

- HUANG, K. (1947). *Proc. Roy. Soc. A* **190**, 102.  
 KANZAKI, H. (1957). *J. Phys. Chem. Solids*, **2**, 107.  
 PECKHAM, G. (1967). *Proc. Phys. Soc.* **90**, 657.  
 PECKHAM, G. (1968). Private communication.  
 PRYOR, A. W. (1966). *Acta Cryst.* **20**, 138.  
 RACCAH, P. M. & ARNOTT, R. J. (1967). *Phys. Rev.* **153**, 1028.  
 SABINE, T. M. (1965). Unpublished results.  
 SABINE, T. M. & KEATING, D. T. (1968). To be published.  
 SUZUKI, T. (1960). *Acta Cryst.* **13**, 279.  
 TOGOWA, S. (1965). *J. Phys. Soc. Japan*, **20**, 742.  
 TOKONAMI, M. (1965). *Acta Cryst.* **19**, 486.  
 WALKER, D. G. & HICKMAN, B. S. (1965). *Phil. Mag.* **12**, 445.  
 WATSON, R. E. (1958). *Phys. Rev.* **111**, 1108.  
 YAMASHITA, J. (1964). Private communication to Dr Tokonami (see Tokonami, 1965).  
 YAMASHITA, J. & KOJIMA, M. (1952). *J. Phys. Soc. Japan*, **7**, 261.  
 YOUNG, R. A. (1965). *Trans. Amer. Cryst. Assoc.* **1**, 42.

*Acta Cryst.* (1969). **A25**, 702

## One and Two-Phonon X-ray Cross-Section Calculations for the Molecular Crystal Hexamethylenetetramine

BY G. S. PAWLEY\*

*Department of Physics, Edinburgh University, Drummond Street, Edinburgh 8, Scotland*

(Received 14 February 1969)

The two-phonon X-ray scattering from hexamethylenetetramine is calculated, and this is compared with the one-phonon result, here independently recalculated. The details of the calculation procedure are fully described, and possible savings in computation discussed. In a few regions of reciprocal space within the Cu  $K\alpha$  reflecting sphere the two-phonon scattering is larger than the one-phonon scattering. It is therefore essential when making quantitative comparisons with experiment that the two-phonon scattering be considered.

### Introduction

Cochran & Pawley (1964) have calculated the one-phonon X-ray scattering cross-section of hexamine (hexamethylenetetramine). Since that time there have been improved measurements of the thermal diffuse scattering (TDS) by Powell (1963) and McMullan (1967). Until the calculation here reported the only comparisons of experiment with theory involved either the one-phonon calculation mentioned above or the Difference Fourier Transform of Amorós, Canut & De Acha (1960). The latter is simply the difference in the squared Fourier transform calculated with and without thermal motion, where the atomic thermal motion is introduced through anisotropic mean-square amplitudes as found by crystallographic structure refinement. The present calculation shows that the effect of the two-phonon process should not be neglected when comparisons with accurate measurements are attempted.

The crystal structure of hexamine is fully described by Becka & Cruickshank (1963). Nearly spherical molecules of symmetry  $\bar{4}3m$ , are placed on a body centred cubic lattice with only one molecule in the primitive unit cell. The planes  $(0kl)$ ,  $(1kl)$  etc. in reciprocal space contain reciprocal lattice points, and it is

customary to make measurements of the diffuse X-ray scattering in the interlayers  $(\frac{1}{2}kl)$ ,  $(\frac{3}{2}kl)$  etc. where there is no Bragg scattering. The present calculations are for the  $(\frac{1}{2}kl)$  interlayer. The one-phonon scattering calculation is here repeated in order to establish a scale.

The model used here is exactly the same as that of Cochran & Pawley (1964), the equations for the calculations coming from Cochran (1963). However, before discussing this in detail mention should be made of a method of calculating in one procedure the effect of all the phonon processes. This has been done for NaCl by Eldridge & Lomer (1967) and Lomer (1966). A model for a small crystal is set up in the computer, and the displacements for all the atoms are calculated for a typical but random set of vibrations. The phonon eigenvectors and eigenvalues are obtained by the use of the model, and therefore the energies in all the possible modes of vibration are known for a given temperature. The displacement configuration is obtained by assigning random phases to all the modes. The total scattering from this small crystal is then found. This must of necessity include all the phonon processes. The calculation is then repeated a number of times, each time taking new random phases, until the averaged calculated intensity becomes stable. The conclusion for NaCl was that most of the TDS is due to one and two phonon processes – calculated separately – but that in some regions the scattering from higher order processes was appreciable. This emphasizes the

\* Present address: Department of Chemistry, Aarhus University, Denmark; on leave of absence.

need for a two-phonon scattering calculation for hexamine.

### Scattering equations

In this section the relevant equations governing the TDS are taken from the review article of Cochran (1963), and moulded to the example of hexamine. The numbering of the equations identifies their source.

The one-phonon and two-phonon scattering cross-sections are  $(d\sigma/d\Omega)^{(1)}$  and  $(d\sigma/d\Omega)^{(2)}$  respectively. The scattering geometries are shown in Fig. 1, defining the phonon wave-vectors  $\mathbf{q}$  and  $\mathbf{q}'$ . For a crystal with  $N$  primitive unit cells with  $n$  atoms in the unit cell, Cochran (1963) shows that

$$\left(\frac{d\sigma}{d\Omega}\right)^{(1)} = \frac{NQ^2}{m} \sum_{j=1}^{3n} \frac{E_j(\mathbf{q})}{\omega_j^2(\mathbf{q})} |G_j^{(1)}(\mathbf{Q})|^2 \quad (1) \quad (\text{C:7-20})$$

where

$$QG_j^{(1)}(\mathbf{Q}) = \mathbf{Q} \cdot \sum_{k=1}^n \hat{\mathbf{U}}_j(k\mathbf{q}) f(k\mathbf{Q}) \exp [i\mathbf{B} \cdot \mathbf{r}(k)] \quad (2) \quad (\text{C:7-19})$$

and

$$\left(\frac{d\sigma}{d\Omega}\right)^{(2)} = \frac{1}{2m^2} \sum_{i,j=1}^{3n} \sum_{\mathbf{q}'} \frac{E_j(\mathbf{q}') E_i(\mathbf{q}-\mathbf{q}')}{\omega_j^2(\mathbf{q}') \omega_i^2(\mathbf{q}-\mathbf{q}')} |G_{ij}^{(2)}(\mathbf{Q})|^2 \quad (3) \quad (\text{C:7-25})^*$$

where we have introduced

$$G_{ij}^{(2)}(\mathbf{Q}) = \sum_{k=1}^n f(k\mathbf{Q}) \exp [i\mathbf{B} \cdot \mathbf{r}(k)] (\mathbf{Q} \cdot \hat{\mathbf{U}}_j(k\mathbf{q}')) (\mathbf{Q} \cdot \hat{\mathbf{U}}_i(k, \mathbf{q}-\mathbf{q}')) \quad (4)$$

$i$  and  $j$  are indices which range over the phonon branches at any point  $\mathbf{q}$  in the Brillouin zone, and  $\omega_j(\mathbf{q})$  is the angular frequency in the  $j$ th branch. The total energy in this branch is

$$E_j(\mathbf{q}) = [n_j(\mathbf{q}) + \frac{1}{2}] \hbar \omega_j(\mathbf{q}) \quad (5) \quad (\text{C:2-19})$$

$$n_j(\mathbf{q}) = [\exp (\hbar \omega_j(\mathbf{q}) / k_B T) - 1]^{-1} \quad (6) \quad (\text{C:2-20})$$

$\mathbf{Q}$  is the X-ray scattering vector, of magnitude  $4\pi \sin \theta / \lambda$ , and  $\mathbf{B}$  is a vector of the reciprocal lattice (Fig. 1). The vector  $\mathbf{r}(k)$  defines the equilibrium position

\* Correction here in the normalizing constant (Cochran, private communication).

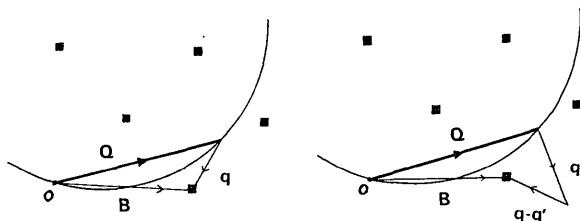


Fig. 1. The geometries for one- and two-phonon scattering. Black squares represent reciprocal lattice points.

of the  $k$ th atom within its cell, for which  $f(k\mathbf{Q})$  is the atomic scattering factor modified by the Debye-Waller factor.

In the equations above we have used normalized wave amplitudes,  $\hat{\mathbf{U}}_j(k\mathbf{q})$ , defined by

$$\sum_k m_k |\hat{\mathbf{U}}_j(k\mathbf{q})|^2 = \sum_k m_k = m \quad (7) \quad (\text{C:2-11})$$

Dividing by  $m$  we get

$$\sum_k \frac{m_k}{m} |\hat{\mathbf{U}}_j(k\mathbf{q})|^2 = 1 = \sum_k \xi_j^2(k\mathbf{q}), \quad (8)$$

giving a relationship with the orthogonalized eigenvectors,  $\xi_j(k\mathbf{q})$ , obtained from the secular equation. It is computationally advantageous to calculate absolute wave amplitudes,  $\mathbf{U}_j(k\mathbf{q})$ , before embarking on any scattering calculation. From equations (C:2-18) and (C:2-19) – not quoted above – we have

$$E_j(\mathbf{q}) = N \omega_j^2(\mathbf{q}) \sum_k m_k |\mathbf{U}_j(k\mathbf{q})|^2 \quad (9)$$

which with equation (8) gives

$$\mathbf{U}_j(k\mathbf{q}) = \sqrt{\frac{E_j(\mathbf{q})}{Nm_k \omega_j^2(\mathbf{q})}} \xi_j(k\mathbf{q}) \quad (10)$$

Equations (1) and (3) then become

$$\left(\frac{d\sigma}{d\Omega}\right)^{(1)} = N^2 \sum_{j=1}^{3n} \left| \sum_{k=1}^n (\mathbf{Q} \cdot \mathbf{U}_j(k\mathbf{q})) f(k\mathbf{Q}) \times \exp [i\mathbf{B} \cdot \mathbf{r}(k)] \right|^2, \quad (11)$$

$$\left(\frac{d\sigma}{d\Omega}\right)^{(2)} = \frac{1}{2} N^2 \sum_{i,j=1}^{3n} \sum_{\mathbf{q}'} \left| \sum_{k=1}^n (\mathbf{Q} \cdot \mathbf{U}_j(k\mathbf{q}')) \times (\mathbf{Q} \cdot \mathbf{U}_i(k, \mathbf{q}-\mathbf{q}')) f(k\mathbf{Q}) \exp [i\mathbf{B} \cdot \mathbf{r}(k)] \right|^2. \quad (12)$$

Now let us turn to the problem of hexamine. If we assume that the molecules move only as rigid bodies, this is equivalent to assuming that the internal modes of vibration of the molecules have negligible amplitudes of motion. Three translational and three librational coordinates, expressed as vectors  $\mathbf{u}$  and  $\boldsymbol{\theta}$ , are then sufficient to describe the displacement of a molecule. The displacement for the atom at  $\mathbf{r}(p)$  in the molecule with centre at  $\mathbf{r}(k)$  in the unit cell defined by  $\mathbf{r}(l)$ , due to the phonon with wave-vector  $\mathbf{q}$ ,  $j$ th branch, is

$$\mathbf{u}(lkp) = \mathbf{u}(lk) + \boldsymbol{\theta}(lk) \times \mathbf{r}(p),$$

$$\begin{pmatrix} \mathbf{u}(lk) \\ \boldsymbol{\theta}(lk) \end{pmatrix} = \begin{pmatrix} \mathbf{U}_j(k\mathbf{q}) \\ \boldsymbol{\Theta}_j(k\mathbf{q}) \end{pmatrix} \exp [i(\mathbf{q} \cdot \{\mathbf{r}(l) + \mathbf{r}(k)\} - \omega_j(\mathbf{q})t)] \quad (13)$$

It should be noted that this travelling wave involves  $\mathbf{q} \cdot \{\mathbf{r}(l) + \mathbf{r}(k)\}$  but not  $\mathbf{q} \cdot \mathbf{r}(p)$ . This, as we shall see,

causes slight differences between the present equations and those of Cochran.

As there is only one molecule in the primitive unit cell we can set  $k=1$ . For any wave-vector  $\mathbf{q}$ , branch  $j$  the eigenvector from the secular equation has six components  $\xi_i$ ,

$$\begin{aligned} \sum_{i=1}^6 \xi_i^2 &= 1, \\ \xi_{1,2,3} &= \sqrt{M} (\hat{\mathbf{U}}_j(\mathbf{q}))_{1,2,3} \\ \xi_{4,5,6} &= \sqrt{I} (\hat{\mathbf{\Theta}}_j(\mathbf{q}))_{1,2,3} \end{aligned} \quad (14)$$

where  $M$  is the molecular mass and  $I$  the moment of inertia. Similar to equation (10) we have

$$\begin{aligned} \mathbf{U}_j(\mathbf{q}) &= \sqrt{\frac{E_j(\mathbf{q})}{NM\omega_j^2(\mathbf{q})}} \xi_{1,2,3} \\ \mathbf{\Theta}_j(\mathbf{q}) &= \sqrt{\frac{E_j(\mathbf{q})}{NI\omega_j^2(\mathbf{q})}} \xi_{4,5,6} \end{aligned} \quad (15)$$

from which we can find  $\mathbf{U}_j(p\mathbf{q})$ , the amplitude for the  $p$ th atom found after performing the vector product of equation (13).

We have to be very careful on introducing  $\mathbf{r}(p)$  into equations (11) and (12). Cochran's expression (C:7-16) is now

$$i \sum_{lp} f(p\mathbf{Q}) \exp [i\mathbf{Q} \cdot \{\mathbf{r}(l) + \mathbf{r}(p)\}] \mathbf{Q} \cdot \mathbf{u}(lp), \quad (16)$$

but the travelling wave to be substituted for  $\mathbf{u}(lp)$  lacks the factor  $\exp [i\mathbf{q} \cdot \mathbf{r}(p)]$ . This causes the  $\mathbf{B} \cdot \mathbf{r}(k)$  in equations (C:7-19) and (C:7-25) to be replaced by  $\mathbf{Q} \cdot \mathbf{r}(p)$ . The equations for the calculations for hexamine therefore become

$$\left( \frac{d\sigma}{d\Omega} \right)^{(1)} = N^2 \sum_{j=1}^6 \left| \sum_p (\mathbf{Q} \cdot \underline{\mathbf{U}}_j(p\mathbf{q})) f(p\mathbf{Q}) \right. \\ \left. \times \exp [i\mathbf{Q} \cdot \mathbf{r}(p)] \right|^2, \quad (17)$$

$$\left( \frac{d\sigma}{d\Omega} \right)^{(2)} = \frac{1}{2} N^2 \sum_{i,j=1}^6 \sum_{\mathbf{q}, \mathbf{q}'} \left| \sum_p (\mathbf{Q} \cdot \underline{\mathbf{U}}_j(p\mathbf{q})) \right. \\ \left. (\mathbf{Q} \cdot \underline{\mathbf{U}}_i(p, \mathbf{q} - \mathbf{q}')) f(p\mathbf{Q}) \exp [i\mathbf{Q} \cdot \mathbf{r}(p)] \right|^2. \quad (18)$$

In this final expression the fact that the vectors  $\mathbf{U}$  are complex in character has been emphasized by underlining.

### Calculation procedure

The one-phonon cross-section, equation (17), is a straightforward calculation for the point  $\mathbf{Q}$  in reciprocal space, whereas the two-phonon cross-section, equation (18), requires a summation over the whole of the Brillouin zone. The first Brillouin zone is a rhombic dodecahedron, Fig.2, and similar dodecahedra placed about each reciprocal lattice point must fill reciprocal space. However this is an awkward shape to compute with when a simpler shape is allowed.

Fig.2 shows how the first Brillouin zone can be fitted into two cubes. In fact any volume with sides 1, 1 and 2 reciprocal lattice units placed along axes  $\langle 100 \rangle$  will be equivalent to the first Brillouin zone. For our purposes we choose a zone with the long side along  $[010]$

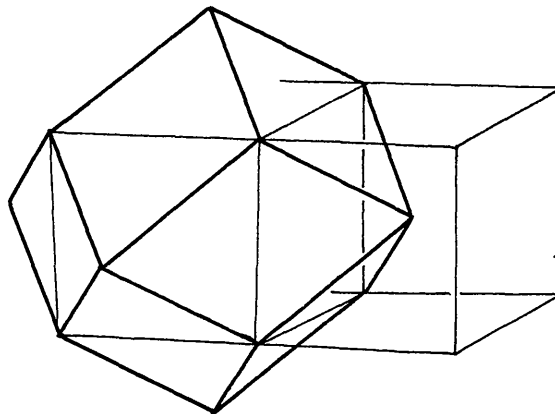


Fig.2. The first Brillouin zone. The rhombic dodecahedron can be considered as a cube with pyramids on all faces. These pyramids can be mapped into the outlined cube.

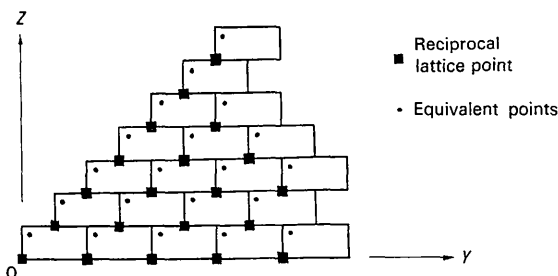


Fig.3. The zones used for the calculations, and the associated reciprocal lattice points.

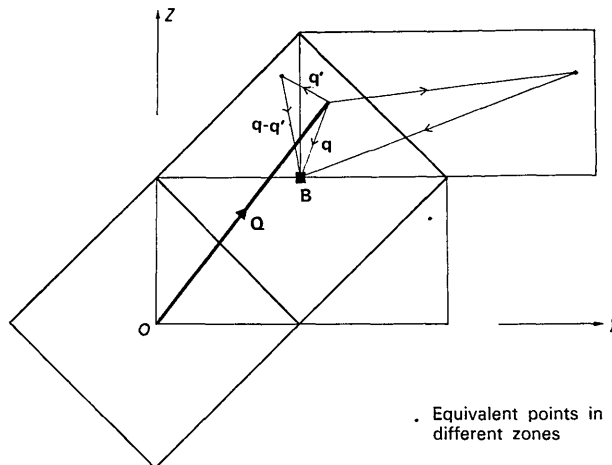


Fig.4. Two-phonon scattering geometry, showing the equivalence of choosing wave vectors related by any reciprocal lattice vector.

and with its origin at a corner. Similar zones with origins at the reciprocal lattice points completely fill reciprocal space. Those zones required in the present calculation are shown in Fig. 3.

We must reassure ourselves that we can choose such a convenient Brillouin zone. Fig. 4 shows the geometry for two-phonon scattering where phonon wave-vectors in different zones are compared. These different wave-vectors yield identical eigenvectors and eigenvalues, though there may be unimportant differences within

the eigenvector phases. There is no part of equation (18) which involves  $\mathbf{q}$  and  $\mathbf{q}'$  except through the eigenvectors and eigenvalues, so the result must be independent of the zone chosen.

When summing over the Brillouin zone use of very long wavelength phonons should be avoided. The acoustic branches in this region have low frequencies and as a result would dominate the calculation. This would be an error because any particular acoustic mode phonon is representative of only a small region of re-

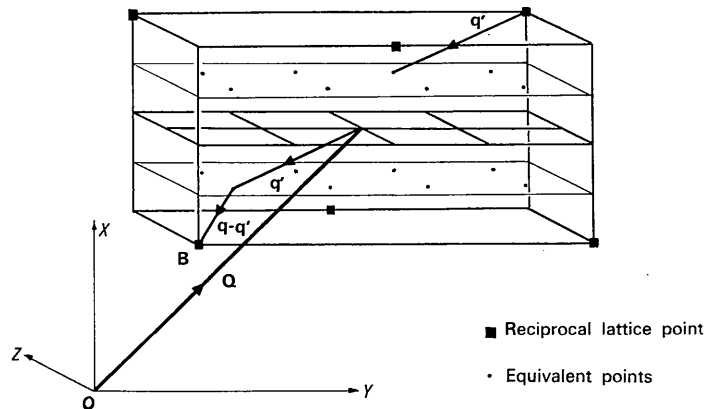


Fig. 5. The  $(\frac{1}{2}kl)$  calculation grid and the points (black dots) whose eigenvectors and eigenvalues need to be calculated.

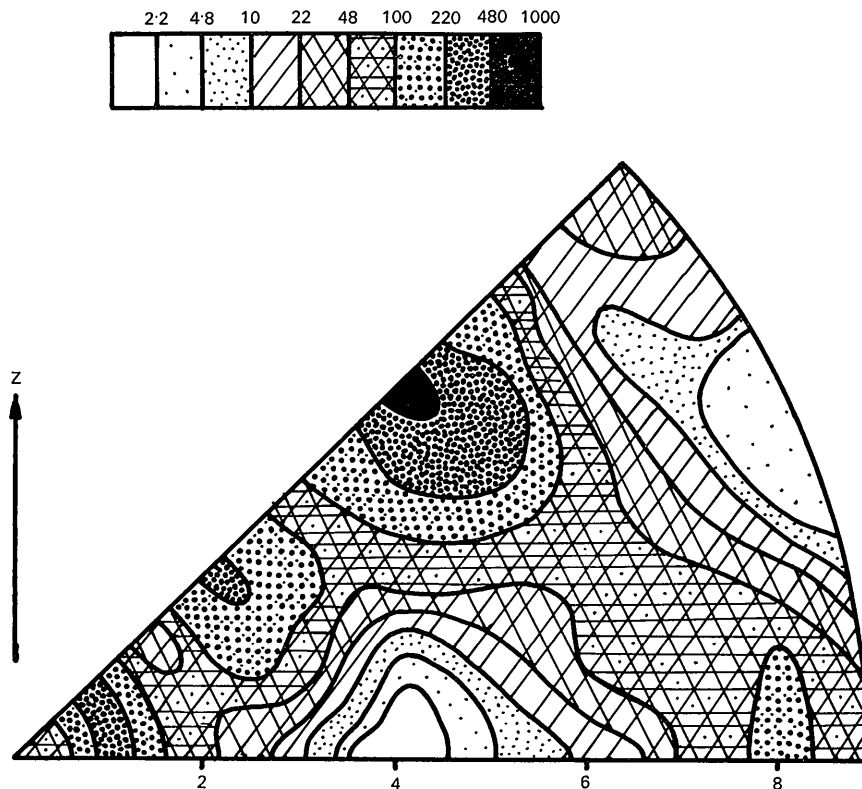


Fig. 6. The one-phonon X-ray TDS, recalculated.  $(\frac{1}{2}kl)$  interlayer. The value of the index  $k$  is indicated.

reciprocal space, but should be representative of a region determined by the sampling interval. Errors of this nature were avoided as follows.

In Fig. 5 we see the grid of the  $(\frac{1}{2}kl)$  interlayer over which the calculation is to be done. The grid points are spaced at  $\frac{1}{2}$ -reciprocal lattice units. Eigenvectors and eigenvalues are calculated at points with coordi-

nates  $h_1/4$ ,  $h_2/4$  and  $h_3/4$  in reciprocal lattice units, where  $h_1$ ,  $h_2$  and  $h_3$  are all odd integers. This gives 16 points in all,  $N=16$ , and no point is too near to  $\mathbf{q}=0$ . The procedure for a sampling interval reduced by a factor of two, giving  $N=128$ , is exactly similar.

Two calculations, one for  $N=16$  and the other for  $N=128$ , were done and compared. For this calculation

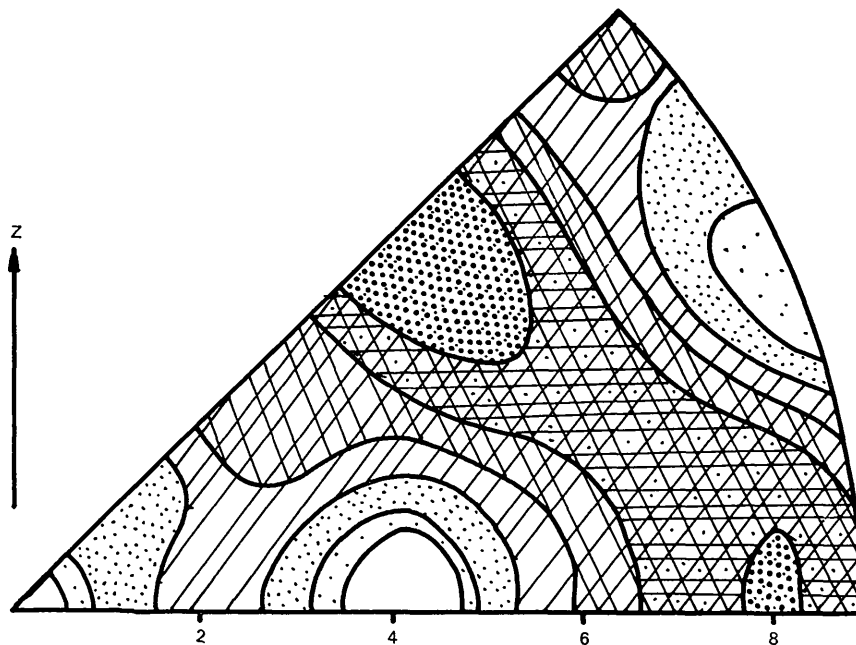


Fig. 7. The two-phonon X-ray TDS, on the same scale as Fig. 6.

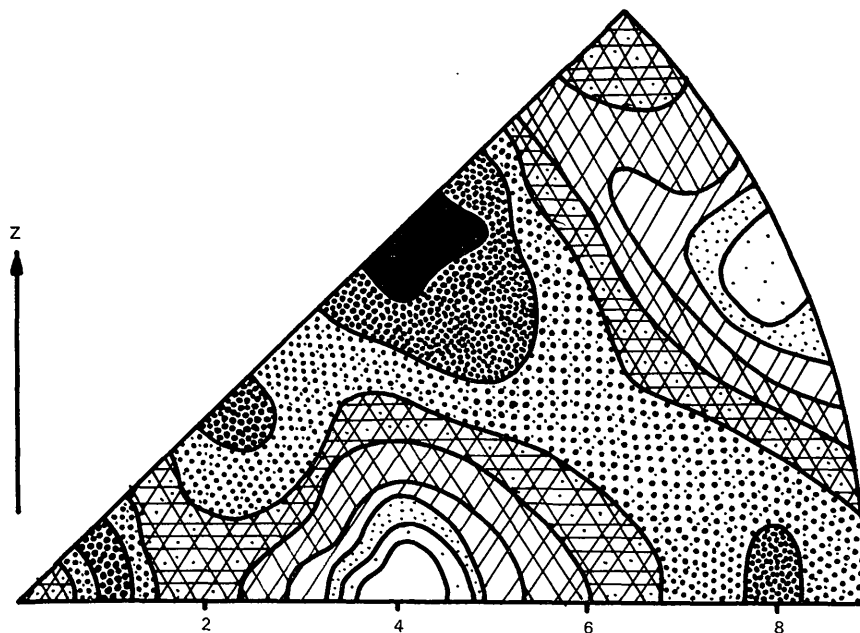


Fig. 8. The sum of Figs. 6 and 7, the total inelastic X-ray scattering neglecting three-phonon and higher order processes.

the hydrogen atoms were all omitted, giving over 50% saving in computer time for the loss of at most 16% of the scattering. Going from  $N=16$  to  $N=128$  increases the computing time by a factor of 32, but the difference in the results was so small that the increase in accuracy was not thought worthwhile. As the larger sampling interval was found to be sufficient (though not quite so for the one-phonon case), the two-phonon calculation was repeated with the inclusion of the hydrogen atoms. Their inclusion was seen to be necessary on comparing the one-phonon calculations done with and without the hydrogen atoms.

### Results

The results of the calculations are shown in Figs. 6–9. Fig. 6 is simply a repeat of the calculation of Cochran & Pawley (1964) done with a completely independent program. The fact that these two results agree is reassuring, and this result establishes the scale shown for Figs. 6–8. The atomic scattering factors used for  $f(kQ)$  were taken without scaling from *International Tables for X-ray Crystallography* (1959). All calculations were terminated at the reflecting sphere for Cu  $K\alpha$  radiation, the most commonly used X-ray source. No account is taken of the X-ray polarization factor, for which X-ray measurements should be corrected before making comparisons.

Fig. 7 gives the two-phonon scattering intensity in the  $(\frac{1}{2}kl)$  interlayer, which when added to Fig. 6 gives Fig. 8. At large scattering angles (large  $Q$ ) the two-phonon intensity is the same order of magnitude as the one-phonon intensity, and in a few places is the main source of scattering. This is shown more clearly

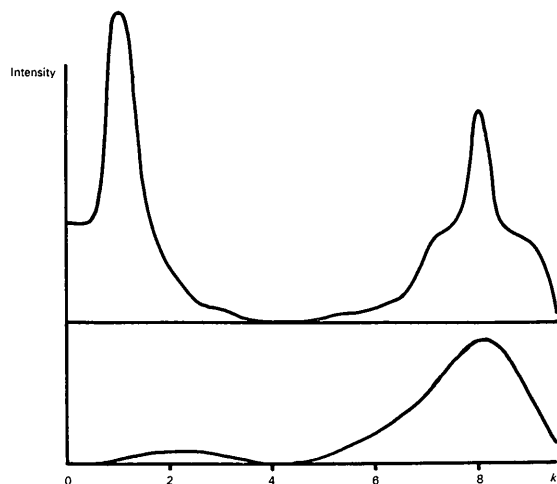


Fig. 9. The one-phonon (upper part) and two-phonon (lower part) TDS along the line  $l=0$  in the  $(\frac{1}{2}kl)$  interlayer, showing that the two-phonon scattering exceeds the one-phonon scattering in some regions of high scattering angle.

in Fig. 9 where both results are plotted separately for the line  $(\frac{1}{2}k0)$  in reciprocal space, which is parallel to a tetrad axis. The two-phonon cross-section is much the smoother function, which is a well-known result.

It should be emphasized that this comparison is only valid at room temperature ( $300^\circ\text{K}$ ), the temperature used in the calculation. The two-phonon intensity varies roughly as  $T^2$  whereas the one-phonon intensity varies as  $T$ , so that any experimental measurements made at liquid nitrogen temperature would involve a contribution of no more than 10% intensity from the two-phonon process.

### Conclusion

The two-phonon cross-section for the molecular crystal hexamine at room temperature is comparable with the one-phonon cross-section at large scattering angles. Cochran & Pawley (1964) point out in their conclusion that experimental measurements would need to be corrected for second order scattering when doing a numerical comparison, and it would now seem advisable to make measurements at lower temperatures to reduce this scattering. However, the measurement exposure or counting times would then be increased, increasing the Compton scattering contribution.

Economies in computing time are best made by choosing a rather coarse interval for calculation because the two-phonon cross-section is a smooth function. No advantage is gained by ignoring the contribution of the hydrogen atoms, although their scattering power is small, when doing a one-phonon calculation. However, Fig. 9 shows that the hydrogen atoms could be ignored for the two-phonon case without much loss as most of the intensity occurs at high scattering angles.

The author wishes to thank the Edinburgh Regional Computing Centre for making the KDF9 computer available, and to thank Professor W. Cochran for valuable discussions.

### References

- AMORÓS, J. L., CANUT, M. L. & DE ACHA, A. (1960). *Z. Kristallogr.* **114**, 39.
- BECKA, L. N. & CRUICKSHANK, D. W. J. (1963). *Proc. Roy. Soc. A* **273**, 435.
- COCHRAN, W. (1963). *Rep. Progr. Phys.* **26**, 1.
- COCHRAN, W. & PAWLEY, G. S. (1964). *Proc. Roy. Soc. A* **280**, 1.
- ELDRIDGE, J. E. & LOMER, T. R. (1967). *Proc. Phys. Soc.* **91**, 459.
- International Tables for X-ray Crystallography* (1959). Vol. II. Birmingham: Kynoch Press.
- LOMER, T. R. (1966). *Proc. Phys. Soc.* **89**, 135.
- MCMULLAN, J. T. (1967). Thesis, Dundee University.
- POWELL, B. M. (1963). Thesis, Queen Mary College, London University.