

For (iii) and (iv) the method of isotopic substitution is used, and the partial structure factors are extracted. The results are presented in momentum (Q) space and in real (r) space. Structural models are presented, for these liquids, to fit the experimental observations. Computer modelling in three dimensions is used to help to interpret the experimental data.

Apart from some work on pure liquid chalcogens there has been no previous study in this detail of the structure of liquid semiconductors.

CHAPTER 1

Liquid Semiconductors

1.1 The Electrical Properties of Liquid Semiconductors

Many semiconductors become metallic on passing into the liquid state. That is to say, they exhibit small thermopowers ($10^{-5} \text{ V}^\circ\text{C}^{-1}$), small Hall coefficients independent of temperature ($R_H \sim 10^{-3} \text{ e.m.u.}$) and fairly high conductivities (of order $5000 \text{ ohm}^{-1} \text{ cm}^{-1}$). Examples of these materials are Bi_2Te_3 , ZnSb , CdSb , Au_2Te and Ge .

On the other hand, there are binary liquid alloys for which the electron transport parameters are outside the range characteristic of the metallic state for at least some compositions. We can refer to those alloys as "true" liquid semiconductors because they exhibit most of the properties that characterise conventional solid semiconductors. These include liquid Cu-Te , Ag-Te , In-Te , Mg-Bi and all liquid alloys involving selenium as one component. Table 1 gives a list of some of the alloy systems that fall into this category, together with the value of their electrical conductivities at the composition of particular interest.

To be specific, we shall focus attention on two groups of liquid alloys that constitute systems of this type. Let M and S refer respectively to pure liquids that have metallic and semi-metallic electrical properties.

The first group comprises M-M systems which are of particular interest because it is possible continually to follow the transition from metallic behaviour to semiconducting behaviour. Liquid Mg-Bi , MgSb , and LiBi represent some of the alloys known to fall into this group.

Experimental results for conductivity

TABLE I

Liquid Semiconductors

<u>Liquid Alloy</u>	<u>Critical Composition</u>	<u>Conductivity</u> $\sigma^{-1} \text{ cm}^{-1}$
S-Ag	Ag_2S	200
S-Pb	PbS	110
S-Cu	Cu_2S	50
S-Sn	SnS	24
S-Ge	GeS	1.35
S-Tl	Tl_2S_3	1.7×10^{-2}
	Tl_2S_3	6.5×10^{-3}
S-Sb	Sb_2S_3	1.5×10^{-2}
Te-Cu	Cu_2Te	200
Te-Ag	Ag_2Te	150
Te-Fe	FeTe_2	400
Te-Tl	Tl_2Te	70
Te-Cd	CdTe	40
Te-Zn	ZnTe	40
Te-In	In_2Te_3	25
Te-Ga	Ga_2Te_3	10
Bi-Mg	Mg_3Bi_2	245
Bi-Li	Li_3Bi	?

References:

Allgaier (1969)

Enderby and Collings(1970)

σ , and for thermoelectric power S , have been reported for liquid Mg-Bi by Enderby and Collins (1970), and a selection of data is given in figures (1.1) and (1.2). At the composition Mg_3Bi_2 the S changes sign, σ falls to a minimum value and $\frac{d\sigma}{dT}$ is positive. It is clear from this evidence and also from thermodynamic data (Haltgeen et al., 1963) that a major change in the bonding characteristics takes place as we proceed from pure liquid magnesium. There is also evidence that substantial electromigration occurs in liquid Mg - Bi, with Mg drifting towards the cathode and Bi drifting towards the anode. (Epstein 1973)

The second group comprises M-S systems which include Ag-Te, Cu-Te (but not Au-Te), Ga-Te and Tl-Te and these are the most widely studied group of Liquid Semiconductors. Phase diagrams for Cu-Te and Tl-Te are available (Hanson, 1958), and a selection of the experimental data due to Dancy (1965) Cutler and Mallon (1966) and Enderby and Simmons (1969) is given in figures (1.3) and (1.4). The conductivity falls to a minimum value for Tl_2Te at which composition elementary valence considerations are satisfied. All alloys within this second group have the following characteristics:

(a) the alloys possess a two-phase liquid region (liquid immiscibility) often in the range $70 \leq X_m \leq 100$ where X_m is the atomic percentage of the metallic component.

(b) R_H/R_{H0} is significantly different from unity; R_H itself is negative at all compositions and achieves a maximum value at the composition of minimum conductivity.

1.2 The Outstanding Problems.

The four most outstanding problems of liquid semiconductors are as follows:

- (1) What is the most useful way to characterise the structure of liquid semiconductors?
- (2) How can the distribution of binary liquid semiconductors (within the periodic table) be understood?
- (3) What will be the form of the density of states as a function of composition and temperature?
- (4) What is the mode of electron transport, particularly around the stoichiometric composition?

This work is concerned with answering the first of these questions; concerning the structure of liquid semiconductors.

CHAPTER 2

The Neutron Scattering Theory

2.1 Introduction

Since the advent of high flux beam reactors the neutron has been used extensively as a tool in the study of both solids and liquids. The purpose of this chapter is to give an account of the theory of neutron scattering, and in particular its application to liquids.

For a more complete understanding of the physical properties of liquids it is necessary to have a precise knowledge of $S(Q)$, the structure factor. Neutron diffraction techniques possess several advantages over other methods in the determination of $S(Q)$. The main advantages are

- (i) that a transmission geometry is used (avoiding problems associated with free liquid surfaces),
- (ii) vanadium is available as a calibration material, and
- (iii) isotopes can be used to determine partial structure factors for some mixtures, (see Chapter 5) since the scattering is nuclear rather than electronic.

However, the following corrections must be considered:

1. Allowance must be made for multiple scattering (this is considerably higher than for x-rays, although it is isotropic).
2. A full analysis of the absorption in the sample and sample holder must be carried out.
3. The connection between the true static structure factor and the effective structure factor must be properly established. This can only be done reliably for the heavier elements, with the aid of the Placzek expansion (equation 2.13). For the lighter elements (e.g. Li, Al, S) the Placzek method is not accurate.

In section 2.2 neutron scattering is treated in terms of the scattering law $S(Q, \omega)$. The "static approximation" which enables one

to obtain the static structure factor $S(Q)$ is outlined in section 2.4, and corrections to the static approximation are described in section 2.5. Since the absorption of neutrons in most elements is small, the probability of a second scattering event occurring can be high. Section 2.6 outlines the methods of correcting for multiple scattering.

2.2 Van Hoves Formulation

The scattering of low energy neutrons from a system of N identical atoms can, in Born approximation, be most usefully described in terms of the scattering law, $S(\underline{Q}, \omega)$. This quantity measures the probability that energy $\hbar\omega$ will be transferred to the neutron if momentum $\hbar\underline{Q}$ is absorbed by the scatterer. Van Hove (1954) showed that the differential scattering cross-section per unit solid angle per unit energy range is

$$\frac{d^2\sigma}{d\omega d\Omega} = N f^2 \frac{\kappa}{\kappa_0} S(\underline{Q}, \omega) \quad (2.1)$$

where $\underline{\kappa}_0$ and $\underline{\kappa}$ are the initial and final wave vectors, $\underline{Q} = \underline{\kappa}_0 - \underline{\kappa}$, f is the scattering length and Ω refers to solid angle. The bound atom scattering cross-section is given by

$$\sigma_s = 4\pi f^2 \quad (2.2)$$

In practice we have both coherent and incoherent scattering; the latter is due to isotope and spin effects.

Let $\langle f \rangle$ represent an average scattering length weighted by spin factors and the isotopic abundance (Bacon, 1962), then equation (2.1) may be re-written as

$$\frac{d^2\sigma^{(inc)}}{d\omega d\Omega} = N \left[\langle f^2 \rangle - \langle f \rangle^2 \right] \frac{\kappa}{\kappa_0} S^{inc}(\underline{Q}, \omega) \quad (2.3)a$$

$$\frac{d^2\sigma^{(coh)}}{d\omega d\Omega} = N \langle f \rangle^2 \frac{\kappa}{\kappa_0} S^{(coh)}(\underline{Q}, \omega) \quad (2.3)b$$

where $\sigma^{(inc.)}$ and $\sigma^{(coh.)}$ refer to the incoherent and coherent cross-sections respectively. In the following section $S(\underline{Q}, \omega)$ is related to the time dependent correlation functions.

2.3 The Time Dependent Correlation Functions

Van Hove obtains his time dependent correlation functions by taking a double Fourier Transform of $S(\underline{Q}, \omega)$ to give

$$G_s(\underline{r}, t) = \frac{1}{(2\pi)^3} \iint S^{(inc)}(\underline{Q}, \omega) e^{-[\underline{Q} \cdot \underline{r} - \omega t]} d\underline{Q} d\omega \quad (2.4)a$$

$$G(r, t) = \frac{1}{(2\pi)^3} \iint S^{(coh)}(\underline{Q}, \omega) e^{-[\underline{Q} \cdot \underline{r} - \omega t]} d\underline{Q} d\omega \quad (2.4)b$$

$G_s(\underline{r}, t)$ is the probability of finding an atom which was at the origin at $t = 0$, at the position $\underline{r}$ at time t . Similarly $G(\underline{r}, t)$ represents the probability of finding any atom at position $\underline{r}$ at time t when it is known that an atom was at the origin at time $t = 0$. We write $G = G_d + G_s$. If an atom is at the origin at $t = 0$ then $G_d(\underline{r}, t)$ is the probability that any other atom is at $\underline{r}$ at time t .

In terms of G the differential scattering cross-section may be written as

$$\frac{d^2\sigma^{(coh)}}{d\Omega d\omega} = \frac{\langle f \rangle^2}{2\pi} N \frac{k}{k_0} \iint d\underline{r} dt e^{j(\underline{Q} \cdot \underline{r} - \omega t)} G(\underline{r}, t) \quad (2.5)a$$

$$\frac{d^2\sigma^{(inc)}}{d\Omega d\omega} = N \left[\frac{\langle f^2 \rangle - \langle f \rangle^2}{2\pi} \right] \frac{k}{k_0} \iint d\underline{r} dt e^{j(\underline{Q} \cdot \underline{r} - \omega t)} G_s(\underline{r}, t) \quad (2.5)b$$

2.4 The Static Approximation

In diffraction experiments the quantity that is measured is the differential scattering cross-section $\frac{d\sigma}{d\Omega}$. In x-ray scattering this quantity is measured automatically in the static approximation, but for neutrons corrections to this approximation are required.

In the static approximation one assumes that the energy transfers are small compared to the incident energy, so that Q is regarded as constant over the range of ω for which energy transfers are important. Equation (2.5)a becomes

$$\frac{d\sigma^{(coh)}}{d\Omega} = \frac{\langle f \rangle^2}{2\pi} N \int d\omega \int dt e^{-j\omega t} \int d\mathbf{r} e^{j\mathbf{Q} \cdot \mathbf{r}} G(\mathbf{r}, t) \quad (2.6)$$

since $\mathbf{K} \simeq \mathbf{K}_0$

Since G in this approximation hardly varies for time intervals less than $1/\omega$ the integration over ω produces $2\pi \delta(t)$ so that

$$\begin{aligned} \frac{d\sigma^{(coh)}}{d\Omega} &= \langle f \rangle^2 N \int dt \delta(t) \int d\mathbf{r} e^{j\mathbf{Q} \cdot \mathbf{r}} G(\mathbf{r}, t) \\ &= \langle f \rangle^2 N \int d\mathbf{r} e^{j\mathbf{Q} \cdot \mathbf{r}} G(\mathbf{r}, 0) \\ &= \langle f \rangle^2 N \left[1 + \int d\mathbf{r} e^{j\mathbf{Q} \cdot \mathbf{r}} g(\mathbf{r}) \right] \end{aligned} \quad (2.7)$$

since $G_s(\mathbf{r}, 0) = \delta(\mathbf{r})$ $G_d(\mathbf{r}, 0) = g(\mathbf{r})$

$g(r)$ is the time independent pair correlation function.

So in the static approximation the structure factor $S(Q)$ is given by

$$\frac{d\sigma^{(coh)}}{d\Omega} = N \langle f \rangle^2 S(Q) \quad (2.8)$$

where

$$S(Q) = 1 + n \int g(r) e^{i\mathbf{Q} \cdot \mathbf{r}} d\mathbf{r} \quad (2.9)$$

By measuring the scattered intensity as a function of scattering angle 2Θ one arrives at the structure factor.

It can be readily verified that

$$\frac{d\sigma^{(inc)}}{d\Omega} = N \left[\langle f^2 \rangle - \langle f \rangle^2 \right] \quad (2.10)$$

in the static approximation.

2.5 Corrections to the Static Approximation

The method described here is due to Placzek. For neutrons of wavelength $\sim 1 \text{ \AA}$ the scattering is centred around the elastic value since the incident energy, E_0 ($\approx 85 \text{ meV}$) is considerably larger than the energy transfer $\hbar\omega$ ($\leq 10 \text{ meV}$).

The Placzek method is to expand K/k_0 and $S(Q, \omega)$ about Q_0 , the value of Q for which $\hbar\omega = 0$, in terms of $\hbar\omega/E_0$. The product of these gives an expansion for $\frac{d^2\sigma}{d\Omega d\omega}$; Placzek then integrates over ω assuming:

- (i) the detector has constant efficiency,
- (ii) the detector has a $1/Q$ dependence.

For (ii) this process yields

$$\left(\frac{d\sigma^{(coh)}}{d\Omega}\right)_{eff} = N \langle f^2 \rangle^2 [S(Q) + f_p(Q)] \quad (2.11)$$

$$\left(\frac{d\sigma^{(inc)}}{d\Omega}\right)_{eff} = N (\langle f^2 \rangle - \langle f \rangle^2) [1 + f_p(Q)] \quad (2.12)$$

where

$$f_p(Q) = \frac{\bar{K}_0}{3\epsilon\mu} - \frac{\bar{K}_0\alpha}{6\epsilon^2} - \frac{\alpha}{2\epsilon} + \frac{\alpha}{2\mu\epsilon} \quad (2.13)$$

Here $\bar{K}_0$ is the average kinetic energy of the atoms in units of $k_B T$

$$\alpha = \hbar^2 k^2 / 2M k_B T, \quad \epsilon = E_0 / k_B T \quad \text{and}$$

μ is the nuclear mass (M)/neutron mass. For heavier metals $f_p(Q)$ can be neglected, but it is important for light elements. It has to be known accurately at low angles where $S(Q)$ and $f_p(Q)$ become comparable.

2.6 The Multiple Scattering of Neutrons

The method used to calculate the multiple scattering was that due to Blech and Averbach (1964).

The solution for multiple scattering of neutrons by infinite slabs of an isotropic scatterer has been derived by Vineyard. He calculated the second order scattering and then estimated the total multiple scattering. Blech and Averbach used the same approach as Vineyard for the case of cylindrical samples completely bathed in a homogeneous neutron beam. The scattering is shown in figure (2.1). The number of neutrons per unit solid angle scattered from a volume dV for an incoming flux J_0 is given by

$$dI_1 = \frac{1}{4\pi} (N_v \sigma_s J_0) e^{-\mu L_1} dV \quad (2.14)$$

where N_v is the number of atoms per cm^3 , σ_s is the scattering cross-section, μ the total absorption and L_1 is the path length of the incoming beam. The total primary scattering I_1 of neutrons for solid angle is given by

$$I_1 = \int_V e^{-\mu L_1} dI_1 \quad (2.15)$$

when L_1 is the path length of the scattered beam.

The secondary intensity from a volume element dV' is given by

$$dI_2 = \left\{ N_v \sigma_s \int \frac{dI_1}{4\pi L^2} e^{-\mu L} dV \right\} dV' \quad (2.16)$$

and the total secondary intensity I_2 is

$$I_2 = \int_V e^{-\mu L''} dI_2 \quad (2.17)$$

Similarly the n th order scattering will be

$$I_n = \int_V e^{-\mu L''} dI_n \quad (2.18)$$

where

$$dI_n = \left\{ N v \sigma_s \int \frac{dI_{n-1}}{4\pi L^2} e^{-\mu L} dV \right\} dV' \quad (2.19)$$

The total scattering is

$$I = \sum_1^{\infty} I_n \quad (2.20)$$

$$\text{Assuming } I_n / I_{n-1} = I_2 / I_1 = \delta' \quad (2.21)$$

the multiple scattering I_m is

$$I_m = I - I_1 = I_2 + I_3 + \dots = I_1 (\delta' / 1 - \delta') \quad (2.22)$$

This equation is true whenever I_2/I_1 is appreciably smaller than unity.

It follows that

$$\delta' = \frac{I_2}{I_1} = \frac{N v \sigma_s}{\mu} \delta = \left(\frac{\sigma_s}{\sigma_t} \right) \delta \quad (2.23)$$

where

$$\delta = \frac{2\mu}{\pi R^2 h} \int_{r=0}^R \int_{r'=0}^R \int_{\theta=0}^{\pi} \int_{z=0}^h \int_{z'=0}^{h-z} \frac{e^{-\mu L}}{L^2} \quad (2.24)$$

$$\text{and } L^2 = z'^2 + r^2 + r'^2 - 2rr' \cos \theta$$

σ_t is the total cross-section (scattering plus absorption).

Then if the multiple scattering cross-section is σ_m we have

$$\sigma_m = \frac{\sigma_s (\sigma_s / \sigma_t) \delta}{1 - (\sigma_s / \sigma_t) \delta} \quad (2.25)$$

The integral in δ is obtained by summing over the two disks.

The quantity finally evaluated is

$$1 + \frac{\sigma_m}{\sigma_s} = \frac{1}{1 - (\sigma_s / \sigma_t) \delta} = 1 + \Delta \quad (2.26)$$

When deciding upon sample size values of R/h were chosen so as to minimize the multiple scattering.

2.7 Sample Absorption and Container Corrections

The corrections due to absorption by the sample and scattering by the container were computed together using the method outlined by Paalman and Pings (1962).

If I denotes a theoretical intensity and I^E the experimental intensity then for scattering off just a container $I_c^E = A_{c,c} I_c$ where $A_{i,j}$ is the absorption factor for scattering in i and the total absorption in j . For a sample in a container we have

$$I_{sc}^E = A_{c,sc} I_c^E + A_{s,sc} I_s \quad (2.27)$$

where sc means sample and container. The true scattered intensity from the sample is given by

$$I_s = \frac{I_{sc}^E}{A_{s,sc}} - \frac{I_c^E A_{c,sc}}{A_{s,sc} A_{c,c}} \quad (2.28)$$

The $A_{i,j}$'s were computed by integrating over all path lengths in the sample and container as described in the paper by Paalman and Pings.

The use of the corrections, described in Sections (2.5), (2.6) and (2.7), to obtain structure factors is illustrated in Chapter 4 and Chapter 5. In Chapter 3 the apparatus and experimental method is described.

CHAPTER 3

Experimental

3.1 Introduction

This chapter deals briefly with the neutron diffraction apparatus, and also deals with the furnace which was used to maintain the samples above their melting points.

The neutron spectrometer and spectrometer control system which were used, form part of the standard Harwell equipment, and no contribution was made to their design or development. The sample holders were designed by the author, and the top plate of the furnace was modified by the author so that samples with high vapour pressures could be used.

3.2 The Neutron Spectrometer

3.2(i) A General Description

The general layout of most crystal spectrometers is similar, and a schematic form is shown in figure (3.1). Neutrons which have a Maxwellian distribution of velocities appropriate to the temperature of the moderator are extracted from the reactor by means of an in-pile collimator. This 'white' radiation impinges on a crystal monochromator which diffracts neutrons of a particular wavelength λ_0 (usually $\sim 1 \text{ \AA}$) at an angle $2\theta_m$, when the Bragg condition for the diffracting planes is satisfied. These mono-energetic neutrons are then used in diffraction experiments, where the neutrons scattered from the sample are detected at an angle 2θ , the maximum scattering angle being about 100° .

Experiments were carried out at the Dido research reactor at Harwell. Four spectrometers were used. These were the Curran, Badger I and Badger II (used for low angle work), and the 10H 'liquids' spectrometer. It is proposed here to give a brief description of the Dido 10H spectrometer (Hance 1973), figure 2.2. This machine was used entirely for elastic scattering $[S(Q)]$.

3.2(ii) The Monochromator

The monochromator consisted of a rectangular aluminium crystal capable of rotation about a vertical axis. It provided mono-energetic neutrons in the range 0.5 to $1.4 \text{ \AA}$. For example, the planes (111), (220) and (311) gave wavelengths of $1.4 \text{ \AA}$, $0.84 \text{ \AA}$ and $0.73 \text{ \AA}$ respectively. The longest wavelength used was $1.2 \text{ \AA}$ (200) which contained no more than 3% second order contamination ($0.6 \text{ \AA}$). The wavelength generally used was $0.84 \text{ \AA}$ which, on this

machine, gave a Q range of 1 to $13 \text{ \AA}^{-1}$, and the second order was undetectable. Shorter wavelengths than this were not used because of the low intensities and long counting times.

3.2(iii) Neutron Beam Collimation

Primary collimation from the monochromator was provided by a set of steel ~~sol~~er slits with separation of about 5 mm giving a resolution of 0.5° . The total aperture was 7 cm by 4 cm. The monochromated beam was sampled by a parallel plate fission chamber, called a monitor, which drove a ratemeter giving a visual indication of the primary beam. The beam size could be altered by means of a pair of cadmium slits situated just after the monitor.

3.2(iv) The Counters

Thermal neutrons are detected via the secondary products produced by their absorption in nuclei. These recoil particles are detected either by ionising a gas or by producing light flashes in a scintillating medium. In Helium-3 proportional counters the reaction may be written as



Figure 2.3 shows a block diagram of the typical arrangement of a counting assembly. The amplifier is usually composed of two sections, a pre-amplifier unit with a fixed gain and a main amplifier section. The amplified pulses are applied to an amplitude discriminator (to separate neutron pulses from the smaller γ -ray pulses) whose output is fed into a counting unit (scaler) and a ratemeter. After reaching a pre-determined number of monitor counts the contents of the scalers were printed out on paper roll and punched on paper tape.

On the Dido 10H spectrometer there were three two-atmosphere Helium-3 detectors. They were mounted 40° apart and scanned from -15° to $+125^\circ$ (w.r.t. the straight through position $2\theta = 0$), with an overlap of 5° . At the start of a run the starting angle, interval and range of scan were fed into the machine memory. Each position was then scanned automatically for a pre-set number of monitor counts until the run was completed.

The role of Soller slit collimators in neutron diffraction work is usually to limit the horizontal divergence of the beam, thus increasing the angular resolution. A compromise is made between the intensity of the diffraction pattern and its resolution (Bacon, 1962). Fine collimation was provided at the counters by a set of Soller slits 15" long and $2\frac{1}{4}$ " high; defining an aperture of $\frac{1}{2}^\circ$.

To protect the counters from stray neutrons and γ -rays they were individually wrapped in cadmium foil. The counter shield was manufactured from tightly fitting Jabroc sections encased on the outside with boral plate. With this shielding the background rate of counting was about one count per second. A graph showing the resolution of the Liquids diffractometer is indicated in figure 3.2c. To determine the resolution a standard nickel sample was used and the quantity plotted is the full width at half-height for the characteristic nickel peaks. If α_1 , α_2 and α_3 denote the collimation angles of the in-pile, pre- and post-sample collimators respectively then Coglioti et al. (1958) conclude that for a good compromise between resolution and intensity $\alpha_1 \leq \alpha_2 < \alpha_3$, with the mosaic spread of the collimator matching $\frac{1}{2}(\alpha_1^2 + \alpha_2^2)^{\frac{1}{2}}$. The resolution of the Curran is better than that of the Liquids diffractometer because:

- (1) the Curran has better collimation at the counter
(α_3 Curran = $15'$ and α_3 Liquids = $45'$) and,
- (2) the take-off angle from the Curran monochromator is 45° ,
whereas for the Liquids machine it is about 15° .

This means that with the Curran we are usually operating nearer the focussing position than with the Liquids machine.

3.3 The Furnace and Sample Holders

3.3(i) The Furnace

The furnace itself was inherited from Sheffield University, but the author was responsible for modifying the top-plate so that samples with high vapour pressure could be held in alumina tubes. With the heating elements used the furnace was capable of temperatures of up to 1250⁰ C.

The shell of the furnace is shown in figure (3.3). The casing was made of aluminium, whilst the top-plate, base plate and funnel were made of brass. To cool the outer shell water jackets were used around the casing and funnel, and a brass pipe ran around the top-plate. The water outlets were joined by plastic piping and water was made to flow in at the bottom of the furnace and out at the top to prevent the formation of air blocks.

The heater was made of tantalum and made of two half-cylinders (figure 3.4) joined at the bottom by a wide tantalum ring. It could take currents of up to 200 amps (r.m.s.). The power dissipated in the heater was 900 watt at 1200⁰C and heat losses were reduced by reflection from a set of three tantalum radiation shields arranged concentrically around the heater. There were also two sets of semi-circular shields clamped to the electrodes above the heating element. For some runs vanadium heat shields were used since these did not give peaks in the diffraction pattern.

3.3(ii) The Power Supply

Power to the furnace was supplied from the 30V secondary of an 8 : 1 step down transformer; there was a 20 amp fuse on the input side and no fuse on the output side. A furnace trip was incorporated in the system in case the water supply failed.

Flexible copper braid capable of carrying the maximum current connected the transformer secondary to the water cooled electrodes of the furnace (figure 3.5).

3.3(iii) The Furnace Performance

All temperatures were measured using cromel-alumel thermocouples connected to a chart recorder, and by using two thermocouples the temperature difference along the axis of the heater was found to be less than 5°C . The furnace temperature was controlled by means of a current switching device and was maintained at the required temperature to about $\pm 5^{\circ}\text{C}$.

The furnace was maintained at temperatures of 1200°C for up to 48 hours; the vacuum was from 10^{-5} to 10^{-6} torr. The furnace did not show signs of deterioration after a run under normal circumstances; it only did this if a sample broke whilst the furnace was hot.

3.3(iv) The Sample Containers

The sample containers were either quartz or alumina tubes which had been machined down to about half the normal wall thickness (i.e. to about 0.5 mm). The quartz tubes holding the sample were sealed off under argon. The alumina tubes were fitted with a metal cap and sealed by welding in an argon environment.

Because the cap was stuck with araldite a large funnel was welded on to the top plate so that the cap remained cool and the glue did not melt.

The tubes were held by supports made of stainless steel (figure 3.6).

Figure 3.7 is a photograph of the furnace and radiation shields. Figure 3.8 is a photograph of the inside of the furnace.

3.4 The Experimental Procedure

In order to determine the structure of a liquid sample experiments were carried out in the following sequence:

- (1) a background run (air scattering) which lasted for about $\frac{1}{2}$ day:
- (2) a vanadium calibration run (using a vanadium rod) $\sim$ 1 day:
- (3) an empty tube held in the furnace under vacuum and at the correct temperature, $\sim$ 1 day:
- (4) the sample held in the furnace at the correct temperature and contained in the calibrated tube (3), $\sim$ 2 days:
- (5) a background run to see if the background scattering has changed with time, $\sim$ $\frac{1}{2}$ day.

This procedure, whereby each of these runs is completed before the next is begun, seems to be the most suitable for furnace work. Although sample changers are used for aqueous solutions work, it is considered that furnaces are at present too large for this method to be possible.

There is, however, one very important improvement which must be made to the experimental method, and this involves the alignment of samples in the neutron beam. Unfortunately, the neutron beam is not homogeneous, so that it is necessary for the sample, container and vanadium rod to be located in exactly the same position in the neutron beam. In this way the sample + container, and container, will see the same neutron intensity profile. Account should also be taken of the smaller width of the vanadium rod compared to most samples; to compare the integrated intensities received by the vanadium rod and samples the beam profile must be accurately known.

In these experiments the samples were aligned using a photographic method. Cadmium was placed around the sample which was then photographed using a scintillation camera. The image of

the cadmium was aligned centrally in the beam using the tilting device (shown in figure 3.3), and the sample was then rotated through 90° and the procedure repeated. This method is only accurate to about ± 1 mm. If more accurate data than those reported here is required then a more accurate method will have to be devised.

CHAPTER 4

The Structure Factors and Radial Distribution Functions of some Liquid Chalcogens

4.1 Introduction

Although this work is concerned with the structure of liquid semiconductors it is important to consider the situation for pure liquid chalcogens.

The structure factor $S(Q)$ can be obtained from diffraction experiments, where the most common radiation probes are X-rays and neutrons. The radial distribution function $g(r)$ is available through Fourier Transformation of $S(Q)$. The procedure used for the analysis of, and corrections to, the experimental data is almost identical to that described by North, Enderby and Egelstaff (1968 a,b), and in particular involves the use of vanadium as a calibration material.

The experimental results for the liquid chalcogens tellurium, selenium and sulphur are presented here, together with results for some tellurium-selenium mixtures. An attempt has been made to interpret the results in terms of structural models. Results are also presented for some computer simulations involving the packing of rigid chains in three dimensions.

4.2 The Theory

For pure liquids the structure factor $S(Q)$ and the radial distribution function $g(r)$ are defined and related by

$$S(Q) = \frac{1}{N} \left\langle \left| \sum_{i=1}^N \exp(jQ \cdot \underline{r}_i) \right|^2 \right\rangle \quad (4.1)$$

$$S(Q) = 1 + \frac{4\pi N}{Q^2 V} \int_0^\infty [g(r) - 1] r \sin Qr dr \quad (4.2)$$

(see Appendix A)

where N is the number of atoms in the volume V , $\underline{r}_i$ is the position of the i th atom $|\underline{Q}| = \frac{4\pi}{\lambda} \sin \theta$ and $r = |\underline{r}_n - \underline{r}_m|$. $\langle \rangle$ denotes a time average and λ is the wavelength of the radiation scattered through an angle 2θ . By inverting equation (4.1) we see that $g(r)$ may be obtained from $S(Q)$ through

$$g(r) = 1 + \frac{1}{2\pi^2 n r} \int_0^\infty [S(Q) - 1] Q \sin Qr dQ \quad (4.3)$$

where n is the number of atoms per unit volume. Since $g(r) \rightarrow 0$ as $r \rightarrow 0$ because of the atomic size we have

$$\int_0^\infty [S(Q) - 1] Q^2 dQ = -2\pi^2 n \quad (4.4)$$

An experimentally determined $S(Q)$ must satisfy equation (4.4).

At large values of Q , $S(Q)$ approaches the asymptotic value of unity. This corresponds to the isotropic scattering expected from an independent atom. On the other hand at low values of Q

4.3 The Determination of the Structure Factor

$S(Q)$ can, in principle, be obtained by measuring the angular distribution of intensity scattered from a sample.

However, a number of correction terms have to be applied to the intensity before a reliable $S(Q)$ emerges. (See Chapter 2)

The observed intensity I at any particular angle is given by

$$I = \alpha(\theta) \left[\sum_n J_{n \text{ coh}} + \sum_n J_{n \text{ inc}} \right] \quad (4.6)$$

where $n = 1, 2, 3$ etc. and J_n is the n th order scattered current and is in absolute units. $\alpha(\theta)$ is a machine constant. Following sect. 2.4 we have

$$J_i = \gamma(\theta) \left(\frac{d\sigma}{d\Omega} \right)_{\text{eff}} \quad (4.7)$$

where $\gamma(\theta)$ is an absorption correction. Equation (4.6) becomes

$$I = \alpha(\theta) \gamma(\theta) \left[\left(\frac{d\sigma}{d\Omega} \right)_{\text{eff}}^{\text{coh}} + \left(\frac{d\sigma}{d\Omega} \right)_{\text{eff}}^{\text{inc}} + \left(\sum_2^{\infty} J_n^{\text{coh}} + \sum_2^{\infty} J_n^{\text{inc}} \right) \gamma^{-1} \right] \quad (4.8)$$

where $\left(\sum_2^{\infty} J_n^{\text{coh}} + \sum_2^{\infty} J_n^{\text{inc}} \right)$ is the multiple scattering.

Incorporating the Placzek corrections we have

$$\left(\frac{d\sigma}{d\Omega} \right)_{\text{eff}}^{\text{coh}} = N \langle f \rangle^2 [S(Q) + f_p(Q)] \quad (4.9)$$

$$\left(\frac{d\sigma}{d\Omega} \right)_{\text{eff}}^{\text{inc}} = N (\langle f^2 \rangle - \langle f \rangle^2) (1 + f_p(Q)) \quad (4.10)$$

(see equation (2.11) and (2.12)).

Combining (4.8), (4.9) and (4.10) we have

$$I = N \alpha(\theta) \gamma(\theta) \left[\sigma_c (S(Q) - 1) + \sigma_s (1 + f_p(Q)) + \text{multiple} \right] \quad (4.11)$$

since $\sigma_c = \langle f \rangle^2$ and $\sigma_s = \langle f^2 \rangle$.

We now replace σ_s by $\sigma_s(1 + \Delta_s)$ to account for multiple scattering (see equation 2.26).

The scattering from the sample may now be written

$$I_s = N_s \alpha(\theta) \gamma(\theta) \left[\sigma_c (S(Q) - 1) + \sigma_s (1 + f_s) (1 + \Delta_s) \right] \quad (4.12)$$

The multiple scattering and Placzek corrections were calculated as described in Chapter 2, and the extraction of I_s from the total scattering is described in 2.7.

A second experiment using a vanadium rod was performed under identical experimental conditions. The scattering from vanadium is entirely incoherent and the scattered intensity may be written

$$I_v = N_v \alpha(\theta) \gamma'(\theta) \sigma_{i_v} (1 + f_v) (1 + \Delta_v) \quad (4.13)$$

By dividing equation (4.12) by equation (4.13) $\alpha(\theta)$ was eliminated and $S(Q)$ was found. The absorption constants γ and γ' are the same as A_s , σ_c and A_v described in 2.7 and were calculated by the method of Pøalman and Pings (1962).

the macroscopic properties of the liquid are reflected (see Landau and Lifshitz, 1958), so that

$$S(0) = nk_B T \chi_T \quad (4.5)$$

where χ_T is the isothermal compressibility at the absolute temperature T . Between these limits $S(Q)$ exhibits an oscillatory behaviour which is a direct consequence of the short range order present in a liquid.

4.4 The Experimental Results.

All the experiments on the Liquid Chalcogens were carried out on the Dido reactor at Harwell, and a summary of the experimental conditions is given in Table 2. All the corrections described were carefully carried out in the analysis of the data. The purity of the samples was in all cases greater than 99.9%. The cross-sections used and the structure data are tabulated in Appendices (B) and (C) respectively.

4.4 (i) The Structure Factors for Liquid Tellurium (m.p. 450°C)

Structure factors for Liquid Te at 500°C and 800°C are shown in figure 4.1. Cylindrical quartz tubes were used as sample containers as these were not corroded by the sample at the temperatures used (quartz was preferred to alumina since it does not give sharp peaks in the diffraction pattern). The tellurium sample was maintained under an inert atmosphere of argon to reduce the rate of evaporation of the sample; the pressure used was one third atmosphere at 20°C (for selenium and sulphur the pressures were 0.5 and 0.8 atmospheres respectively).

For the high angle work (on the Liquids diffractometer) a diffraction pattern was taken from a quartz tube with the same wall thickness as that used to contain the tellurium, and this pattern was then subtracted from the diffraction pattern of sample + container (see 2.7). In all the other experiments the containers were individually calibrated before being loaded with a sample.

It was found that the best results were obtained by hand-smoothing the data before the final analysis. The small oscillations at high Q became better defined when this was done, rather than when the data was processed with all the statistical errors included in it. High and low angle work was done on the Liquids and Badger diffractometers respectively.

TABLE 2

Liquid	Temp. °C	Sample	Instrument	Q-range
Te	500	9 mm cylinder in .5 mm quartz	DIDO Liquids	1.5 - 11
	500	"	DIDO Badger	0.5 - 2.5
	800	"	DIDO Liquids	1.5 - 11
	800	"	DIDO Badger	0.5 - 2.5
Se	230	"	DIDO Liquids	1.5 - 13
	230	"	DIDO Badger	0.5 - 2.5
	350	"	DIDO Liquids	1.5 - 13
	350	"	DIDO Badger	0.5 - 2.5
S	150	10 mm cylinder in .5 mm quartz	DIDO Liquids	1.0 - 8
	400	"	DIDO Liquids	1.0 - 8
Se _{.5} Te _{.5}	500	11 mm cylinder in 1 mm quartz	DIDO Liquids	1 - 8.5
Se _{.95} Te _{.05}	500	"	DIDO Liquids	1 - 8.5

EXPERIMENTAL CONDITIONS FOR THE LIQUID CHALCOGENS

4.4 (ii) The Structure Factors for Liquid Selenium (m.p. 217°C)

Structure factors are shown in figure (4.3) at 230°C and 350°C. These were deduced from both high and low angle measurements, and the overlap from the two measurements and the statistical errors are shown in figure (4.2).

4.4 (iii) The Structure Factors for Liquid Sulphur (m.p. 119°C)

Due to the low neutron scattering from liquid sulphur measurements were taken at a wavelength of 1.2 Å on the Liquids Machine (fig. 4.4). This wavelength was associated with a higher flux than that used for liquids Te and Se (0.84 Å) but had a lower range in Q. No low angle work was attempted on liquid sulphur because of the low neutron scattering cross-section.

4.4 (iv) The Structure Factors for Liquid $\text{Te}_{1-x}\text{Se}_x$ where $x = 0.5$ and 0.05

Both these experiments were carried out at 500°C on the Dido Liquids Machine and the results are shown in figure (4.5). The quantity obtained is the total structure factor $F(Q)$ (equation (4.21)). The extraction of $F(Q)$ from the experimental data is described in (4.12).

4.5 Experimental Errors

As stated by North, Enderby and Egelstaff (1968) random errors (i.e. those due to counting statistics) are relatively unimportant (except at small Q). The real difficulties arise from systematic or calibration errors, particularly in the determination of $\alpha(\theta)$.

To see how these systematic errors can affect the final answer, North considered two structure factors $S_1(Q)$ and $S_2(Q)$ calculated from

$$\begin{aligned} I_1(Q) &= \alpha_1(S_1(Q) + \Delta_1) \\ I_2(Q) &= \alpha_2(S_2(Q) + \Delta_2) \end{aligned} \quad (4.14)$$

Setting $I_2(Q) = I_1(Q) \pm \epsilon$ $\alpha_2 = \alpha_1(1 \pm 0.05)$

(for a typical calibration error of 5%).

North finds

$$(1 \pm 0.05) \left\{ \frac{S_2(Q) + \Delta_2}{S_1(Q) + \Delta_1} \right\} = 1 \pm \frac{\epsilon}{I_1} \quad (4.15)$$

Two regions of Q space may be distinguished.

(i) $Q \geq 2 \text{ \AA}^{-1}$ In this region ϵ / I_1 is usually small and, since $S_2(Q)$ and $S_1(Q)$ approach unity as $Q \rightarrow \infty$ we find from (4.15) that

$$S_1(Q) - 1 = (1 \pm 0.05)(S_2(Q) - 1) \quad (4.16)$$

provided Δ is isotropic.

(ii) $Q < 2 \text{ \AA}^{-1}$ Here I is small so that ϵ / I_1 is large and statistical errors begin to dominate the problem. The statistical and systematic errors are indicated in Table 3.

TABLE 3

Experimental Errors in S(Q) and F(Q)

Liquid	Temp °C	$0 < Q < 2 \text{ \AA}^{-1}$	$2 < Q < 13 \text{ \AA}^{-1}$	
		Total Error	Systematic Error	Random Error
Te	500	± 0.02	$(1 \pm 0.05)(S(Q)-1)$	± 0.015
	800	± 0.02		
Se	230	± 0.02	$(1 \pm 0.05)(S(Q)-1)$	± 0.02
	350	± 0.02		± 0.02
S	150	± 0.05	$(1 \pm 0.05)(S(Q)-1)$	± 0.04
	400	± 0.05		± 0.04
$\text{Te}_{1-x}\text{Se}_x$	500	± 0.02	$(1 \pm 0.05)F(Q)$	± 0.015

4.6 The Radial Distribution Functions for Liquids Te, Se and S

4.6 (i) Method of Calculation

The radial distribution function is related to $S(Q)$ through equation (4.3). A smooth curve was drawn through the experimental values of the structure factor and the curve tabulated in steps of $0.05 \text{ \AA}^{-1}$ in Q . The numerical transform was performed using a standard Fourier Transform routine. For reasons which will become clear in section 4.6(ii) a second radial distribution function $g_w(r)$ was calculated for each liquid through

$$g_w(r) = 1 + \frac{1}{2\pi^2 nr} \int_0^\infty [S(Q) - 1] w(Q) Q \sin Qr dQ \quad (4.17)$$

where $w(Q)$, a "window" function, is defined by

$$w(Q) = \frac{1}{2} \left[1 + \cos \left(\frac{\pi Q}{Q_m} \right) \right] \quad (4.18)$$

and Q_m is the maximum value of Q for which data was taken.

4.6 (ii) The Influence of Systematic, Random and Truncation Errors

The form of $g(r)$ is dominated by the Q space data beyond $2 \text{ \AA}$ (North, Enderby and Egelstaff, 1968), so that the uncertainty in $g(r)$ from calibration errors can be calculated directly from the scale factor shown in the fourth column of Table 3. The random errors give rise to errors in the transform which appear as increasingly violent oscillations in $g(r)$ as r tends to zero.

There is a third major source of error which is particularly severe for the liquid chalcogens, namely, the need to truncate the integral in equation (4.3) at Q_m ($\sim 12 \text{ \AA}^{-1}$ in these experiments).

The structure factors of all three chalcogens oscillate strongly at Q_m (the strongest being liquid selenium) so that putting $(S(Q)-1) = 0$ for $Q > Q_m$ in equation (4.3) leads to severe truncation errors. These appear as high frequency oscillators throughout $g(r)$. (i.e. the transform of a step function) The problem is to decide which features in the $g(r)$ are due to truncation and which represent real structure.

Ideally, measurements should be continued out to much higher values of Q using, for example, the LINAC facility at Harwell (Sinclair and Dore, 1972). But until such measurements are made we have adopted a scheme which allows those features in $g(r)$ which represent true structure to be identified. $S(Q)$ was first multiplied by a window function and then transformed. An example of $g_w(r)$ for liquid selenium is given in figure (4.7). A comparison with figure (4.6) shows that certain features have disappeared. These features must be truncation errors and were eliminated from $g(r)$, which was then back-transformed to $S(Q)$. This last step was iterated until the experimental data were reproduced.

Radial distribution functions produced by the above method are shown for liquid Te (figure 4.8), liquid Se (figure 4.9) and S (figure 4.10).

4.6 (iii) Comparison with previous work

The $g(r)$ for liquid Se is in general agreement with the results of Moscinski, Renninger and Averbach (1973). A similar comparison holds when the data for liquid sulphur is compared with data due to Thompson and Gingrich (1959). In the case of liquid Te, however, the $g(r)$ found differs from that due to Tourand and Brueil (1971), figure (4.11). A comparison can be made between

the $g(r)$ given here at 500°C and theirs at 675°C. Tourand and Breuil have in addition to peaks at 3.01 and 4.52 Å a peak at 3.82 Å. We at Leicester believe that this last peak is due to truncation errors, and does not represent real structure. (see 4.8(ii))

In the following sections possible structural models are outlined for liquid Te and liquid Se.

4.7 Non-Central Forces

The structure of liquid chalcogens cannot be explained in terms of simple pair forces. This is clear from an examination of the structure factors given here.

For hard spheres $g(r)$ has a sharp edge at the hard sphere diameter. However, $g(r)$ for real liquids has a finite slope where the atoms overlap. As a result of this $S(Q)$, for real liquids, obtained by Fourier Transformation of $g(r)$, has oscillations to high Q which are damped out more rapidly than $S(Q)$ for a hard sphere liquid. It is also expected that these oscillations will move out of phase with respect to hard sphere oscillations as the damping increases. This has been demonstrated by Page et al. (1969) who compared $S(Q)$'s for liquids argon and rubidium. It was observed that the oscillations for rubidium were damped out more rapidly than those for argon, and there was a more pronounced phase shift. This is consistent with the rather soft inter-atomic potential which characterises alkali metals.

For the chalcogens tellurium, selenium and sulphur there are large deviations from the behaviour of hard spheres. There is less damping in the $S(Q)$ for selenium than for hard spheres, and since the hard sphere damping is a minimum for simple liquids, selenium cannot be discussed in terms of central pairwise interactions. This argument also applies to liquid tellurium.

Hence theories for the structure of liquid chalcogens must be discussed in terms of non-central forces. Possible models involve rings, chains and other bonded structures. Computer models for chains and molecules were produced using a Monte-Carlo method, and structure factors were determined for these models. These models provided some assistance in the interpretation of the experimental data for the chalcogens and for the binary systems.

4.8 The Computer Models

Computer models were produced to represent closely packed 3-dimensional systems of: (a) short chains, and (b) molecules. Structure factors were then determined for these models so that comparisons could be made with the structure factors obtained by diffraction experiments. The computer which was used was the ICL 4130 at Leicester University. The method used involved the use of random numbers i.e. a Monte-Carlo method.

4.8 (i) Chain Models

Three-dimensional chain models were produced within the computer memory, with up to three atoms per chain. The chains were either rigid or flexible. The main problem which was encountered was to make the chains pack closely to each other. This was done by building the model outwards from a central chain as indicated in figure (4.13a). The steps were as follows:

(1) The first chain was produced with successive atoms in contact with each other. The orientation of all the chains with respect to the co-ordinate system was chosen at random i.e. values of θ^c and ϕ^c were generated by the expressions:

$$\begin{aligned} \theta^c &= \text{random number} \times \pi \\ \text{and } \phi^c &= \text{random number} \times 2\pi \end{aligned}$$

where the random numbers lie between 0 and 1. For rigid chains

Θ and ϕ were constant along the chain, and for flexible chains they were allowed to vary continuously between well defined limits.

(2) A second chain was produced so that its first atom lay between the distances $2R$ and $2R + A$ of the atom numbered one. This is equivalent to the box potential of figure (4.13)b. Other chains were produced from the first atom in the same way, and subject to the condition that no atoms overlapped. One thousand attempts were made to produce chains from a given atom, so as to saturate the volume with chains.

(3) Other chains were produced from atoms 2,3,4... etc. and a structure was built up from chain units.

If equations A.4 and A.7 are combined we have a relationship between the co-ordinates of the atoms in the model and the structure factor of the model.

$$S(Q) = 1 + \sum_{m,n}' \frac{\sin Q r_{mn}}{Q r_{mn}} \quad (4.19)$$

To reduce truncation errors, due to the finite size of the models, a window function was used.

$$S(Q) = 1 + \sum_{m,n}' \frac{\sin Q r_{mn}}{Q r_{mn}} \omega(r) \quad (4.20)$$

$$\omega(r) = \frac{1}{2} \left[1 + \cos \left(\frac{\pi r}{r_{\max}} \right) \right] \quad r \leq r_{\max}$$

and $\omega(r) = 0$ for $r > r_{\max}$.

The computer memory held all the co-ordinates of the atoms, and the computer programme determined the distances r_{mn} and calculated $S(Q)$ from equation (4.20).

Two values of the radius of an atom were used, namely 1.7 and 1.1, to represent tellurium and selenium respectively. Also, the width, A, of the potential was varied to alter the packing density of the chains.

Figures (4.14), (4.15) and (4.16) show structure factors for rigid chains of three atoms, where the value of A has values of 0.5, 1.7 and 3.4 respectively. The first peak is at a Q value of 2.0, corresponding to the first peak in tellurium. As A is increased this peak broadens and then splits into two peaks I and II. In figure (4.17) the radius was changed to 1.1 with A at 3.4. A Fourier Transformation of one of these curves to a radial distribution function is shown in figure (4.18).

4.8 (ii) Molecular Models (discussed in Chapter 5)

Three-dimensional computer models of closely packed molecules, of two kinds of atom, were produced. Once again the model was built up from a central molecule to ensure close packing. The models contain about 750 atoms, and a two-dimensional analogue is shown in figure (4.19). Three partial structure factors were obtained from the co-ordinates of the atoms (see equation 4.20). The two smaller atoms in the molecules were arranged at 90° to each other to represent p-orbital bonding (figure (4.13)c).

Three partial structure factors are shown in figures (4.20, a, b and c). Each structure factor has a δ -function at the origin due to the finite size of the models, but it is free of truncation errors since window functions were used.

These models were helpful with the interpretation of the experimentally determined structure factors for Cu_2Te and Ag_2Te .

4.9 The Structure of Liquid Tellurium

It has been proposed by many workers (Hodgson, 1961), Cutler and Mallon (1962), Ioffe and Regel (1960)) that liquid tellurium is a semiconductor, the semiconducting state being due to retention of the chain structure of the solid (Buschert, 1955). However, recent measurements of the Knight shift (Cabane and Froidevaux, 1969) and Hall effect (Enderby and Walsh, 1966) show that the density of conduction electrons at the Fermi level is so large that a metallic description of these states is more applicable. Cabane and Friedel analyse the structural data of Tourand and Brueil and other structure related information, such as the viscosity and inelastic scattering of neutrons. They conclude that although the interatomic forces are not of a simple pair-wise type, the theory that independent and well defined chains exist in liquid tellurium is incorrect. They favour a covalently bonded network in which the co-ordination number is between 2 and 3.

With some reservations it is felt that the theory of Cabane and Friedel (1971) does present a likely model for the structure of liquid tellurium. It is intended to discuss this model and also to suggest some modifications to it.

4.9 (i) The Theory of Cabane and Friedel

Cabane and Friedel use the structural data of Tourand and Brueil and also the electronic properties to argue against the existence of independent chains in liquid tellurium.

Three basic difficulties occur with chain models. Co-ordination numbers found experimentally for the first peak (i.e. the number of nearest neighbours) are between 2.5 and 3, whereas for independent chains this quantity would be about 2. (A random hard sphere model would give about 10 nearest neighbours). Secondly, chain models imply the existence of rather long structural

relaxation times, which is in conflict with the observed low viscosity and high diffusion coefficient and with the inelastic neutron scattering spectra. Thirdly, the density of states at the Fermi level is far too large to be explained by chain models. Knight shift and Hall effect measurements indicate $n(E_f) \sim 2.6$ electron per atom at 750°C , whereas a chain of 10 atoms would give only 0.2 "free-electrons" per atom (each chain has two unpaired electrons). It is concluded that long independent chains cannot exist in liquid tellurium.

However, a completely random structure would give much too large a co-ordination number. Cabane and Friedel propose that local order in liquid tellurium consists of sites with two or three first neighbours, joined by bonds with a strong covalent character. In space the local order persists up to the second neighbours; in time it is of short duration (relaxation time $\sim 10^{-12}$ s).

At 900°C they note that the number of nearest neighbours is 3, and they propose the structure indicated in figure (4.21). The number of second nearest neighbours is 6, and these all come into the peak at $4.52 \text{ \AA}$. There is still some space for 3 or 4 more atoms, somewhat further than the first neighbours and in opposite directions; they go into the peak at $3.82 \text{ \AA}$, figure (4.11). The model does not involve any molecules or clusters: the network of bonds extends over the whole liquid.

When the temperature is lowered from 900°C to 490°C the average number of first neighbours falls from 3 to 2.5, which suggests that near the melting point many atoms have only 2 nearest neighbours. For example, at 490°C the average co-ordination is 2.5 ± 0.2 corresponding to about equal concentration of binary

and tenary sites, figure (4.21d). The fact that the second and third peaks are quite insensitive to temperature variations is consistent with the model, since the positions and numbers of the neighbours corresponding to the second and third peaks in $g(r)$ are almost the same for binary and ~~tenary~~ sites.

This model is consistent with the observed dynamical properties of liquid tellurium.

The short lifetime of the covalent bonds explains the low viscosity, large self-diffusion coefficient and the absence of vibrational modes which give a 'smeared' spectra for inelastic neutron scattering.

The density of states proposed by Cabane and Friedel is shown in figure (4.22). At high temperatures three p-bonds are formed by each tellurium atom using up, together with the two s-states, five electrons per atom, leaving one to go into the conduction band. It is also assumed that the conduction and valence bands overlap to give a density of states of 2 to 3 electrons per atom, thus explaining the observed Hall coefficients and Knight shifts.

4.9 (ii) Modifications to the Theory of Cabane and Friedel

The radial distribution function presented here differs from that due to Tourand and Brueil in that

- (i) there is no peak at $3.82 \text{ \AA}$, and
- (ii) the third peak at $4.52 \text{ \AA}$ is much broader.

The peak at $4.52 \text{ \AA}$ is due to second nearest neighbours and its broadness is probably due to the bonds not being so rigid as those suggested by Cabane and Friedel. The absence of a peak at $3.82 \text{ \AA}$ could be due to the fact that vacancies in the structure of Cabane and Friedel at about this distance are simply not filled.

A further difficulty concerns the topology of the structure. It is not clear why ordinary hard-sphere packing cannot take place (at least between some atoms) in the Cabane-Friedel structure, figure (4.21), and so increase the co-ordination number. A possible explanation is that the directional covalent bonds draw the atoms together to a distance less than that for normal random packing, so that if this occurs it does not affect the number of nearest neighbours.

The co-ordination number for nearest neighbours was found to be 3.0 ± 0.5 at 500°C and 800°C . This is similar to the value quoted by Tourand and Breuil but does not support their temperature dependent co-ordination numbers.

The computer models indicate that liquid tellurium does not consist of short rigid chains, since structure factors obtained for these do not resemble those for liquid tellurium. This is also apparent from the $g(r)$'s for liquid tellurium.

Evidence that the peak in the French $g(r)$ at $3.82 \text{ \AA}$ does not represent real structure is indicated in figure (4.12). It is shown that the experimental data can be regenerated by back-transforming the French $g(r)$ for liquid tellurium without this peak.

It is concluded that liquid tellurium has a network structure of some description. It certainly does not consist of chains, or of completely random packing as found in liquid metals.

4.10 The Structure of Liquid Selenium

The structural data for liquid selenium at 230°C and 350°C is interpreted to consist mainly of flexible chains. Some rings may be introduced into the structure at 350°C.

Consider the radial distribution functions of figures (4.9) and (4.7). The first peak is well defined and gives a co-ordination number of 2.0 ± 0.1 , which would be the same for rings or chains. The second peak in $g(r)$ is also well defined, and rather stronger at 350°C than at 230°C. But there is almost a complete absence of structure after the second peak, and this can be explained by a flexible chain model and not by a ring model, (as indicated in figure (4.23)). It is seen that in 6-membered rings there would be three well defined distances, and these are not found experimentally. However, flexible chains would have only two well defined distances. Because of the rotation of the atoms about the bonds the third distance in $g(r)$ is not well defined. Hence, a flexible chain model is in agreement with the experimental results. These chains must be long to explain the low conductivity of liquid selenium, which is an insulator. Some structure beyond the second peak does appear at 350°C, which could indicate some ring formation as the temperature is increased. Viscosity measurements on liquid selenium show that this quantity is always an order of magnitude greater than that for monatomic liquids. This is interpreted as ring formation.

4.11 The Structure of Liquid Sulphur

The neutron diffraction measurements obtained for pure liquid sulphur at 150°C and 400°C are not as accurate as those for tellurium and selenium because of the small elastic scattering cross-section of sulphur. But it is clear that, like selenium, the $g(r)$ does have a well defined first peak, and the number of nearest neighbours is 2.0 ± 0.2 . This could suggest rings or chains for the structure of liquid sulphur. Measurements of electrical resistance versus temperature for liquid sulphur (G.C.Vezzoli, 1972) suggest that chain fission may occur as the temperature is increased, and it was noted here that the colour changed from orange (at 150°C) to black (at 400°C). A small difference in the structure factors was found at the two temperatures, but the data was not sufficient in extent or accuracy to postulate a definite structural model. To do this much better counting statistics and Q range must be obtained e.g. by using the high flux beam reactor at Grenoble in France.

4.12 The Structure of $\text{Te}_{1-x}\text{Se}_x$

The quantity which can be extracted from a single diffraction experiment on a liquid containing two species, a, b (Enderby, North and Egelstaff, 1966) is the total structure factor $F(Q)$ defined by

$$F(Q) = C_a^2 f_a^2 (S_{aa} - 1) + C_b^2 f_b^2 (S_{bb} - 1) + 2C_a C_b f_a f_b (S_{ab} - 1) \quad (4.21)$$

where C_a and C_b are the atomic concentrations of the two species, f_a and f_b are the neutron scattering lengths and S_{aa} , S_{bb} and S_{ab} are the partial structure factors which are related to the radial distribution functions for one atom type with respect to another atom type by

$$S_{\alpha\beta} = 1 + \frac{4\pi N}{V} \int_0^\infty (g_{\alpha\beta} - 1) r \sin Qr dr \quad (4.22)$$

where $\alpha, \beta = a \text{ or } b$

The total structure factor for $\text{Te}_{.95}\text{Se}_{.05}$ looks like the $S(Q)$ for pure tellurium (apart from a reduction in the height of the first peak and a broadening of the second peak), so that the addition of 5% selenium has not greatly altered the tellurium structure. However, $F(Q)$ when $x = 0.5$ looks more like the structure factor for pure selenium.

Two possible models are the substitutional model and the inhomogeneous model. For $\text{Te}_{0.5}\text{Se}_{0.5}$ the substitutional model says that the tellurium network is absorbed into the selenium structure. This was tested by putting $S_{aa} = S_{bb} = S_{ab} = S_{\text{selenium}}$ in equation (4.21)

But, as is shown in figure (4.24), this does not produce the experimental $F(Q)$. In the dilute limit, where we postulate that the selenium is absorbed into the tellurium network, this model also fails. In the inhomogeneous model we have islands of selenium in tellurium, so that in equation 4.21 we put:

$S_{aa} = S_{\text{tellurium}}$, $S_{bb} = S_{\text{selenium}}$, $S_{ab} = 1$ (assuming that there is no interaction between the atoms of tellurium and selenium).

Unfortunately, this model does not give the experimental $F(Q)$ either. (figure (4.24))

It is planned to obtain more, and better, diffraction data on tellurium - selenium mixtures. The work here was performed simply to see if there were gross deviations from the substitutional model.

CHAPTER 5

The Structure of the Liquid Semiconductors Cu_2Te , CuTe and Ag_2Te

5.1 Introduction

The existence of the isotopes ^{63}Cu , ^{65}Cu and ^{107}Ag , ^{109}Ag enables a full structural analysis to be made of the Cu-Te and Ag-Te systems. These two systems are typical of a wide range of liquid semiconducting systems, so that conclusions drawn from them may be considered to be generally valid.

The partial structure factors and partial radial distribution functions (R.D.F.'s) are presented for liquids Cu_2Te (at 1200°C), CuTe (at 700°C) and Ag_2Te (at 1000°C). These results are compared with the predictions of models involving clusters, ionic bonding, covalent bonding, and also with computer model predictions.

5.2 The Theory

Faber and Ziman (1964), for example, wrote the intensity of radiation scattered coherently from a liquid alloy as

$$I = \left\langle \sum_a \sum_b f_a f_b \exp jQ \cdot (r_a - r_b) \right\rangle \quad (5.1)$$

where f_a , f_b are the coherent scattering lengths of atoms a and b, $Q = \frac{4\pi \sin \Theta}{\lambda}$ (where 2Θ is the scattering angle) and $\langle \rangle$ denotes a time average. It follows from equation (5.1) that I may be written as

$$I = N \left\{ C_a^2 f_a^2 + C_b^2 f_b^2 + F(Q) \right\} \quad (5.2)$$

where $F(Q) = C_a^2 f_a^2 (S_{aa} - 1) + C_b^2 f_b^2 (S_{bb} - 1) + 2C_a C_b f_a f_b (S_{ab} - 1)$

C_a and C_b are the atomic concentrations of the two constituents, N is the total number of scattering atoms and S_{aa} , S_{bb} and S_{ab} are the three partial structure factors for the binary alloy.

It was the aim of the experiments to extract $S_{\alpha\beta}$ (where $\alpha, \beta = a$ or b), from the diffraction data. This can be done in principle by varying the scattering lengths of one or both of the components in such a way as to provide three total structure factors F_1 , F_2 and F_3 , which are sufficiently different to enable three linear equations to be solved for S_{aa} , S_{bb} and S_{ab} . The scattering lengths can be varied by using isotopes since neutrons are scattered from the nuclei of atoms and the scattering length depends on the make-up of the nucleus. In this work isotopes of copper and silver were used; the enrichment and scattering lengths are shown in Table 4.

The equations to be solved may be written in the matrix form

$$[A] \cdot [X(Q)] = [F(Q)] \quad (5.3)$$

$$\text{where } A = \begin{bmatrix} C_a^2 f_a^2 & C_b^2 f_b^2 & 2C_a C_b f_a f_b \\ C_a^2 (f'_a)^2 & C_b^2 f_b^2 & 2C_a C_b (f'_a) f_b \\ C_a^2 (f''_a)^2 & C_b^2 f_b^2 & 2C_a C_b (f''_a) f_b \end{bmatrix}$$

$$[X] = \begin{bmatrix} (S_{aa}-1) \\ (S_{bb}-1) \\ (S_{ab}-1) \end{bmatrix} = \begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix}$$

TABLE 4

Isotope	Enrichment	Scattering Length 10^{-12} cm
Cu ^{nat}	-	0.76
Cu ⁶³	99%	0.67
Cu ⁶⁵	99%	1.11
Ag ^{nat}	-	0.61
Ag ¹⁰⁷	99%	0.83
Ag ¹⁰⁹	99%	0.43
Te ^{nat}	-	0.54

SCATTERING LENGTHS OF THE ISOTOPES

TABLE 5

Liquid	Temp ^o C	Sample	Instrument	Q-range $\text{\AA}^{-1}$
CuTe	700	9 mm diameter cylinder in quartz 0.5 mm thick	DIDO Liquids	1.1 - 12.8
	700	9 mm cylinder in 0.5 mm quartz	DIDO Curran	0.6 - 2.7
Cu ₂ Te	1200	9 mm cylinder in 0.5 mm alumina	DIDO Liquids	0.5 - 12.5
	1200	9 mm cylinder in 0.5 mm alumina	DIDO Badger	0.2 - 3.3
Ag ₂ Te	1000	6.25 mm cylinder in 0.5 mm alumina	DIDO Liquids	0.8 - 7

EXPERIMENTAL CONDITIONS

$$\text{and } [F] = \begin{bmatrix} F_1 \\ F_2 \\ F_3 \end{bmatrix}$$

The formal solution of (5.2) is

$$[X] = [A]^{-1} [F] \quad (5.4)$$

and is in principle unique because $[A] \neq 0$. However, one column of $[A]$ contains identical elements which tends to make $[A]$ rather small, so that small errors in $[F]$ can produce large errors in $[X]$. In the experiments reported here, for example, the form of $[A]$ is such that the uncertainties are greatest for $[X_2]$ and least for $[X_1]$.

5.3 The Results

5.3 (i) Experimental Details

The isotopes were provided by D. Boreham at A.E.R.E. Harwell, who also prepared all the samples. The three samples of CuTe (i.e. the natural and ~~two~~ isotopes) were contained in turned-down quartz tubes, whilst the samples of Cu₂Te and Ag₂Te were contained in turned-down alumina tubes because of the higher temperatures involved. (Quartz was preferred as a container material because it does not give any sharp peaks in diffraction experiments ; alumina gives several peaks and so was a second choice). The liquids Cu₂Te and Ag₂Te did not attack the alumina at the temperatures used. All the samples were contained under argon at about 1 atmosphere pressure at the temperatures of the run. Details of the diffractometers used and the ranges of Q covered are given in Table 5.

5.3 (ii) The Extraction of the Structure Factors and Radial Distribution Functions

For binary systems the quantity obtained by neutron scattering is the total structure factor $F(Q)$ (equation 4.21). This quantity is connected to the measured intensity through the equation

$$I_s = \alpha N_s [4\pi F(Q) + \Delta + \sigma_s \Delta_s] \quad (5.5)$$

where $\Delta = C_a f_a^2 + C_b f_b^2 + \text{incoherent scattering}$.

α is the machine constant and Δ_s the multiple scattering. I_s is the scattered intensity from the sample after corrections for container scattering and absorption in the sample and container. (see equation 2.28). The incoherent scattering for the binary sample is related to the incoherent scattering intensities of the components by the relation

$$\text{incoherent scattering} = \frac{\sigma_{a \text{ inc}}}{4\pi} + \frac{\sigma_{b \text{ inc}}}{4\pi} \quad (5.6)$$

The machine constant α was found by using vanadium as a calibration material as described in 4.3. Hence an $F(Q)$ was found for each experiment. The experimental errors in $F(Q)$ are indicated in Table 6. The experimentally determined $F(Q)$'s, with the experimental errors, are shown in figures (5.1), (5.2) and (5.3).

In order to explain the numerical procedures which were used to extract the partial structure factors from $F(Q)$ let us focus attention on liquid Cu_2Te . Solutions were found to the equation

$$[X \pm x] = [A]^{-1} [F \pm f] \quad (5.7)$$

where $[f]$ is the experimental error in $[F]$ and $[x]$ the corresponding uncertainty in $[X]$. The components of $[f]$ were allowed to vary between the limits corresponding to the random error (see Table 6), and subject to the condition that no component of $[X \pm x]$ can fall outside the range defined in figure (5.4), or violate

the conditions derived by Enderby et al (1966), which are

$$C_a + C_a^2 (S_{aa} - 1) > 0 \quad (5.8)$$

and

$$C_b + C_b^2 (S_{bb} - 1) - \frac{C_b^2 C_a^2 (S_{ab} - 1)^2}{C_a + C_a^2 (S_{aa} - 1)} > 0 \quad (5.9)$$

Equations (5.8) and (5.9) are a result of the fact that the measured intensities must be positive. Values of $X_1 (= S_{CuCu} - 1)$ obtained by this procedure were determined to an accuracy shown in figure (5.5). Since S_{CuCu} was the best determined partial structure factor, smooth curves were drawn through the error bars such that the sum rule

$$\int (S_{aa} - 1) Q^2 dQ = -2\pi^2 n \quad (5.10)$$

was satisfied. By choosing any one of these smooth curves, it was possible to limit the values of $[f]$ and so reduce the uncertainty in $X_3 (\equiv S_{CuTe} - 1)$. Since S_{CuTe} must itself satisfy a sum rule, equivalent to that defined in equation (5.10) the choice of possible S_{CuCu} was restricted. Partial structure factors derived from these results must yield R.D.F.'s which behave properly at small r . The best estimate of S_{CuCu} which satisfies this criterion and which is consistent with the above error analysis is shown by the dotted line in figure (5.6).

Once the form of S_{CuCu} is defined, the uncertainty in S_{CuTe} is reduced to ± 0.1 (figure 5.6). It is therefore possible to derive the cross R.D.F. which is well behaved at small r . In the case of S_{TeTe} the uncertainties which remain are substantial and the R.D.F.'s obtained by inversion are very approximate. Partial structure factors obtained by identical techniques are given in figures (5.7) and (5.8) for liquid CuTe and liquid Ag_2Te . In all cases the partial structure factors shown generate the measured $F(Q)$ within the experimental errors listed in Table 6. Partial R.D.F.'s are shown in figures (5.9), (5.10) and (5.11).

TABLE 6.

The Experimental Errors in $F(Q)$

Liquid	Temp. °C	$0 < Q < 2 \text{ \AA}^{-1}$	$2 < Q < 12 \text{ \AA}^{-1}$ *	
		Total Error	Systematic Error	Random Error
$\text{Cu}^{\text{nat}}\text{Te}$	700	± 0.01	$(1 \pm 0.1)F(Q)$	$\pm 0.01 - .02$
Cu^{63}Te	700	± 0.01	$(1 \pm 0.1)F(Q)$	$\pm 0.01 - .02$
Cu^{65}Te	700	± 0.01	"	$\pm 0.01 - .02$
$\text{Cu}_2^{\text{nat}}\text{Te}$	1200	± 0.02	"	$\pm 0.03 - .04$
$\text{Cu}_2^{63}\text{Te}$	1200	± 0.02	"	$\pm 0.03 - .04$
$\text{Cu}_2^{65}\text{Te}$	1200	± 0.02	"	$\pm 0.03 - .04$
$\text{Ag}_2^{\text{nat}}\text{Te}$	1000	-	"	$\pm 0.02 - .03$
$\text{Ag}_2^{107}\text{Te}$	1000	-	"	$\pm 0.02 - .03$
$\text{Ag}_2^{109}\text{Te}$	1000	-	"	$\pm 0.02 - .03$

* Varies from angle to angle

Values given are representative

5.4 The limit in $S\alpha\beta(Q)$ as $Q \rightarrow 0$

In a paper on the resistivity of liquid binary alloys Bhatia and Thornton (1970) derived expressions for the zero wave vector limit of the partial structure factors of Faber and Ziman (1964). The formulae are

$$S_{11}(0) = \Phi - \frac{C_2}{C_1} + A \left(\delta - \frac{1}{C_1} \right)^2 \quad (5.11)$$

$$S_{22}(0) = \Phi - \frac{C_1}{C_2} + A \left(\delta + \frac{1}{C_1} \right)^2$$

$$S_{12}(0) = \Phi + 1 + A \left(\delta - \frac{1}{C_1} \right) \left(\delta + \frac{1}{C_2} \right)$$

where $\Phi = \frac{Nk_B T K_T}{V}$, $\delta = \frac{1}{V_m} \left(\frac{\partial V_m}{\partial C_1} \right)_N$

and $A = C_2 \left\{ \frac{1}{a_1} \left(\frac{\partial a_1}{\partial C_1} \right)_{T,P} \right\}^{-1} = C_1 \left\{ \frac{1}{a_2} \left(\frac{\partial a_2}{\partial C_2} \right)_{T,P} \right\}^{-1}$

V_m is the molar volume, and C_1 , C_2 and a_1 , a_2 are the fractional compositions and thermodynamic activities of species 1 and 2 respectively. The activity a_i is defined as the ratio of the vapour pressure of the species i in the mixture to that of the pure material at the same temperature. The contribution of Φ to the partial structure factors is small and it will be neglected in further calculations involving the calculation of $S\alpha\beta(0)$.

These equations were used to fix the values of $S\alpha\beta(0)$ for CuTe, Cu_2Te and Ag_2Te . For Cu_2Te and Ag_2Te it was assumed that

A = 0. We then have

$$S_{11} = -\frac{C_2}{C_1} = -2$$

$$S_{22} = -\frac{C_1}{C_2} = -\frac{1}{2}$$

$$S_{12} = 1$$

(1 $\equiv$ Te, 2 $\equiv$ Cu or Ag)

No data was available for CuTe, but it was assumed that the thermodynamic quantities were similar to those of liquid TlTe. With this assumption we have

$$S_{11} = -0.19 + \overline{\Phi} = -0.17 \quad (\overline{\Phi} \approx 0.02)$$

$$S_{22} = -0.026 + \overline{\Phi} = 0.00$$

$$S_{12} = 0.112 + \overline{\Phi} = 0.13$$

These results for $S_{\alpha\beta}(0)$ were particularly useful in obtaining the partial structure factors for very low Q, where it was not possible to obtain experimental data.

5.5 The Partial Structure Factors for Cu₂Te, CuTe and Ag₂Te

On examination of all the partial structure factors and partial radial distribution functions of Cu₂Te, CuTe and Ag₂Te the following features become evident:

(1) the nearest neighbour distances in $g_{\text{Te-Te}}(r)$ are highly correlated in all cases. This distance is less in Cu₂Te than in CuTe.

(2) the nearest neighbour distances in $g_{\text{Cu-Te}}(r)$ and $g_{\text{Ag-Te}}(r)$ is highly correlated.

(3) the nearest neighbour distance in $g_{\text{Cu-Cu}}(r)$ for CuTe is not well correlated, but this correlation does increase slightly in Cu_2Te and Ag_2Te :

(4) the partial structure factors and R.D.F.'s are very similar to those for CuCl (Page et al 1972):

(5) $S_{\text{Cu-Cu}}(Q)$ for Cu_2Te and CuTe, and $S_{\text{Ag-Ag}}(Q)$ have only a single major peak:

(6) in all cases the cross-terms move to higher Q values than that predicted by hard-sphere interactions:

(7) there is absence of a definite feature in any of the partial structure factors for Cu_2Te corresponding to the pre-peak in $F(Q)$ at $Q = 1 \text{ \AA}^{-1}$ (in the past pre-peak maxima in $F(Q)$ have been used as evidence of long-range order):

(8) there is little to distinguish between the results for Cu_2Te and Ag_2Te , so that the same model may be used for both liquids, at least as a first approximation.

5.6 Structural Models for the Liquid Cu-Te system and for Ag_2Te

The experimental results will be discussed in terms of models for liquid semiconductors. These are cluster models, and ionic and molecular models.

5.6 (i) Cluster Models

Models based on clusters to describe liquid semiconductors have been used by Hodgkinson (1970, 1971). For the Cu-Te system we imagine that islands of semiconducting Cu_2Te are dispersed in a semi-metallic Te or vice versa. This model has been applied with considerable success to liquid semiconductors by combining the structural features of the model with ideas derived from classical percolation theory (Cohen and Sak, 1972).

In either of the two arrangements described above the structure can be represented by six partial structure factors. Let Te^{I} represent

a tellurium atom in the stoichiometric compound and Te^{II} a tellurium atom in the semi-metallic liquid (see figure 5.12). The total structure factor $F(Q)$ for the equi-atomic alloy CuTe is given by

$$F(Q) = \left(\frac{1}{2}\right) f_{\text{Cu}}^2 (S_{\text{CuCu}}^{\text{II}} - 1) + \left(\frac{1}{8}\right) f_{\text{Cu}} f_{\text{Te}} (S_{\text{CuTe}}^{\text{I}} - 1) + \frac{1}{16} f_{\text{Te}}^2 (S_{\text{TeTe}}^{\text{I}} - 1) + \frac{1}{16} f_{\text{Te}}^2 (S_{\text{TeTe}}^{\text{II}} - 1) + \frac{1}{16} f_{\text{Te}}^2 (S_{\text{TeTe}}^{\text{I}} - 1) + \frac{1}{8} f_{\text{Cu}} f_{\text{Te}} (S_{\text{CuTe}}^{\text{II}} - 1) \quad (5.12)$$

Now for Cu_2Te we have

$$F_{\text{Cu}_2\text{Te}} = \frac{4}{9} f_{\text{Cu}}^2 (S_{\text{CuCu}}^{\text{II}} - 1) + \frac{2}{9} f_{\text{Cu}} f_{\text{Te}} (S_{\text{CuTe}}^{\text{I}} - 1) + \frac{1}{9} f_{\text{Te}}^2 (S_{\text{TeTe}}^{\text{I}} - 1) \quad (5.13)$$

Hence F_{CuTe} may be written as

$$F_{\text{CuTe}} = \frac{9}{16} F_{\text{Cu}_2\text{Te}}(Q) + a X(Q) + b Y(Q) + \frac{1}{16} f_{\text{Te}}^2 (S_{\text{TeTe}}^{\text{II}} - 1) \quad (5.14)$$

Hence $C(Q) = a X(Q) + b Y(Q)$ (5.15)

where $C(Q) = F(Q) - \frac{9}{16} F_{\text{Cu}_2\text{Te}} - \frac{1}{16} f_{\text{Te}}^2 (S_{\text{TeTe}}^{\text{II}} - 1)$ can be obtained directly by measuring the total structure factors for liquid Te , CuTe and Cu_2Te .

$$X(Q) = (S_{\text{TeTe}}^{\text{I}} - 1) \quad \text{and}$$

$$Y(Q) = (S_{\text{CuTe}}^{\text{II}} - 1) \quad \text{are the two unknowns, and}$$

$$a = \left(\frac{1}{8}\right) f_{\text{Te}}^2 \quad \text{and} \quad b = \left(\frac{1}{4}\right) f_{\text{Cu}} f_{\text{Te}} \quad \text{are constants}$$

independent of Q . The total structure factor for $^{\text{nat}}\text{CuTe}$, $^{63}\text{CuTe}$ and $^{65}\text{CuTe}$, $^{\text{nat}}\text{Cu}_2\text{Te}$, $^{63}\text{Cu}_2\text{Te}$ and $^{65}\text{Cu}_2\text{Te}$, yield three equations relating the two unknowns X and Y . These can be tested for consistency by calculating the determinant

$$\Delta = \begin{vmatrix} a & b_1 & c_1 \\ a & b_2 & c_2 \\ a & b_3 & c_3 \end{vmatrix} \quad (5.16)$$

where b_1 , b_2 , b_3 and c_1 , c_2 , c_3 are the values of b and c evaluated for ^{nat}Cu , ^{63}Cu and ^{65}Cu . The cluster model, in its primitive form, implies that $\Delta = 0$ except for $Q \leq 0.1 \text{ \AA}^{-1}$ when size effects might become significant ($Q = 0.1$ corresponds to a distance of $\sim 60 \text{ \AA}$ in real space when cluster-cluster correlation is important).

It is easily shown that the maximum error in (Δ) is $\sim 2a(b_3 - b_2) \times \delta c$. Hence $\delta \Delta = 2 \times 0.037 \times 0.059 \times 0.02 \approx 10 \times 10^{-5}$. The values given in Table 7 show how Δ varies with Q . Since these values do not lie outside $\pm 10 \times 10^{-5}$ the cluster model has not been disproved (with the present experimental errors). However, the cluster model predicts that $S_{\text{CuCu}}(Q)$ is the same in liquids CuTe and Cu_2Te . Since this is not the case the cluster model is inconsistent with the experimental data.

5.6 (ii) An Ionic Model

In a purely ionic model for these liquid semiconductors we imagine a random mixture of Cu (or Ag) and Te ions in which substantial electron transfer has taken place. But this model fails for Cu_2Te , CuTe and Ag_2Te for the following reasons:

- (1) The nearest neighbour distance in $g_{\text{Te-Te}}(r)$ is too highly correlated in all three cases (e.g. compared to the predictions of $g(r)$ by Woodcock (1971) for an ionic liquid).
- (2) In the Cu-Te system the ionic model predicts that the nearest neighbour distance in $g_{\text{Te-Te}}(r)$ should increase as we approach Cu_2Te , due to repulsion of the Te^{2-} ions. In fact this distance decreases.

TABLE 7

$Q(R^{-1})$	$\Delta \times 10^{-5}$
1.0	-3.33
1.5	0.74
2.0	-6.14
2.2	-2.04
2.3	0.15
2.4	-1.07
2.5	3.22
2.6	1.37
2.7	0.67
2.8	4.30
3.0	-1.59
3.5	-0.70
4.0	0.33
4.5	0.63
5.0	0.22
5.5	1.70
6.0	-3.37
7.0	-0.56
8.0	1.33

(Q) FOR THE LIQUID Cu-Te SYSTEM

(3) There is no evidence of charge oscillations as predicted by Woodcock. In the ionic model $g_{\text{Cu-Cu}}(r)$ and $g_{\text{Cu-Te}}(r)$ move out of phase because of alternative +ve and -ve charges.

(4) The first peak in $g_{\text{Cu-Cu}}(r)$ sharpens as we pass from CuTe to Cu_2Te , which means that there is greater order in copper atoms at the inter-metallic composition. This would not be expected with the ionic model, where the copper-copper distances would reflect the repulsive potential.

(5) In neither Cu_2Te , CuTe nor Ag_2Te does the nearest neighbour distance in $g_{\text{Te-Te}}(r)$ have the same value. With the ionic model this should be so.

For these reasons a purely ionic model is not acceptable. But there may be some ionicity, and (2) suggests that CuTe is more ionic than Cu_2Te (a point also suggested by the N.M.R. work of Warren on the Cu-Te system (1972)).

5.6 (iii) Covalent Models

A possible covalent model for Cu_2Te and Ag_2Te might consist of randomly packed molecules of Cu_2Te or Ag_2Te . Unfortunately, such a model is not acceptable since it predicts

(1) a well defined copper-copper distance corresponding to copper distances within a molecule (similarly for Ag_2Te),

(2) a second peak in $g_{\text{Cu-Cu}}(r)$ to account for copper-copper distances between molecules (similarly for Ag_2Te),

(3) a Te-Te nearest neighbour distance which is not especially sharp,

Also the computer models for packed molecules do not produce the experimental structure factors. (see figure 4.20 a, b and c)

A better model is one in which a majority of atoms form molecules of Cu_2Te (or Ag_2Te). The remainder are ionically and metallically bonded (the conductivities of Cu_2Te and Ag_2Te indicate

that there are free carriers present). In CuTe the proportion of molecules would be less than in Cu₂Te.

Difficulties with this model are that it predicts a well correlated copper-copper (or silver-silver) distance, and also a second major peak in $S_{\text{Cu-Cu}}(Q)$ (or $S_{\text{Ag-Ag}}(Q)$).

Another possible covalent model is one in which the complex covalent structure of tellurium (see Chapter 4) is largely retained, and the copper atoms fit into spaces in this structure. Hence, the copper atoms become slightly more ordered as we approach Cu₂Te. When all the spaces are full the system will not dissolve more copper, and we have a miscibility gap. The conductivity falls as more copper tellurium bonds are formed. The Te-Te distances are reduced due to bonding with the copper atoms. Also, in this model, the copper-tellurium (or Ag-Te) and Te-Te nearest neighbour distances are well correlated. But the copper-copper distance is not so well correlated as the other two. The nearest neighbour distance in $g_{\text{Te-Te}}(r)$ becomes sharper as the tellurium atoms are pushed together by the copper (or silver) atoms.

This model is the one which is most consistent with the structural data, although considerably more analysis must be done before definitive conclusions can be reached.

5.7 Suggestions for further work

Structural models have been presented for the liquid chalcogens and for tellurium-based liquid semiconductors. There is considerable scope for further experimental work on liquid semiconductors, which could take the form of

- (1) examining structurally a wider range of materials and,
- (2) improving the counting statistics (e.g. by using the high-flux beam reactor at Grenoble) and,

(3) looking at structural variations with temperature.

More specifically, it would be rewarding to look at the structure of liquid AgTe (using silver isotopes), so that the liquid Ag-Te system could be better compared structurally with the liquid Cu-Te system. Also, the change in the structure of liquid tellurium due to the addition of an impurity could be examined directly by using nickel of zero scattering cross-section. (Nickel of this kind can be made by mixing nickel isotopes Ni^{60} and Ni^{62} in suitable proportions)

Electro-diffusion is a technique which can be used to indicate the degree of ionicity of a mixture, and could be usefully employed for liquid semiconductors to verify the interpretation of the structural data. It would also be useful to obtain more thermodynamic data on these materials for the same reason.

APPENDIX A

The Radial Distribution Function

As indicated by March (1968) the coherently scattered neutron or x-ray intensity may be written as:

$$I = \sum_n \sum_m f_n f_m \exp \left[j\mathbf{Q} \cdot (\mathbf{r}_m - \mathbf{r}_n) \right] \quad (\text{A.1})$$

where $\mathbf{r}_m$, $\mathbf{r}_n$ are the positions of the atoms m and n , and f_n and f_m are the scattering lengths. Equation (A.1) may be written as:

$$I = \sum_n \sum_m f_n f_m \exp \left[jQ r_{mn} \cos \alpha \right] \quad (\text{A.2})$$

where α is the angle between $\mathbf{r}_m - \mathbf{r}_n$ and $\mathbf{Q}$ ($\mathbf{Q} = \mathbf{K} - \mathbf{K}_0$). Since the vector $\mathbf{r}_m - \mathbf{r}_n$ can take on all orientations we must average over α , and we find that:

$$I = \sum_n \sum_m f_n f_m \left\{ \frac{\sin Q r_{mn}}{Q r_{mn}} \right\} \quad (\text{A.3})$$

For liquids composed of atoms of only one type $f_m = f_n = f$. For a liquid containing N atoms we have:

$$I = Nf^2 \left[1 + \sum' \frac{\sin Q r_{mn}}{Q r_{mn}} \right] \quad (\text{A.4})$$

where the summation excludes $r_{mn} = 0$.

Now if $\rho(r)$ is the density of atoms at distance r from an atom we are 'sitting on' we can replace the summation of (A.4) by an integration and we obtain:

$$I = Nf^2 \left[1 + \int_0^R 4\pi r^2 \rho(r) \frac{\sin Qr}{Qr} dr \right] \quad (\text{A.5})$$

where r is the (very large) radius of the liquid sample. If we denote

the average density by ρ_0 then (A.5) becomes

$$I = Nf^2 \left[1 + \int_0^R 4\pi r^2 [\rho(r) - \rho_0] \frac{\sin Qr}{Qr} dr + \int_0^R 4\pi r^2 \rho_0 \frac{\sin Qr}{Qr} dr \right] \quad (A.6)$$

The second integral denotes the scattered intensity from a uniform density and is all concentrated in the small angle region (giving a δ function at the origin in the limit $R \rightarrow \infty$).

We now define a liquid structure factor $S(Q)$ by the relation

$$S(Q) = I / Nf^2 \quad (A.7)$$

Equation (A.6) may be written

$$S(Q) = 1 + \int_0^\infty 4\pi r^2 [\rho(r) - \rho_0] \frac{\sin Qr}{Qr} dr \quad (A.8)$$

where the δ -function has not been considered further. The radial distribution function $g(r)$ is defined by setting the number of atoms in a spherical shell of radius r and thickness dr to $\rho_0 g(r) 4\pi r^2 dr$ so that

$$S(Q) = 1 + \rho_0 \int_0^\infty 4\pi r^2 [g(r) - 1] \frac{\sin(Qr)}{Qr} dr \quad (A.9)$$

which is equation (4.2).

APPENDIX B

The Coherent Scattering Lengths For The Liquid Chalcogens

Liquid Chalcogen	Scattering Length $\times 10^{-12}$ cm
Tellurium	0.543
Selenium	0.780 .
Sulphur	0.285

(February 1971 M.I.T.)

APPENDIX C

F(Q)'s for Liquid $\text{Te}_{1-x}\text{Se}_x$ at 500°C

Q	F(Q)	
	x = 0.5	x = 0.05
1.0	-.35	-.29
1.2	-.25	-.25
1.4	-.14	-.2
1.6	-.05	-.12
1.8	.02	-.035
2.0	.055	.055
2.2	.05	.07
2.4	.035	.015
2.6	.025	-.01
2.8	.05	.02
3.0	.095	.04
3.2	.115	.035
3.4	.115	0
3.6	.08	-.03
3.8	.02	-.05
4.0	-.05	-.045
4.2	-.09	-.025
4.4	-.1	0
4.6	-.09	.015
4.8	-.075	.025
5.0	-.055	.025
5.2	-.04	.02
5.4	-.025	.005
5.6	-.02	-.01
5.8	-.03	-.02
6.0	-.055	-.025
6.2	-.07	-.025
6.4	-.08	-.02
6.6	-.075	-.015
6.8	-.07	-.005
7.0	-.06	0
7.2	-.045	.005
7.4	-.03	.01
7.6	-.015	.01
7.8	.005	.015
8.0	.02	.015
8.2	.035	.015
8.4	.045	.015

LIQUID Te

500°C				800°C			
Q (Å ⁻¹)	S(Q)	Q (Å ⁻¹)	S(Q)	Q (Å ⁻¹)	S(Q)	Q (Å ⁻¹)	S(Q)
0.2	(0.03)	5.6	0.94	0.2	0.03	5.6	0.97
0.4	(0.03)	5.8	0.95	0.4	0.03	5.8	0.97
0.6	0.03	6.0	0.965	0.6	0.03	6.0	0.972
0.8	0.04	6.2	0.98	0.8	0.03	6.2	0.985
1.0	0.045	6.4	0.995	1.0	0.04	6.4	1.005
1.2	0.08	6.6	1.00	1.2	0.11	6.6	1.02
1.4	0.21	6.8	1.02	1.4	0.24	6.8	1.025
1.6	0.44	7.0	1.03	1.6	0.51	7.0	1.02
1.8	0.84	7.2	1.03	1.8	0.83	7.2	1.01
2.0	1.38	7.4	1.01	2.0	1.24	7.4	0.99
2.2	1.32	7.6	0.985	2.2	1.27	7.6	0.977
2.4	1.09	7.8	0.975	2.4	1.04	7.8	0.97
2.6	0.98	8.0	0.97	2.6	0.973	8.0	0.96
2.8	0.985	8.2	0.97	2.8	1.01	8.2	0.962
3.0	1.08	8.4	0.97	3.0	1.07	8.4	0.97
3.2	1.105	8.6	0.975	3.2	1.05	8.6	0.98
3.4	0.98	8.8	0.99	3.4	0.98	8.8	0.995
3.6	0.89	9.0	1.01	3.6	0.93	9.0	1.00
3.8	0.89	9.2	1.02	3.8	0.935	9.2	1.003
4.0	0.95	9.4	1.02	4.0	1.00	9.4	1.004
4.2	1.04	9.6	1.02	4.2	1.07	9.6	1.01
4.4	1.10	9.8	1.01	4.4	1.11	9.8	1.01
4.6	1.13	10.0	1.005	4.6	1.13	10.0	1.01
4.8	1.125	10.2	1.005	4.8	1.125	10.2	1.005
5.0	1.10	10.4	0.99	5.0	1.10	10.4	1.00
5.2	1.035	10.6	0.98	5.2	1.04		
5.4	0.965			5.4	0.995		

LIQUID Se

230°C				350°C			
Q (Å ⁻¹)	S(Q)	Q (Å ⁻¹)	S(Q)	Q (Å ⁻¹)	S(Q)	Q (Å ⁻¹)	S(Q)
0.2	(0.049)	6.6	0.965	0.2	0.04	6.6	0.925
0.4	(0.047)	6.8	0.95	0.4	0.032	6.8	0.955
0.6	0.045	7.0	0.942	0.6	0.03	7.0	0.96
0.8	0.095	7.2	0.94	0.8	0.10	7.2	0.92
1.0	0.21	7.4	0.94	1.0	0.24	7.4	0.91
1.2	0.42	7.6	0.947	1.2	0.47	7.6	0.915
1.4	0.625	7.8	0.96	1.4	0.655	7.8	0.94
1.6	0.82	8.0	0.98	1.6	0.80	8.0	0.975
1.8	0.98	8.2	1.005	1.8	0.93	8.2	1.01
2.0	0.995	8.4	1.035	2.0	0.98	8.4	1.05
2.2	0.905	8.6	1.05	2.2	0.91	8.6	1.06
2.4	0.85	8.8	1.045	2.4	0.84	8.8	1.05
2.6	0.835	9.0	1.025	2.6	0.835	9.0	1.03
2.8	0.87	9.2	0.995	2.8	0.87	9.2	1.00
3.0	0.975	9.4	0.97	3.0	0.995	9.4	0.975
3.2	1.12	9.6	0.947	3.2	1.14	9.6	0.95
3.4	1.26	9.8	0.937	3.4	1.225	9.8	0.95
3.6	1.28	10.0	0.94	3.6	1.245	10.0	0.95
3.8	1.18	10.2	0.943	3.8	1.15	10.2	0.965
4.0	1.01	10.4	0.955	4.0	0.955	10.4	0.99
4.2	0.89	10.6	0.98	4.2	0.825	10.6	1.02
4.4	0.815	10.8	1.00	4.4	0.77	10.8	1.045
4.6	0.795	11.0	1.025	4.6	0.75	11.0	1.060
4.8	0.855	11.2	1.037	4.8	0.80	11.2	1.07
5.0	0.965	11.4	1.035	5.0	0.885	11.4	1.065
5.2	1.045	11.6	1.027	5.2	0.98	11.6	1.052
5.4	1.105	11.8	1.01	5.4	1.07	11.8	1.035
5.6	1.155	12.0	0.985	5.6	1.095	12.0	1.005
5.8	1.16	12.2	0.960	5.8	1.045	12.2	0.98
6.0	1.11	12.4	0.940	6.0	0.98		
6.2	1.04	12.6	0.93	6.2	0.93		
6.4	0.995			6.4	0.915		

LIQUID S

150°C				400°C			
Q (A ⁻¹)	S(Q)	Q (A ⁻¹)	S(Q)	Q (A ⁻¹)	S(Q)	Q (A ⁻¹)	S(Q)
0.2	(0.03)	3.6	1.01	0.2	0.03	3.6	1.00
0.4	(0.03)	3.8	1.10	0.4	0.03	3.8	1.06
0.6	(0.04)	4.0	1.14	0.6	0.05	4.0	1.10
0.8	(0.07)	4.2	1.13	0.8	0.11	4.2	1.10
1.0	0.22	4.4	1.095	1.0	0.28	4.4	1.08
1.2	0.46	4.6	1.04	1.2	0.55	4.6	1.06
1.4	0.62	4.8	0.97	1.4	0.65	4.8	1.035
1.6	0.77	5.0	0.93	1.6	0.665	5.0	0.97
1.8	0.89	5.2	0.94	1.8	0.68	5.2	0.91
2.0	0.78	5.4	0.96	2.0	0.675	5.4	0.91
2.2	0.63	5.6	1.00	2.2	0.625	5.6	0.94
2.4	0.55	5.8	1.04	2.4	0.59	5.8	1.00
2.6	0.54	6.0	1.09	2.6	0.585	6.0	1.045
2.8	0.58	6.2	1.12	2.8	0.615	6.2	1.085
3.0	0.67	6.4	1.12	3.0	0.68	6.4	1.12
3.2	0.79	6.6	1.08	3.2	0.785	6.6	1.135
3.4	0.90	6.8	1.04	3.4	0.91	6.8	1.12

LIQUID CuTe
700°C

Q (Å ⁻¹)	F _N (bns)	F ₆₃ (bns)	F ₆₅ (bns)	Q (Å ⁻¹)	F _N (bns)	F ₆₃ (bns)	F ₆₅ (bns)
0.2	(-0.37)	(-0.32)	(-0.53)	5.2	0.055	0.05	0.08
0.4	(-0.36)	(-0.30)	(-0.52)	5.4	0.05	0.04	0.065
0.6	(-0.355)	(-0.295)	(-0.51)	5.6	0.02	0.02	0.035
0.8	-0.35	-0.29	-0.49	5.8	-0.01	0.00	0.00
1.0	-0.33	-0.29	-0.48	6.0	-0.035	-0.02	-0.03
1.2	-0.315	-0.28	-0.46	6.2	-0.05	-0.03	-0.05
1.4	-0.29	-0.27	-0.43	6.4	-0.05	-0.04	-0.065
1.6	-0.25	-0.21	-0.40	6.6	-0.04	-0.04	-0.06
1.8	-0.20	-0.14	-0.32	6.8	-0.03	-0.025	-0.04
2.0	-0.10	-0.05	-0.20	7.0	-0.015	-0.01	-0.01
2.2	-0.03	-0.01	-0.09	7.2	0.005	0.00	0.015
2.4	0.01	0.015	0.02	7.4	0.02	0.015	0.03
2.6	0.06	0.04	0.14	7.6	0.025	0.02	0.035
2.8	0.14	0.11	0.25	7.8	0.025	0.02	0.035
3.0	0.20	0.17	0.325	8.0	0.025	0.015	0.03
3.2	0.15	0.12	0.23	8.2	0.025	0.015	0.025
3.4	0.025	0.01	0.03	8.4	0.02	0.01	0.015
3.6	-0.07	-0.05	-0.12	8.6	0.01	0.01	0.01
3.8	-0.10	-0.08	-0.17	8.8	0.00	0.005	-0.005
4.0	-0.11	-0.09	-0.16	9.0	-0.01	0.00	-0.01
4.2	-0.09	-0.075	-0.13	9.2	-0.015	-0.01	-0.01
4.4	-0.055	-0.04	-0.07	9.4	-0.015	-0.015	-0.005
4.6	-0.02	-0.02	-0.02	9.6	-0.01	-0.015	0.00
4.8	0.02	0.01	0.03	9.8	0.00	-0.015	0.005
5.0	0.04	0.04	0.07	10.0	0.005	-0.01	0.005

Liquid Cu₂Te
1200°C

Q (Å ⁻¹)	F _N (Q) (bns)	F ₆₃ (Q) (bns)	F ₆₅ (Q) (bns)	Q (Å ⁻¹)	F _N (Q) (bns)	F ₆₃ (Q) (bns)	F ₆₅ (Q) (bns)
0.2	(-0.35)	(-0.03)	(-0.72)	5.2	0.02	0.02	0.05
0.4	(-0.30)	(-0.028)	(-0.62)	5.4	0.03	0.02	0.05
0.6	(-0.28)	(-0.026)	(-0.56)	5.6	0.03	0.01	0.04
0.8	-0.26	-0.023	(-0.52)	5.8	0.00	0.00	-0.01
1.0	-0.27	-0.23	-0.52	6.0	-0.01	-0.01	-0.03
1.2	-0.275	-0.23	-0.52	6.2	-0.03	-0.025	-0.06
1.4	-0.29	-0.23	-0.525	6.4	-0.04	-0.035	-0.07
1.6	-0.28	-0.23	-0.52	6.6	-0.04	-0.03	-0.07
1.8	-0.25	-0.20	-0.45	6.8	-0.03	-0.02	-0.05
2.0	-0.20	-0.17	-0.33	7.0	-0.02	-0.01	-0.02
2.2	-0.11	-0.10	-0.19	7.2	0.00	0.01	0.02
2.4	0.00	0.00	0.01	7.4	0.02	0.02	0.05
2.6	0.12	0.11	0.20	7.6	0.025	0.03	0.06
2.8	0.22	0.19	0.39	7.8	0.03	0.03	0.06
3.0	0.21	0.15	0.40	8.0	0.03	0.025	0.05
3.2	0.04	0.02	0.09	8.2	0.02	0.02	0.03
3.4	-0.06	-0.06	-0.11	8.4	0.01	0.00	0.01
3.6	-0.12	-0.11	-0.20	8.6	0.00	-0.015	-0.01
3.8	-0.15	-0.13	-0.26	8.8	-0.01	-0.02	-0.02
4.0	-0.16	-0.12	-0.26	9.0	-0.01	-0.025	-0.02
4.2	-0.15	-0.11	-0.24	9.2	-0.015	-0.015	-0.02
4.4	-0.12	-0.09	-0.18	9.4	-0.02	0.00	-0.01
4.6	-0.08	-0.07	-0.14	9.6	0.02	0.01	0.00
4.8	-0.05	-0.04	-0.07	9.8	0.02	0.015	0.005
5.0	-0.01	0.00	0.00	10.0	0.015	0.015	0.01

LIQUID Ag_2Te

1000°C

Q ($\text{\AA}^{-1}$)	F _N (bns)	F ₁₀₇ (bns)	F ₁₀₉ (bns)	Q ($\text{\AA}^{-1}$)	F _N (bns)	F ₁₀₇ (bns)	F ₁₀₉ (bns)
0.2	(-0.32)	(-0.51)	(-0.20)	4.2	-0.04	-0.05	-0.02
0.4	(-0.31)	(-0.495)	(-0.19)	4.4	-0.01	0.00	0.00
0.6	(-0.30)	(-0.46)	(-0.185)	4.6	-0.015	0.04	0.02
0.8	(-0.28)	(-0.44)	(-0.18)	4.8	0.04	0.07	0.025
1.0	-0.27	-0.42	-0.18	5.0	0.055	0.08	0.025
1.2	-0.26	-0.40	-0.17	5.2	0.045	0.065	0.02
1.4	-0.235	-0.36	-0.145	5.4	0.025	0.02	0.01
1.6	-0.205	-0.32	-0.125	5.6	0.00	-0.01	0.00
1.8	-0.155	-0.255	-0.085	5.8	-0.01	-0.03	-0.015
2.0	-0.10	-0.13	-0.05	6.0	-0.025	-0.04	-0.02
2.2	-0.02	-0.03	0.01	6.2	-0.03	-0.04	-0.025
2.4	0.09	0.20	0.065	6.4	-0.015	-0.025	-0.015
2.6	0.205	0.35	0.13	6.6	-0.01	-0.01	-0.005
2.8	0.225	0.33	0.14	6.8	0.005	0.01	0.005
3.0	0.10	0.14	0.07	7.0	-0.015	0.025	0.01
3.2	-0.015	0.00	0.01	7.2	0.015	0.03	0.01
3.4	-0.08	-0.115	-0.03	7.4	0.02	0.03	0.01
3.6	-0.095	-0.14	-0.045	7.6	0.015	0.025	0.005
3.8	-0.085	-0.115	-0.045	7.8	0.005	0.02	0.00
4.0	-0.065	-0.10	-0.03				

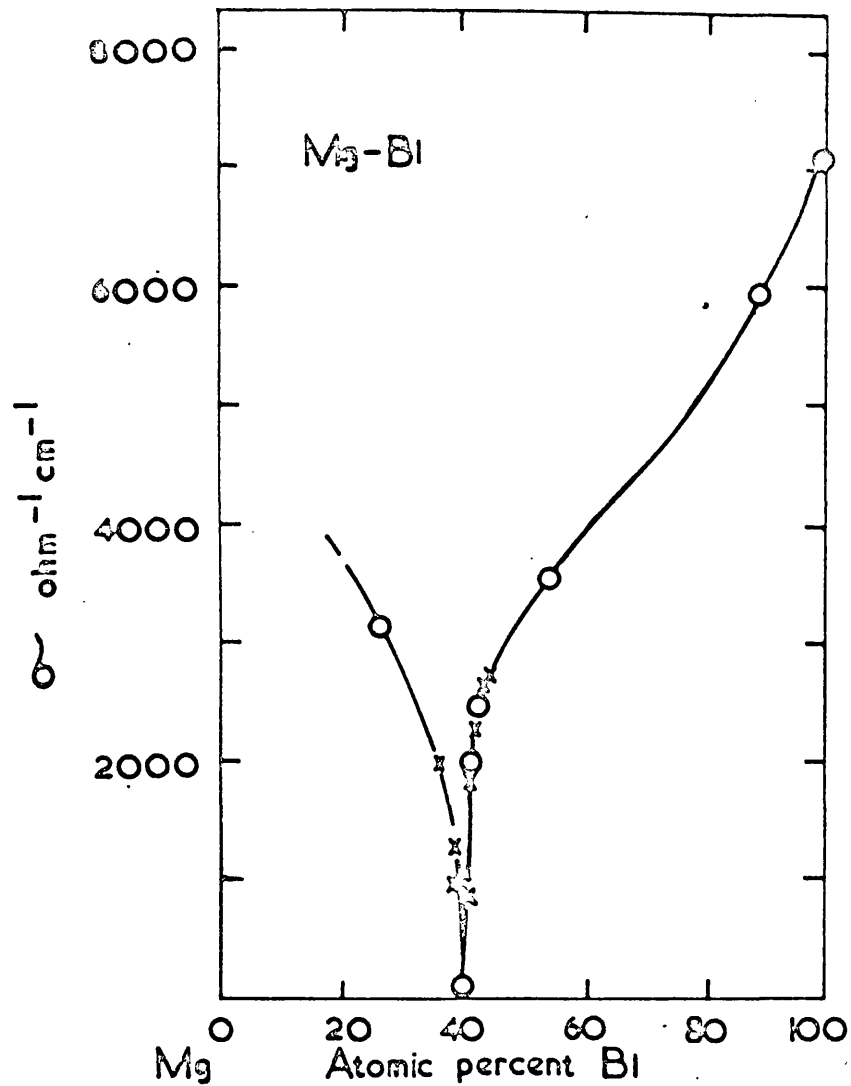
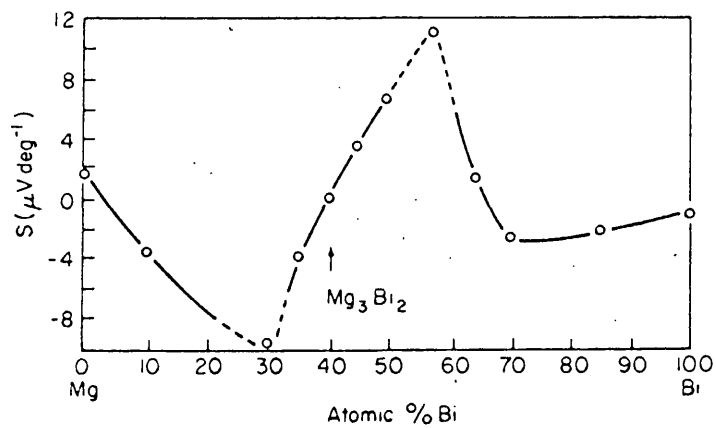


FIG. 1.1 The conductivity of liquid Mg-Bi
 x - Ilschner and Wagner (1953). o - Enderby and Collings (1970).



The thermoelectric power of liquid Mg-Bi as a function of composition at temperatures 100°C above the liquidus.

[after Enderby 1973]

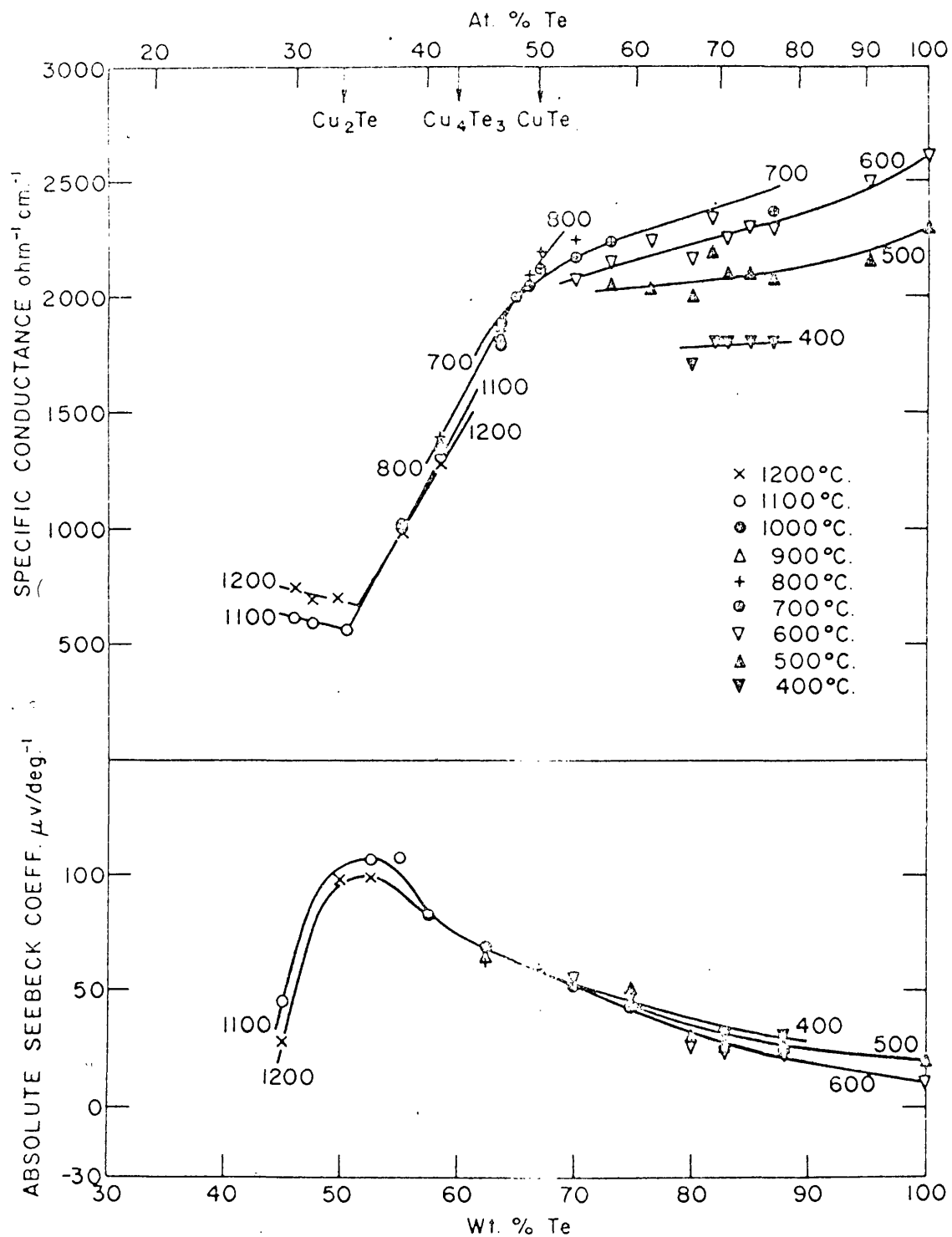


FIG. 1.2a —The specific conductance and absolute Seebeck coefficient of the molten Cu-Te system.

[after Dancy 1965]

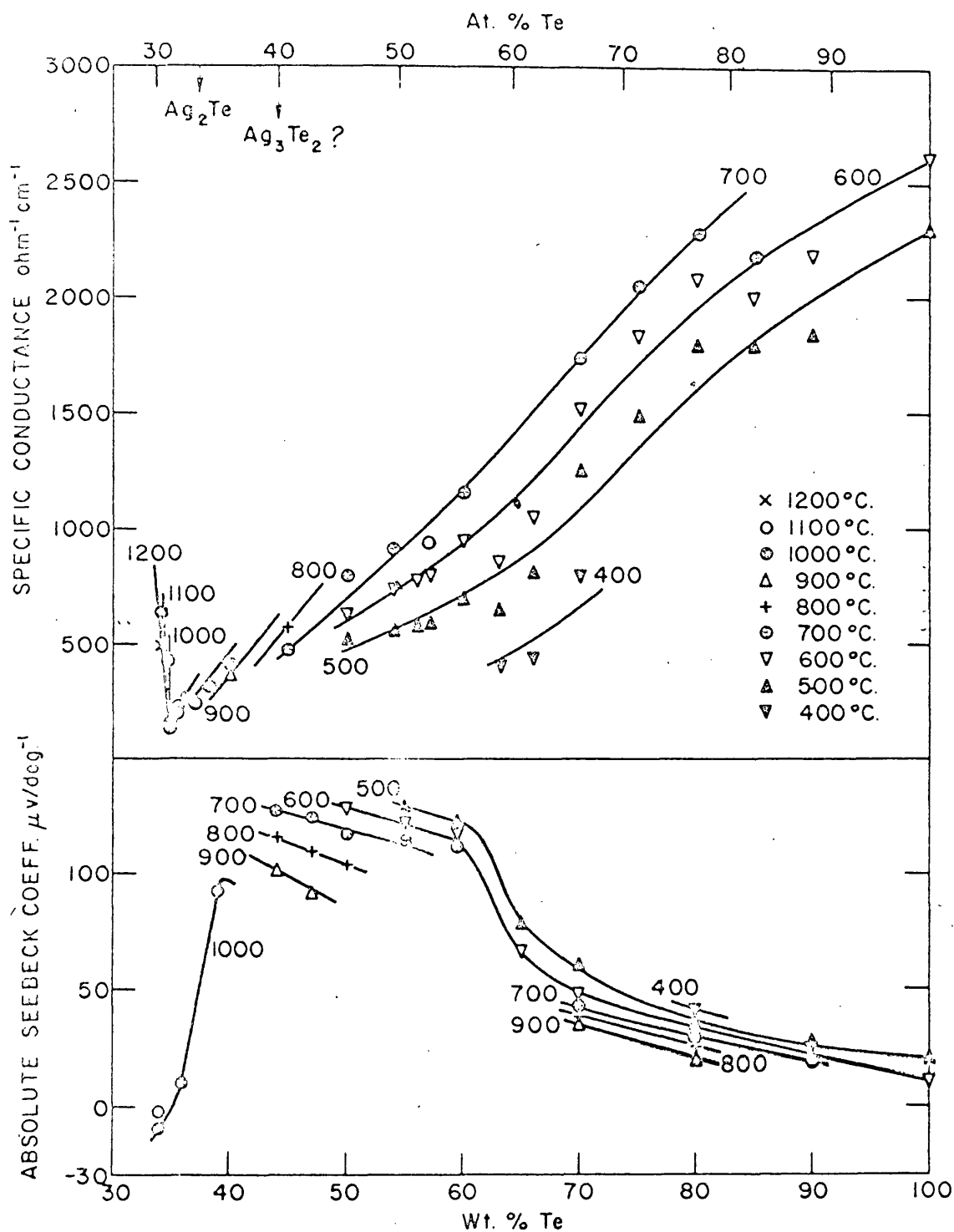


FIG. 1.2b -The specific conductance and absolute Seebeck coefficient of the molten Ag-Te system. [after Dancy 1965]

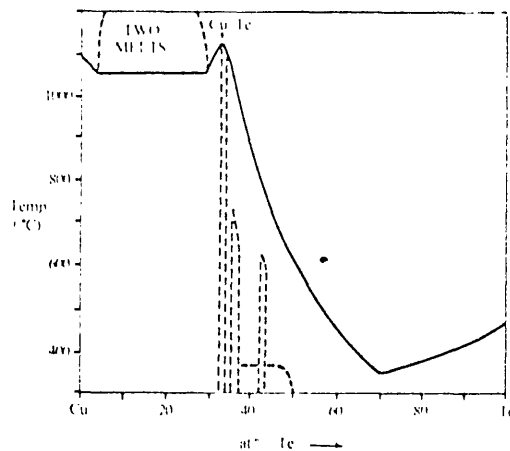


Fig. 1.3. Simplified form of the phase diagram for Cu-Te. A detailed diagram has been given by Hanson (1958)

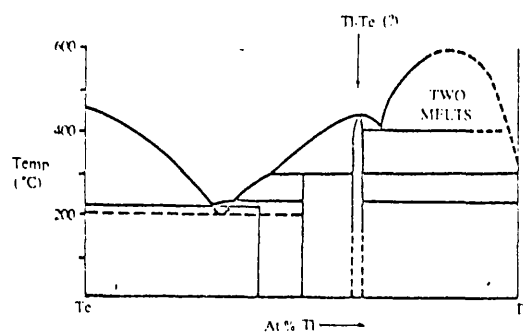


Fig. 1.4. Simplified form of the phase diagram for Tl-Te. A detailed diagram has been given by Hanson (1958)

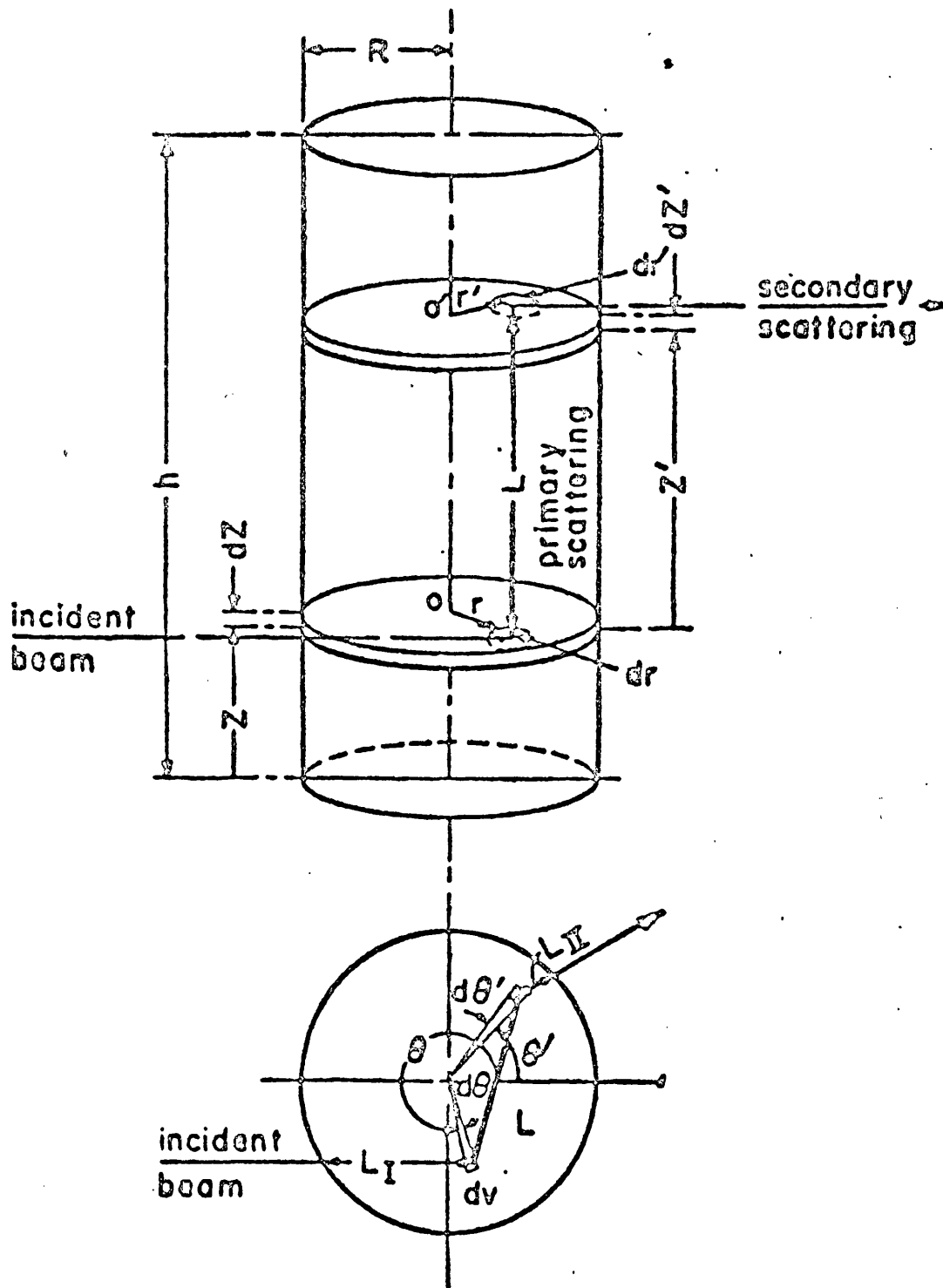
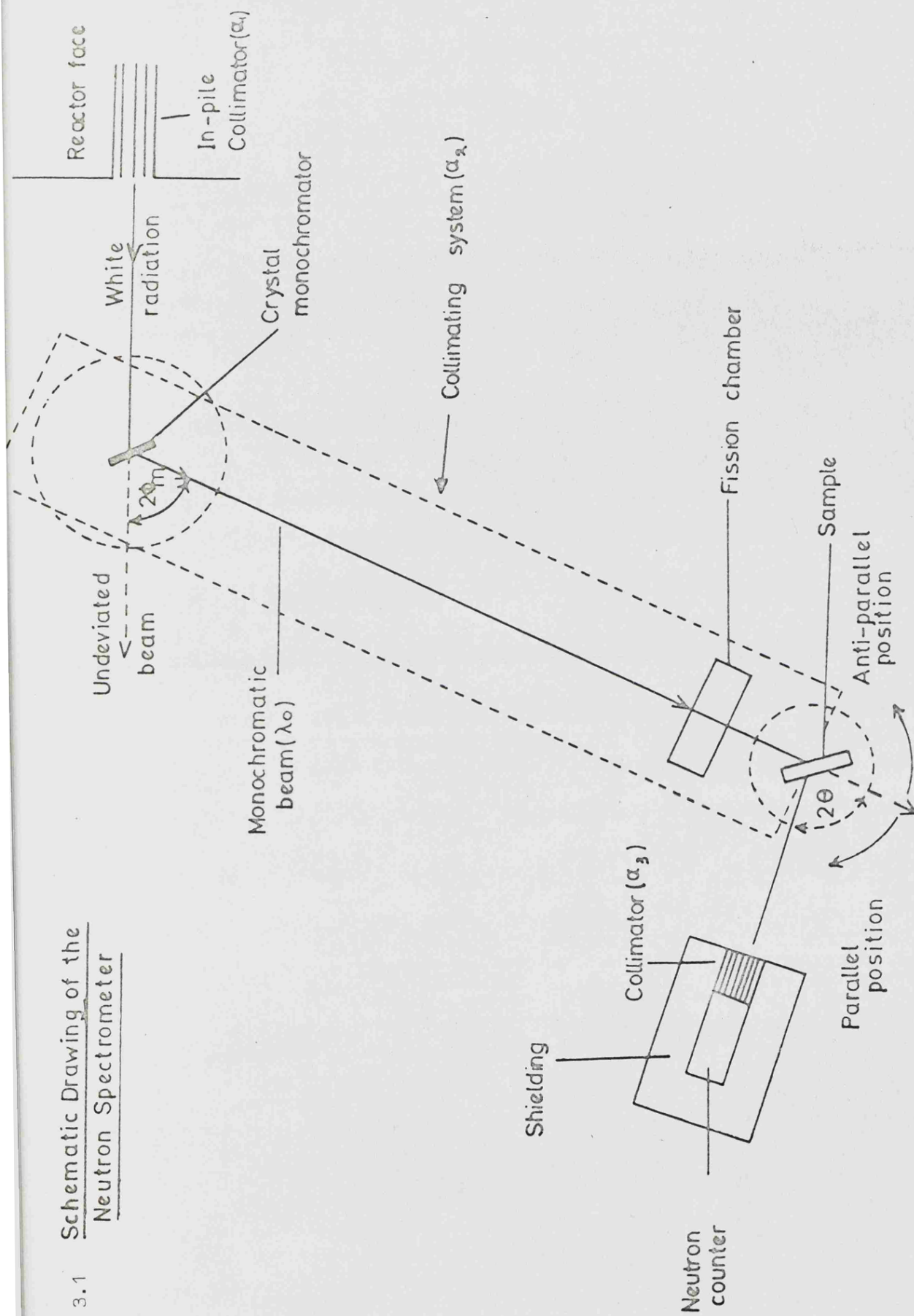
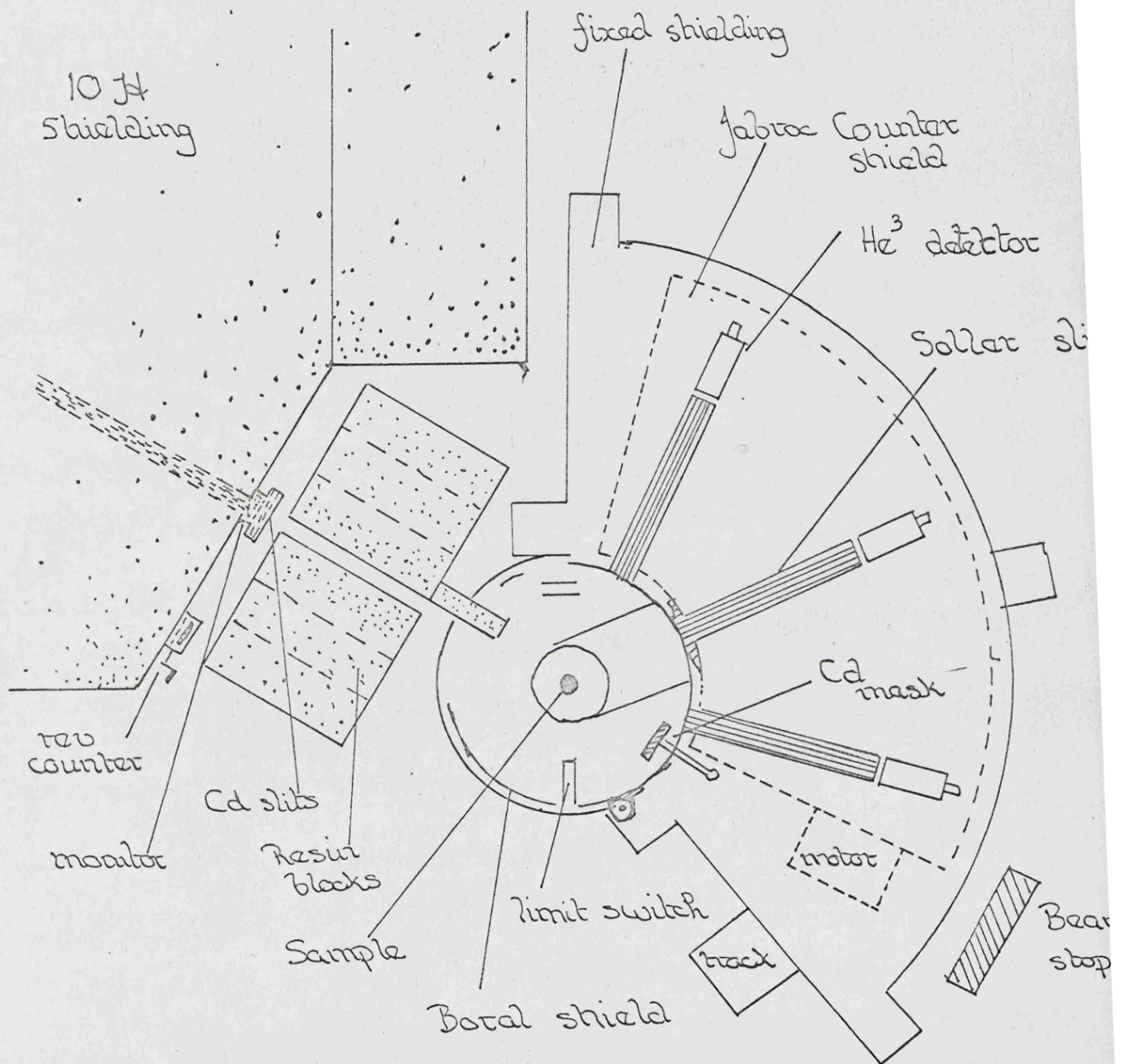


FIG. 2.1 SECONDARY SCATTERING IN CYLINDRICAL SAMPLES

FIG. 3.1 Schematic Drawing of the
Neutron Spectrometer



Liquids Diffractometer (10H Dido)



scale = 1:12

Fig 3.2a

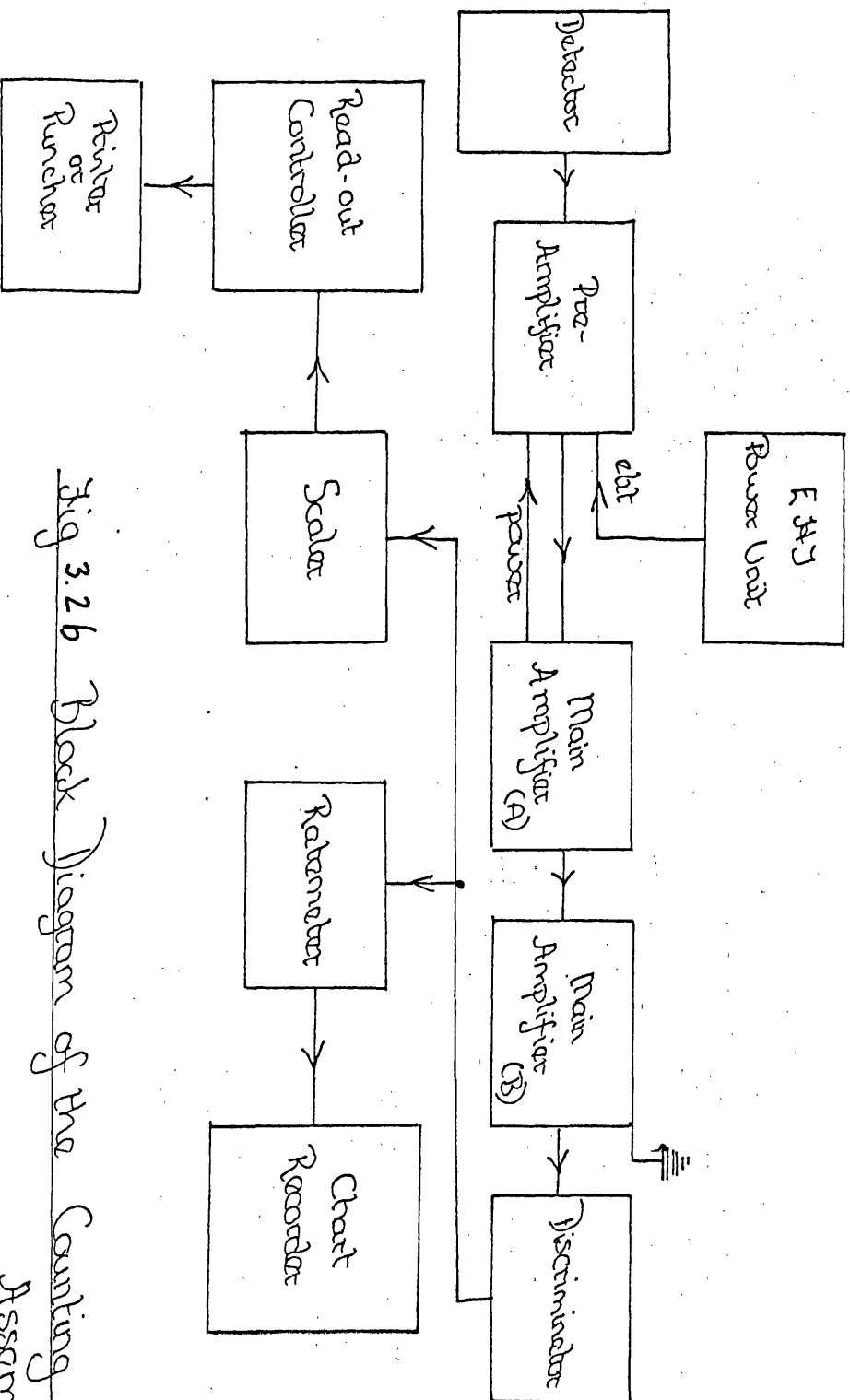
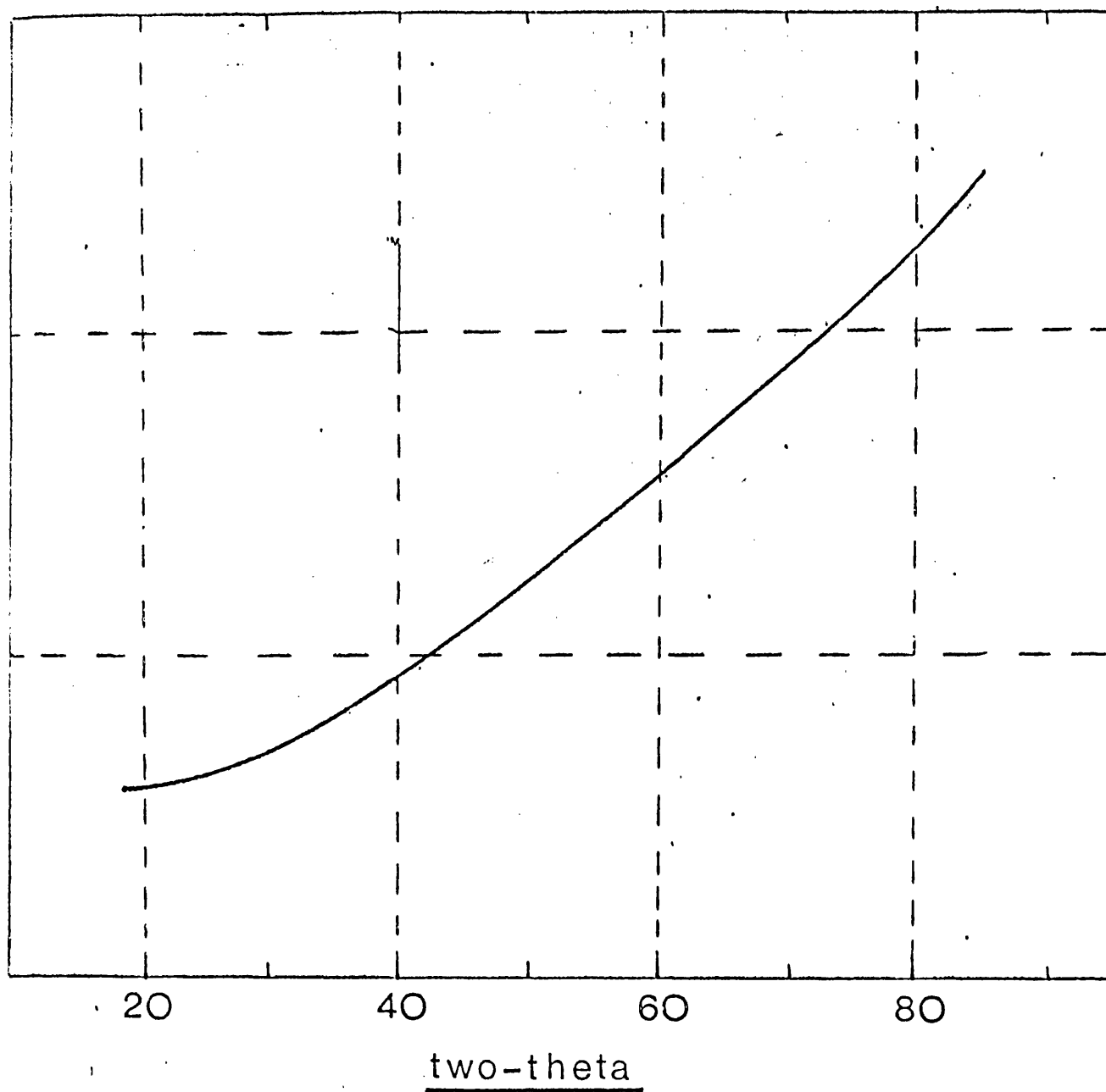


Fig 3.26 Block Diagram of the Counting Assembly

ig 3.2c

Resolution Curve for the
Liquids Machine

Width at half-height v. Two-theta



(w_0 = width at half height)

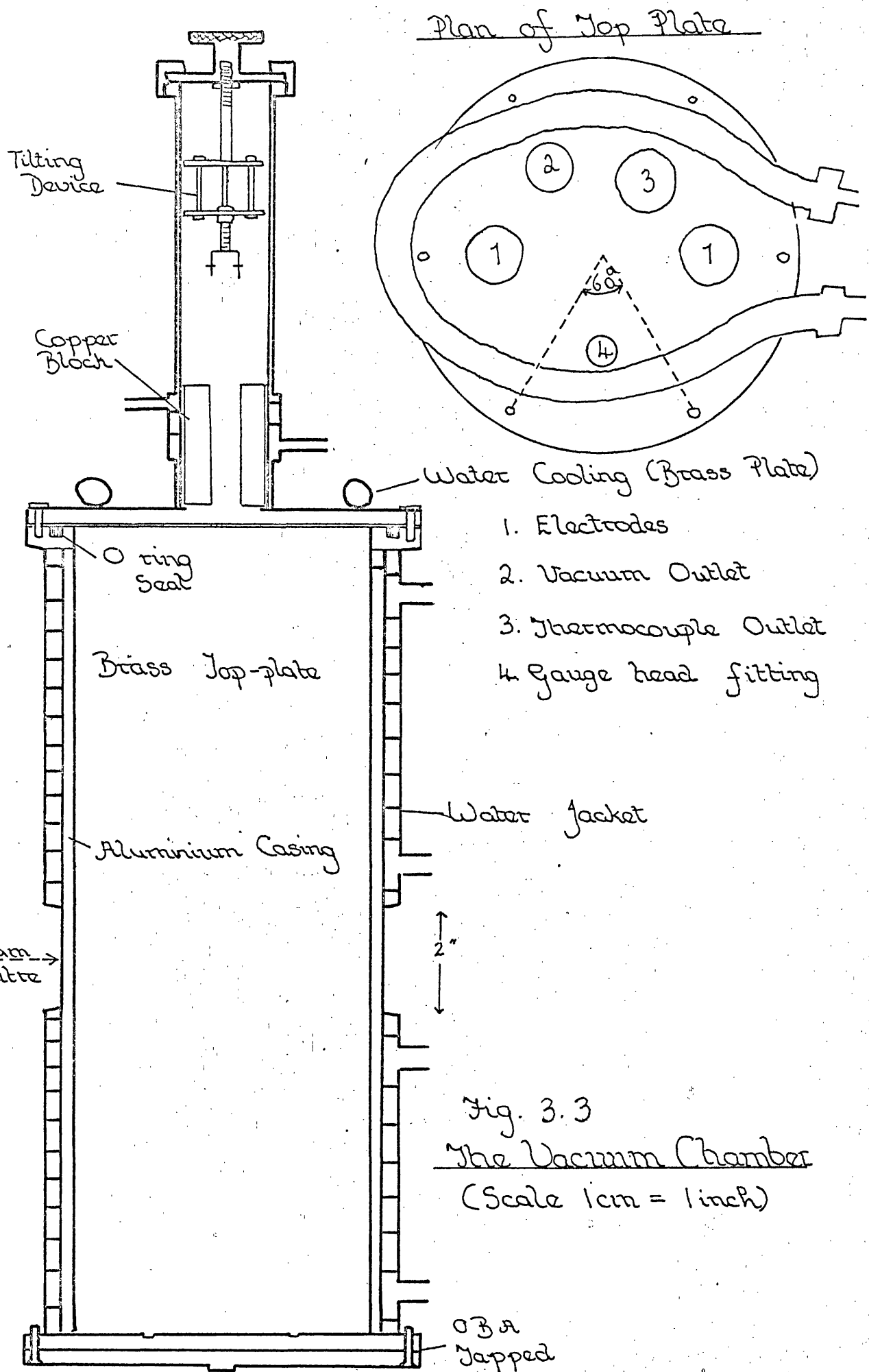


Fig 3.4 The Vacuum Furnace (Scale 2cm $\equiv$ 1")

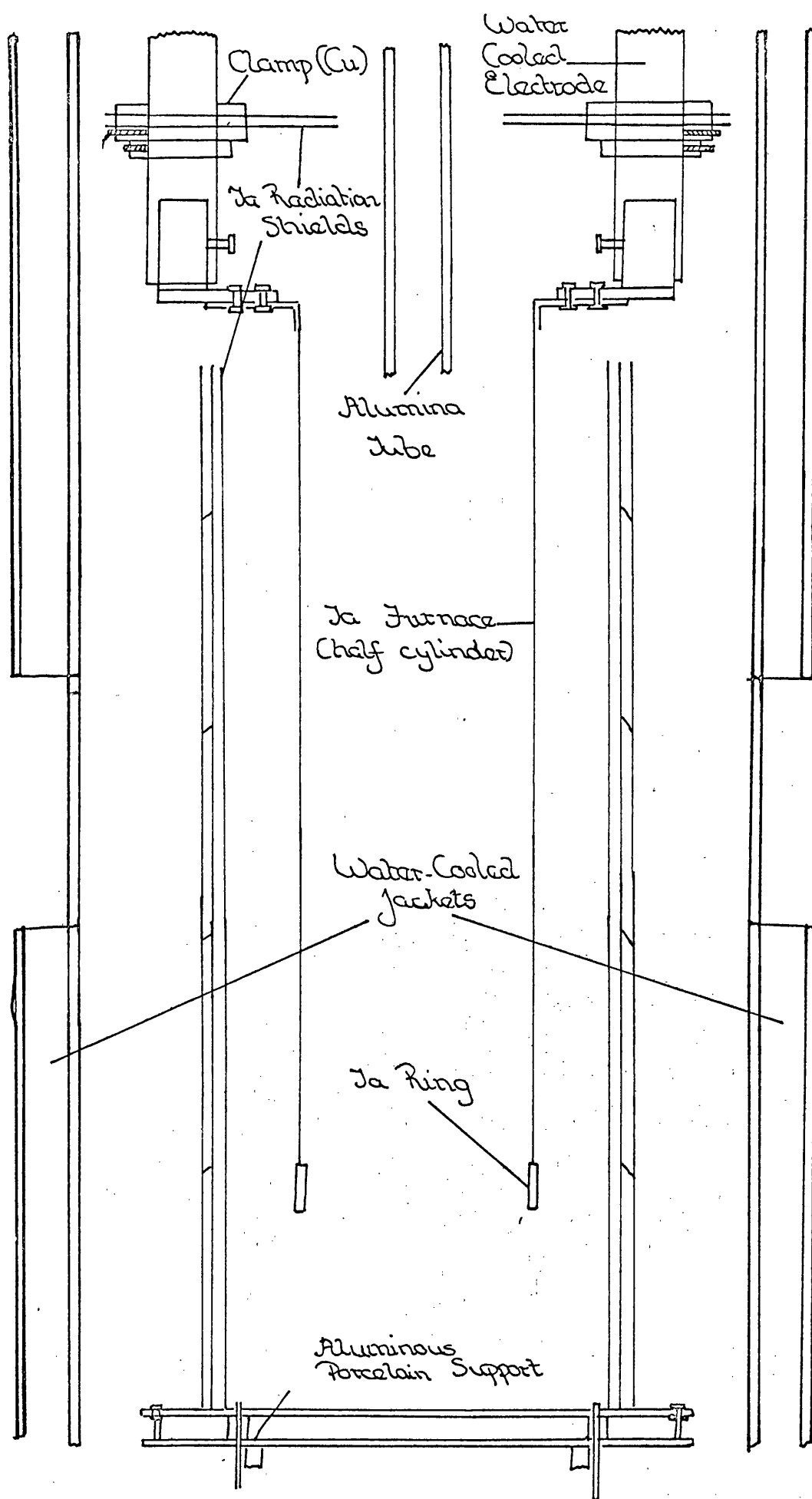


Fig 3.5 Water cooled
Electrode

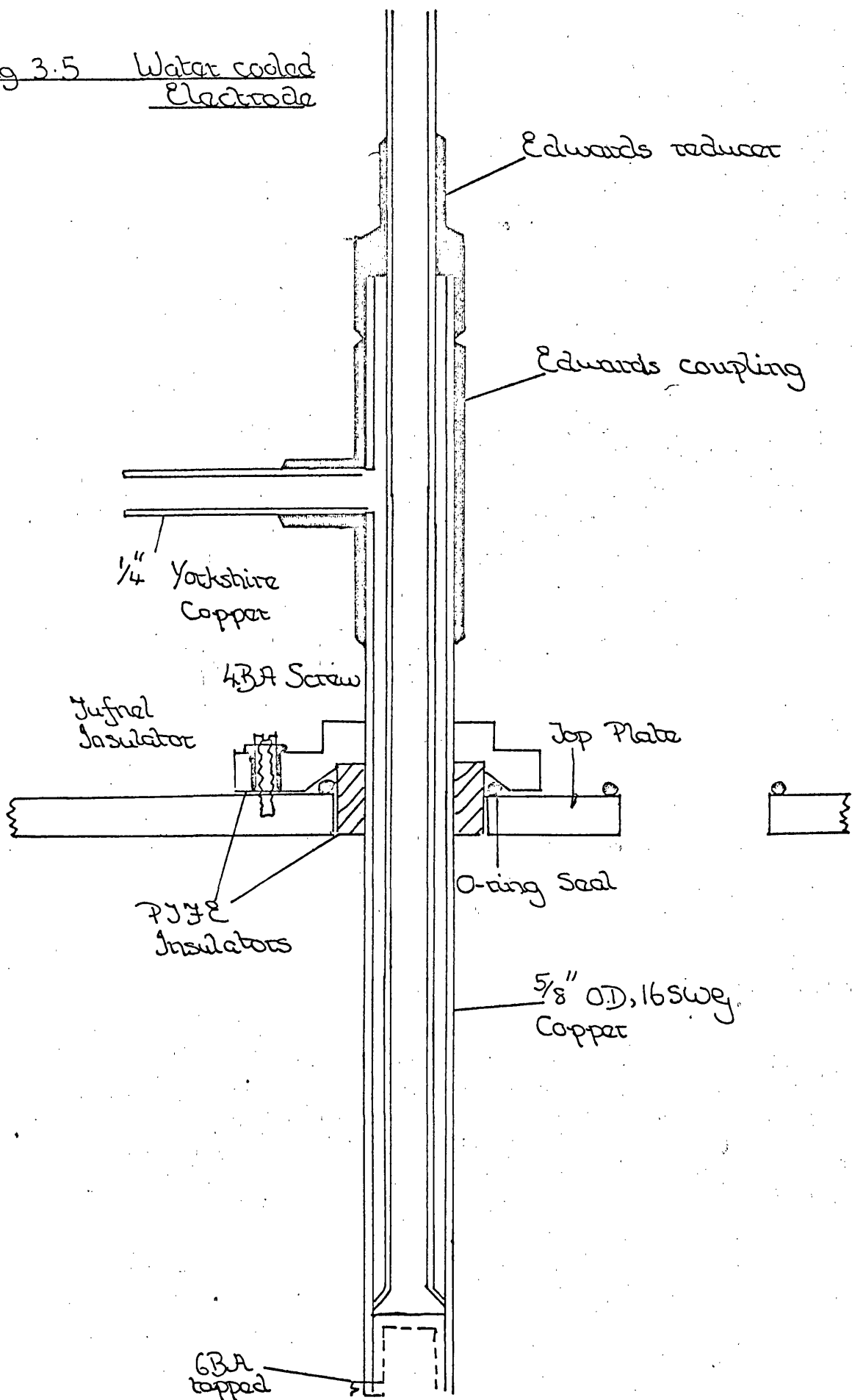
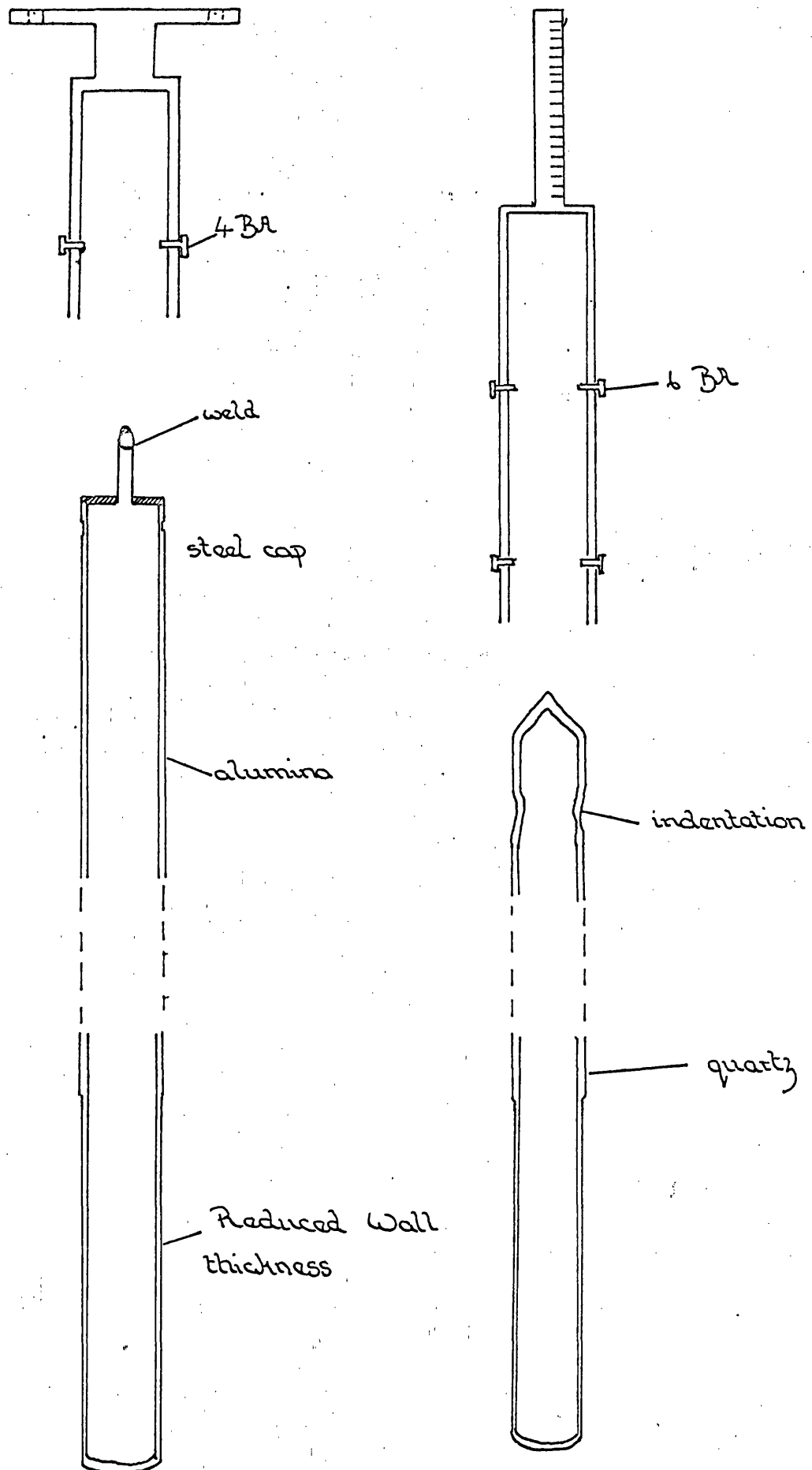


Fig 3.b Sample Containers (actual size)



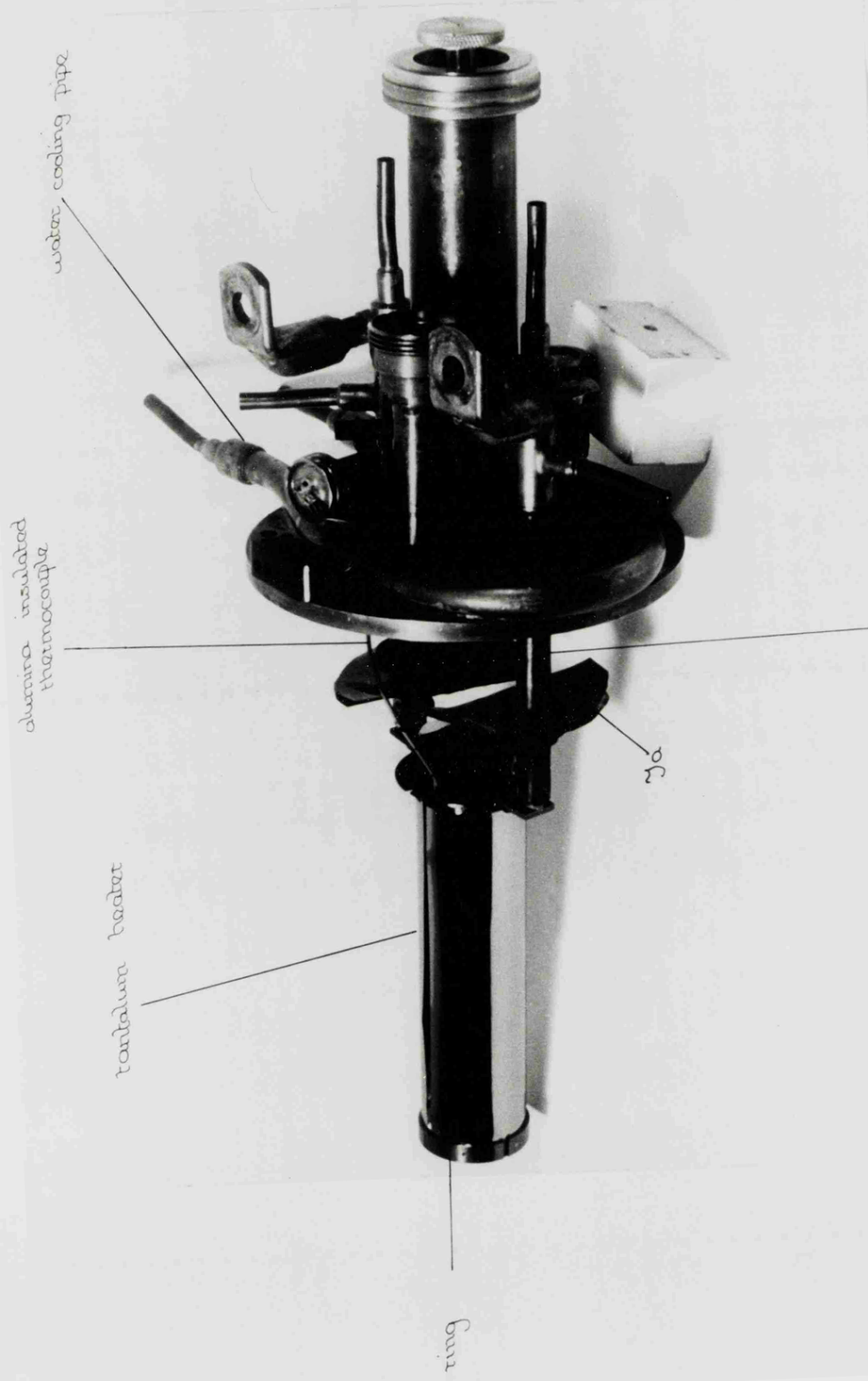


Fig 3.7 Photograph of the furnace

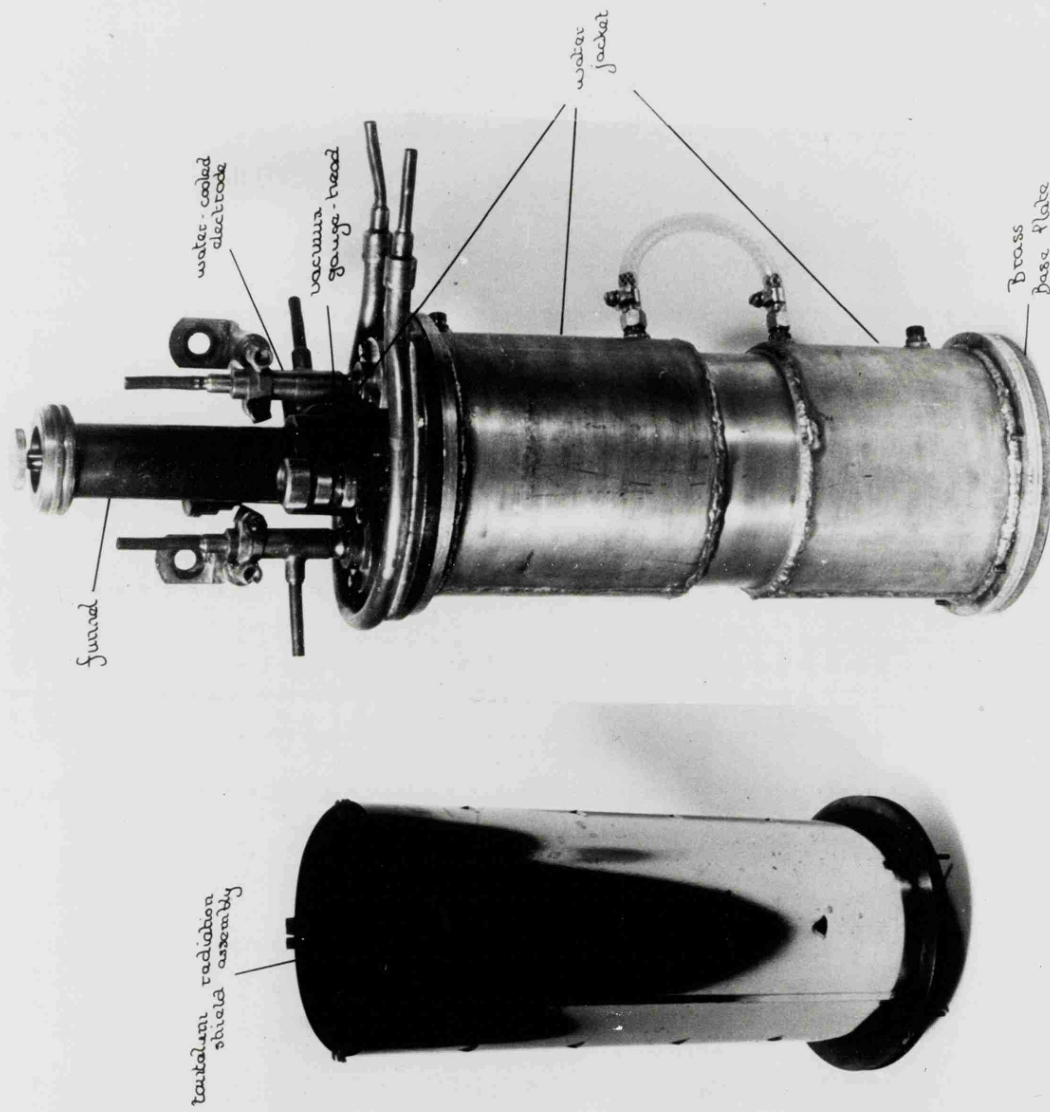


Fig. 38 Photograph of the Furnace and Radiation Shields

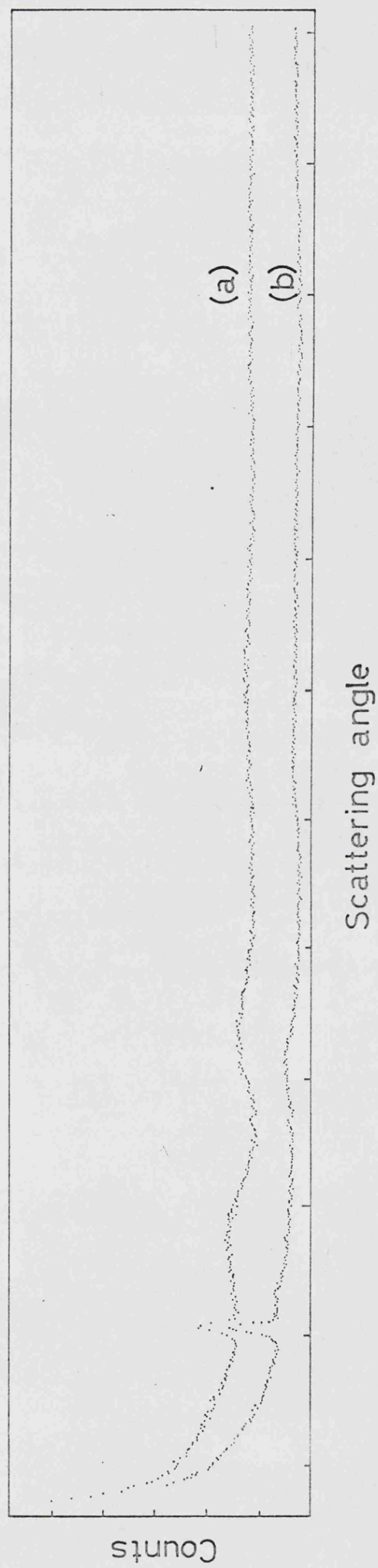


FIG. 4.0 AN EXAMPLE OF EXPERIMENTAL DATA SHOWING SCATTERING FROM (a) SAMPLE + CONTAINER AND (b) CONTAINER

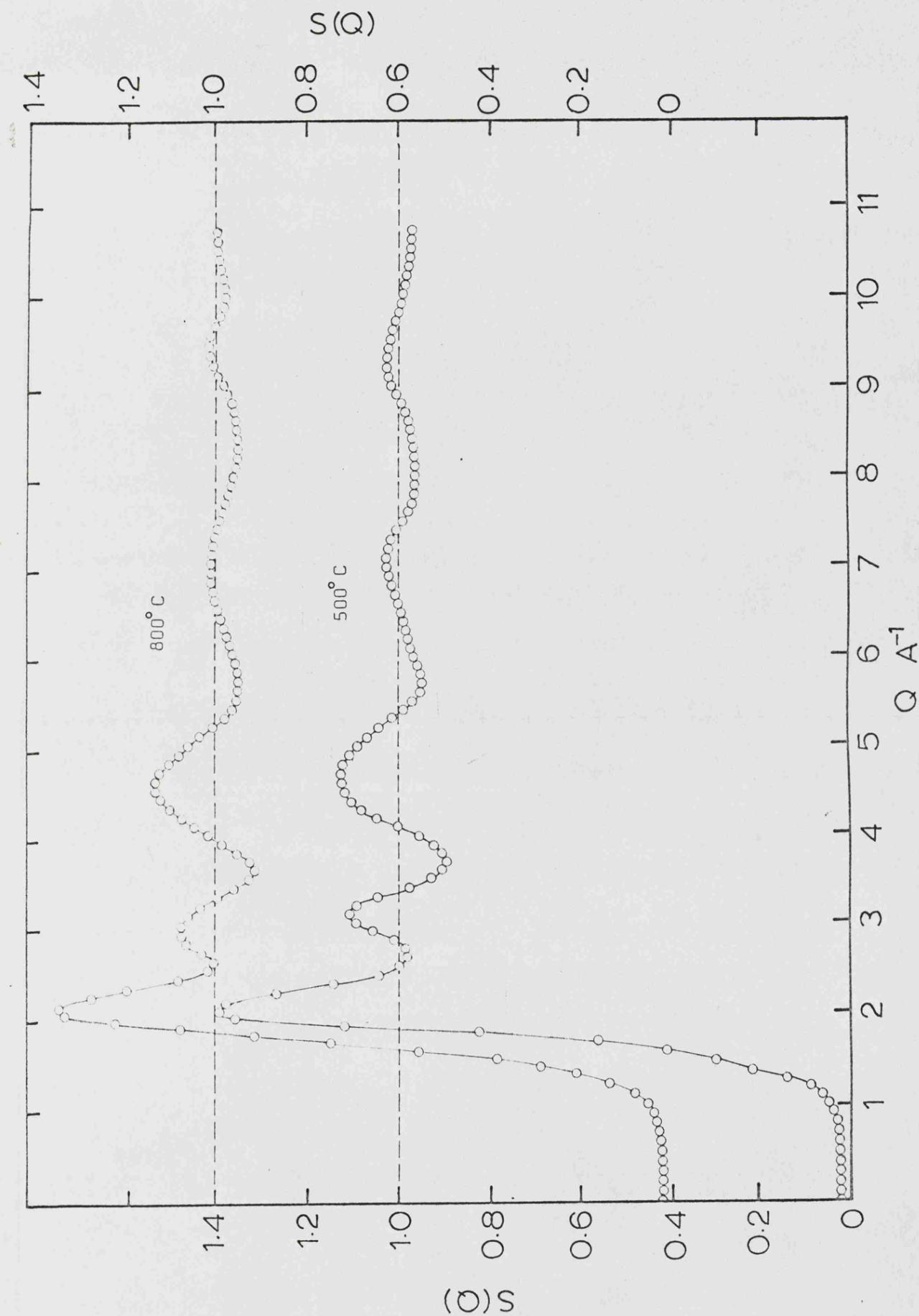


fig. 4.1 Structural Factors for pure Liquid Tellurium.

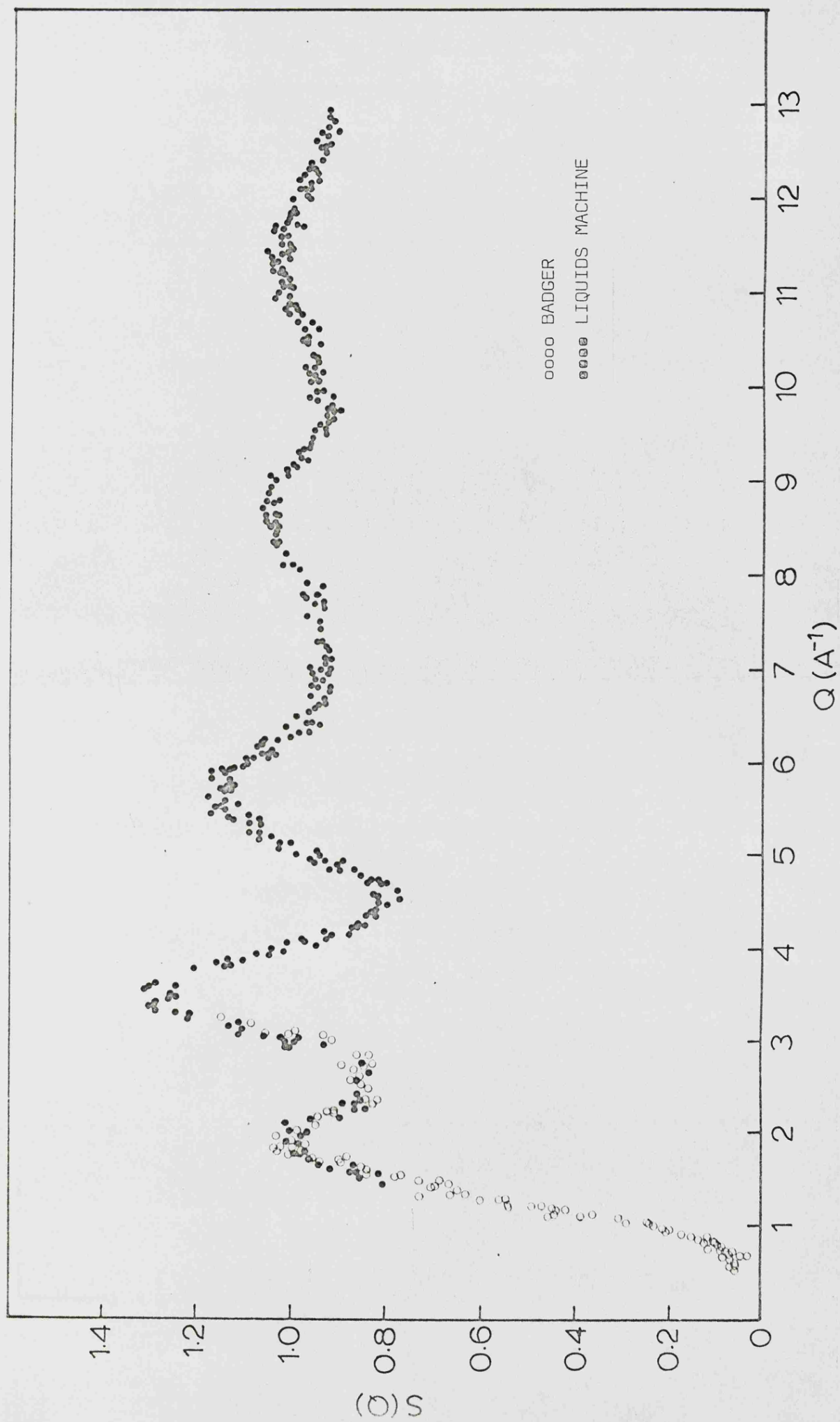


fig. 4.2 $S(Q)$ for Liquid Selenium with Statistical Errors.

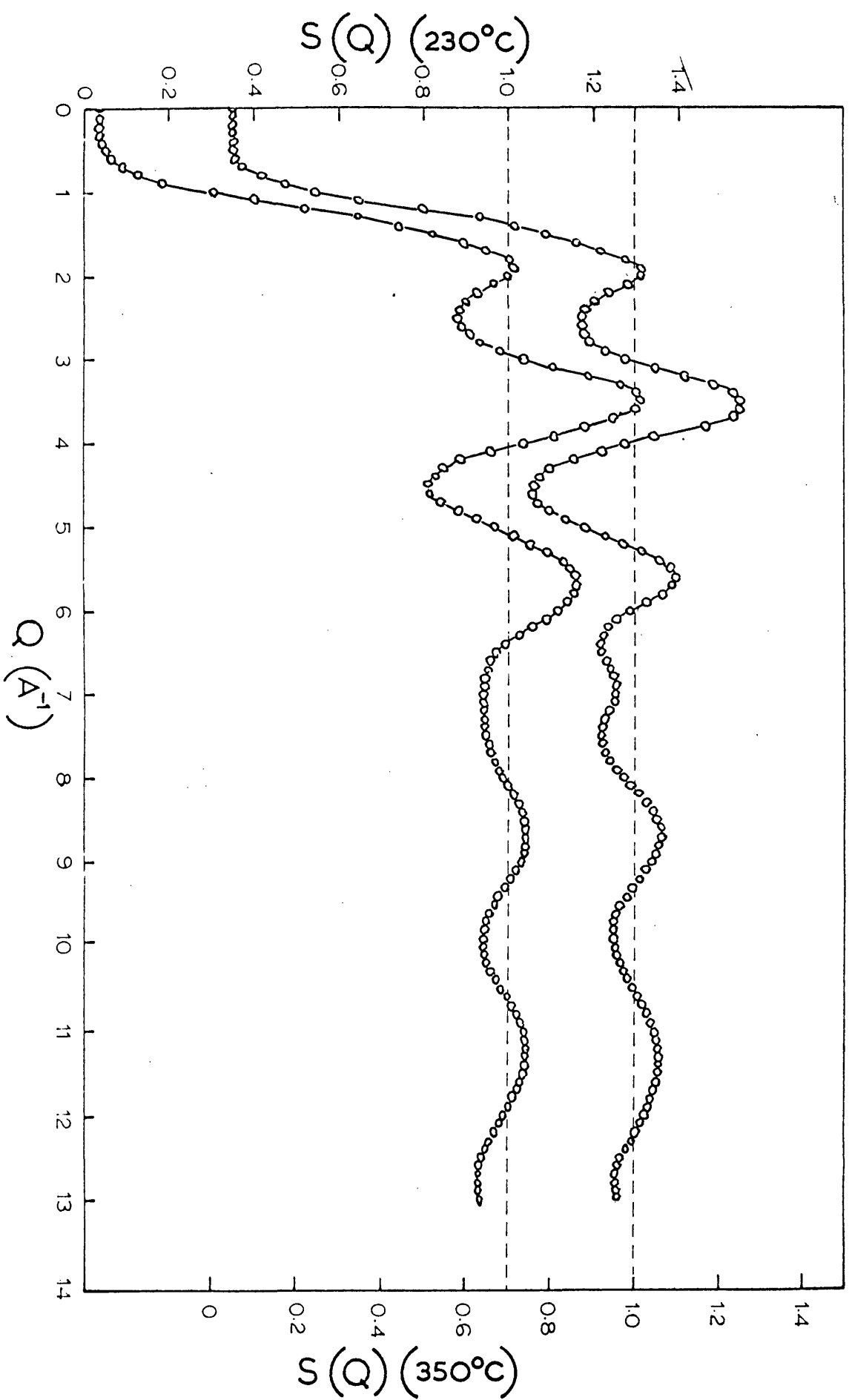


fig. 4.3 Structure Factors for pure Liquid Selenium.

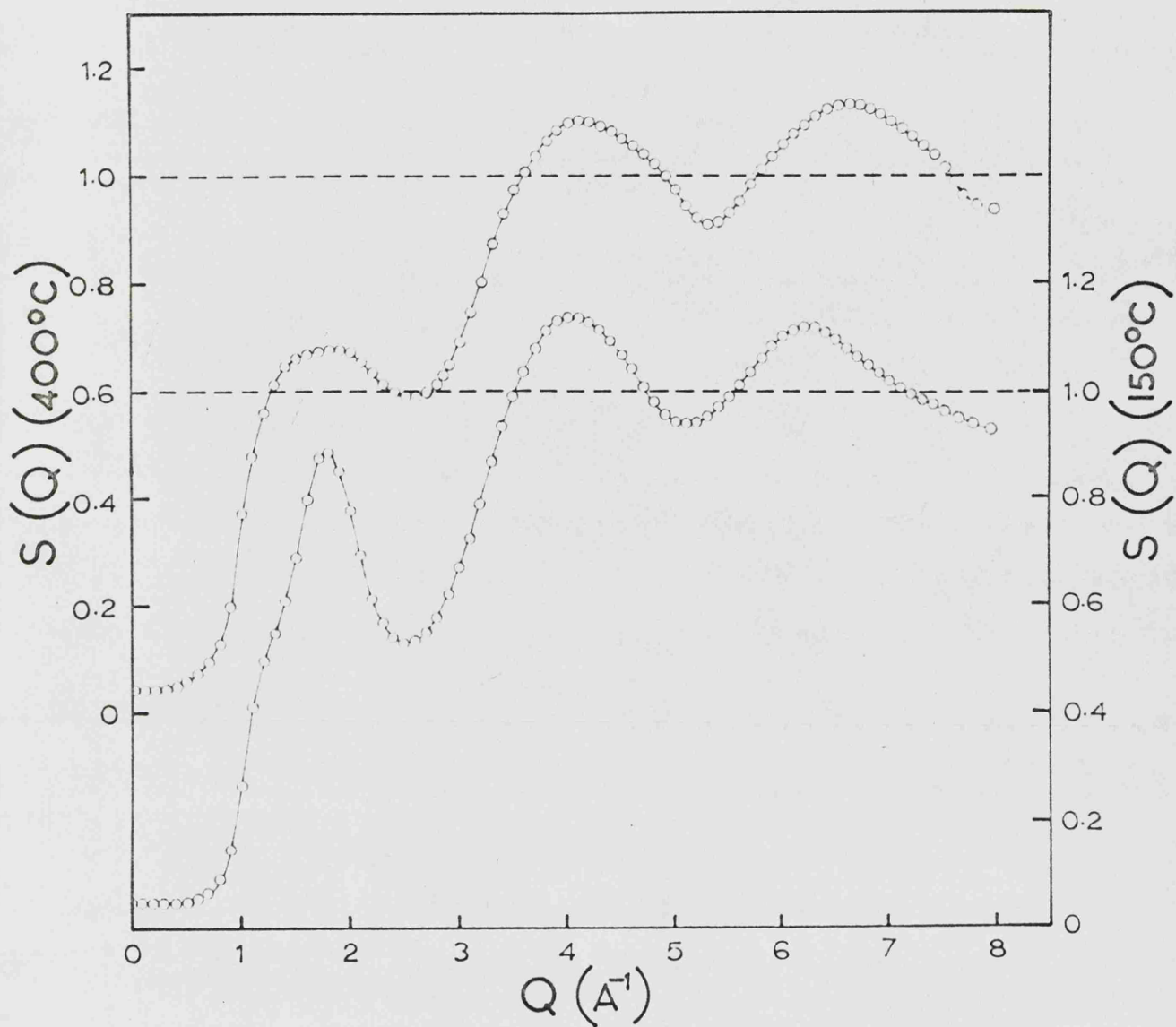


fig.4.4 Structure Factors for pure Liquid Sulphur.

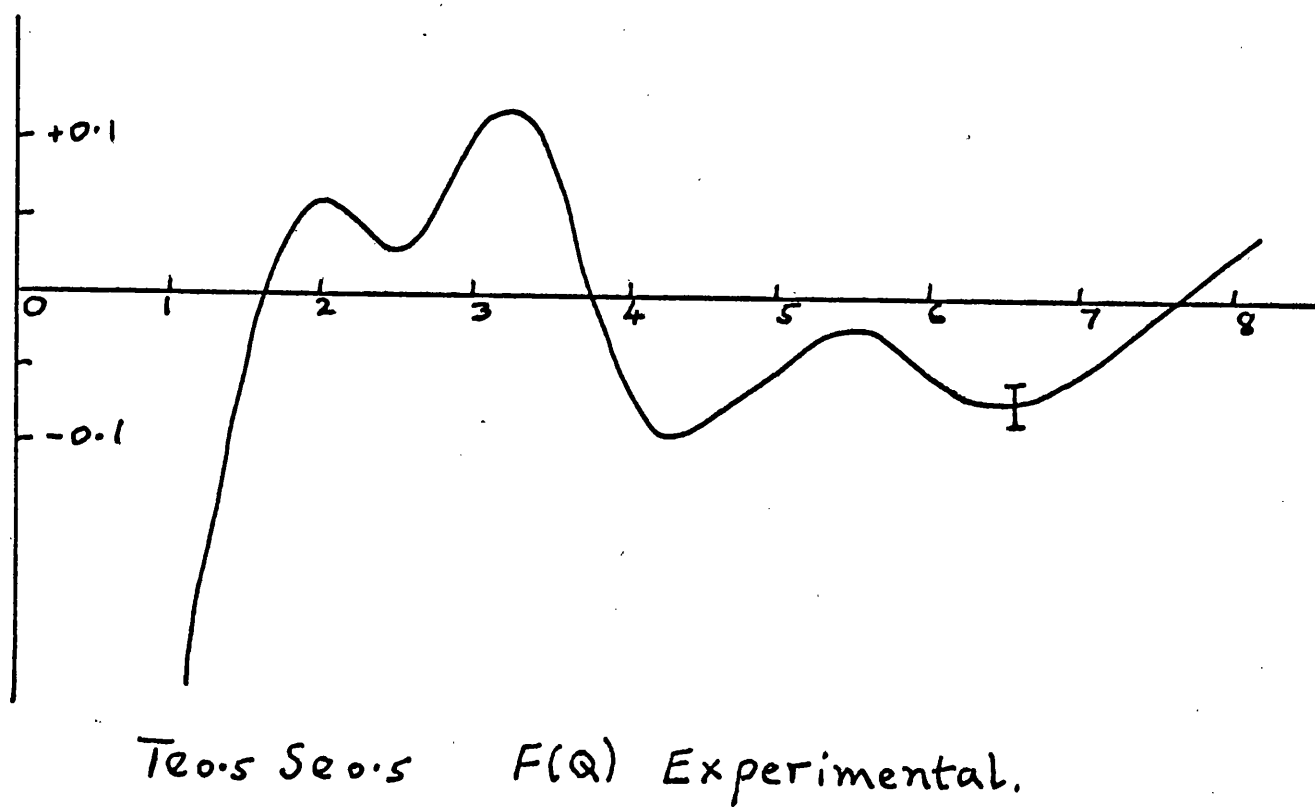
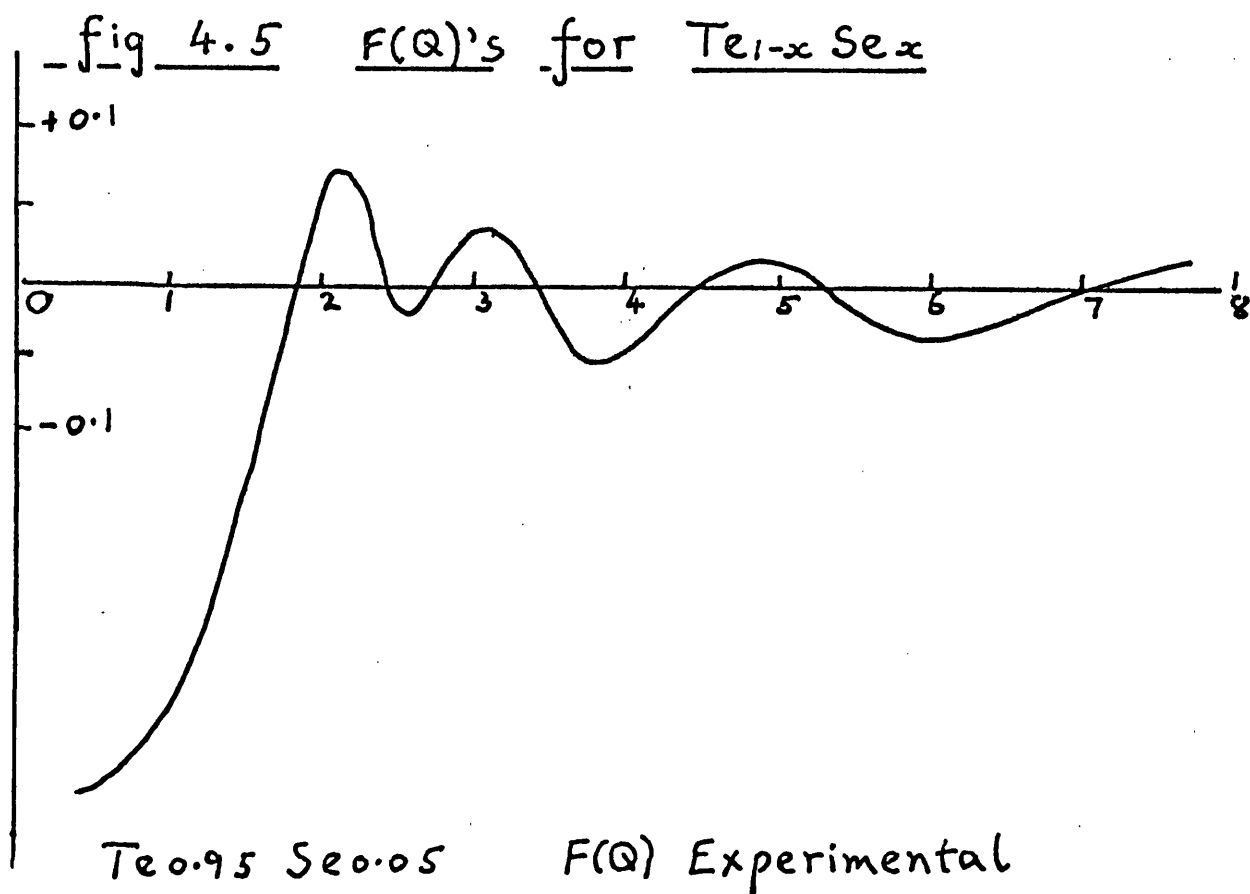
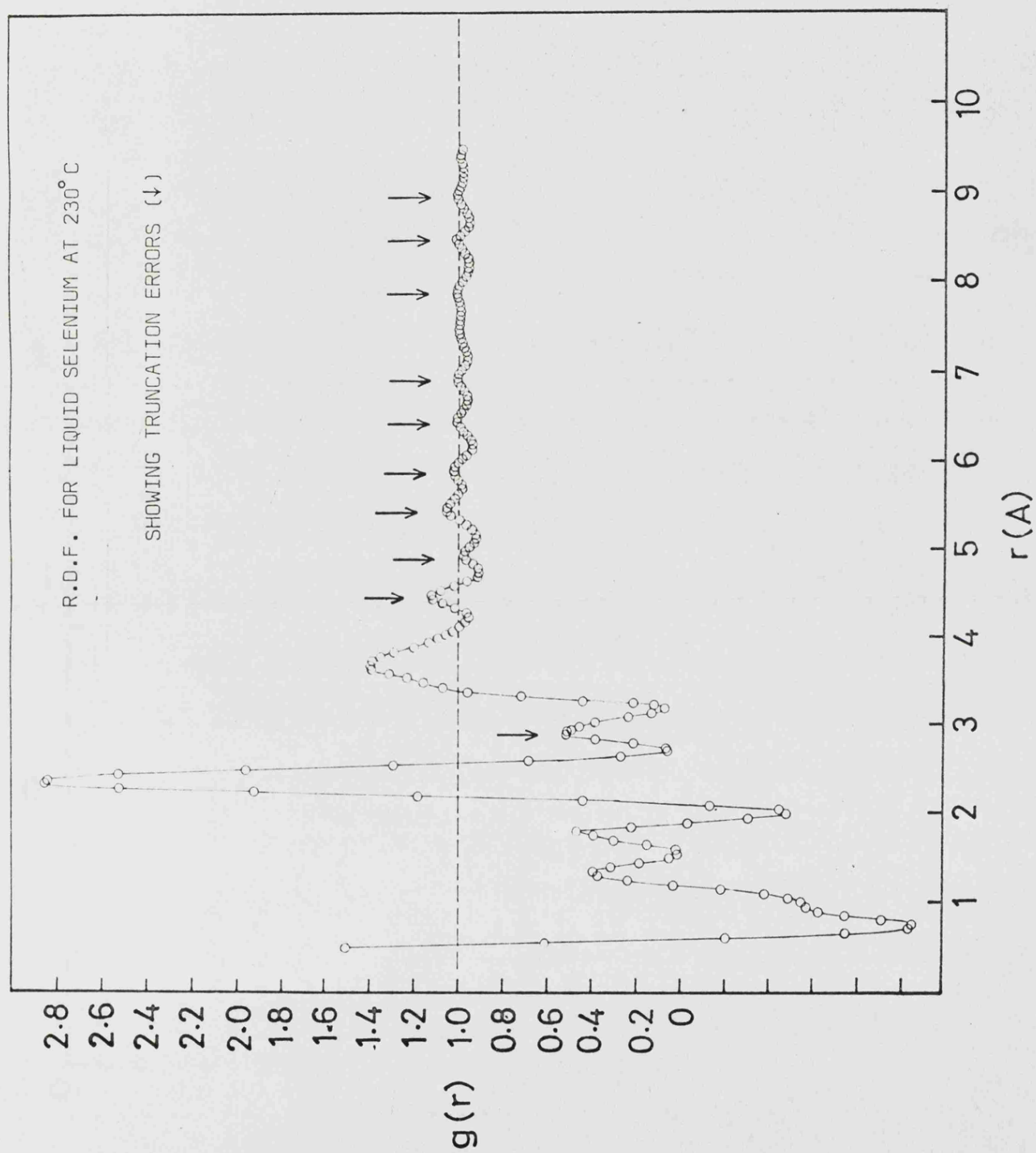


FIG. 4.6



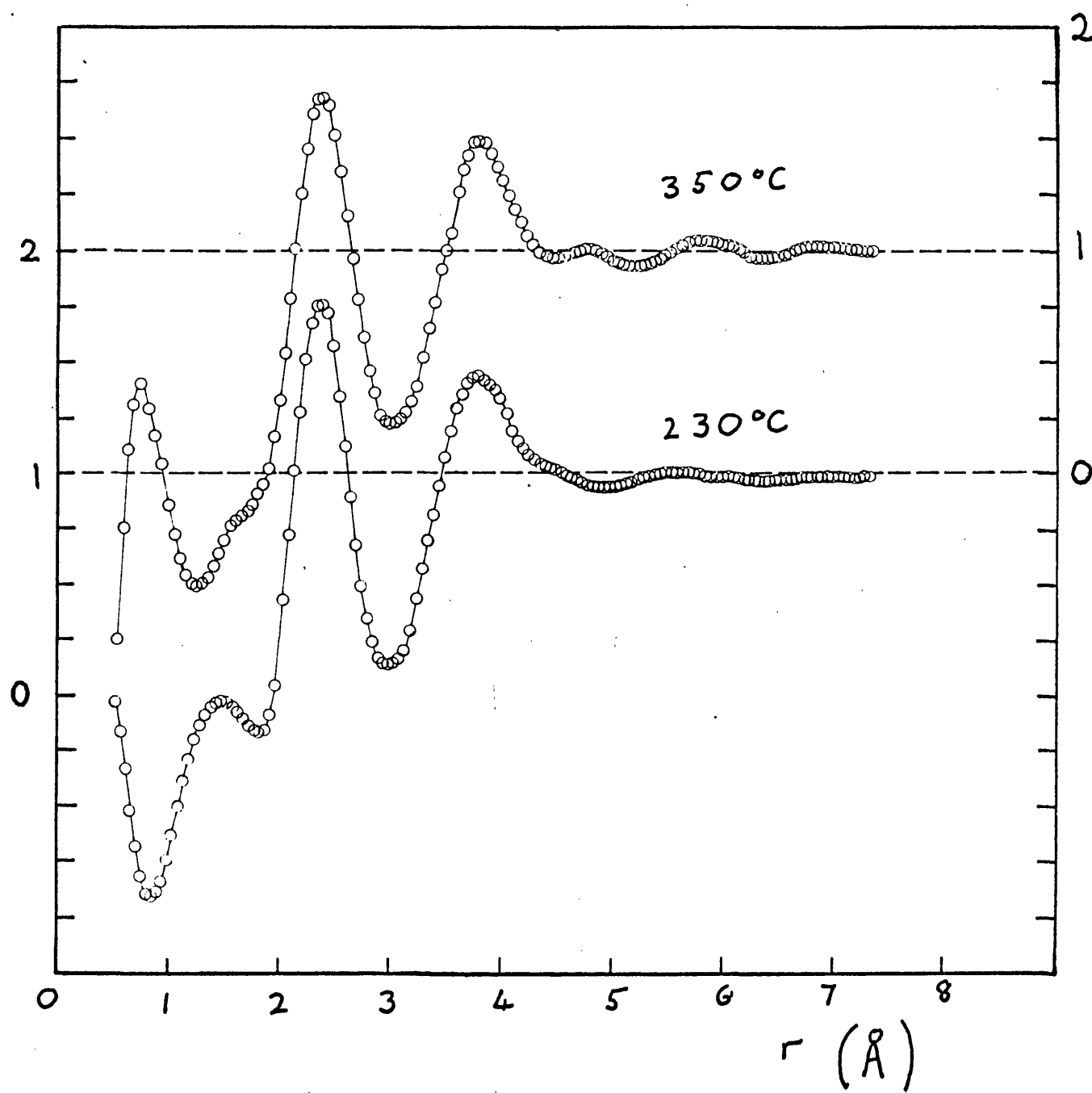


fig. 4.7 $g(r)$'s for Liquid Selenium using a window function $W = \frac{1}{2} \left(1 + \cos \left(\frac{\pi Q}{Q_m} \right) \right)$.

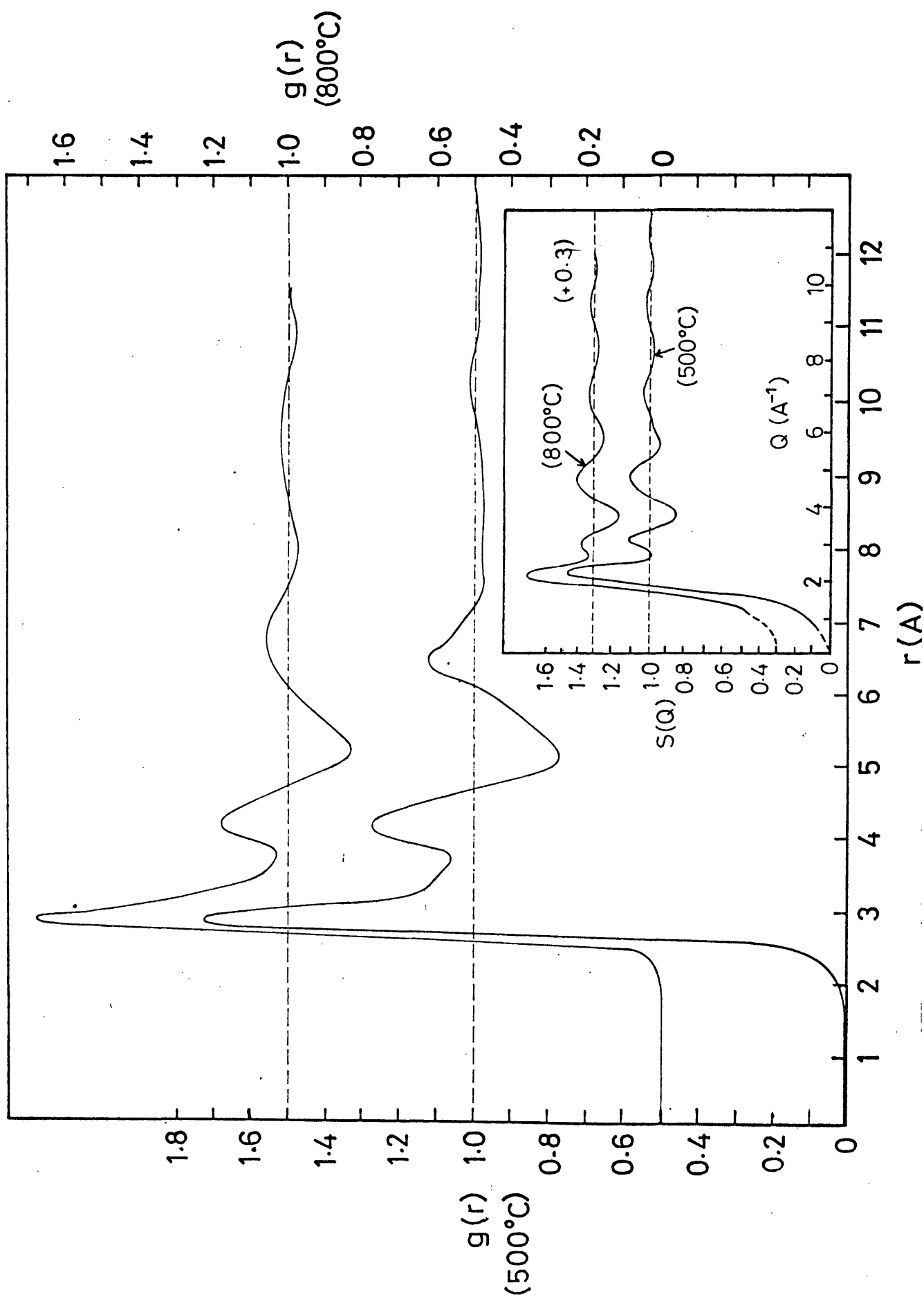


fig.4.8 $g(r)$'s for pure Tellurium with regenerated $S(Q)$'s.

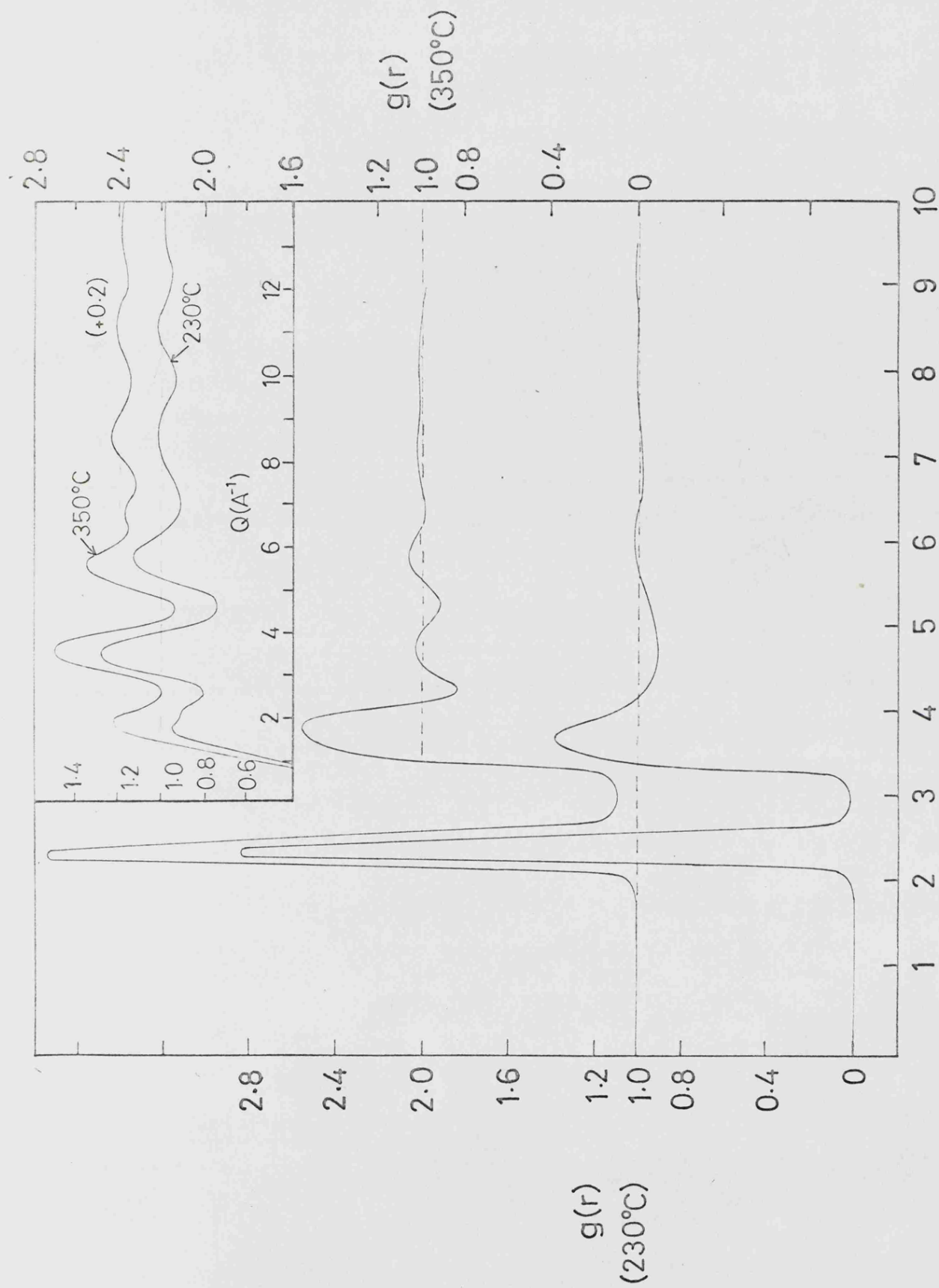


fig.4.9 Radial Distribution Functions for pure Liquid Selenium.

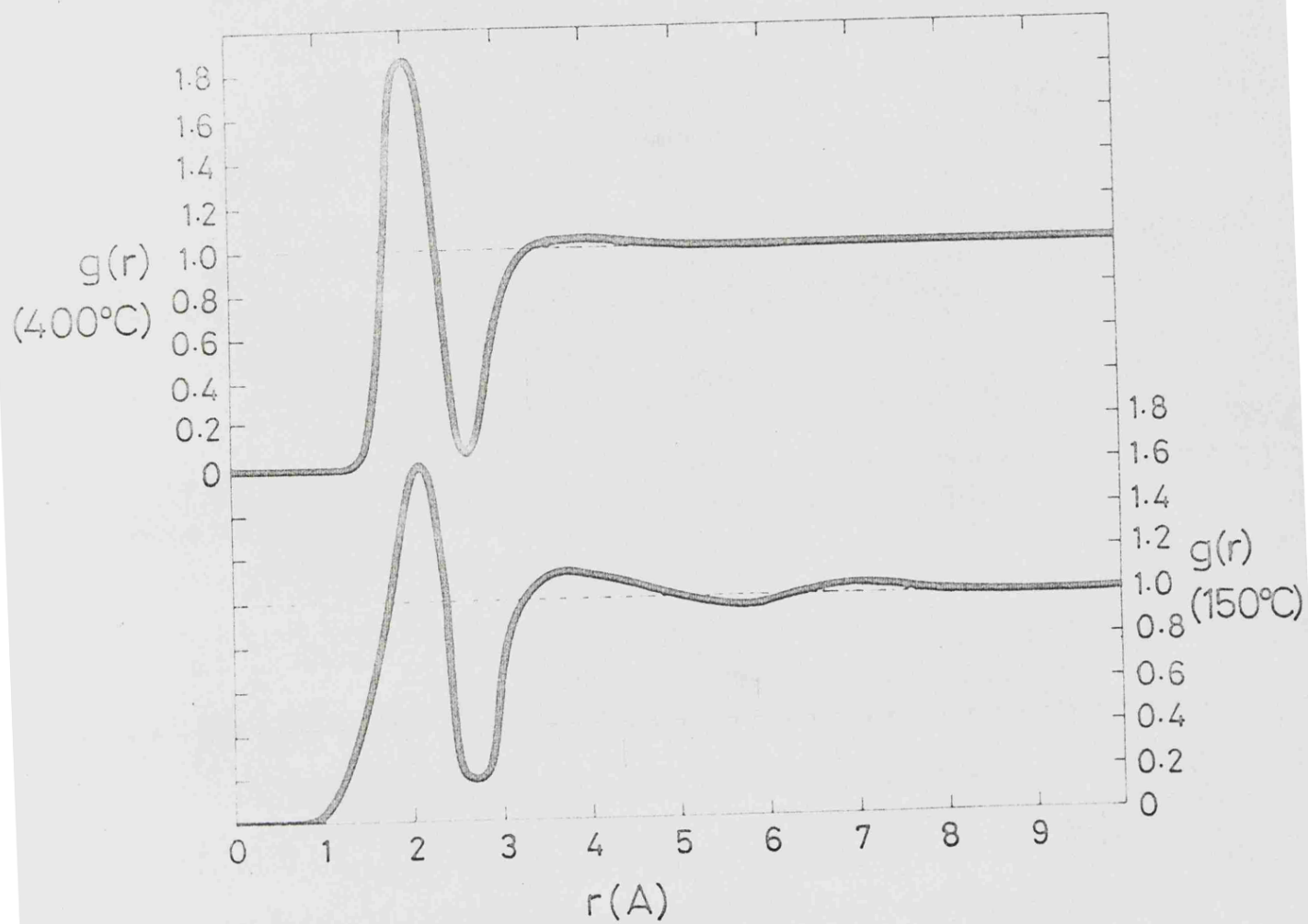


FIG. 4.10 R.D.F. FOR PURE LIQUID SULPHUR

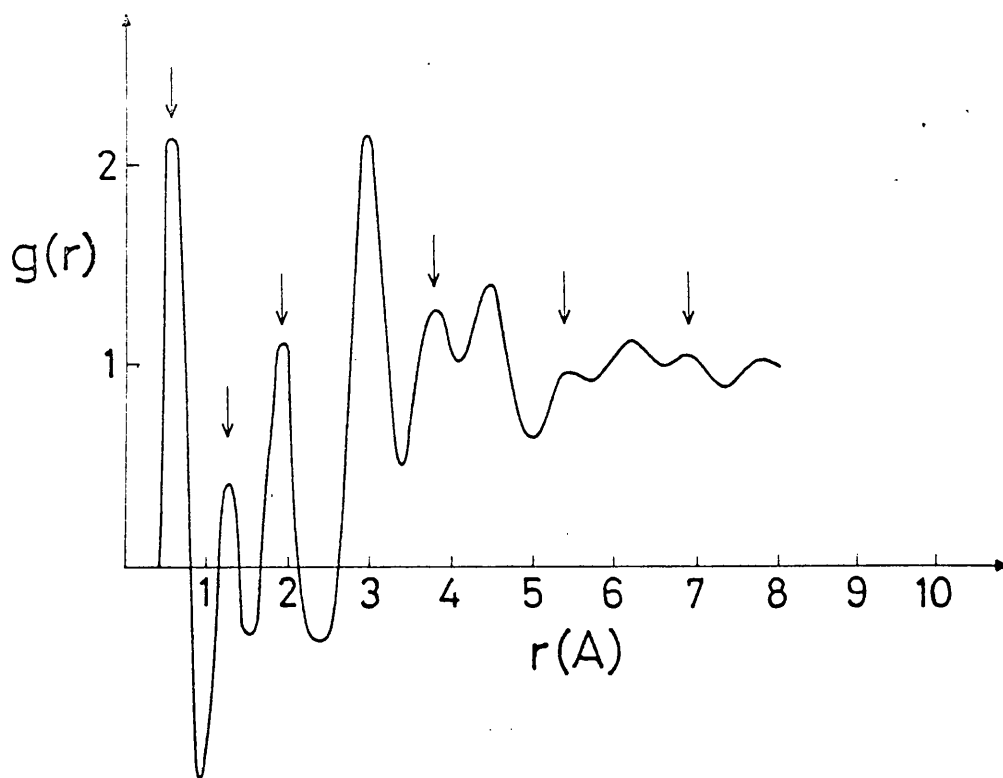


Figure 4.11. FRENCH $g(r)$ FOR LIQUID TELLURIUM AT 675°C
SHOWING TRUNCATION ERRORS. (↓)

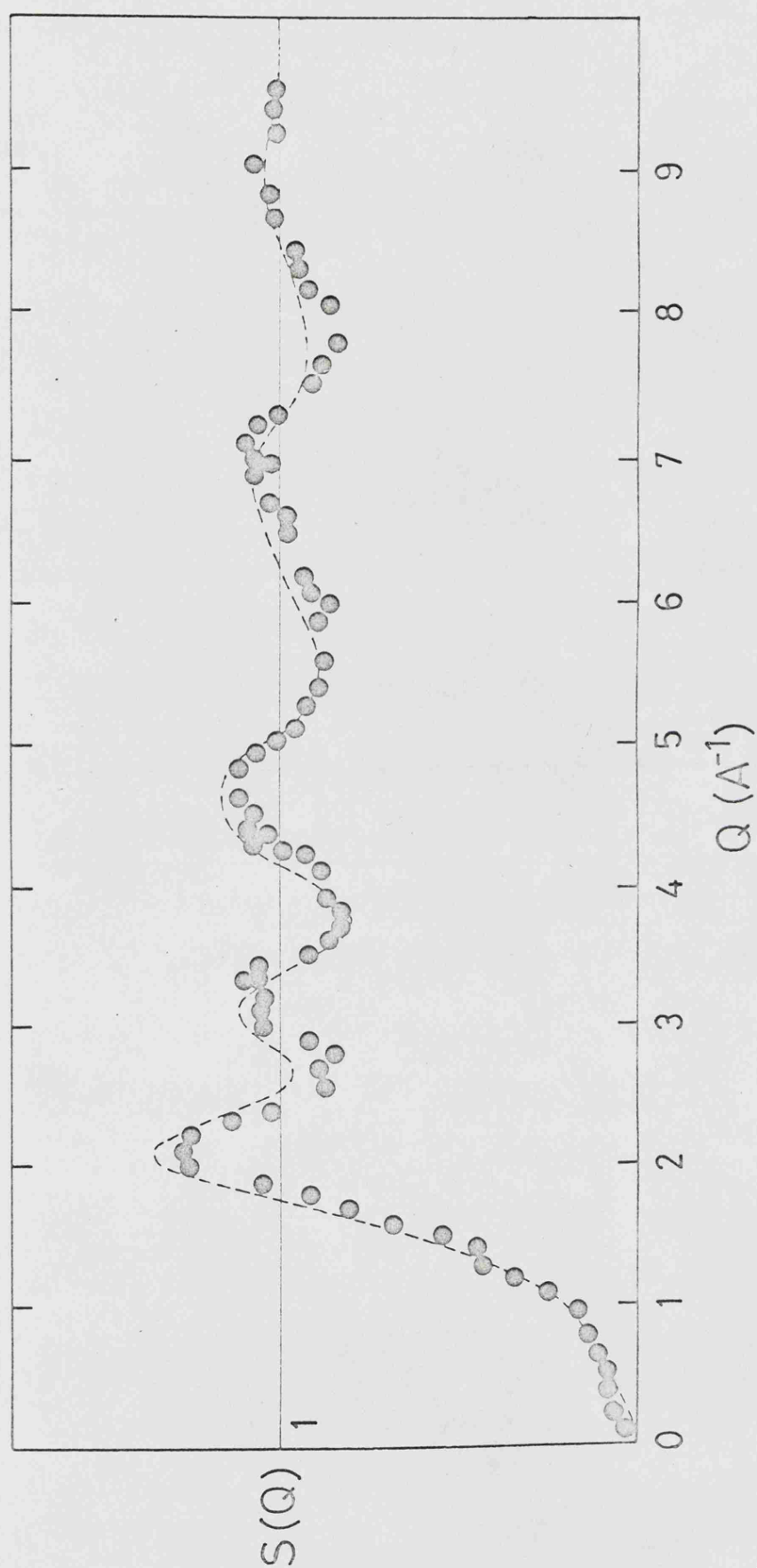


FIG. 4.12 FRENCH STRUCTURE FACTORS FOR LIQUID TELLURIUM AT 675°C

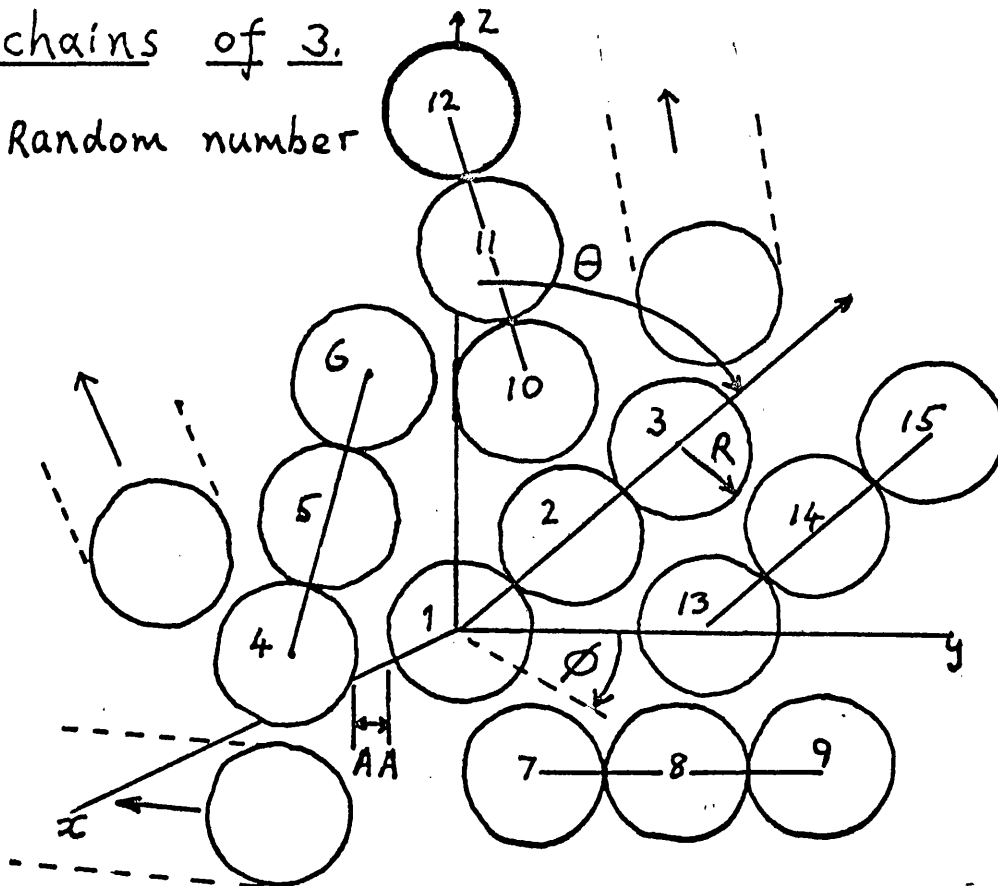
oooo data points

----- $S(Q)$ regenerated from $g(r)$ without peak at $3.82 \text{\AA}$

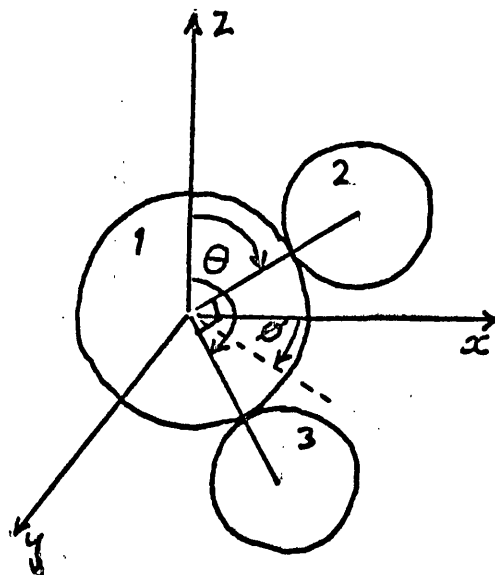
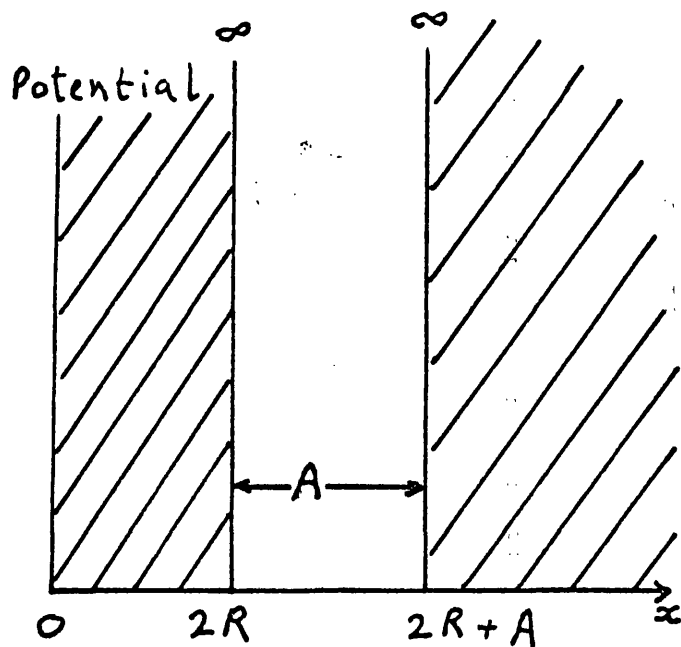
fig. 4.13 Computer Models in 3D.

a) Rigid chains of 3.

$$AA = A \times \text{Random number}$$



b) Box Potential
used for the models.



x = distance from
atomic centre.

Fig- 4.14 Rigid chains of 3 atoms in 3-dimensions

Radius = 1.7 $A = 0.5$

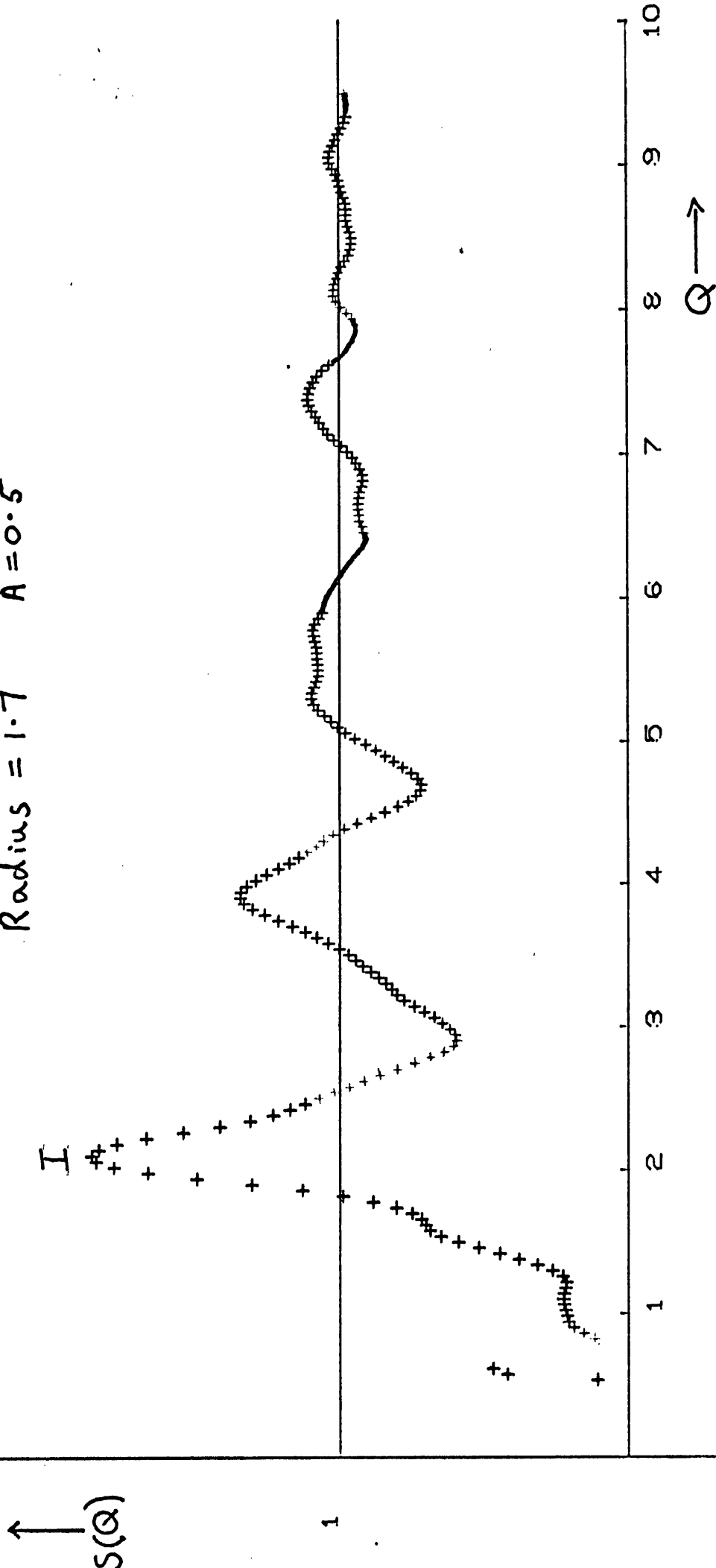


Fig. 4.15. Rigid chains of 3 in 3-dimensions

Radius = 1.7 A = 1.7

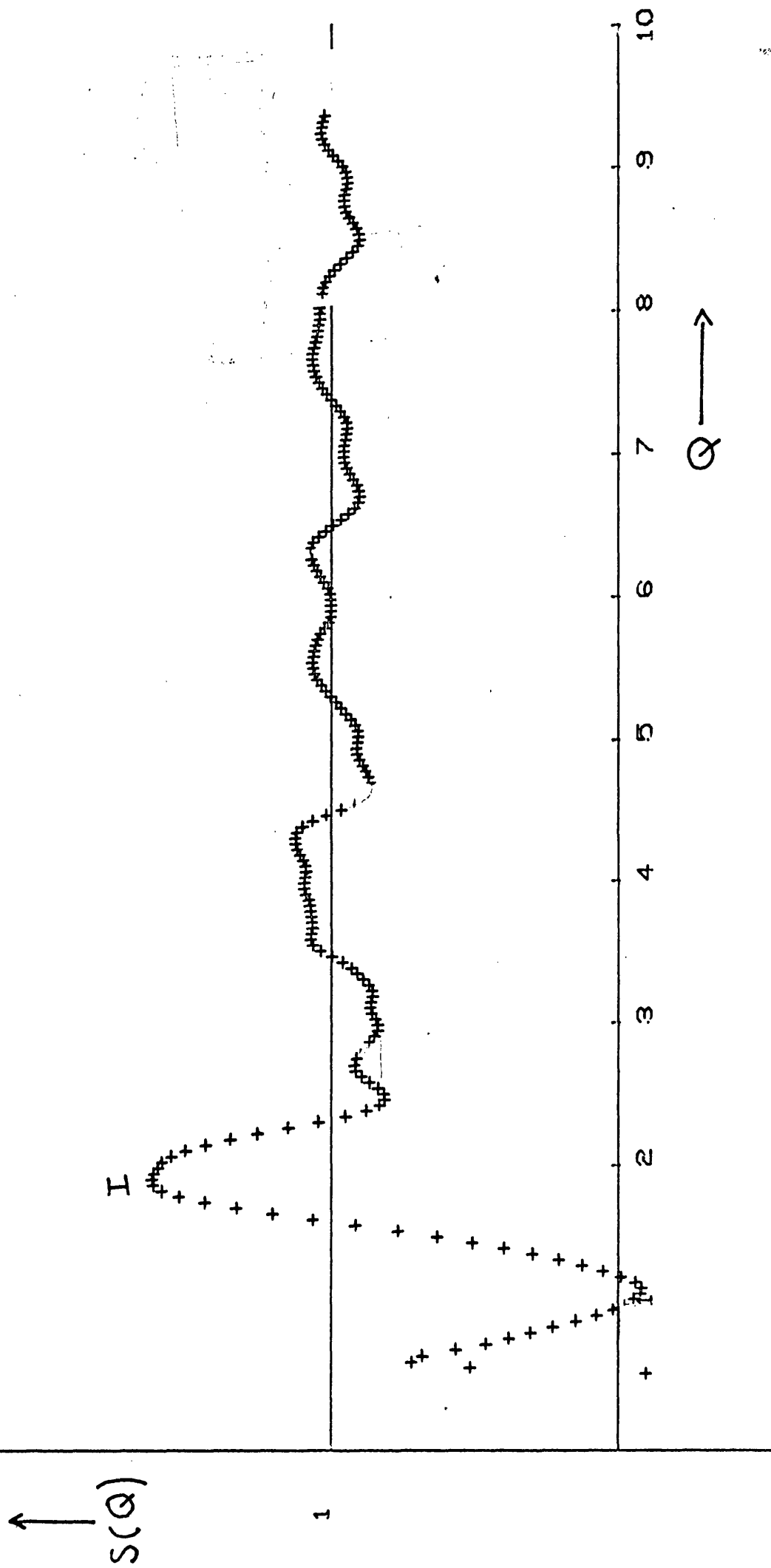


Fig 4.16 Rigid chains of 3 in 3-dimensions

$$R = 1.7 \quad A = 3.4$$

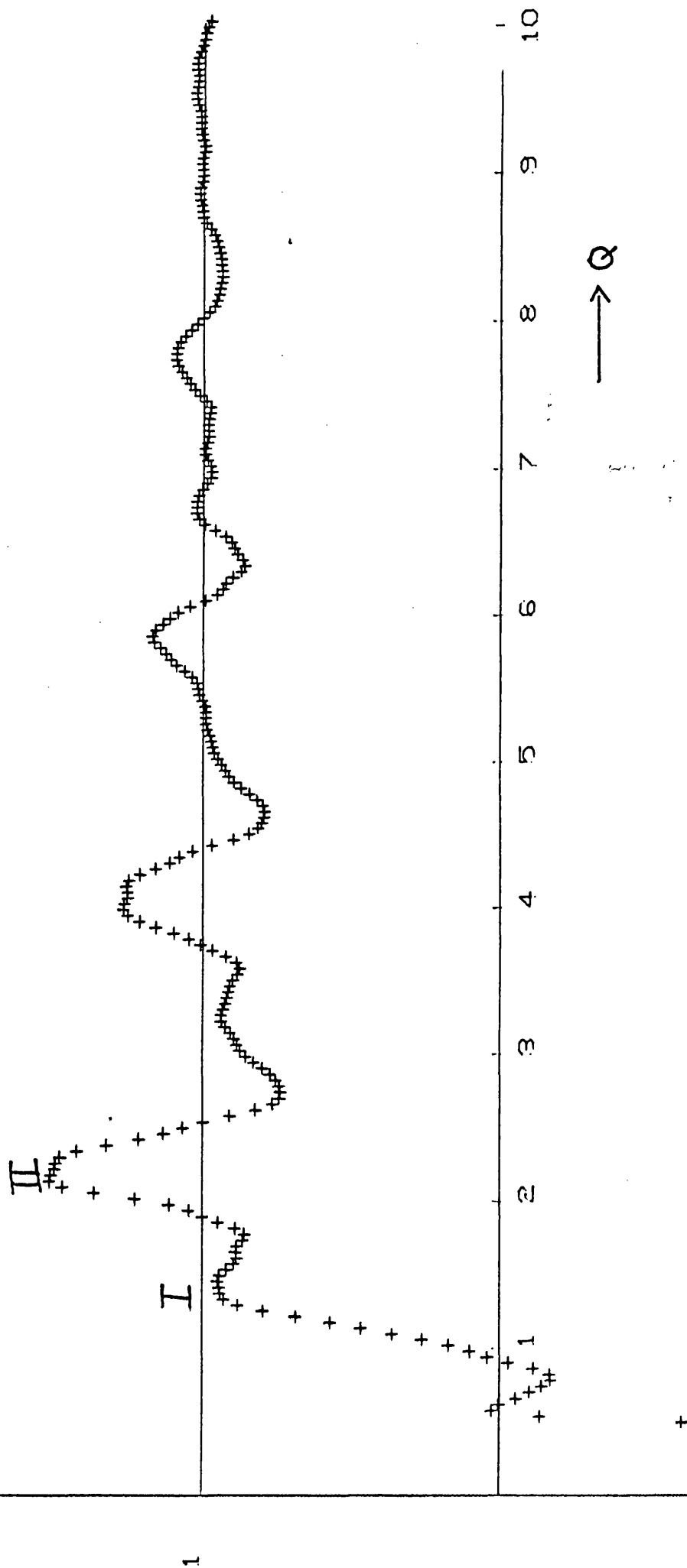
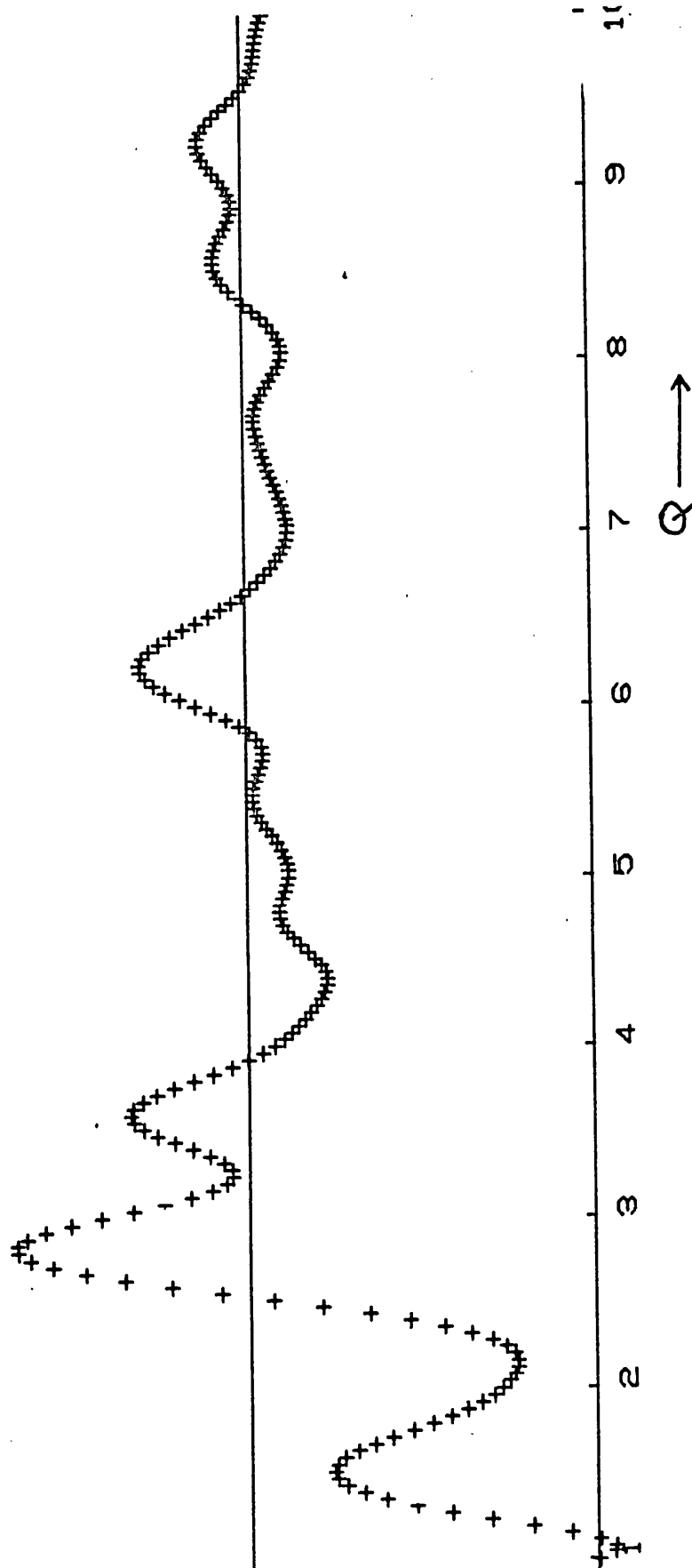
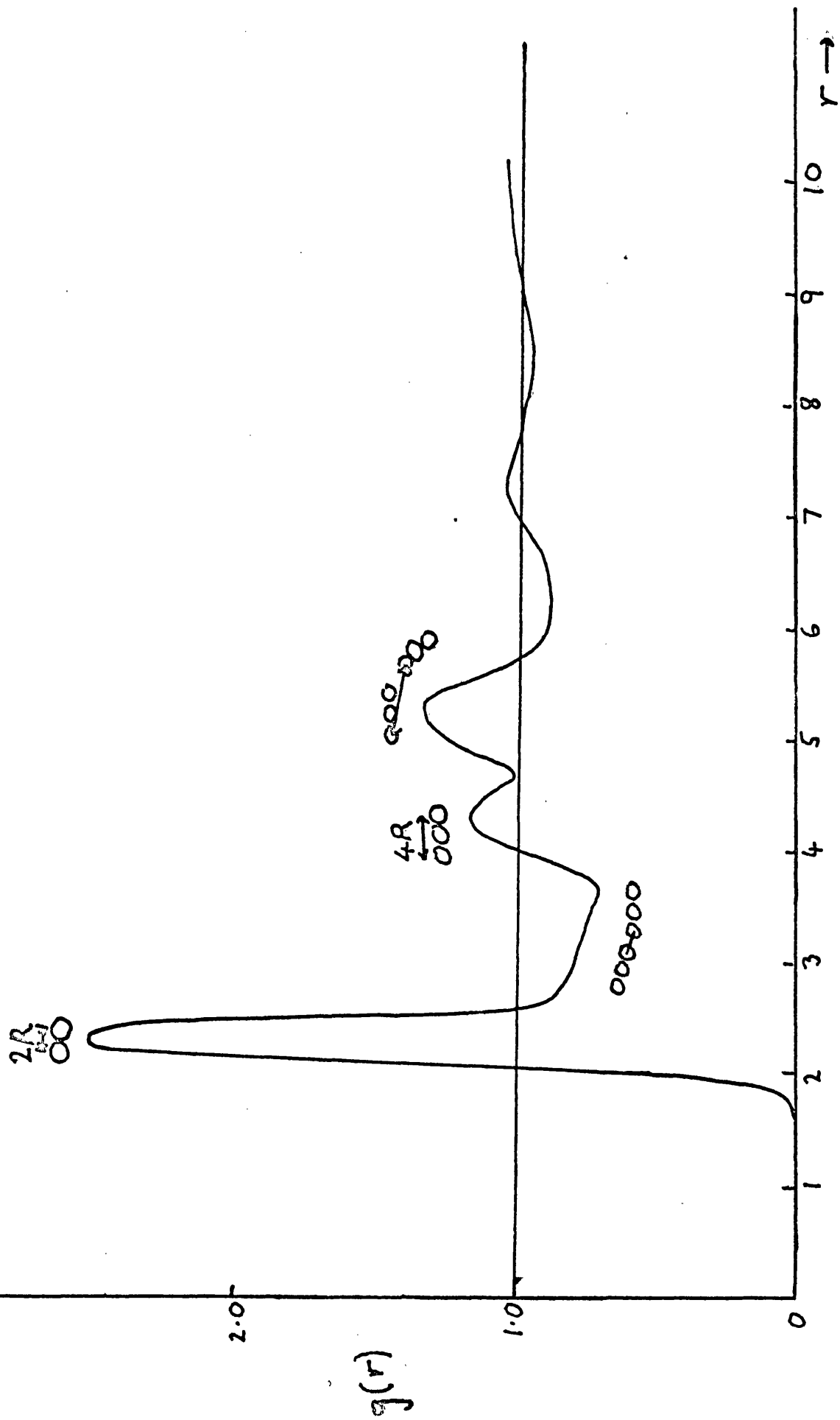


fig-4.17 Rigid chains of 3 in 3-dimensions

$$R = 1.1 \quad A = 3.4$$





-fig. 4.18. R.D.F. for rigid chains of 3 in 3D.
 $R = 1.1$ (Average over 2 central chains)

fig 4.19. Molecular Models.

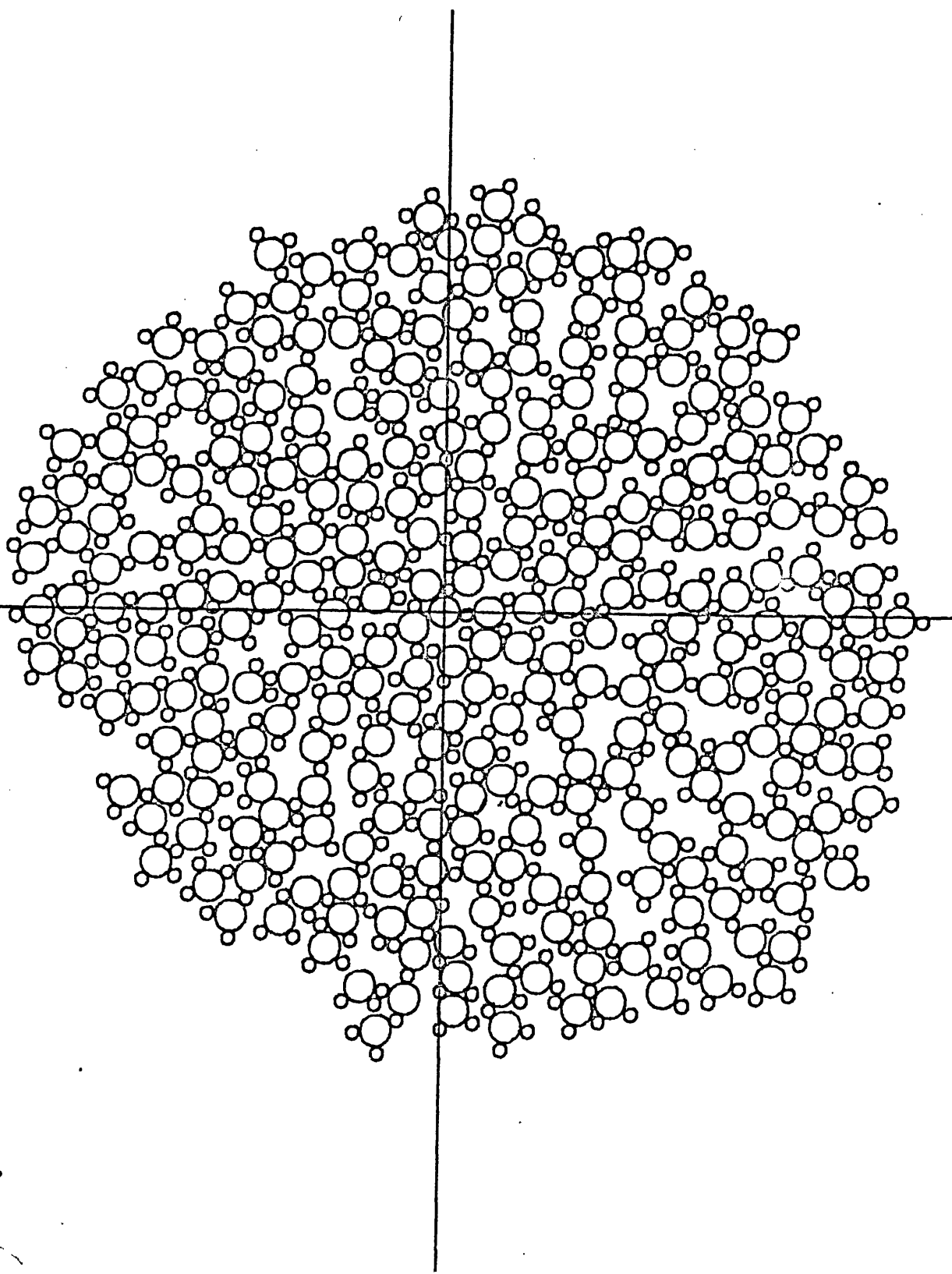


fig. 4.20a Molecular Models

$S_{Cu-Cu}(Q)$ for Cu_2Te molecules

$$R_{Te} = 1.405 \quad R_{Cu} = 1.225 \quad A = 0.5$$

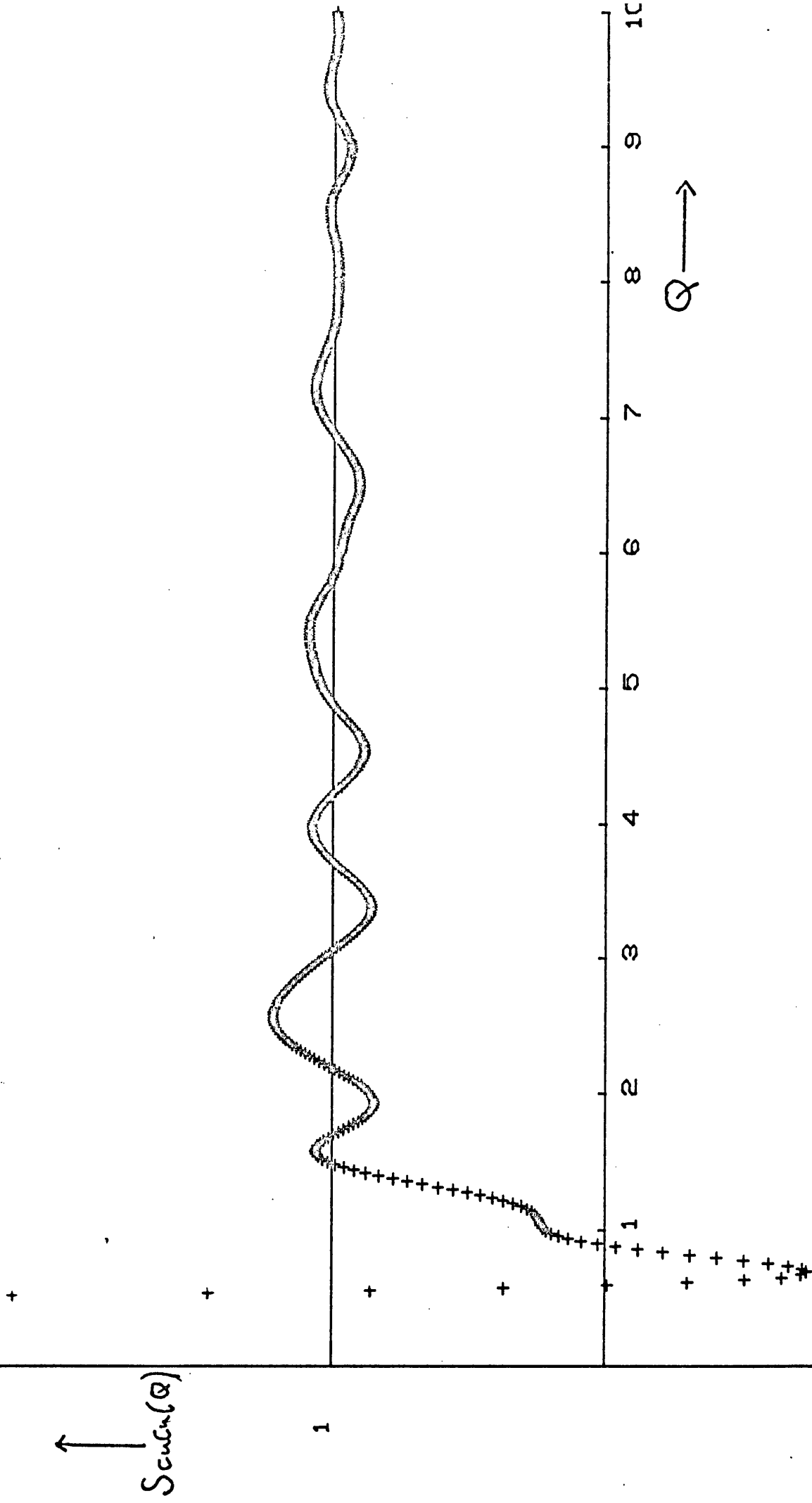


fig- 4.20b Molecular Models
 $S_{CuTe}(Q)$ for $CuTe$ molecules

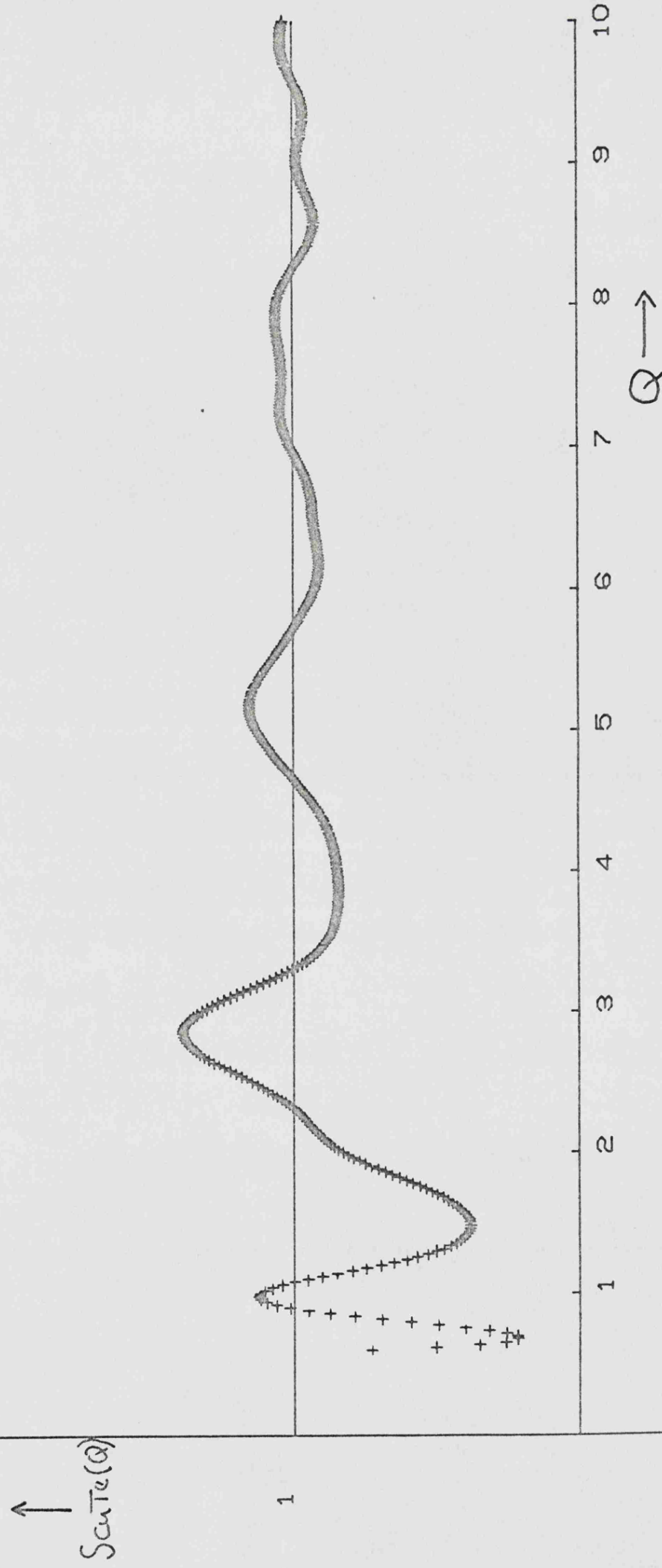


fig 4.20c Molecular Models
 $S_{Te-Te}(Q)$ for Cu_2Te molecules.

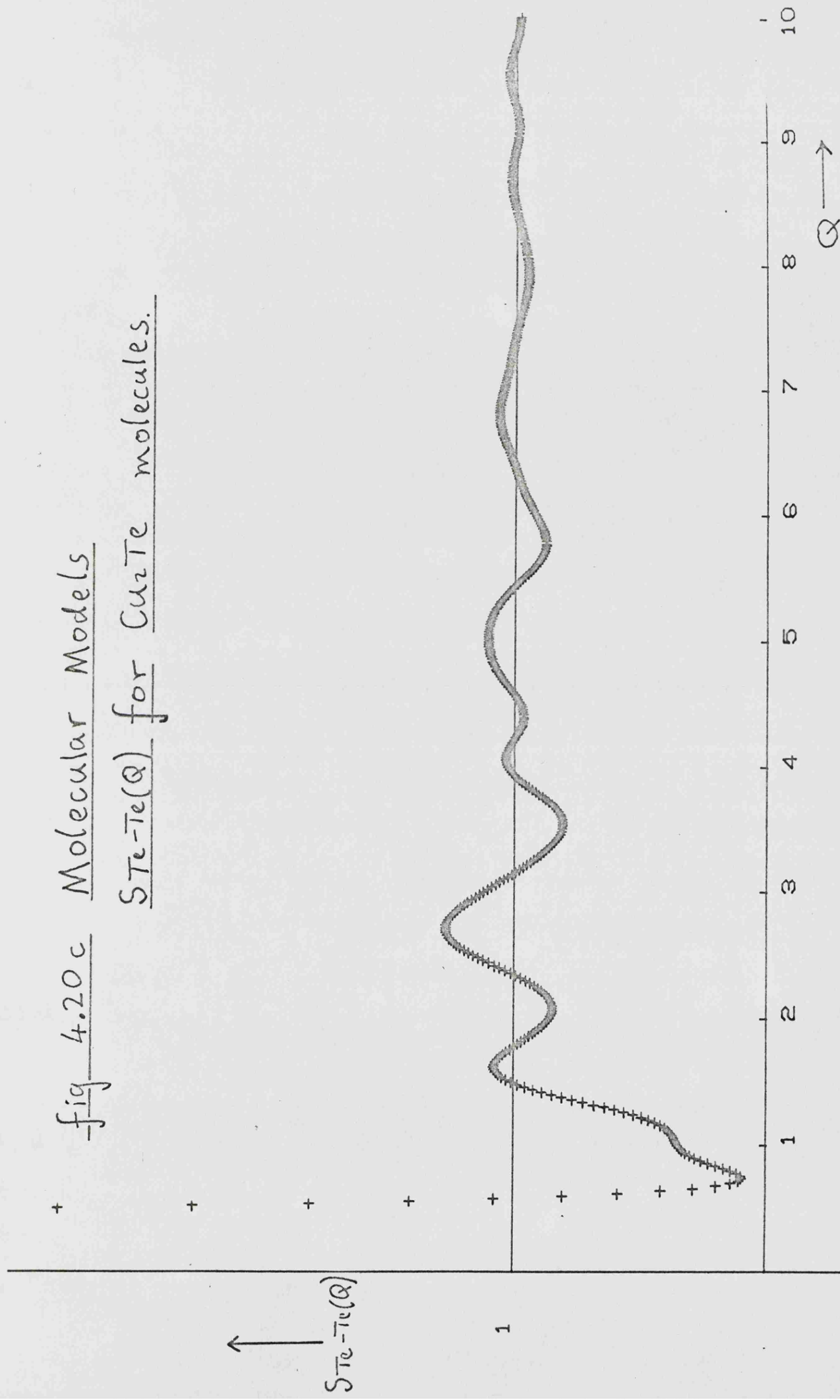
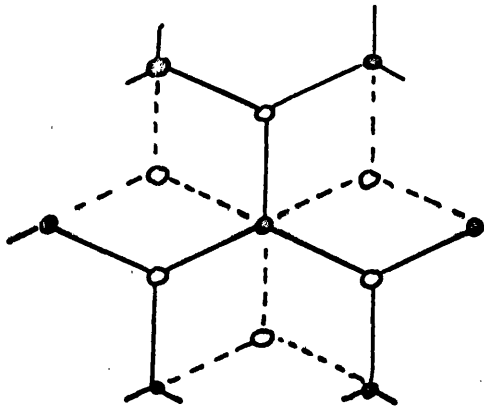
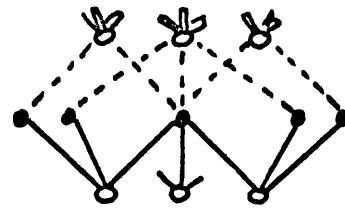


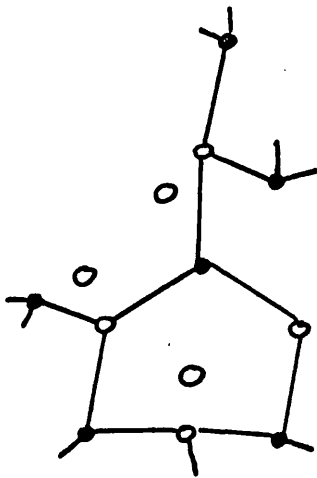
Fig 4.21 Structure of Liquid Tellurium
according to Cabane and Friedel.



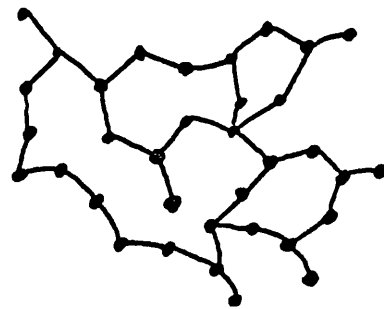
a) top



b) side



c) distorted structure



d) structure at
intermediate temperatures.

a, b and c show the high temperature structure, where covalent bonds join each atom to its 3 nearest neighbours (from Cabane and Friedel 1970).

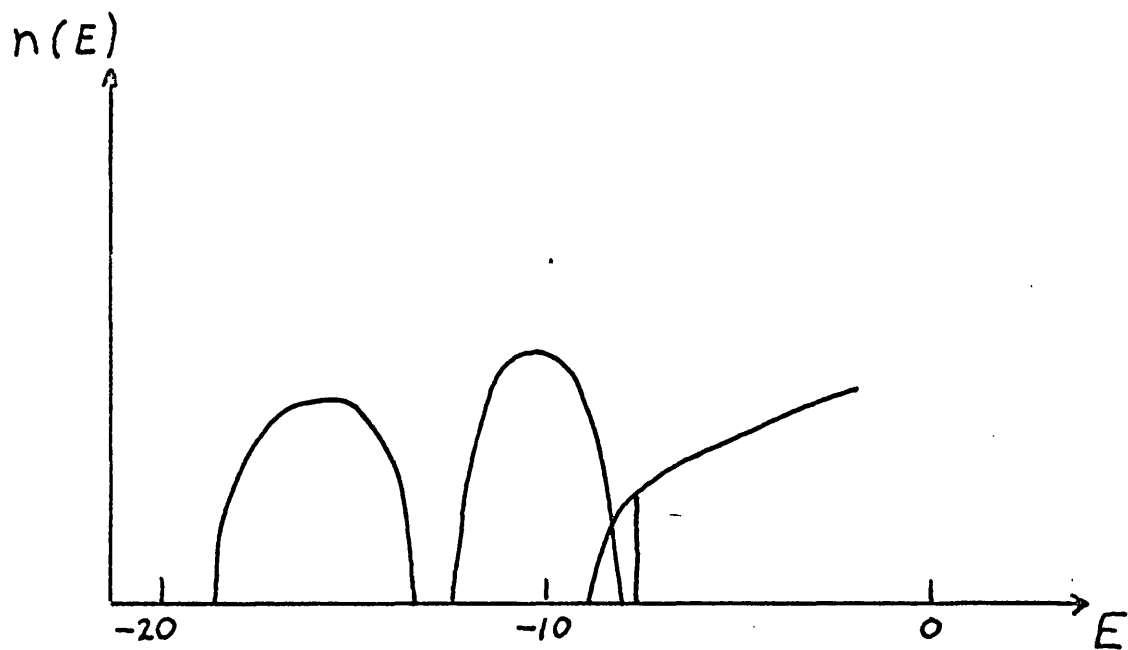
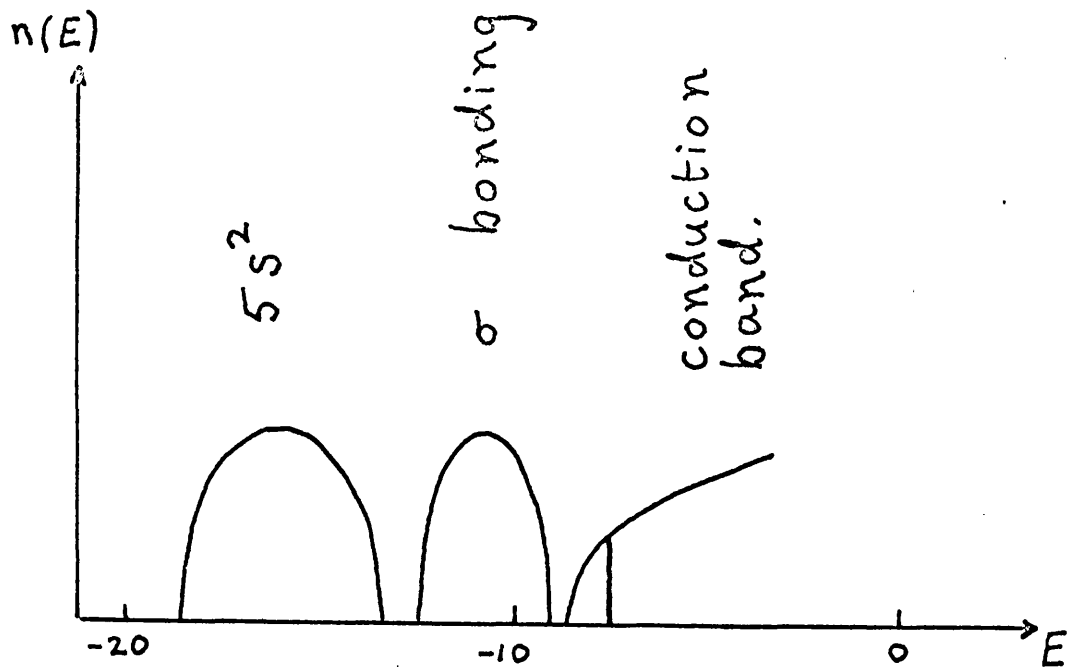
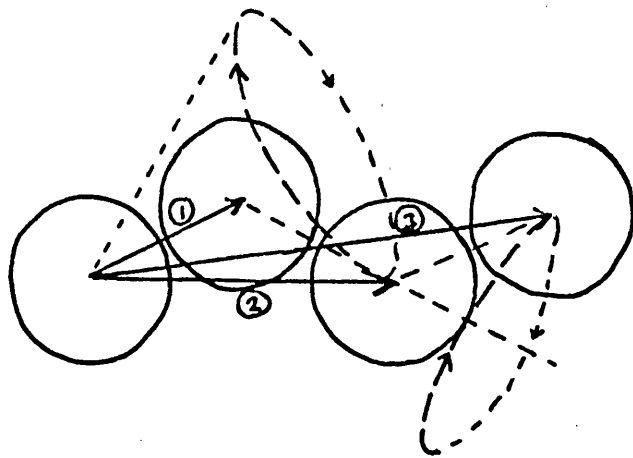
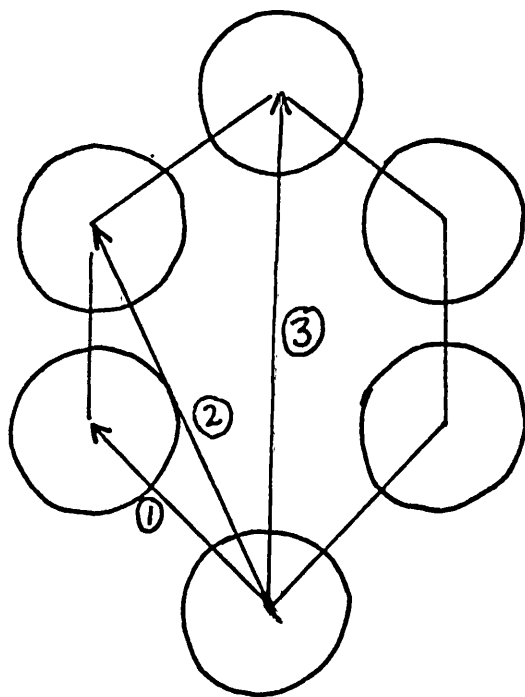


fig. 4.22. Density of states for a
network of ternary sites.
for liquid Tellurium

fig- 4.23 The structure of Liquid Selenium



a) A flexible chain with rotation about the bonds gives only 2 clearly defined distances.



b) Rings will produce at least 3 well defined distances.

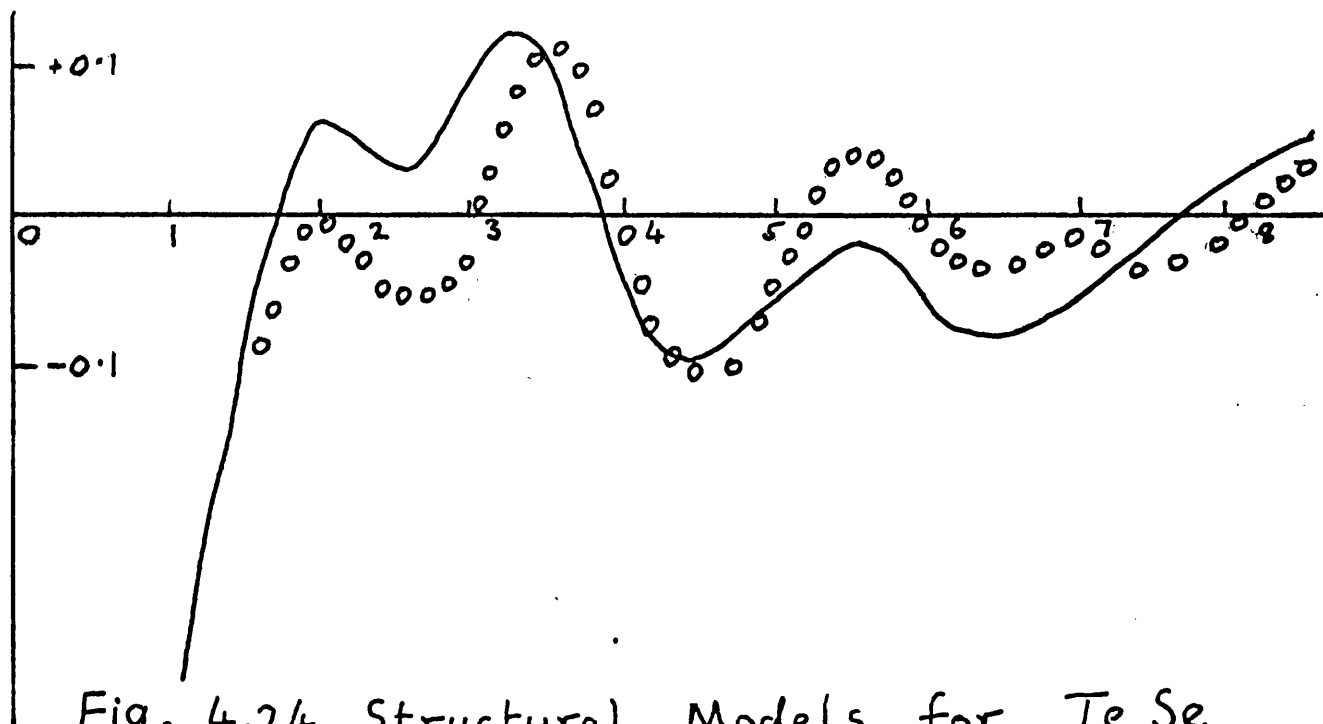


Fig. 4.24. Structural Models for Te Se

———— $F(Q)$ Experimental

oooooo $F(Q)$ Substitution model.

xxxxxx $F(Q)$ Inhomogeneous model.

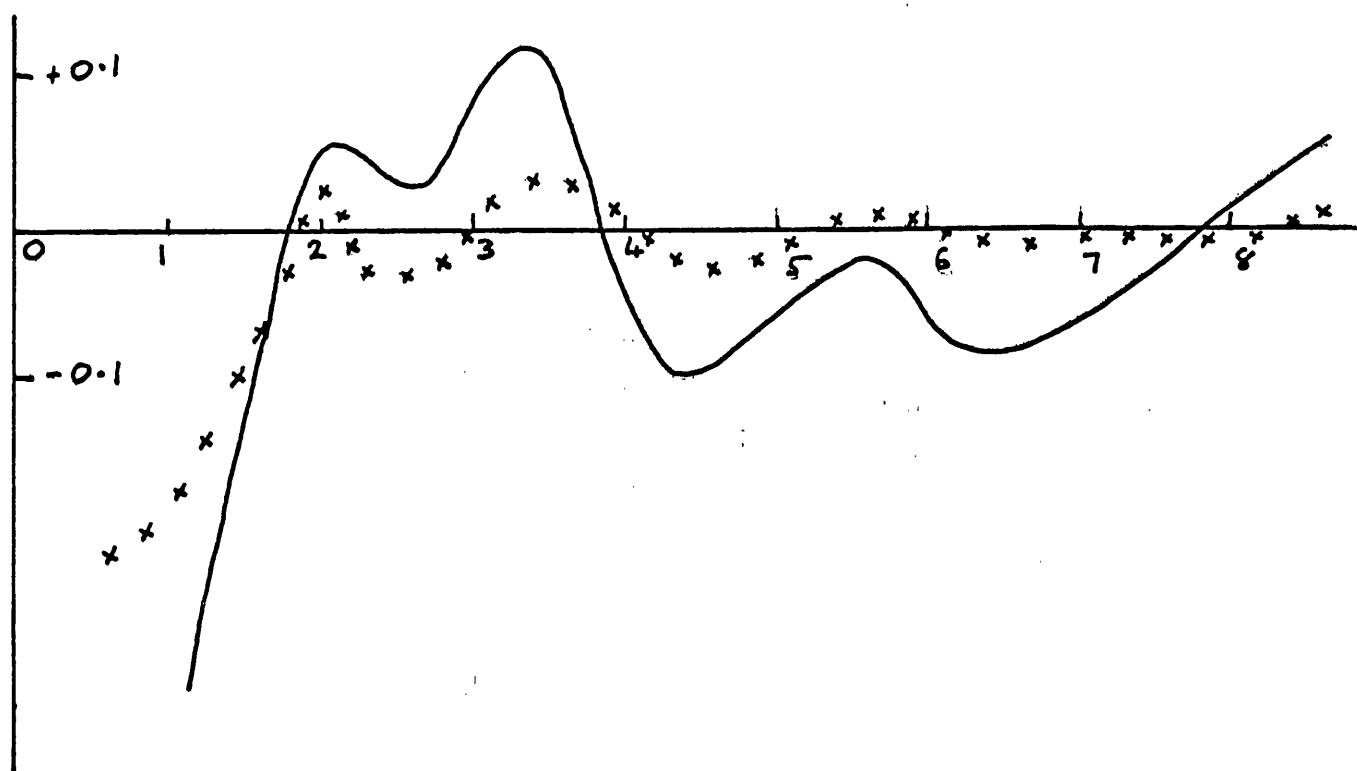
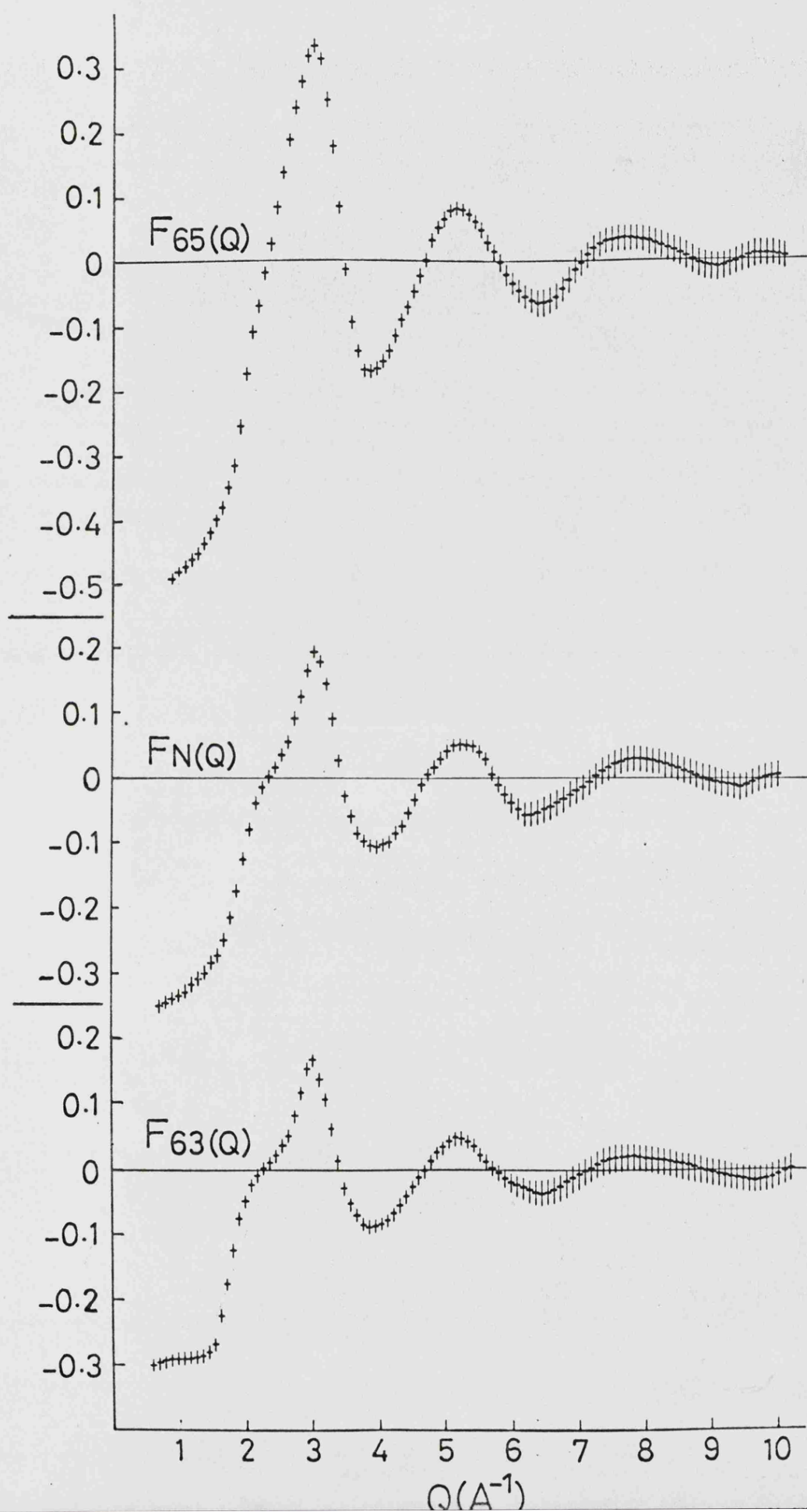


FIG. 5.1 EXPERIMENTAL $F(Q)$'s FOR LIQUID CuTe AT 700°C USING COPPER ISOTOPES



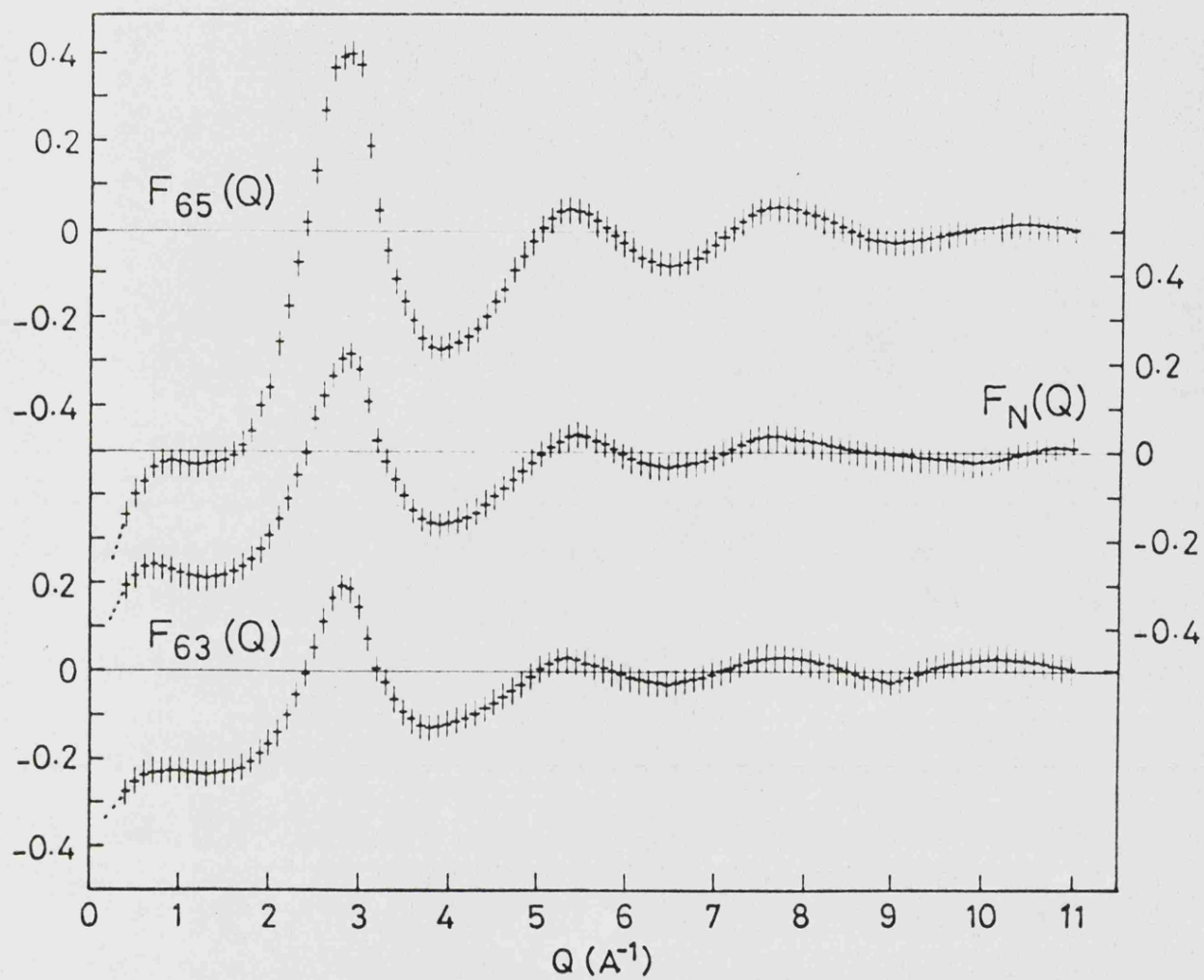


FIG. 5.2 EXPERIMENTAL $F(Q)$'s FOR LIQUID Cu_2Te AT 1200°C USING COPPER ISOTOPES

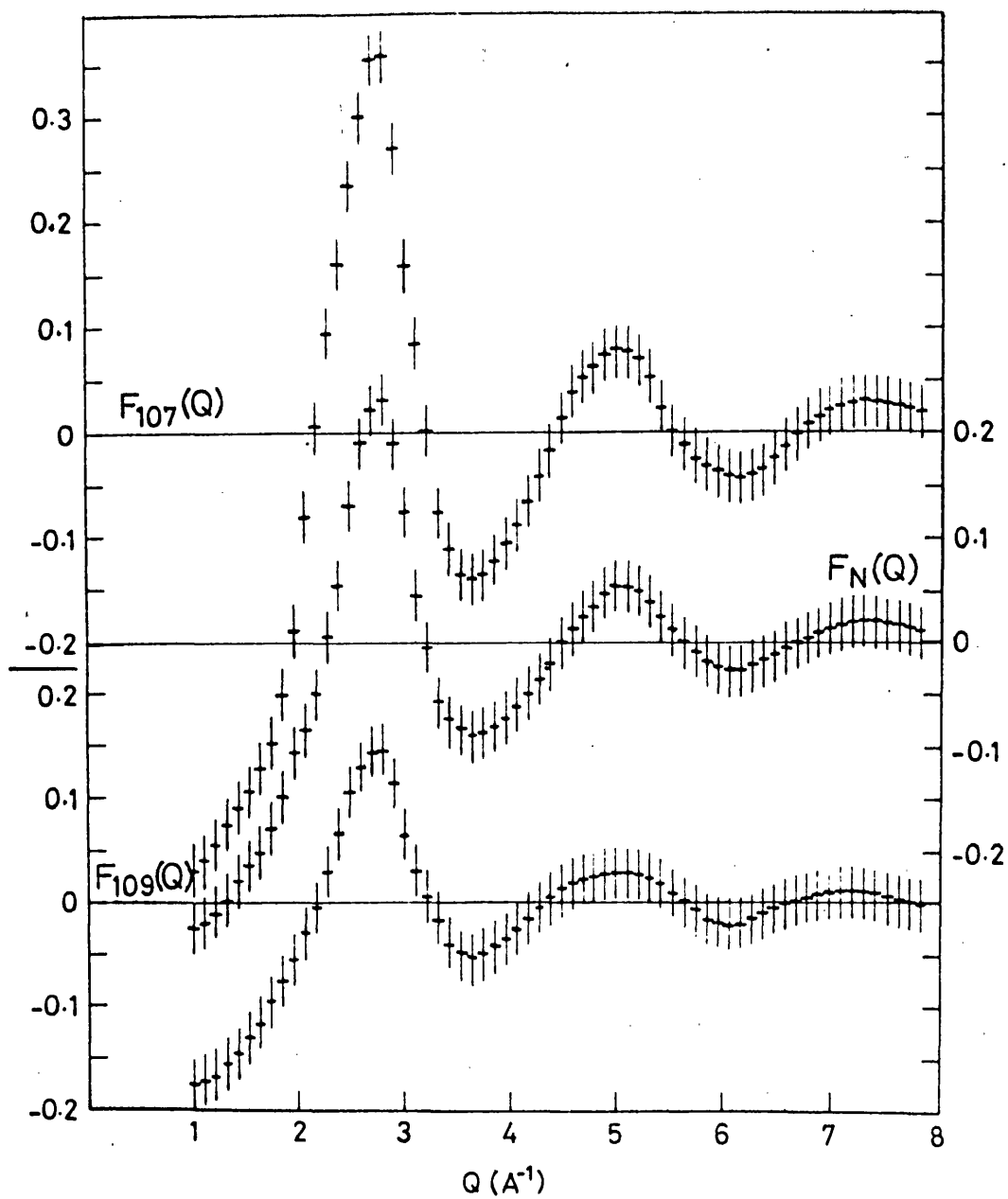


FIG. 8

FIG. 5.3 EXPERIMENTAL $F(Q)$'s for LIQUID Ag_2Te USING SILVER ISOTOPES

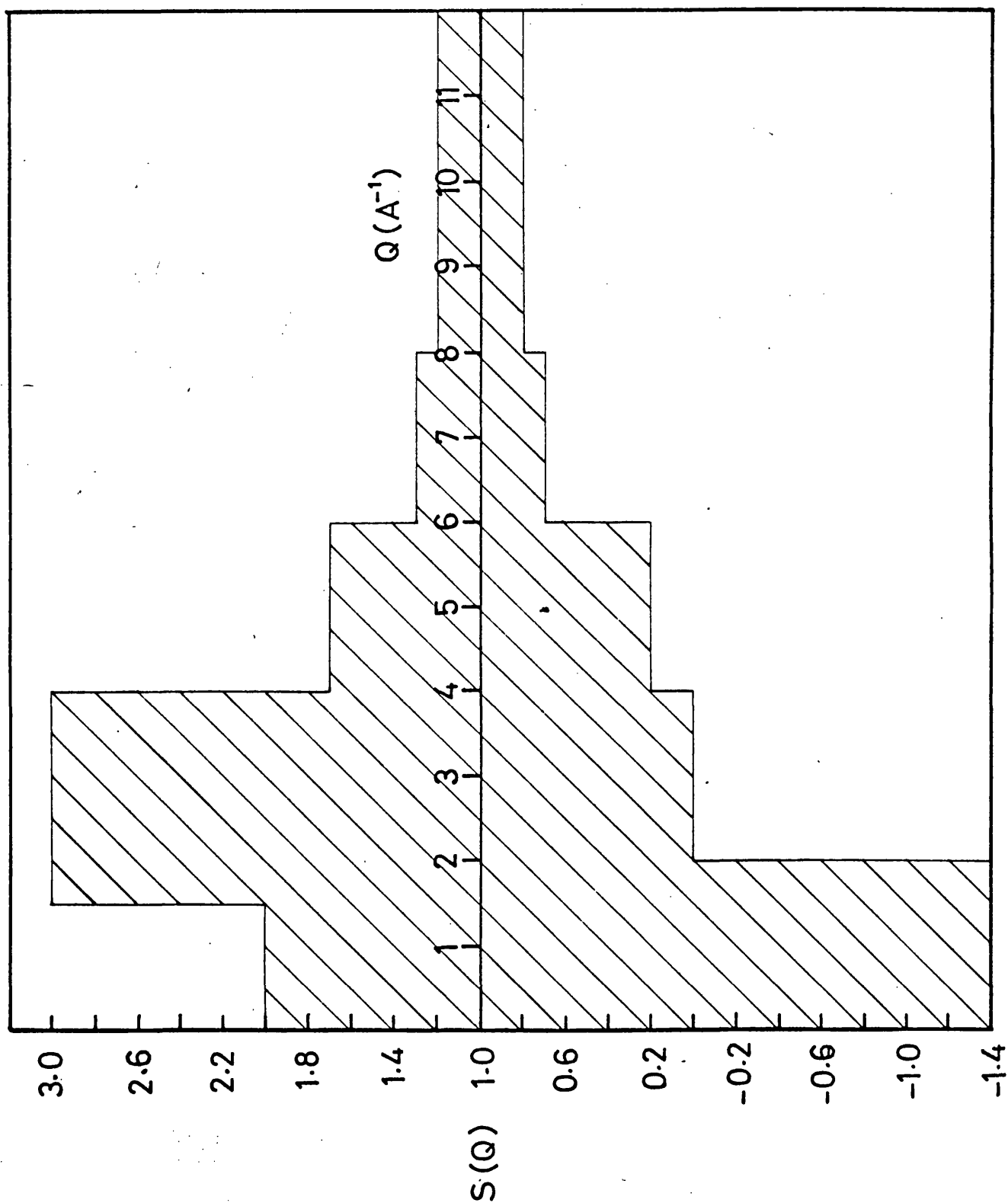


FIG. 5.4 LIMITS FOR THE PARTIAL STRUCTURE FACTORS

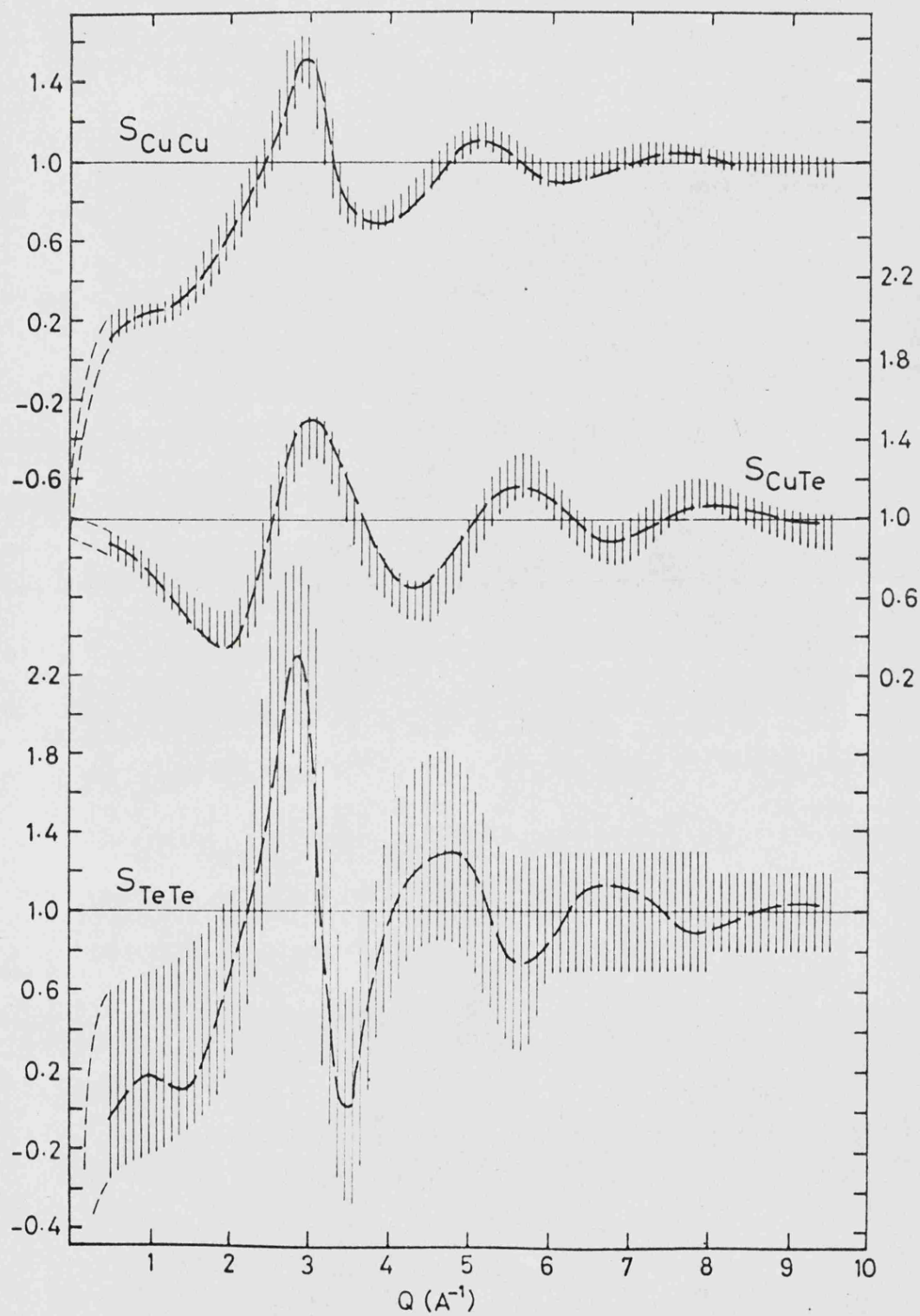
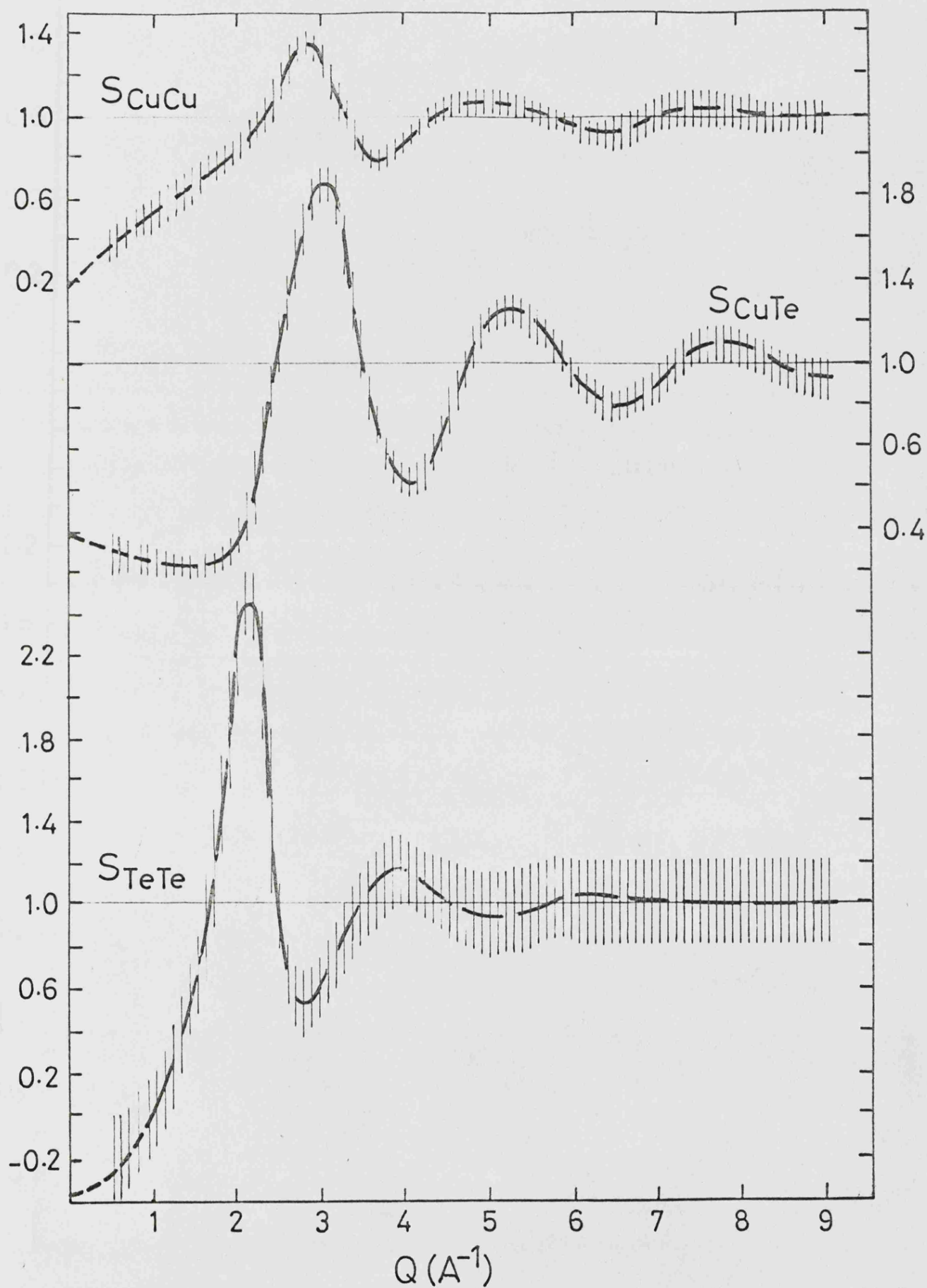
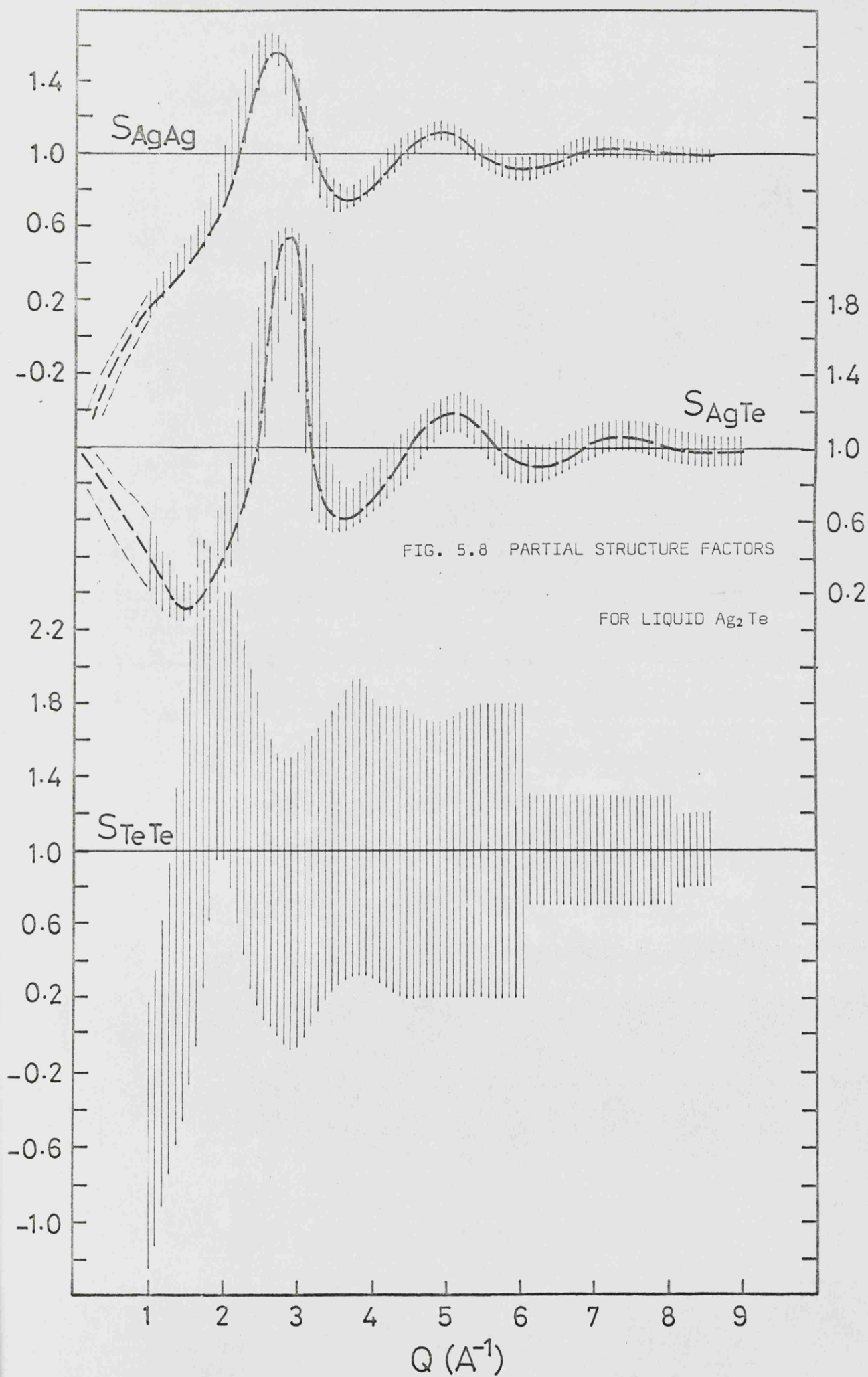


FIG. 5.6 PARTIAL STRUCTURE FACTORS FOR LIQUID Cu_2Te

FIG. 5.7 PARTIAL STRUCTURE FACTORS FOR LIQUID CuTe





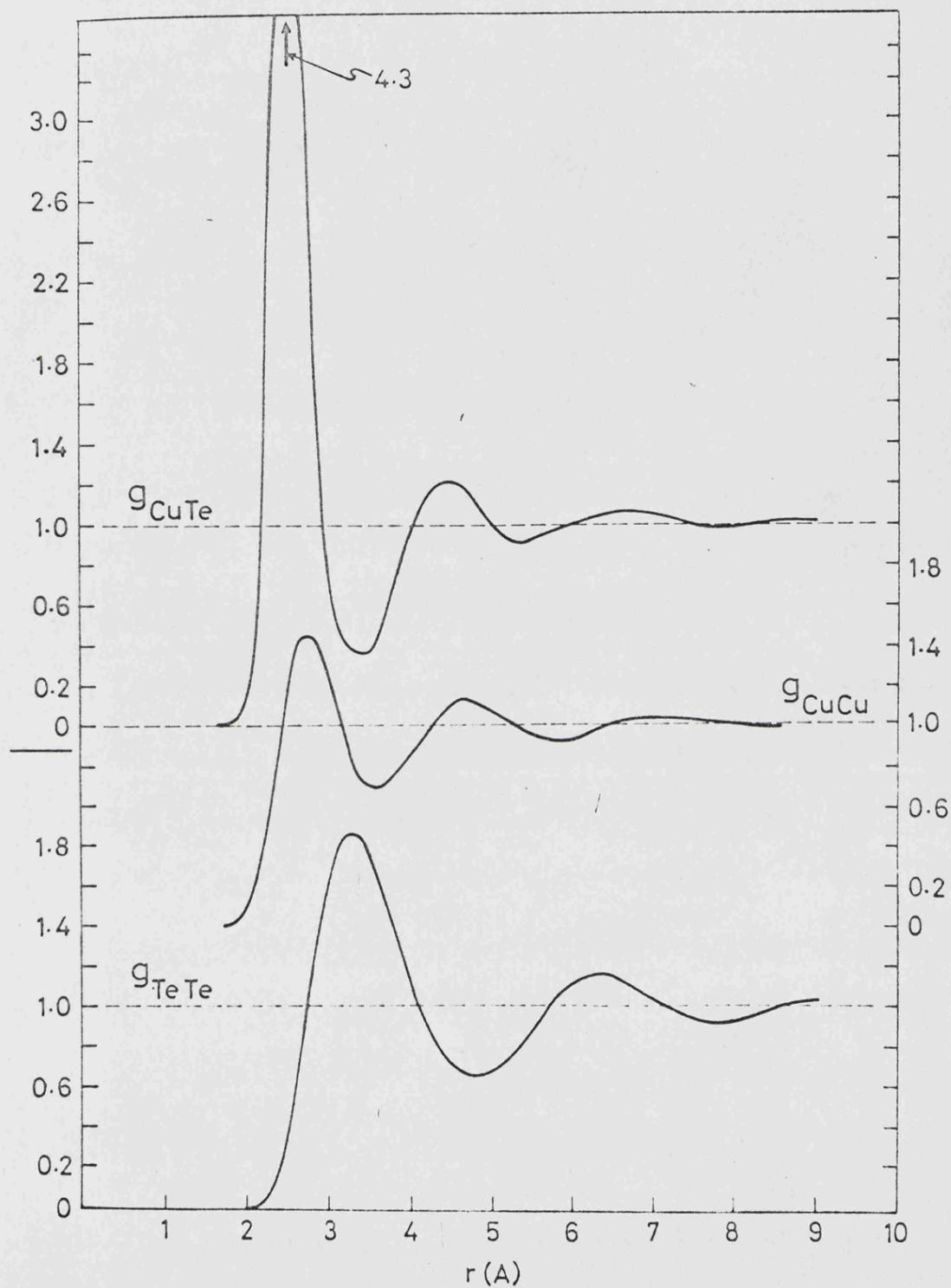
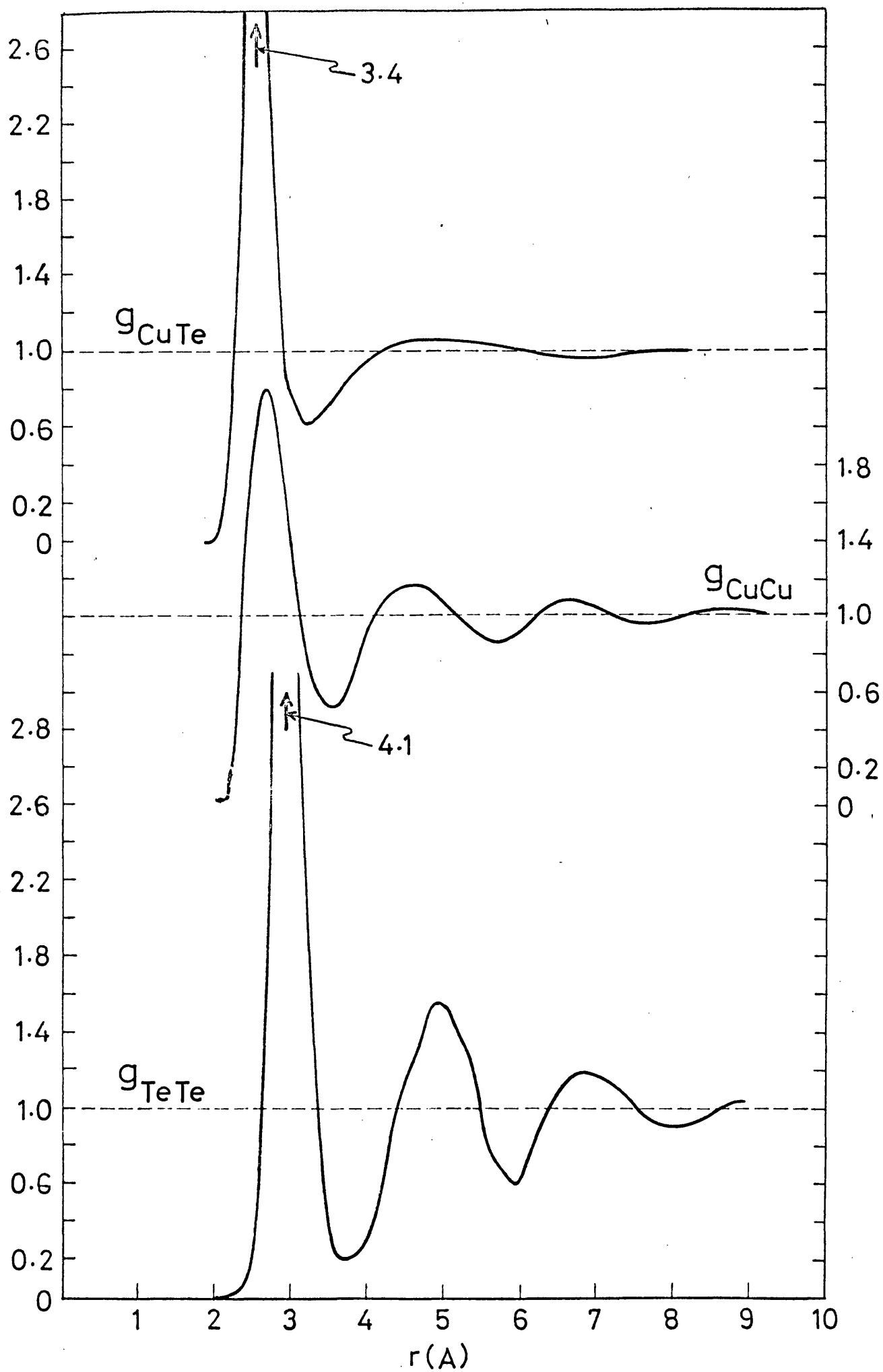


FIG. 5.9 PARTIAL R.D.F.'s for LIQUID CuTe

FIG. 5.10 PARTIAL R.D.F.'s for LIQUID Cu_2Te



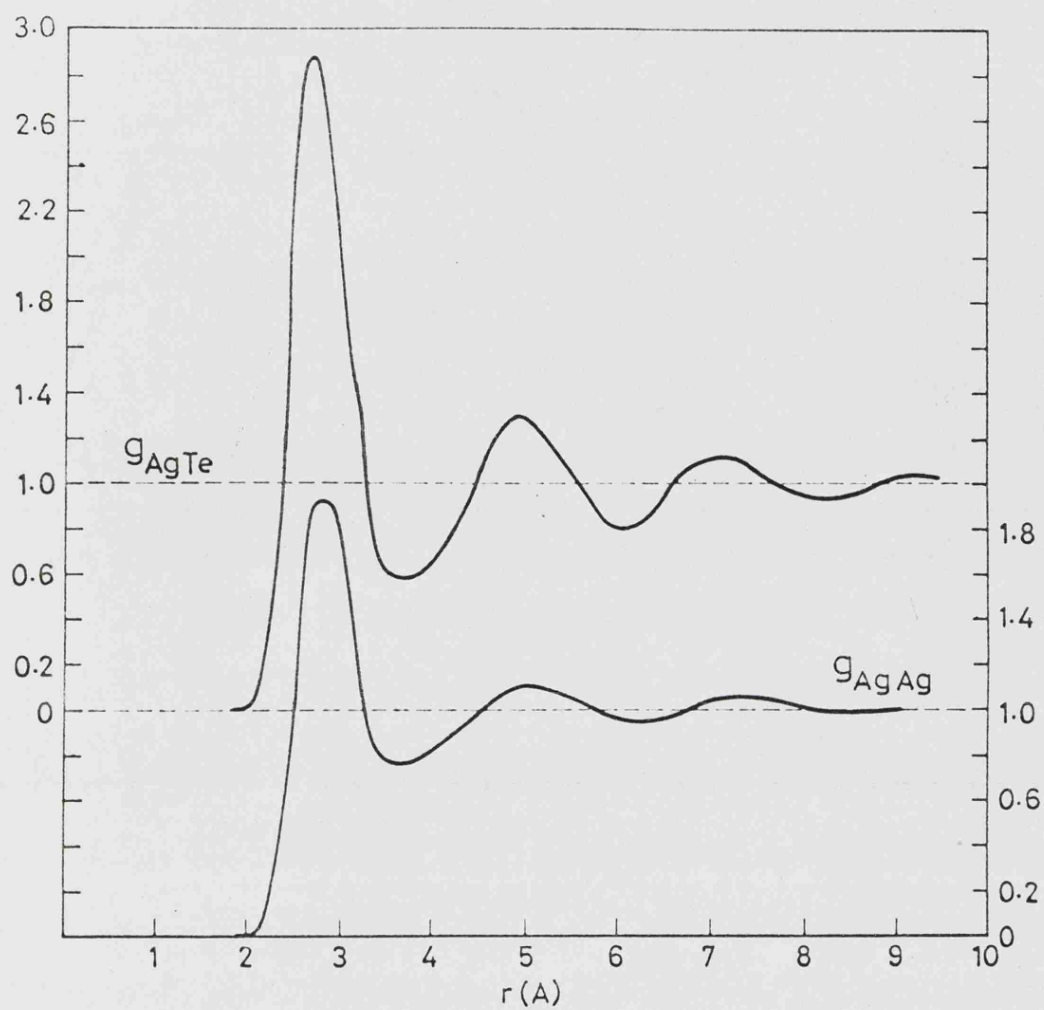


FIG. 5.11 PARTIAL R.D.F.'s FOR LIQUID Ag_2Te

REFERENCES

1. Allgaier, R.S., (1969) Phys. Rev., 185, 227.
2. Bacon, G.E., (1962) Neutron Diffraction, Clarendon Press, Oxford.
3. Bhatia, A.B. and Thornton, D.E., (1970) Phys. Rev. B, 2, 3004-3012.
4. Blech, I.A. and Averbach, B.L., (1965) Phys. Rev. 137, A113.
5. Bushert, R.E., (1957) (Thesis Purdue Univ.)
6. Cabane, B. and Friedel, J., (1971) Jnl. de Physique, 32, 73.
7. Cabane, B. and Froidevaux, C., (1969) Phys. Letts. 29A, 512.
8. Cohen, M.H. and Sak, J., (1972) J. Non-Cryst. Solids 8 - 10, 696.
9. Cutler, M. and Mallon, C.E., (1962) J. Chem. Phys. 37, 2667.
10. Cutler, M. and Mallon, C.E., (1966) Phys. Rev. 144, 642.
11. Dancy, E.A., (1965) Trans. Met. Soc. Aime, 227, 1034.
12. Enderby, J.E., (1974) Amorphous and Liquid Semiconductors, Ed. J. Tans (London Plenum Press).
13. Enderby, J.E. and Collings, E.W., (1970) Jnl. Non-Cryst. Solids, 4, 161.
14. Enderby, J.E., North, D.M., and Egelstaff, P.A., (1966) Phil. Mag., 14, 961.
15. Enderby, J.E. and Simmons, C.J., (1969) Phil. Mag., 20, 125.
16. Enderby, J.E. and Walsh, L., (1966) Phil. Mag. 14, 991.
17. Epstein, S.G., (1972) Liquid Metals, Ed. S.Z. Beer, Marcel Dekker, inc., New York.
18. Faber, T.E. and Ziman, J.M., (1964) Phil. Mag. 11, 153.
19. Hultgreen, R., Orr, R.L., Anderson, P.D. and Kelly, K.K., (1963) 'Selected values of thermodynamic properties of metals and alloys'; J. Wiley, New York.
20. Hance, N.J., (1973) Internal Harwell Publication.
21. Hanson, H.P., (1958) Constitution of Binary Alloys, McGraw-Hill, New York.
22. Hodgkinson, R.J., (1970) Phil. Mag. 22, 1187; (1971) 673-686.
23. Hodgson, J.N., (1961) Phil. Mag. 6, 509.

24. Joffe, A.F. and Regel, A.R., (1960) Progress in Semiconductors (A.F. Gibson, editor) J. Wiley, New York.
25. Landau, L.D. and Lifshitz, E.M., (1958) Statistical Physics (London: Pergamon Press).
26. March, P.A., (1968) Liquid Metals. Oxford, London: Pergamon Press.
27. McAlister, S.P. and Turner, R., (1972) J. Phys. F. Metal Phys., 2, L51-L54.
28. Moscinski, J., Renninger, A. and Averbach, B.L., (1972) Phys. Letters. 42, 453-454.
29. North, D.M., Enderby, J.E. and Egelstaff, P.A., (1968a) J. Phys. C. 1, 784.
30. Paalman, H.H. and Pings, C.J., (1962) J. App. Phys. 33, 2635.
31. Page, D.I. and Mika, K., (1972) J. Phys. C. Solid State Phys. 4, 3034-3044.
32. Placzek, G., (1952) Phys. Rev. 86, 377.
33. Sinclair, R.N., Dore, J.C., and Wright, A.C., (1971) Annual Report of the Neutron Beam Research Committee (S.R.C., London).
34. Thompson, C.W. and Gingrich, N.S. (1959) Jnl. of Chem. Physics) 31, 1528-1604.
35. Tourand, G., (1973) Le Jnl. de Physique, 34, 937.
36. Tourand, G. and Brueil, M., (1970) C.R. Acad. Sci. Paris, B270, 109.
37. Turner, R., (1973) J. Phys. F: Metal Phys., 3, L57-L60.
38. Van Hove, L., (1954) Phys. Rev. 95, 249.
39. Vezzoli, G.C., (1972) The Journal of the American Ceramic Society, 55(2), 65-67.
40. Warren Jnr., W.W., (1972) The Properties of Liquid Metals (Proceedings of the 2nd International Conference, Tokyo, 3-8 September 1972).
41. Woodcock, L.V., (1971) Proc. R. Soc. Lond. A 328, 83-95.