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by

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Chalk River, Ontario

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LIQUID DYNAMICS FROM NEUTRON SPECTROMETRY<sup>†</sup>

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and N. K. Pope<sup>\*\*\*\*</sup>

## ABSTRACT

Recent experiments carried out at Chalk River on the dynamics of liquids using neutron inelastic scattering are reviewed, including one by Sakamoto et al. in which the Van Hove self-correlation functions in water at 25°C and 75°C were determined, and another in which the correlation functions in liquid argon near its triple point were studied.

The possible occurrence of short wavelength phonons in classical liquids is discussed, in analogy with their existence in the quantum liquid He<sup>4</sup>, and in connection with incomplete experiments on liquid tin.

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## 1. INTRODUCTION

In this paper we present an experimental review of the more recent Chalk River work on the dynamics of liquids. The work has been directed by the philosophy that one should attempt to deduce information directly from the experiments, as far as possible by inversion procedures rather than by comparison with calculations based on models which are almost certain to be much over-simplified.

At the time the paper was scheduled for the conference we hoped to be able to discuss the results of two new experiments: one an experiment to determine the pair correlation function in liquid argon, and the other, on liquid tin, to study the question of the existence of phonons in liquids. Because of circumstances beyond our control, the experiments were not finished in time for the conference and we present here preliminary and incomplete results of the experiments.

We first briefly review the familiar notation and ideas of the Van Hove formalism [ 1 ] for discussing the dynamics of classical liquids. The fundamental variables are the momentum transfer or wave vector transfer  $Q = |\underline{Q}|$ , and the energy transfer  $h\omega$ . The scattering function,  $S(Q, \omega)$ , the intermediate scattering function,  $I(Q, t)$ , and the correlation functions,  $\underline{G}_s(r, t)$  (the self-correlation) or  $G(r, t)$  (the pair-correlation), are linked by the Fourier transformation equations

$$G(r, t) = \frac{1}{2\pi^2} \int_0^{\infty} I(Q, t) \frac{\sin Qr}{Qr} Q^2 dQ$$

$$I(Q, t) = \int_{-\infty}^{+\infty} S(Q, \omega) \cos \omega t d\omega$$

and their inverses.

## 2. THE SELF-CORRELATION FUNCTION FOR THE PROTONS IN WATER

The first experiments were carried out on water, in which it was found that there exists a quasi-elastic component to the scattering which, however, is only quasi-elastic; there is an energy broadening, and this broadening is related to the diffusion of the atoms in the liquid [ 2 ]. Figure 1 shows energy distributions obtained several years ago [ 3 ], with curves for water at 6°C and at room temperature, and for ice at -50°C. The distribution for water at room temperature is broader than that for water at 6°C which, in turn, is broader than that for ice. The pattern for ice represents strictly elastic scattering broadened by the instrument resolution function, so that it is actually the resolution function for the other patterns. The width as a function of temperature varies somewhat as the experimental coefficient of self diffusion for water, but is a little smaller, and a theoretical interpretation of these facts was given on the basis of the specific nature of the diffusive motions.

A little later it was proposed by other workers, first by Hughes et al. [ 4 ] at Brookhaven, that in fact the quasi-elastic peak is not

broadened but split. Now the statistics in Figure 1 are not very good, and while it is not likely that the broadening is in fact interpretable as a splitting of the line into three components, it is perhaps conceivable. However, the curves shown in Figure 1 are Lorentzian functions broadened by Gaussian resolution, with a single parameter (the width of the Lorentzian) fitted to the distribution in each case. Thus the curves apparently have shapes close to the Lorentzian shape expected for a broadened line.

It was exceedingly difficult to understand how the components of the split line could simulate this behaviour in the two patterns of Figure 1 as well as in several other patterns at different temperatures and Q's [ 3 ]. It was, in any case, difficult to understand why the splitting should have been observable in the Brookhaven experiments and not in the Chalk River experiments, in view of the facts that the resolutions in the two series of experiments were the same, about  $3 \times 10^{-4}$  ev, and that our experiments utilized a line method rather than the edge method employed at Brookhaven.

More recently, work has been carried out on water at 25°C and 75°C by Sakamoto et al. [ 5 ] using a resolution of about  $2 \times 10^{-4}$  ev. Figure 2 shows a wavelength distribution, one of about 20 taken at 25°C (though not to the same statistical accuracy) using  $4.06\text{\AA}$  neutrons and the rotating crystal spectrometer [ 6 ]. The arrows on either side of

the elastic position show the presumed positions of the two extra components of the quasi-elastic line. The other arrows indicate the positions of other sharp lines also reported [ 4 ]. No evidence for any of them was visible in the patterns.

From distributions such as that shown in Figure 2, the scattering functions  $S(Q, \omega)$  for water at 25°C and at 75°C were constructed [ 5 ]. The parts of the functions involving small energy transfers are shown in Figure 3. The broadening with increasing  $Q$  that is expected from diffusion, and the strong increase in that broadening with increasing temperature, are both visible.

The Van Hove transformations were carried out on these data [ 7 ], and the self-correlation functions for the protons were obtained, as shown in Figure 4. There is not much that one can say directly from these curves, but it is perhaps pleasant to have a mapping of the motions of the atoms in this way.

From the curves of Figure 4, the mean square distance the atom moves as a function of time can be computed. This is perhaps better carried out by means of a mathematical trick [ 5 ], using data further back in the transformation process, namely the intermediate scattering function. (The mathematical trick is of such a nature that a fairly accurate value for the mean square displacement is obtained.) In Figure 5

the mean square distance the atom has travelled from its position at the origin at time zero, is plotted as a function of time. On such a log-log plot calculations for various simple models appear as straight lines. Figure 5 shows calculated lines for several models: for a gas of mass one atoms at room temperature, for a gas of mass 18 atoms at the two temperatures, and for atoms obeying the diffusion equation [ 1, 8 ] with coefficients of self-diffusion equal to those measured at the two temperatures by means of nuclear magnetic resonance [ 9 ]. For times greater than a few times  $10^{-12}$  secs the experimental points agree with the calculations for simple diffusion. It is more informative, however, to look at the ordinate (displacement)<sup>2</sup> scale. For both temperatures it appears that the diffusion equation is obeyed after the atoms have undergone mean square displacements of about  $5\text{\AA}^2$ , roughly corresponding to R. M. S. displacements of one intermolecular separation.

### 3. THE SCATTERING FUNCTION FOR LIQUID ARGON

Wavelength distributions of  $4.06\text{\AA}$  neutrons scattered by liquid argon under its own vapour pressure (550 mm pressure, equivalent to a temperature of  $84.5^\circ\text{K}$ ) have been measured for about twenty angles of scattering between  $17^\circ$  and  $110^\circ$  using the rotating crystal spectrometer [ 6 ]. Typical distributions at three angles are shown in Figure 6, together with similar patterns taken with the specimen container empty. For both series, the fast neutron background was monitored at short intervals

by inserting cadmium in the beam, and has been subtracted. The approximate magnitudes of the fast neutron backgrounds are indicated by the horizontal straight lines. The resolution at the incoming energy was approximately 2% in wavelength or  $2 \times 10^{-4}$  eV.

Figure 7 shows an idealized picture of the scattering function for liquid argon at 84.5°K, obtained from patterns similar to those of Figure 6.

For convenience of the ordinate and abscissa scales, the data are presented as  $S(Q, \lambda^{-1})$  instead of  $S(Q, \omega)$ . Resolution functions are shown for  $Q = 0$  and  $Q = 2 \text{ \AA}^{-1}$ .

We had considerable difficulty from more or less trivial causes in these experiments, and they have taken quite a lot of time. This was partly due to a mistake in the basic design which may be worth recounting. In all our experiments we have been very concerned with the influence of multiple scattering, and in this experiment we took good care that there was very little; in fact we estimate that multiple scattering amounts to only about 3% of the primary scattering at larger  $Q$ 's. We achieved this low level by putting horizontal cadmium absorbers in the argon specimen chamber, as suggested to one of us by Dr. G. H. Vineyard (private communication), but in eliminating multiple scattering we also eliminated too much of the primary scattering. As a result the statistics are not as good as we would have wished, and the background

subtractions are not as accurate. Not only this but the counting times were so long that difficulty was encountered in getting sufficiently compatible experimental results, due to equipment failures and changes. Nevertheless, we think that the results are sufficiently accurate that we will have errors of only 5%, or at worst 10%, in the transformed quantities in the regions of interest.

Figure 8(a) shows the full width at half maximum of the curves of Figure 7, corrected for resolution, and plotted as a function of  $Q$ , with bars indicating estimated errors in  $W$  and resolution in  $Q$ .

Figure 8(b) shows the integrated intensity. At small  $Q$  the scattering comes largely from the incoherent component of the scattering cross section. In this region the width has approximately the value  $2\pi DQ^2$  expected [ 2] from diffusion, using the value of the coefficient of self-diffusion  $D = 1.53 \times 10^{-5} \text{ cm}^2/\text{sec}$  measured by Cini-Castagnoli and Ricci [ 10]. (It should be pointed out, however, that other workers [ 11] have given values about 30% higher.)

At larger values of  $Q$ , in the region of the first diffraction peak, the scattering is predominantly coherent, and the coherent narrowing of the energy distribution is visible. In the region of  $Q = 1.5 \text{ \AA}^{-1}$  the width makes a transition between the two types of behaviour as the scattering changes from predominantly incoherent at small  $Q$ , to coherent in the vicinity of the peak.

The narrowing of the distribution due to coherence, predicted by DeGennes [ 12 ] and observed earlier in liquid lead [ 13 ] , is striking. (This entire phenomenon, it should be noted, is outside the scope of the convolution approximation [ 8 ].)

We hope to complete these experiments by extending the range of  $Q$ , and to have in the near future complete scattering and correlation functions for liquid argon near the melting temperature.

#### 4. A SEARCH FOR PHONONS IN LIQUID TIN

Finally we discuss an experiment designed to study the question "Is a liquid dynamically like a solid in any realistic and quantitative sense?" From the experiments of Larsson et al. [ 14 ] in particular, it is known that the frequency distribution (in the sense of Egelstaff [ 15 ] ) for the liquid, must be very similar to that for the solid. In our view, however, this fact does not provide an answer to the question posed; a liquid has roughly the same volume as the corresponding solid, the potentials between the atoms in the liquid are the same as those in the solid, so the motions are necessarily constrained in much the same way and the Fourier components of the motion must be nearly the same for the two. The real question can be posed as "Does there exist in a classical liquid something akin to the dispersion relation for the normal modes of a solid?" Since a liquid is isotropic the dispersion curve - if it exists - can depend only on the magnitudes of  $Q$ .

For the quantum liquid  $\text{He}^4$  it is known that such a dispersion relation exists. Experiments by Palevsky et al. [ 16 ] at Stockholm, Yarnell et al. [ 17 ] at Los Alamos, and Henshaw et al. [ 18 ] at Chalk River, are in very good agreement as to the form of the curve. Figure 9 shows the points of Yarnell et al. as crosses and of Henshaw and Woods as closed circles. The integrated intensity (structure factor) of the liquid as measured by Henshaw [ 19 ] is also shown, as open circles. The dispersion curve starts at small  $Q$  with the slope given by the measured velocity of sound, shows a maximum at the position of the first zone boundary\* in the liquid, falls rather symmetrically on the other side of the zone boundary to a minimum near the structure factor maximum, then rises again towards a possible second maximum near the structure factor minimum, all in rather close analogy to the behaviour of the dispersion curve in a crystal.

The question to be answered by the experiments is: "Can we see at least vestiges of such a dispersion curve in a classical liquid?" We know that longitudinal sound waves can be propagated in a liquid so we know that the initial part of the dispersion curve exists. We know that for at least some solids, at temperatures near the melting temperature, the phonons for wave vectors near the zone boundary are very much

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\* The spherical zone is defined to contain one degree of freedom per atom. For liquid helium at 1.15°K this leads to a value  $1.09 \text{ \AA}^{-1}$  for the zone boundary.

energy broadened due to short lifetimes for the phonons. In a liquid the lifetime of a phonon can hardly be longer than that for the corresponding phonon in the solid, so we expect any phonon groups near to, or beyond, the first zone boundary, to be very broad at best.

Liquid tin was selected as the subject for the experiments because it is a convenient material whose scattering is almost completely coherent, and especially because of the fact that one can reduce multiple scattering effects in liquid tin by dissolving cadmium in it without much altering other properties of the liquid. This is discussed in detail later.

Figure 10 indicates the main facts known a priori about the "dispersion curve" in liquid tin. It must start off at small  $Q$  with the slope given by the velocity of sound in liquid tin, 2464 m/sec, and at the "zone boundary",  $1.28 \text{ \AA}^{-1}$ , should have an energy certainly no greater than that corresponding to the Debye temperature of solid (white) tin, 170°K. If we accept a prescription of Mott [ 20 ], the Debye temperature of the liquid would be expected to be 110°K corresponding to the quantum energy indicated in the figure. The dispersion curve would then be expected to bend over symmetrically about the zone boundary and take a small energy near the position,  $\sim 2.2 \text{ \AA}^{-1}$ , of the main diffraction peak.

On the figure we have plotted several lines which correspond to the energies and wave vectors which would be observed in conventional

experiments at energy loss for several outgoing energies,  $E'$ , at a scattering angle of 10 degrees, perhaps the minimum reasonable scattering angle one can use. (At smaller angles similar lines would occur to the left of those shown, at larger angles, to the right.) Even for  $E' = 36.2$  meV we could not observe phonons on the linear part of the dispersion curve, although we could within the first zone.

The experiments are made difficult by the fact that we wish to study the region of  $Q$  before the first diffraction peak, the very region that one ordinarily considers to have almost zero primary intensity. Indeed under ordinary conditions most of the scattering observed in this region is multiple scattering, so to study phonons in liquids one must try to minimize the multiple scattering, and then make a reasonably accurate correction for what remains. In our experiments we used a thin specimen of tin ( $T \approx 87\%$ ) in which sufficient cadmium ( $0.78\%$ ) was dissolved to lower the transmission to about 50%. Cadmium dissolves in liquid tin to any amount, the two substances are both metals with approximately the same atomic weight, and we hope that the cadmium acts in liquid tin simply as another isotope but one that converts the tin to an isotopic form which has a large absorption and therefore for which the multiple scattering is reduced [ 21 ] .

To take background we place a duplicate empty specimen container at the position of the specimen, and at the same time place in the

beam a thin cadmium absorber with approximately the same transmission as the specimen. This is done automatically at each spectrometer position and background is subtracted directly from the signal point-by-point. By this means we obtain a background correction which takes accurate account in one operation of the fast neutron background and of container and air scattering.

Figure 11 shows a preliminary set of results obtained at  $Q = 1.4 \text{ \AA}^{-1}$  and  $1.8 \text{ \AA}^{-1}$  (after background subtraction) using the constant  $Q$  method and the triple axis spectrometer [ 6 ]. The dashed curves represent multiple scattering computed in an approximation which assumed that two scatterings occurred, both at angles of scattering of  $90^\circ$ , and that the energy distribution for each scattering was that for a tin gas at  $250^\circ\text{C}$ . Even with this improved specimen, most of the scattering seems to be multiple scattering. If sharp phonons existed in the liquid we calculate that they should be seen with the intensity and approximate shape indicated by the triangles. At  $Q = 1.8 \text{ \AA}^{-1}$  it is clear that there are no sharp phonons in the region of interest but, as discussed earlier, we do not expect sharp phonons anyway. At  $Q = 1.4 \text{ \AA}^{-1}$  there are no sharp phonons below about 10 meV, which at any rate is above the Mott estimate. The statistics and accuracy of the experiments done so far do not allow more definite statements to be made. We have patterns with better statistics but the experiments were interrupted before the absolute normalization

necessary could be carried out. We hope that the completed experiments will allow convincing evidence to be produced for what we think is the case; that there are no sharp phonon groups near the zone boundary, but rather a continuous distribution of intensity (with perhaps some slight structure). We think that the quasi-elastic scattering observed in Figure 11 is probably just the result of an extremely broad phonon line, a line so broadened that there is little sense in calling it a phonon at all.

#### 5. ACKNOWLEDGMENTS

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#### FIGURE CAPTIONS

- Fig. 1. Energy distributions from water at 6°C and 24.5°C and from ice at -50°C (open circles) (Ref. (3)).
- Fig. 2. Wavelength distribution of 4.06 Å neutrons scattered by room temperature water (Sakamoto et al. , Ref. (5)).  
The resolution function, as measured by elastic scattering from vanadium, is shown as open circles.
- Fig. 3. The scattering function  $S(Q, \omega)$  for water at 25°C and 75°C (Sakamoto et al. , Ref. (5)). The resolution functions are shown as dashed curves.
- Fig. 4. The self-correlation function  $G_s(r, t)$  for water at 25°C and 75°C.

- Fig. 5. Mean square displacement of protons in water at 25°C and 75°C as a function of time (Sakamoto et al. , Ref. (5)).
- Fig. 6. Energy distributions from liquid argon at 3 angles of scattering.
- Fig. 7. Scattering function  $S(Q, \lambda')$  for liquid argon.
- Fig. 8. (a) Energy width of scattering function, corrected for resolution.  
(b) Integrated intensity as function of  $Q$ .
- Fig. 9. The dispersion curve and integrated intensity for liquid  $\text{He}^4$ .
- Fig. 10. Information on "dispersion curve" in liquid tin and experimental constructions.
- Fig. 11. Energy distributions from liquid Sn at  $Q = 1.4$  and  $1.8 \text{ \AA}^{-1}$ .

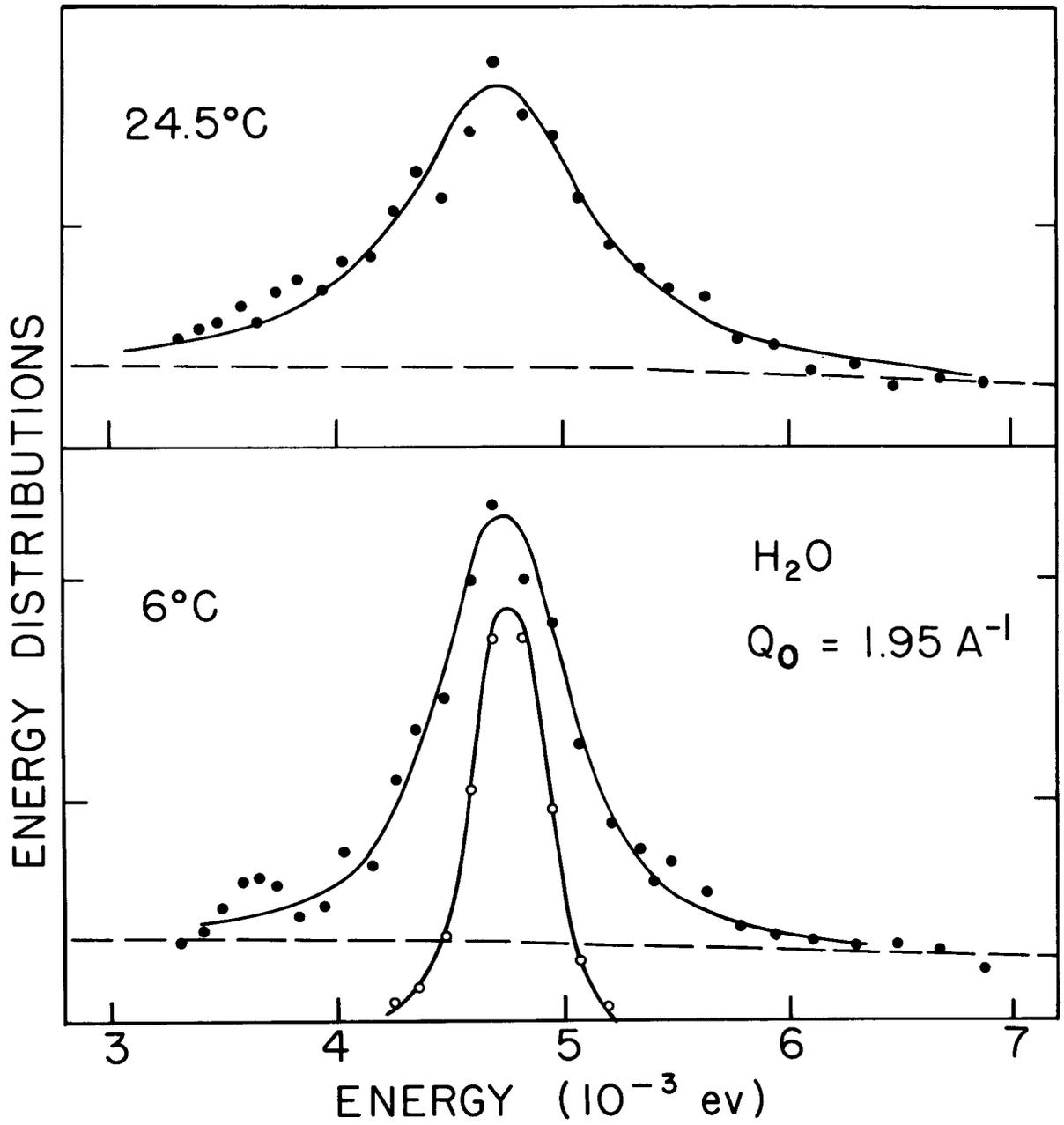


Figure 1

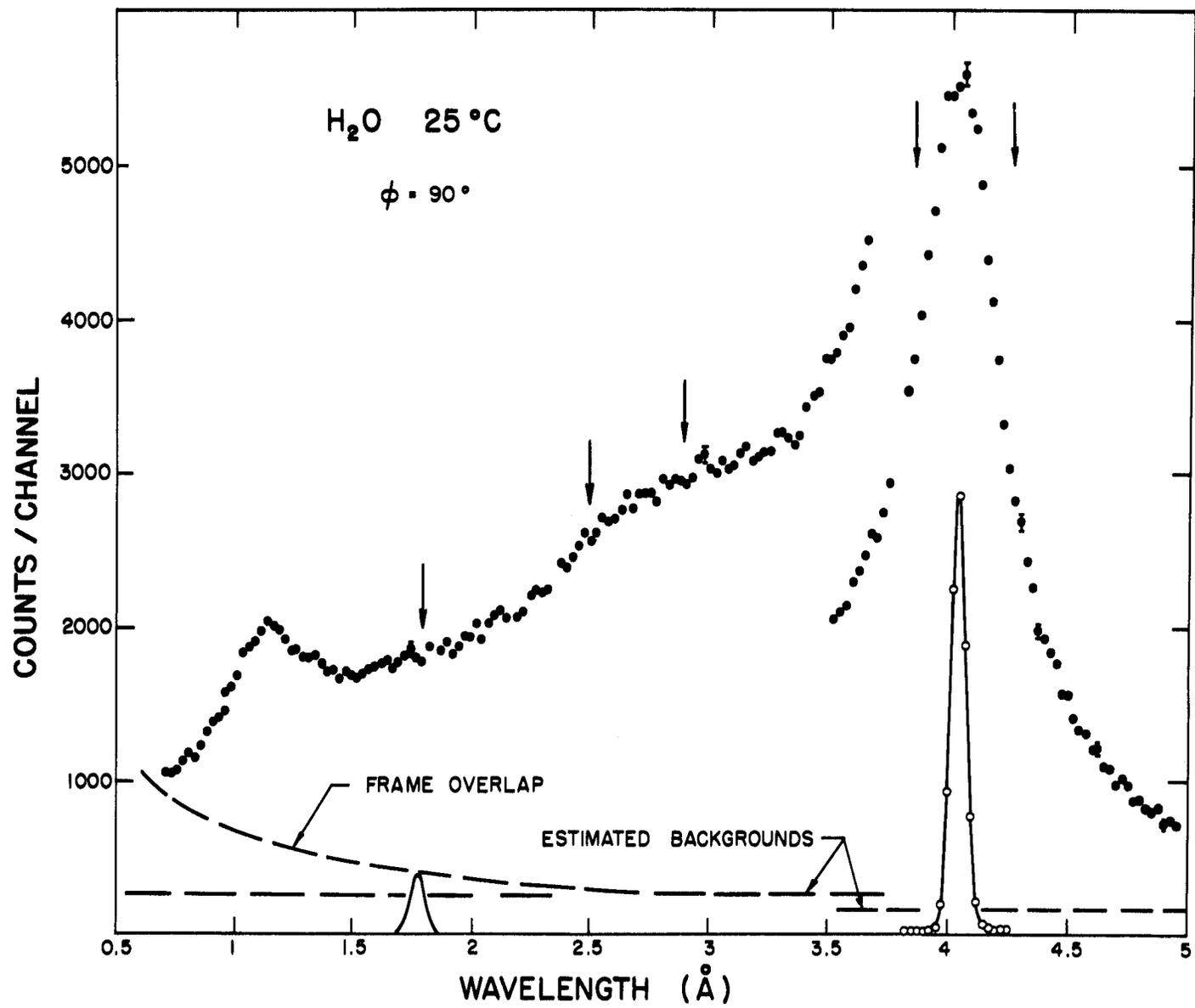
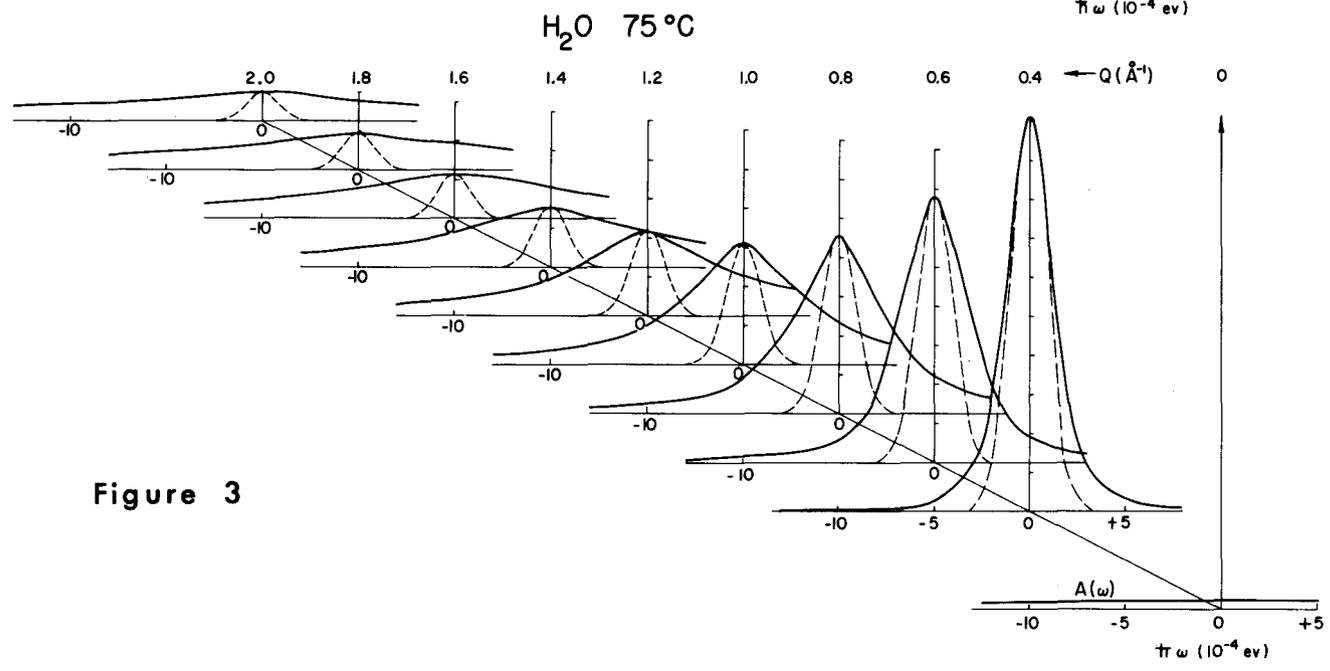
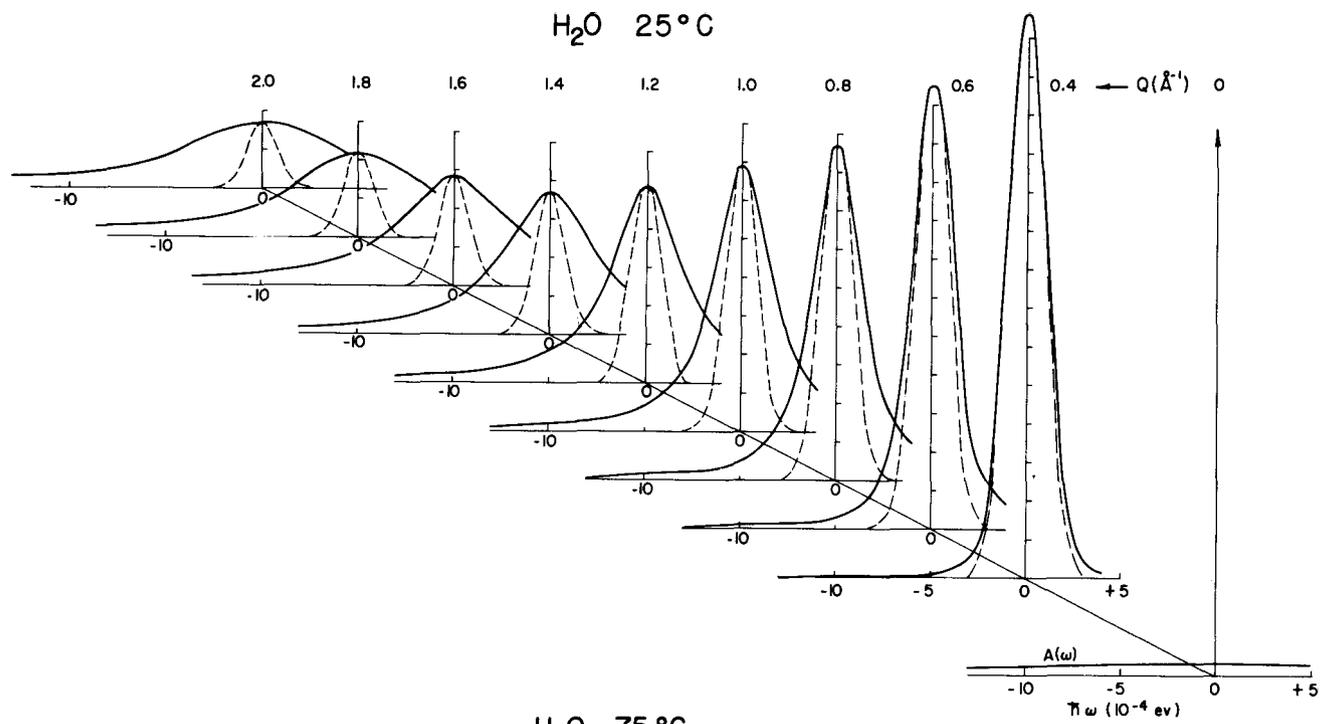


Figure 2



**Figure 3**

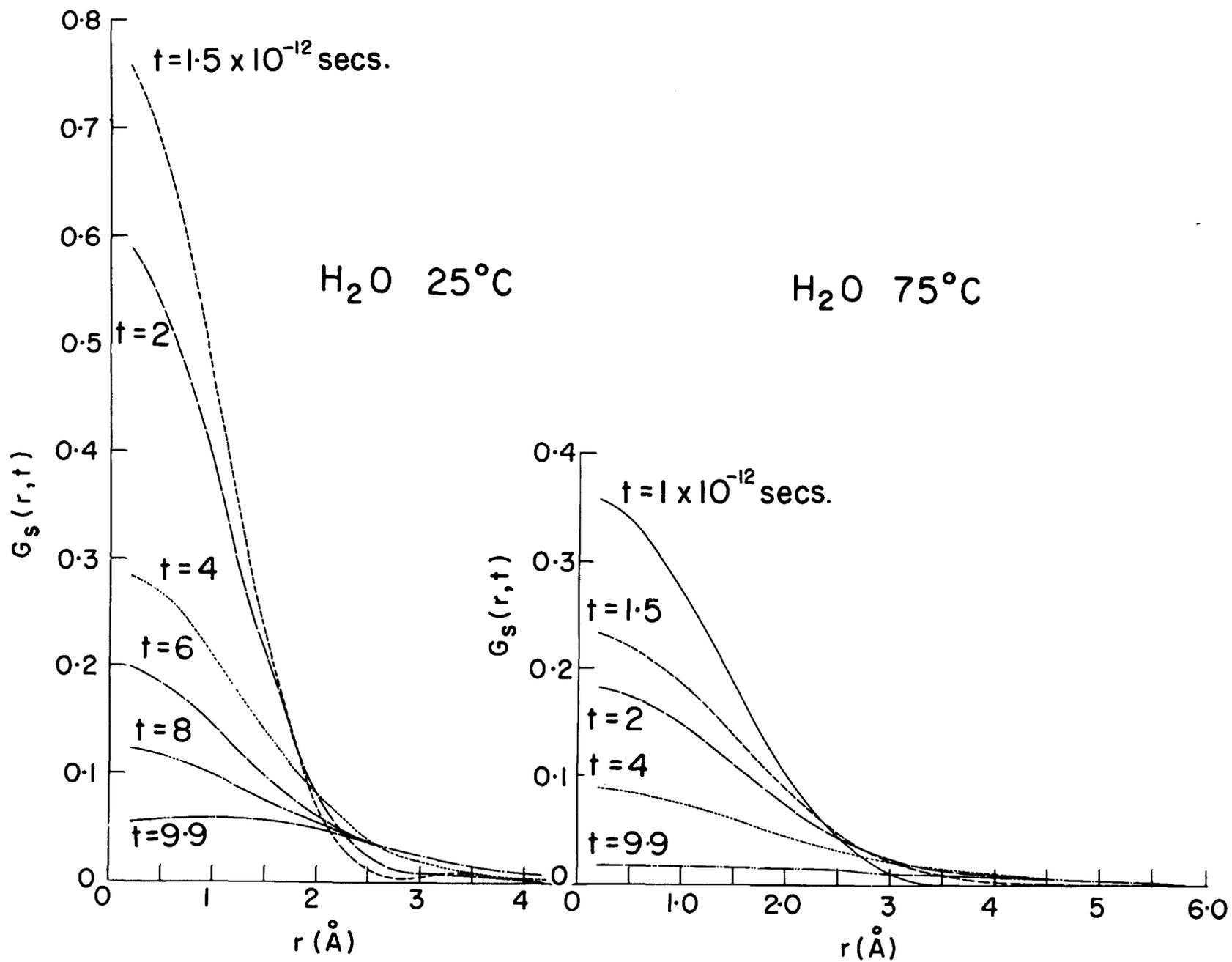


Figure 4

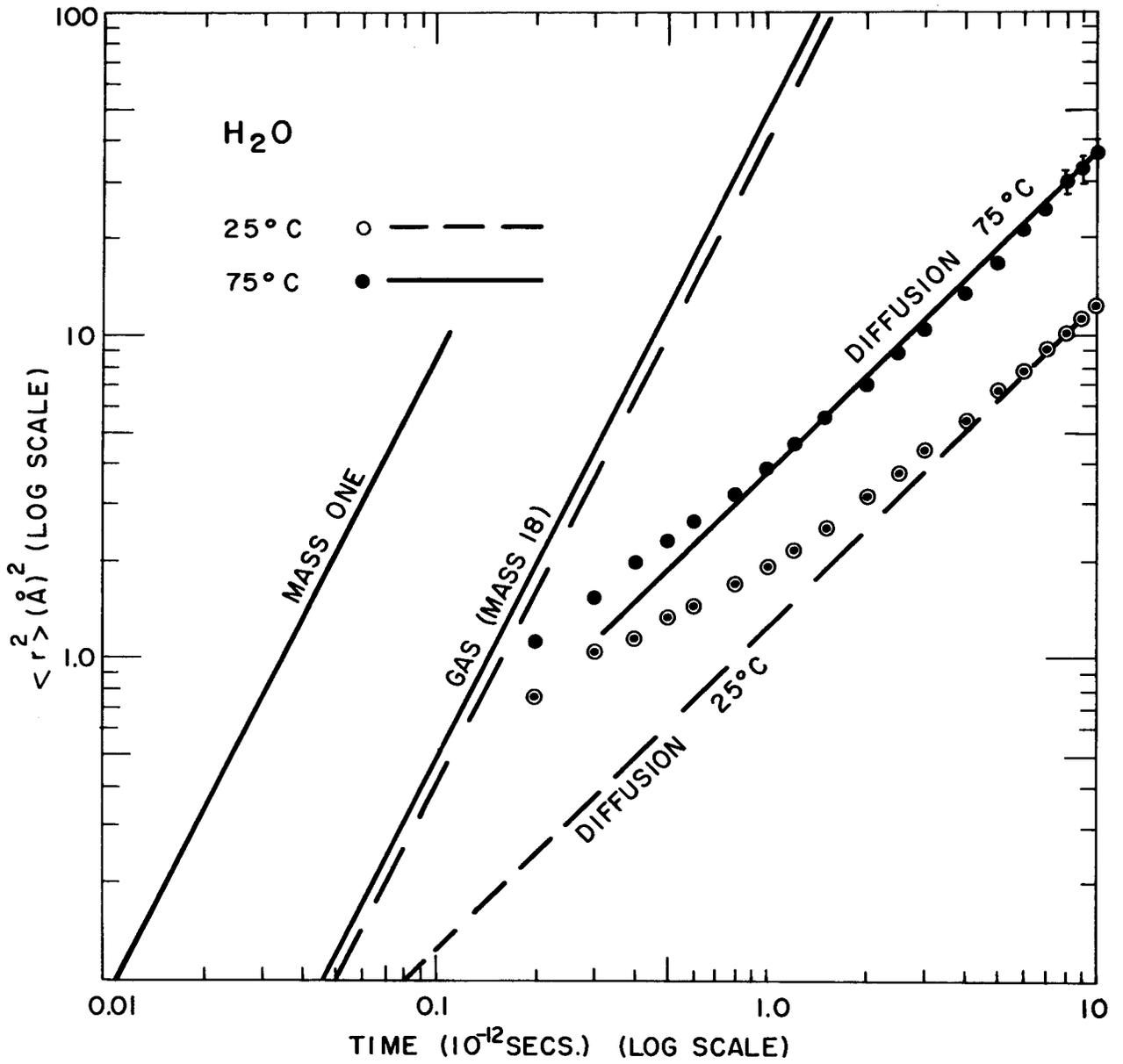


Figure 5

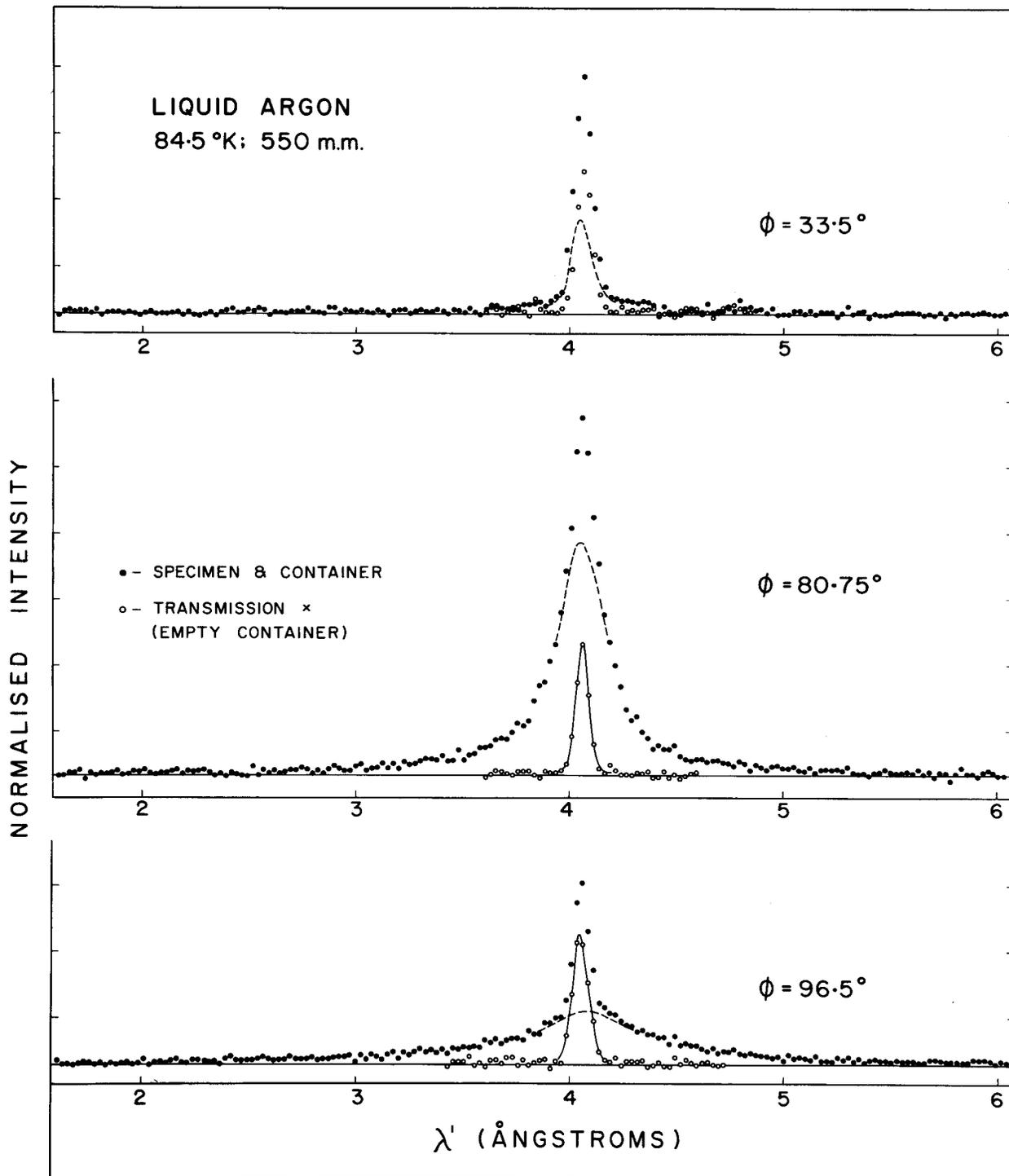


Figure 6

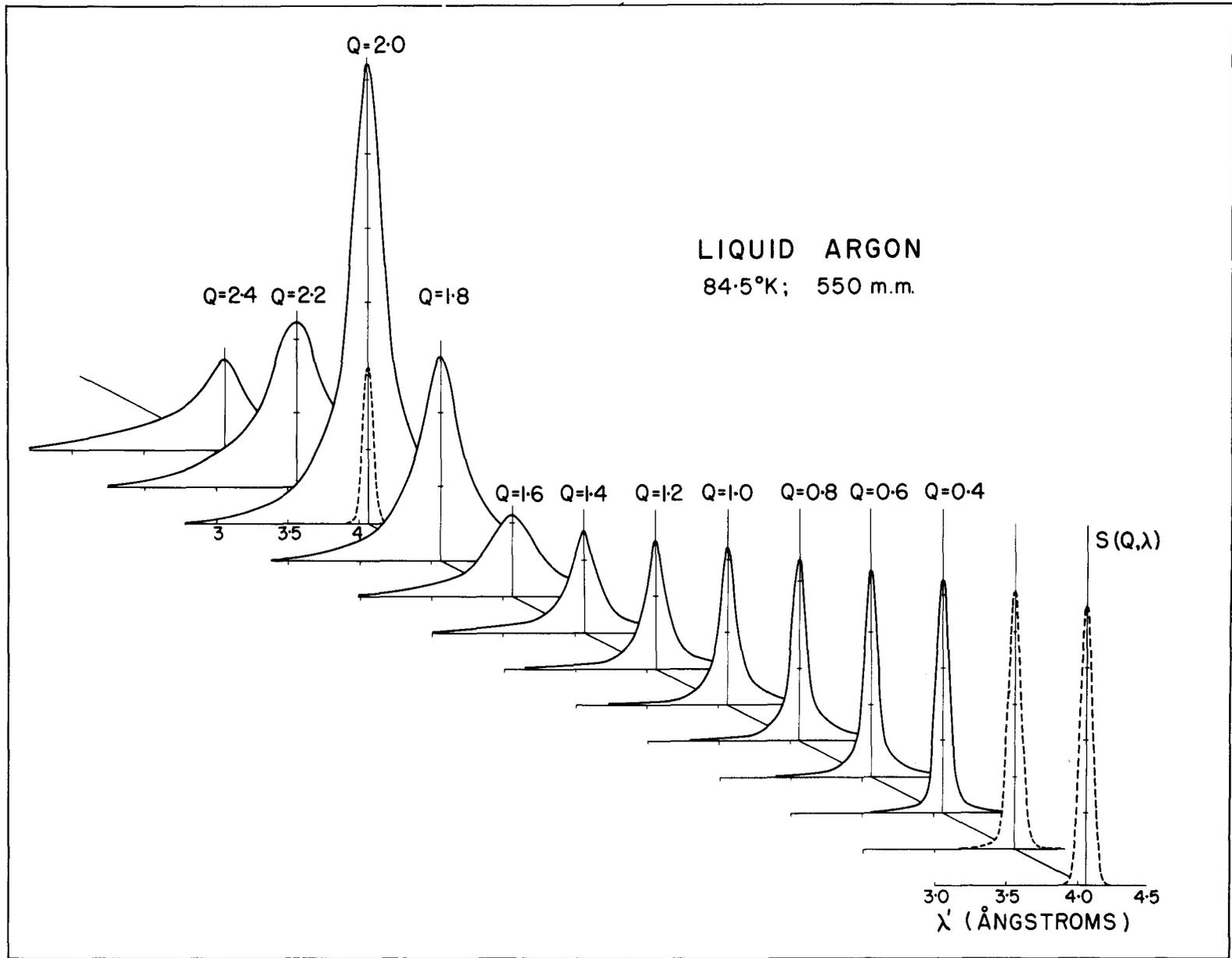


Figure 7

LIQUID ARGON (84.5°K; 550 mm)

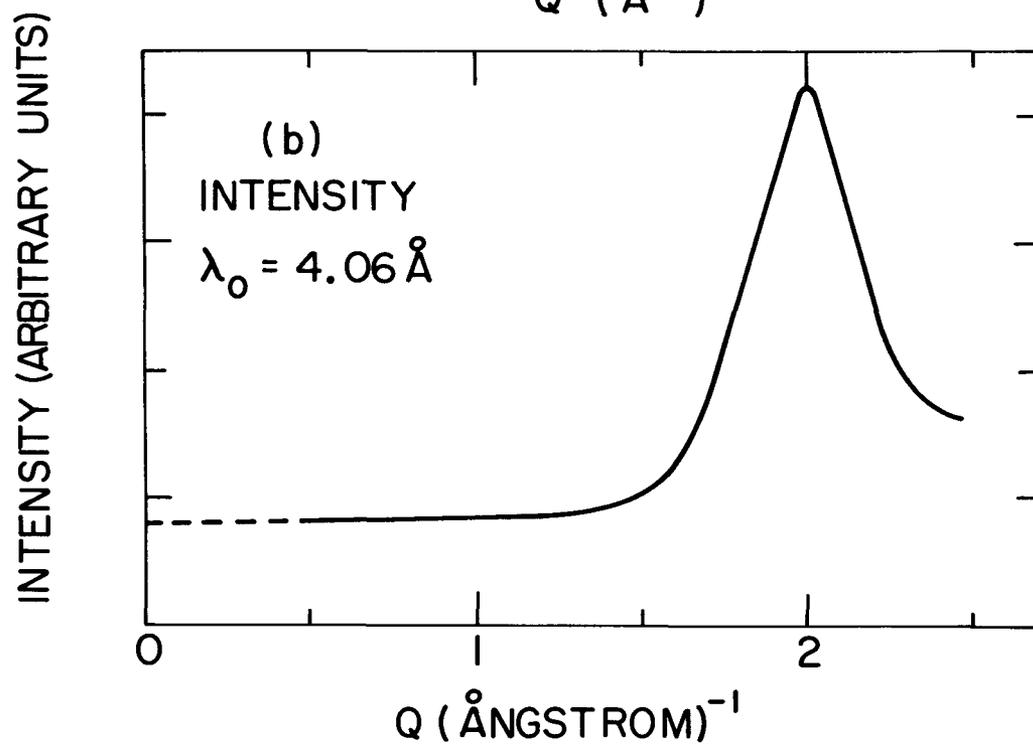
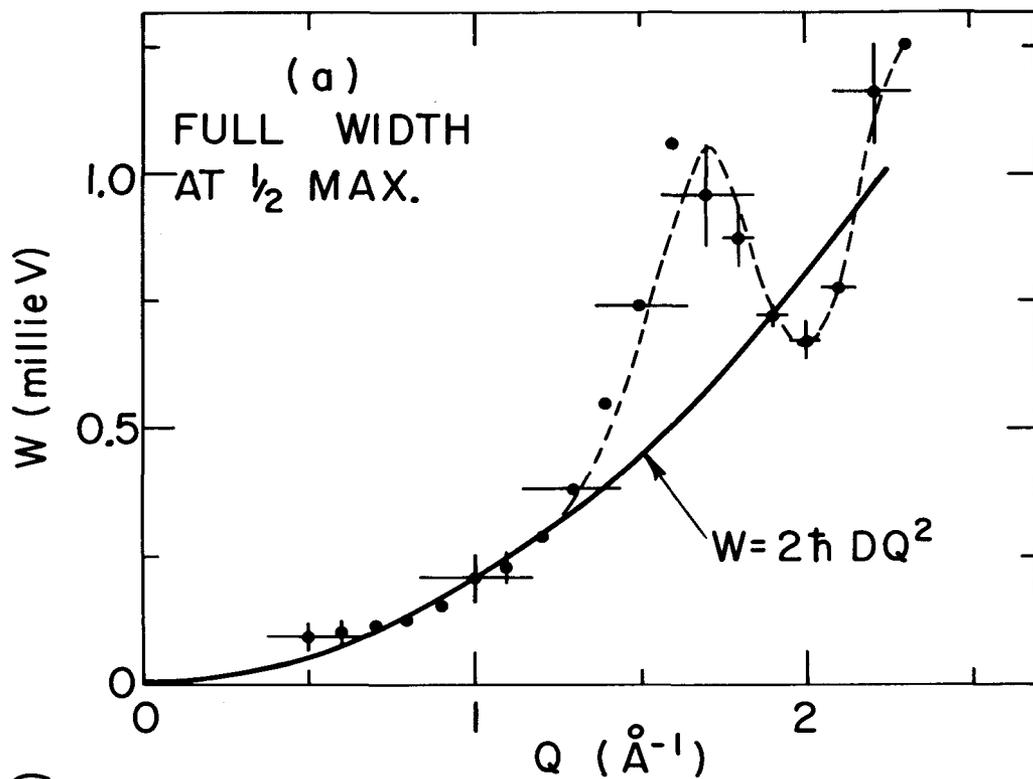


Figure 8

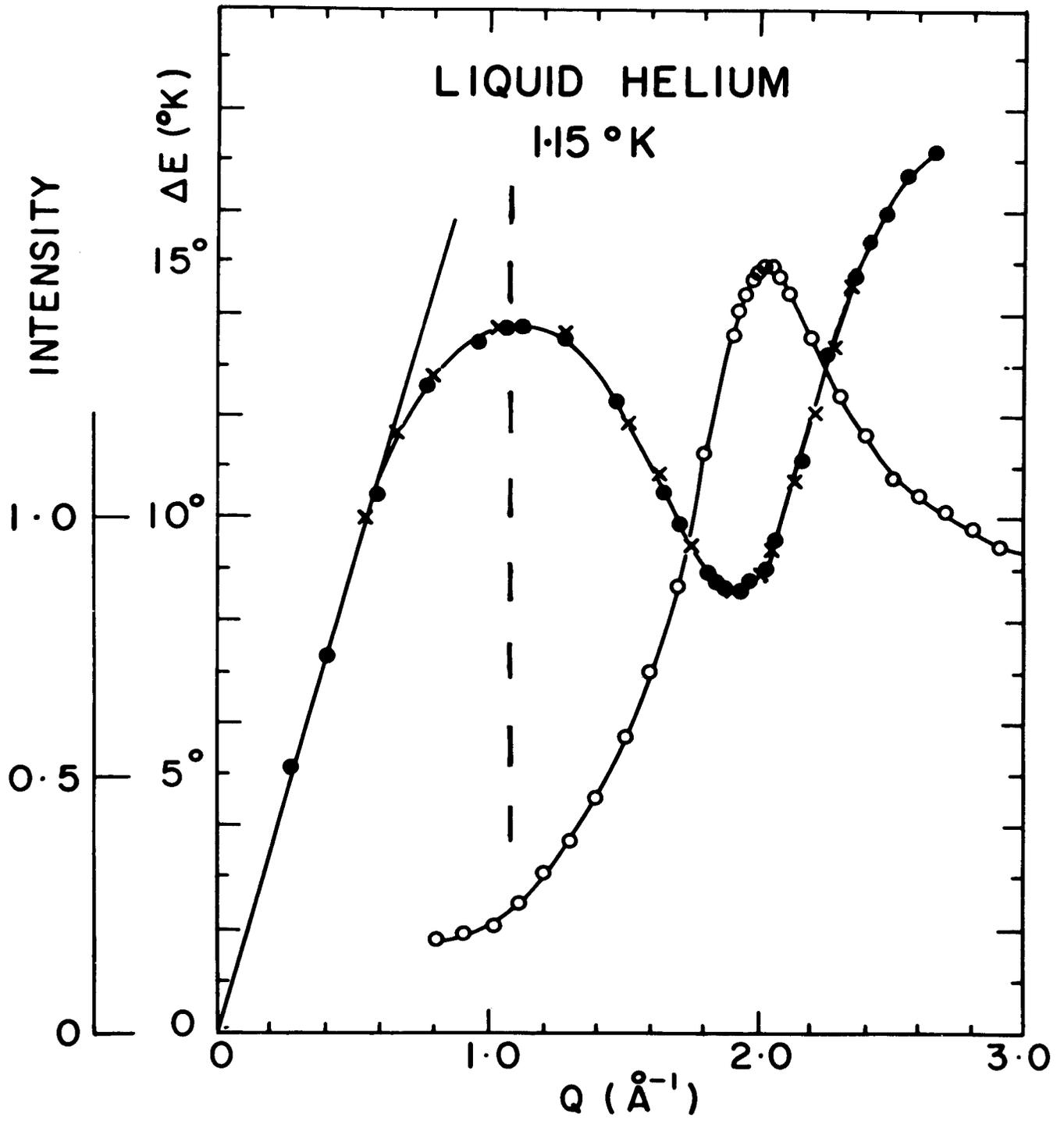


Figure 9

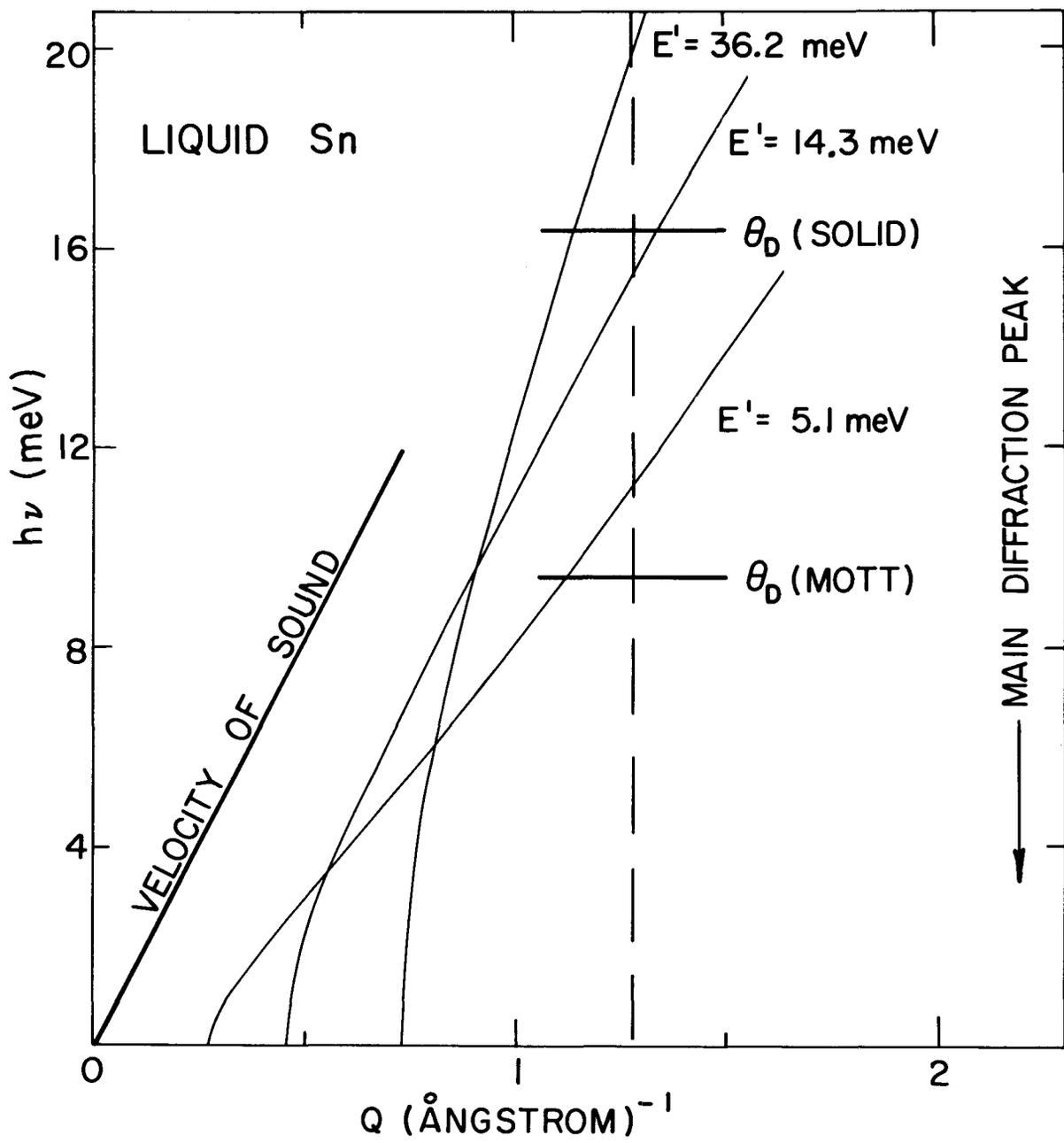


Figure 10

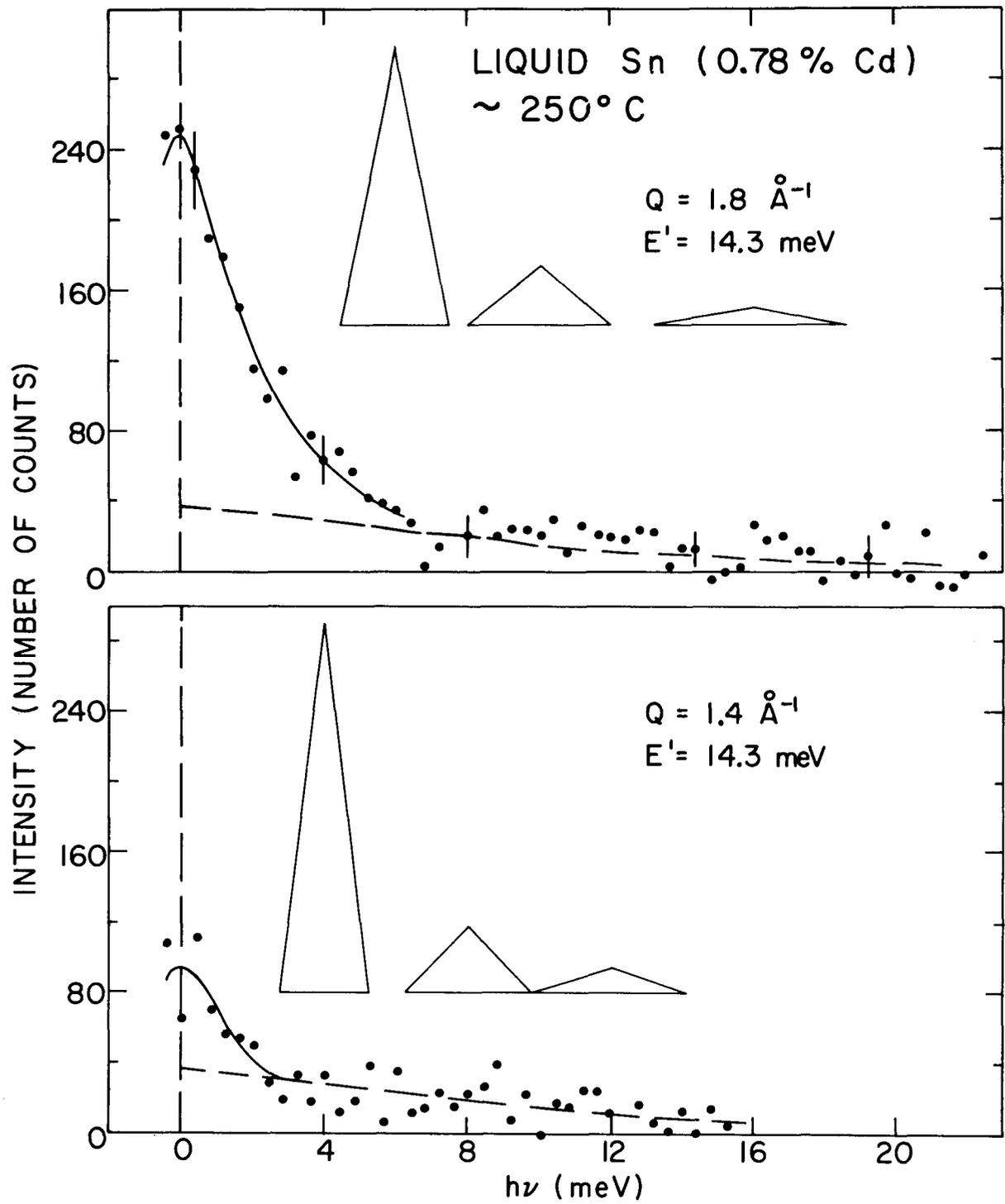


Figure 11