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MASTER

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Abstract

A neutron diffraction investigation has been carried out of the structures of several naturally occurring glasses, viz.
Libyan Desert glass, a Fulgurite, Wabar glass, Lechatelierite from Cañon Diablo, a Tektite, Obsidian (3 samples), and Macusani glass. Libyan Desert sand has also been examined, together with crystalline α-quartz and α-cristobalite. A comparison of data for the natural glasses and synthetic vitreous silica (Spectrosil "B") in both reciprocal and real space allows a categorisation into Silicas, which closely resemble synthetic vitreous silica, and Silicates, for which the resemblance to silica is consistently less striking. The data support the view that Libyan Desert glass and sand have a common origin, while the Tektite has a structure similar to that of volcanic glasses.

1. Introduction

The structure of glass is a function of composition and thermal history. Thus a knowledge of structure and composition may provide a basis from which the thermal history, and hence the melting processes by which a particular natural glass formed, may be deduced. Obsidian, Fulgurites and impact glass (Lechatelierite) recovered from meteorite craters are examples of natural glasses for which processes of formation are well established. Although the preponderance of opinion[1] attributes Tektites and Libyan Desert glass to formation by impact of meteorites some[2] have suggested that the physical properties of these glasses cannot be due to shock melting. These two glasses are not found in meteorite craters. Tektites are found in many parts of the world[3] unrelated to any meteorite crater. Libyan Desert glass is found only in the southwest of Egypt[4], again unrelated to any meteorite crater.

In an effort to tell whether detailed knowledge of the atomic structure of natural glasses could be related to the processes by which they were formed, the structure of samples of a variety of natural glasses have been studied using neutron diffraction techniques. Data have been obtained for Lechatelierites (Cañon Diablo[5] and Wabar[6]), a Fulgurite[7], a Tektite (Indochinite)[8], Obsidian (Rift Valley, Kenya and Lipari Island, Italy)[9], Macusani glass [10,11] and Libyan Desert glass [12]. These glasses were formed by meteorite impact events (Lechatelierites), volcanic eruptions (Obsidian and Macusani (probably)), lightning (Fulgurite) and by unidentified events (Tektite and Libyan Desert glass).

It has been suggested that some of the properties of Libyan Desert glass are inconsistent with shock melting or shock melting and vaporisation with subsequent rapid cooling [13,14]. The samples studied are representative of those processes by which natural glasses have been formed. Their compositions also vary widely, ranging from high silica (Libyan Desert glass ∿ 98% SiO_2) to low silica (Obsidian and Tektites ∿ 70% SiO_2). Because of the time required to perform the measurements and analyse the data the number of samples of each type which have been investigated is small. It is, of course, possible that some of the samples are atypical, although they are typical in their observable gross properties (morphology, colour and source) and also the neutron diffraction technique is insensitive to low level impurities.

2. Theoretical Outline

For an amorphous solid the neutron diffraction pattern is measured as a function of the magnitude of the scattering vector $\underset{\sim}{Q}$,

$$Q = \frac{4\pi}{\lambda} \sin\theta \qquad (1)$$

in which λ is the incident wavelength and 2θ the scattering angle. In real space the structure may be expressed in terms of the correlation function $T(r)$. In order to obtain this function from the normalised, corrected diffraction pattern, $I(Q)$, it is first necessary to calculate the interference function.

$$Qi(Q) = Q\left[I(Q) - \sum_j \overline{b_j^2}\, p_j(\lambda, 2\theta)\right] \qquad (2)$$

where $\overline{b}_j$ is the isotopically averaged neutron scattering length of atom j and the summation is taken over the atoms in the chemical composition unit. $p_j(\lambda, 2\theta)$ is the well known Placzek [15] correction for departures from the static approximation. The real space correlation function $T(r)$ is then found by Fourier transformation of $Qi(Q)$.

$$T(r) = 4\pi r \rho^{o}\left(\sum_{j} \bar{b}_{j}\right)^{2} + \frac{2}{\pi}\int_{0}^{\infty} Qi(Q)\,M(Q)\sin rQ\,dQ \qquad (3)$$

$M(Q)$ is a modification function, necessary because measurements are limited to a finite maximum value of Q, and the constant ρ^{o} is the average number of composition units per unit volume. The modification function due to Lorch [16] was used in the present work. A detailed account of the theory of neutron diffraction, as applied to amorphous solids, has been given by Wright [17] and Wright and Leadbetter [18].

3. Measurements

The samples used in the diffraction experiments varied widely in appearance, physical dimensions, and natural locations as detailed in Table 1. Cylindrical samples were machined from the larger irregular specimens and the average bulk density of each sample was measured by the water displacement method. Data were also acquired for high purity Spectrosil "B" synthetic vitreous silica (Thermal Syndicate Ltd.), Libyan Desert sand, α-quartz and α-cristobalite. Powder samples were contained in a thin-walled vanadium can (wall thickness 0.1 mm).

The diffraction pattern for α-quartz was measured at an incident wavelength of 1.54 Å ($0.5 \leq Q \leq 6.8$ Å^{-1}), using the PANDA powder diffractometer (PLUTO reactor, A.E.R.E., Harwell), while those for all other samples were obtained with the lower resolution CURRAN diffractometer (DIDO reactor; $\lambda = 1.04$ Å; $0.2 \leq Q \leq 9.7$ Å^{-1}). In each case the scattered intensities were measured relative to an incident beam monitor and the data were corrected for diffractometer background. For the powder samples it was also necessary to subtract the scattering from the vanadium can.

4. Results and Discussion

The position and relative intensities of the Bragg powder diffraction peaks for Libyan Desert sand and α-quartz in the range 1 to 6.5 Å^{-1} were found to be in excellent agreement. No extra peaks were observed for the Libyan Desert sand and thus it may be considered isomorphous with α-quartz. Low concentrations of impurities might exist in the sand, but these are not observed here.

Some useful conclusions about the structures of the natural glasses can be made by comparing their diffraction patterns with that for Spectrosil "B". This sample was prepared by melting at $\sim$ 1950°C, annealing at $\sim$ 1060°C for 60 hours, and then cooling to ambient temperature over 20 hours [19]. The diffraction patterns for the natural glasses were normalised to that for Spectrosil "B" at the third peak on account of its relative insensitivity to variations in intermediate range order. The result of scaling the patterns as indicated is to allow a clear categorisation of the glasses into those which closely resemble silica and are referred to as Silicas (figure 1) and those for which the resemblance is less striking and are referred to as Silicates (figure 2).

Although comparisons between the glasses should strictly be made on the experimentally corrected and normalised intensities, some general statements on the structures are possible from a consideration of the raw diffraction patterns. No suggestion of small angle scattering was observed at the lowest measured values of Q ($\sim$ 0.2 Å^{-1}). Apart from slight evidence of crystallinity in the Fulgurite and Wabar samples (probably due to quartz contamination of the surfaces), all the patterns are those of well homogenised glasses (at least on a scale up to tens of Ångstroms, as suggested by the absence of significant small angle scattering at $\sim$ 0.2 Å^{-1}).

Among the natural silica glasses, Libyan Desert glass and Cañon Diablo are similar to each other in that the first peak in each pattern is slightly more intense than in Spectrosil "B". This implies increased intermediate range order relative to Spectrosil "B", which may have been caused by a slower rate of cooling or by oxidising conditions during formation[20]. Apart from the slight trace of α-quartz, the diffraction patterns of Fulgurite and Wabar, are indistinguishable from that of Spectrosil "B". This resemblance is surprising in that both glasses are known to have been very rapidly quenched.

As the natural silica glasses clearly belong to a single group only one member was further analysed. The diffraction pattern for the Libyan Desert glass was corrected for absorption, multiple scattering and self-shielding and then normalised to absolute units using the Krogh-Moe - Norman technique[21,22]. The resulting interference function is given in figure 3 and the correlation function in figure 4 together with that for Spectrosil "B". The differences between the two correlation functions are small and within the experimental uncertainties. For the Libyan Desert glass, the composition (∿ 98% SiO_2 plus trace impurities[14]) and bulk density are sufficiently close to the values for silica that the latter were used in the data analysis. The first two peaks in T(r) were fitted to Gaussians appropriately broadened to account for measurement to a finite maximum value of Q. This yielded an Si - 0 bond length of 1.61_2 Å and an r.m.s. bond length variation of 0.07_2 Å compared with values of 1.61_0 Å and 0.05_0 Å respectively for Spectrosil "B"[23].

The diffraction patterns in Figure 2 all possess a first peak that is less intense and shifted to higher Q than the corresponding feature for Spectrosil "B", thus implying a more compacted but less ordered intermediate range structure than in the laboratory prepared silica. In each case the second peak is shifted to lower Q, with a slightly sharper low Q edge, and there is extra scattering between 4 and 5 $Å^{-1}$.

The Macusani glass sample was chosen for further analysis and the interference and correlation functions are displayed in figures 5 and 6. The composition assumed was that given by Elliot and Moss [24] which for the purposes of the data analysis was simplified to $Li_{0.01}\ F_{0.01}\ K_{0.02}\ Na_{0.03}\ Al_{0.07}\ Si_{0.24}\ O_{0.62}$. Also shown in figure 6 is the correlation function of Spectrosil "B" appropriate to the silica content of one composition unit of Macusani glass. The silica correlation function accounts for all the features in that for Macusani glass and thus it may be concluded that the silicate framework is closely related to that in high purity silica. The first peak in T(r) for the Macusani glass is at slightly higher r (1.62_8 Å) and has an area ∿ 20% greater than for vitreous silica due to interference from other interactions (e.g. Al - O).

5. Conclusion

Neutron diffraction experiments on a series of natural glasses have led to their classification into two groups; Silicas, having structures closely related to high purity vitreous silica, and Silicates, having structures related to vitreous silica but consistently different from it. This classification was first made by comparing the diffraction patterns of the glasses to that of silica and then confirmed by comparisons of real space correlation functions. The categorisation could prove to be useful in considerations of different theories of formation of these glasses.

The near identical correspondence of Libyan Desert sand to α-quartz and Libyan Desert glass to vitreous silica may be taken as a good indication that the glass and sand have a common origin. From the first diffraction peak, it is concluded that both Libyan Desert glass and Cañon Diablo have either cooled at a slower rate than Spectrosil "B" or formed under oxidising conditions.

Further information on the formation conditions of Libyan Desert glass and the other natural silicas could be obtained by extending the diffraction patterns to much lower scattering vectors and, in particular, by determining the zero Q limit, I(0), which is closely linked to thermal history [25,26]. It would be possible to make this measurement with either neutrons or X-rays. The advantages of neutrons are that they can be used to probe bulk samples and that, by using long wavelengths ($\lambda \sim 10 \mathring{A}$) the experiment can be performed at larger scattering angles. The disadvantage is that I(0) is very sensitive to hydrogen contamination, due to the very large neutron scattering cross-section for hydrogen at low Q. An effective correction for -OH scattering would therefore require an accurately known -OH content and a determination of the scattering due to -OH using samples with varying -OH content and identical thermal histories. X-rays, on the other hand, are relatively insensitive to hydrogen but suffer the disadvantage that it is necessary to work at much lower angles with thin samples which may be unrepresentative of the bulk.

Glasses belonging to the Silicate group have more compact but less well ordered intermediate-range structures than the Silicas. The structural similarity of the Tektite with other members of its group would not rule out the possibility of a volcanic origin for Tektites, but their chemical compositions leave this open to doubt [27]. The presence of a large number of components may lead to phase separation. Thus an extension of the present measurements to much lower Q would again be of great value.

Finally, the conclusions reached here serve to illustrate the potential of neutron scattering techniques as non-destructive probes of bulk irregularly shaped solids of compositional complexity.

Acknowledgements

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Table 1. Natural Glass Samples

Sample	Shape	Diameter (mm)	Bulk density (gm./cm^3)	Natural location	Physical Appearance
Libyan Desert glass	rod	7.39	2.208	Libyan Desert	Yellow, translucent, bubble free.
Lechatelierite (Cañon Diablo)	irreg. rod	∿ 8.8	0.819	Meteor Crater (Northern Central Arizona, U.S.A.)	White, perforated.
Wabar glass	irregular	-	1.167	Rub 'al Khali (Saudi Arabia)	Greyish-white glassy.
Fulgurite	irreg. tube	-	2.187	Sand Sea Libyan Desert 25° 17'N, 25° 36'E.	Brownish-yellow with shiny vitreous surface on inner wall.
Macusani glass	rod	7.50	2.359	Peru, 14° 4'S 70° 27'W	Grey translucent with reddish strands in body of glass.
KW6 Obsidian	rod	7.51	2.474	Kenya rift valley	Black, glassy.
KN18 Obsidian	rod	7.51	2.384	Kenya rift valley	Black, glassy.
Lipari Obsidian	rod	7.51	2.360	Lipari (Italy)	Black, glassy with white spots (bubbles).
Tektite (TC-14-42)	irregular	-	2.401	Ban Huai Ung (Thailand)	Black coal-like shine with pitted surface.
Libyan Desert Sand	powder$^{a)}$	7.28	-	Western Egyptian Desert	White powder.
α-quartz	powder$^{a)}$	7.28	-	-	White powder.
α-cristobalite	powder$^{a)}$	7.28	-	-	White powder.
Spectrosil "B" (Thermal Syndicate Ltd.)	rod	7.50	2.201	-	Colourless, transparent.

a) Contained in thin-walled vanadium can.

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Figure Captions

Figure 1. Diffraction patterns for natural silica glasses (●), compared to that for Spectrosil "B" (——), and also for Libyan Desert sand. Note suppressed zero on Q scale.

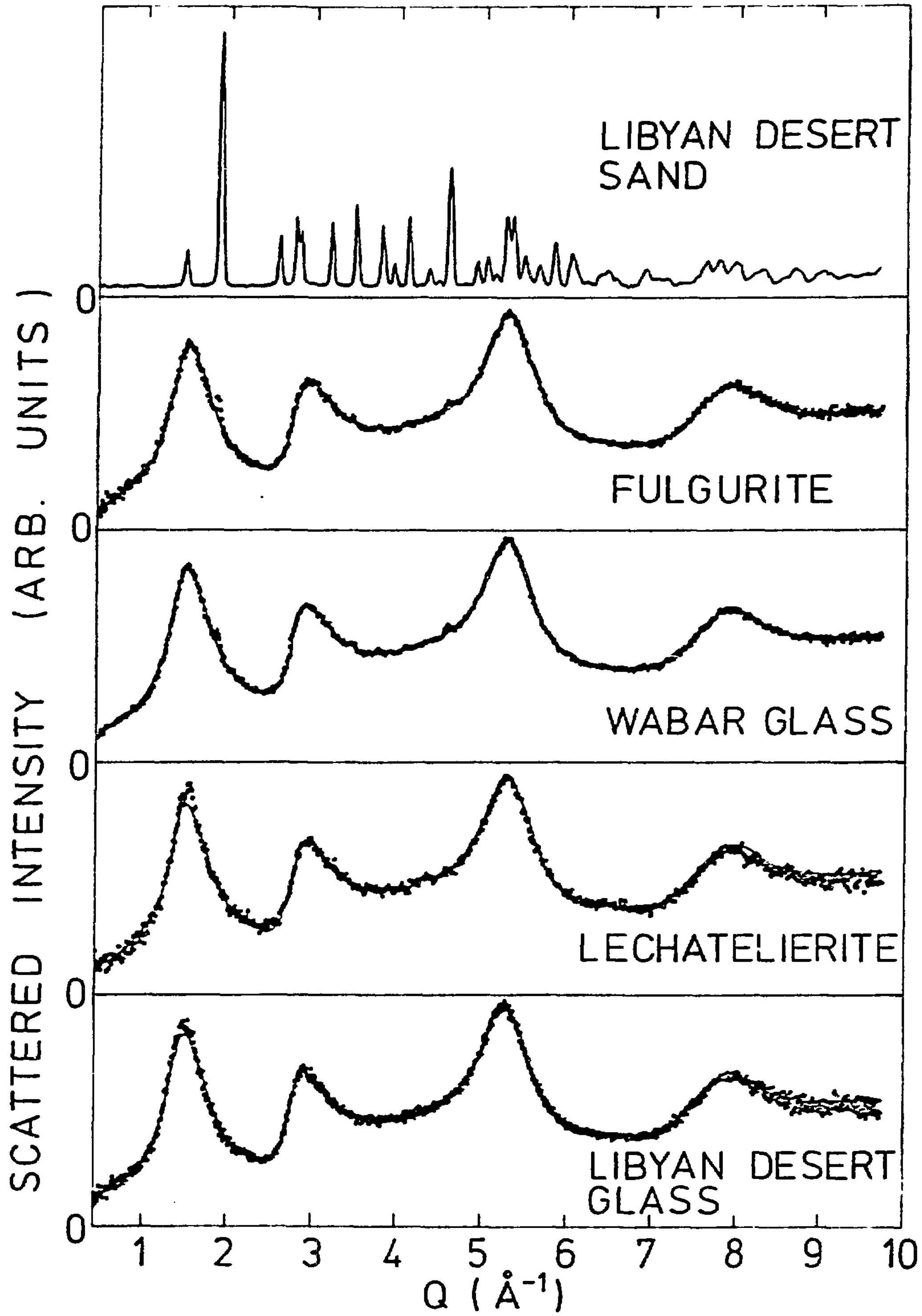
Figure 2. Diffraction patterns for natural silicate glasses (●) and Spectrosil "B" (——).

Figure 3. Interference function for Libyan Desert glass (●), together with cubic spine fit (——).

Figure 4. Correlation function for Libyan Desert glass (——) and Spectrosil "B" (---).

Figure 5. Interference function (●) and cubic spline fit (——) for Macusani glass.

Figure 6. Correlation function for Macusani glass (——) and Spectrosil "B" (---)



LIBYAN DESERT SAND
FULGURITE
WABAR GLASS
LECHATELIERITE
LIBYAN DESERT GLASS
0
0
0
0
0
SCATTERED INTENSITY (ARB. UNITS)
1
2
3
4
5
6
7
8
9
10
Q (Å^{-1})

Figure 1.

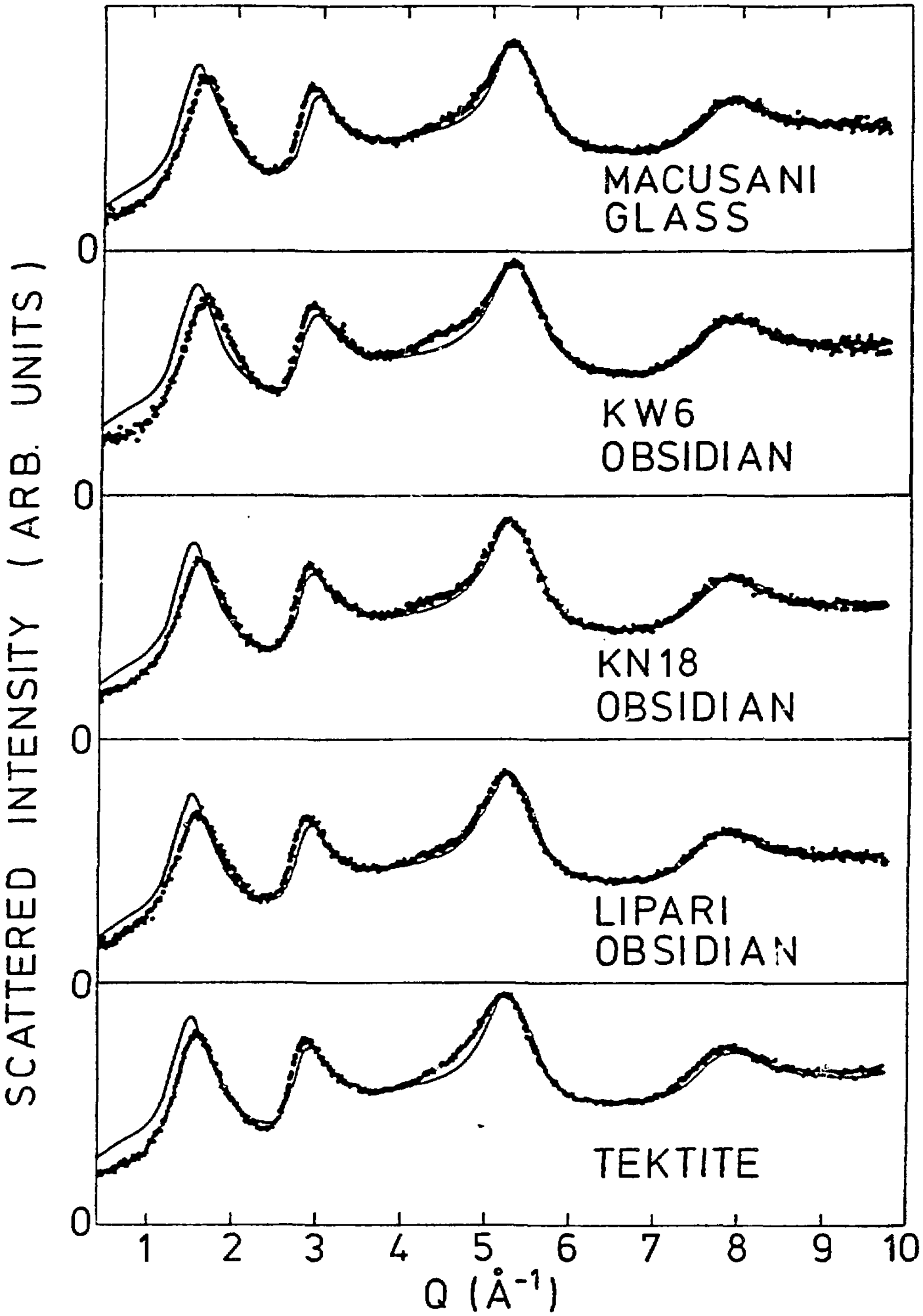

MACUSANI GLASS
KW6 OBSIDIAN
KN18 OBSIDIAN
LIPARI OBSIDIAN
TEKTITE
0
0
0
0
0
SCATTERED INTENSITY (ARB. UNITS)
1
2
3
4
5
6
7
8
9
10
Q (Å^{-1})

Figure 2.

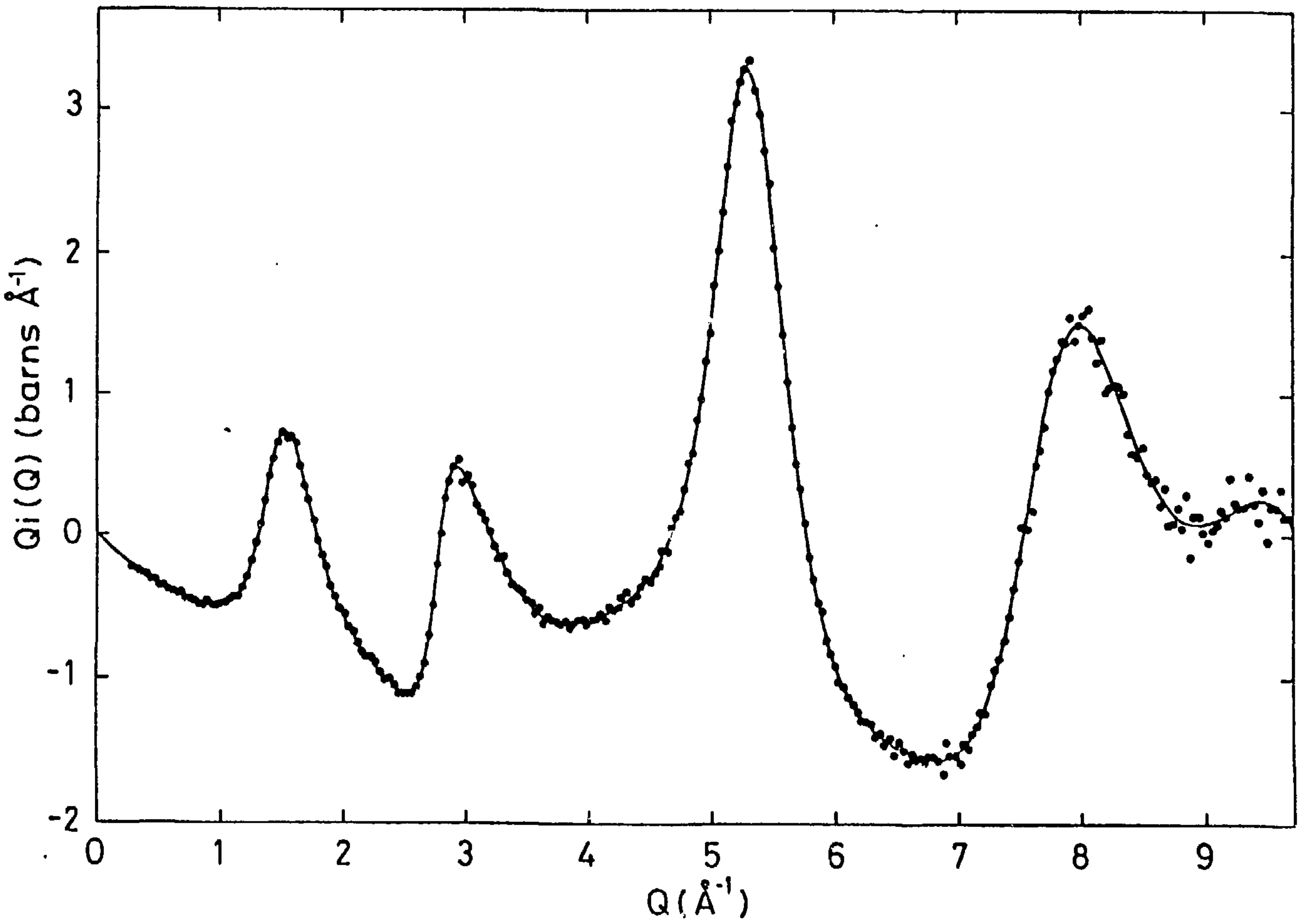


Figure 3.

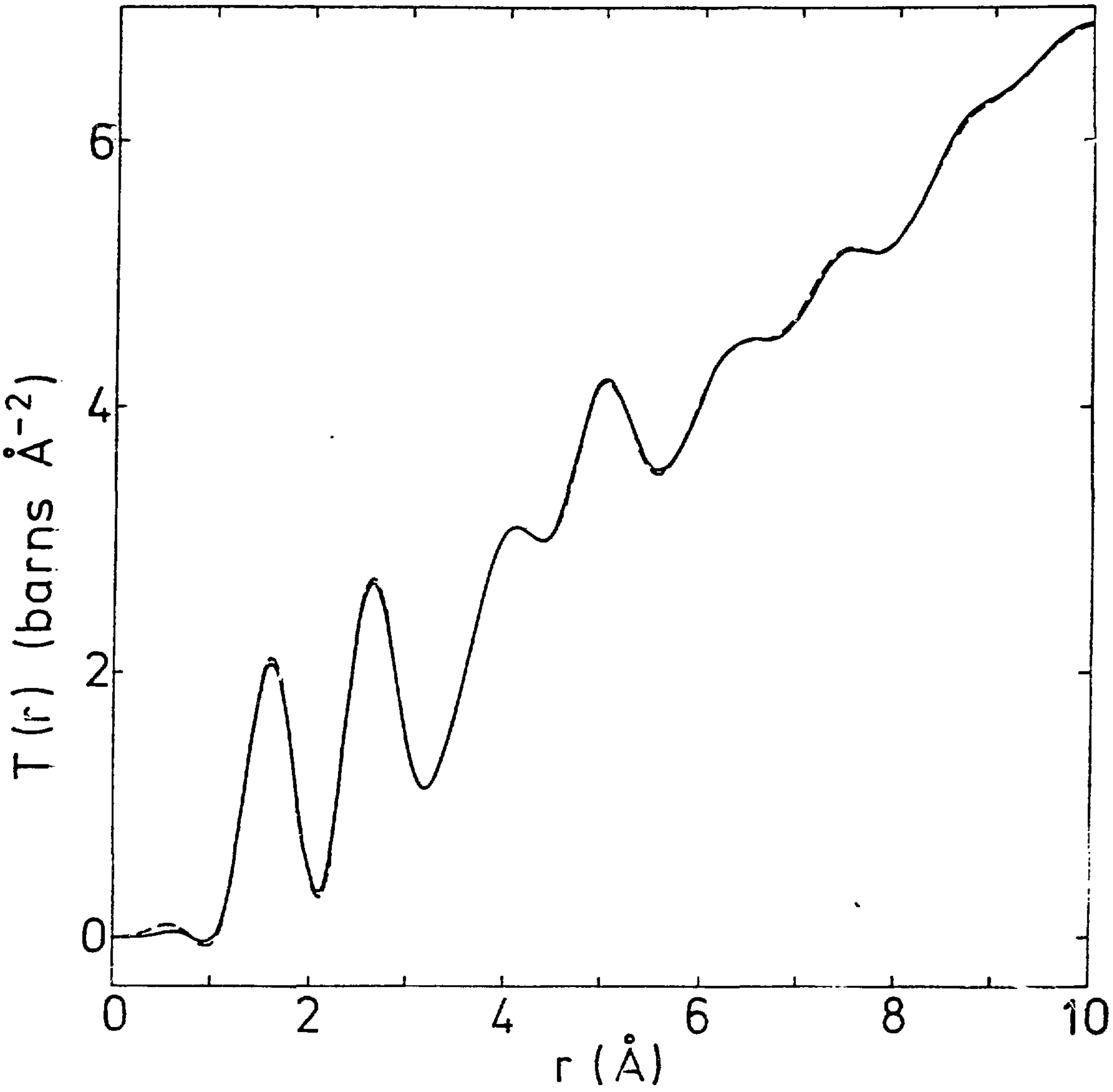


Figure 4.

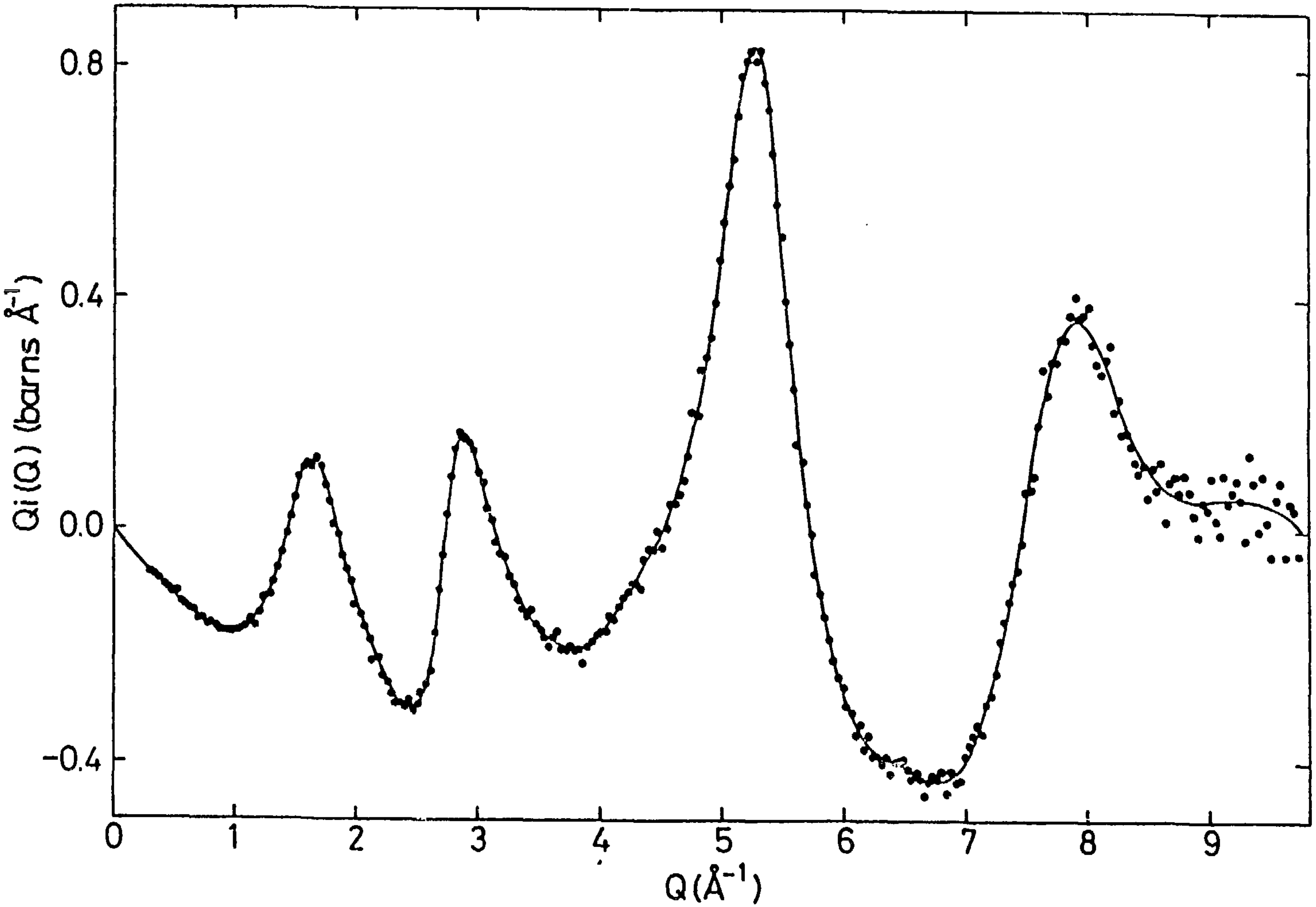


Figure 5.

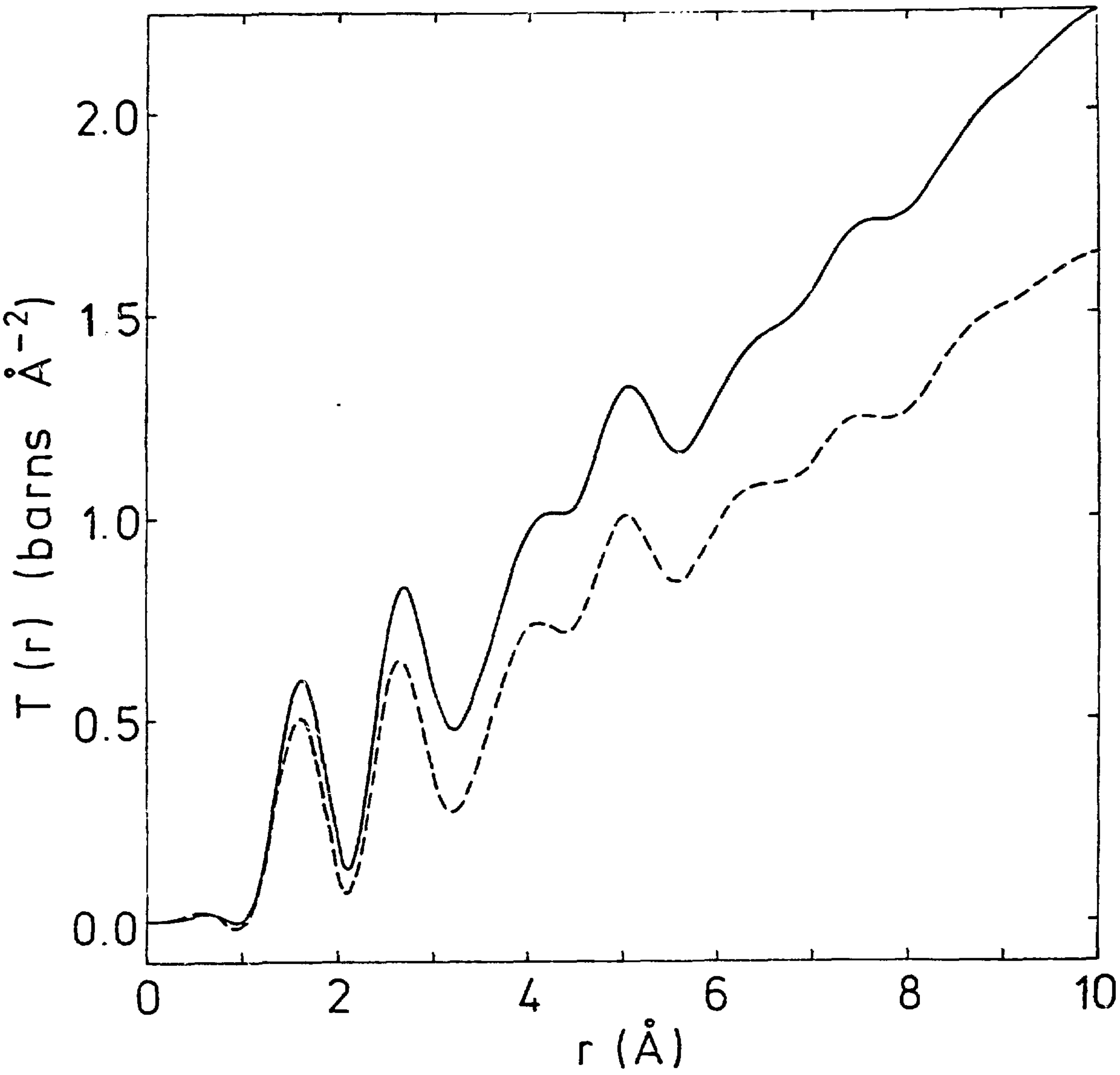


Figure 6.