

## A Study of Second-Order Thermal Diffuse X-ray Scattering Effects and the Elastic Properties of Cubic Single Crystals

BY B. W. LUCAS

*Department of Physics, University of Queensland, St. Lucia, Brisbane, Queensland, Australia*

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The elastic constants of certain single crystals may be obtained by the measurement of thermal diffuse X-ray scattering variation in regions close to reciprocal-lattice points. A method has been given which allows for second-order contributions to the total diffuse intensity by use of a least-squares procedure. The refinement was simplified by equating two functions, each depending on the elastic properties of the crystal, the nearby lattice point to the positions of observation and the direction along which the intensity variation is measured. For cubic crystals, there is an exact equality between appropriate powers of these functions for several important crystallographic directions, while for other directions some approximation results. The present paper includes a simple method of allowing for the deviation from equality in the latter cases.

### Introduction

Measurement of thermal diffuse scattering variation in certain directions close to reciprocal lattice points of strong to medium scattering power has been shown to provide values for the elastic constants of crystals which are in reasonable agreement with values obtained by other methods for several cubic and a few other lower

symmetry single crystals of an atomic rather than molecular nature (Wooster, 1962).

The relationship between the contribution to the observed thermal diffuse intensity due to a single interaction of a phonon with the incident X-ray photon (*i.e.* a first-order scattering process) and the theoretically calculated contribution, which is associated with the appropriate elastic constants of the crystal, is a

Table 1. Expressions for  $\Delta$  corresponding to the major

[ABC]	100	010	001	110	101	011
(hkl)				2	2	
h00	0	0	0	$\frac{2}{\left(\frac{s_3}{s_4} + \frac{s_4}{s_3}\right)}$	$\frac{2}{\left(\frac{s_3}{s_4} + \frac{s_4}{s_3}\right)}$	0
0k0	0	0	0	$\frac{2}{\left(\frac{s_3}{s_4} + \frac{s_4}{s_3}\right)}$	0	$\frac{2}{\left(\frac{s_3}{s_4} + \frac{s_4}{s_3}\right)}$
00l	0	0	0	0	$\frac{2}{\left(\frac{s_3}{s_4} + \frac{s_4}{s_3}\right)}$	$\frac{2}{\left(\frac{s_3}{s_4} + \frac{s_4}{s_3}\right)}$
hh0	$\frac{2}{\left(\frac{s_1}{s_2} + \frac{s_2}{s_1}\right)}$	$\frac{2}{\left(\frac{s_1}{s_2} + \frac{s_2}{s_1}\right)}$	1	0	$\frac{2(1 + s_4/s_2 + s_4/s_3)}{\left(\frac{s_2}{s_3} + \frac{s_3}{s_2} + \frac{s_4}{s_2} \cdot \frac{s_4}{s_3}\right)}$	$\frac{2(1 + s_4/s_2 + s_4/s_3)}{\left(\frac{s_2}{s_3} + \frac{s_3}{s_2} + \frac{s_4}{s_2} \cdot \frac{s_4}{s_3}\right)}$
0kk	1	$\frac{2}{\left(\frac{s_1}{s_2} + \frac{s_2}{s_1}\right)}$	$\frac{2}{\left(\frac{s_1}{s_2} + \frac{s_2}{s_1}\right)}$	$\frac{2(1 + s_4/s_2 + s_4/s_3)}{\left(\frac{s_2}{s_3} + \frac{s_3}{s_2} + \frac{s_4}{s_2} \cdot \frac{s_4}{s_3}\right)}$	$\frac{2(1 + s_4/s_2 + s_4/s_3)}{\left(\frac{s_2}{s_3} + \frac{s_3}{s_2} + \frac{s_4}{s_2} \cdot \frac{s_4}{s_3}\right)}$	0
l0l	$\frac{2}{\left(\frac{s_1}{s_2} + \frac{s_2}{s_1}\right)}$	1	$\frac{2}{\left(\frac{s_1}{s_2} + \frac{s_2}{s_1}\right)}$	$\frac{2(1 + s_4/s_2 + s_4/s_3)}{\left(\frac{s_2}{s_3} + \frac{s_3}{s_2} + \frac{s_4}{s_2} \cdot \frac{s_4}{s_3}\right)}$	0	$\frac{2(1 + s_4/s_2 + s_4/s_3)}{\left(\frac{s_2}{s_3} + \frac{s_3}{s_2} + \frac{s_4}{s_2} \cdot \frac{s_4}{s_3}\right)}$
hhh	$\frac{2(2 + s_2/s_1)}{\left(\frac{s_1}{s_2} + 2 \frac{s_2}{s_1}\right)}$	$\frac{2(2 + s_2/s_1)}{\left(\frac{s_1}{s_2} + 2 \frac{s_2}{s_1}\right)}$	$\frac{2(2 + s_2/s_1)}{\left(\frac{s_1}{s_2} + 2 \frac{s_2}{s_1}\right)}$	$\frac{2}{\left(\frac{s_2}{s_4^{(1)}} + \frac{s_4^{(1)}}{s_2}\right)}$	$\frac{2}{\left(\frac{s_2}{s_4^{(1)}} + \frac{s_4^{(1)}}{s_2}\right)}$	$\frac{2}{\left(\frac{s_2}{s_4^{(1)}} + \frac{s_4^{(1)}}{s_2}\right)}$

relatively direct one. Unfortunately, second and higher order interactions contribute to the overall observed diffuse intensity distribution. Recently, a method has been proposed by which the contribution for second-order thermal diffuse scattering may be allowed for in the determination of the elastic constants of crystals using a least-squares refinement technique (Lucas, 1968). The method consists of refining a quantity (which involves the unknown elastic constants, details of the reciprocal lattice point under investigation and the direction along which the intensity variation is being measured) in the theoretical expression for first- and second-order photon-phonon interactions to the observed thermal diffuse scattering intensity. Calculation of the contribution due to second-order interaction requires, in general, a summation over the overlap volume of two Brillouin zones, the origins of which are each displaced with respect to one another by differing amounts, for each point of intensity observation. The resulting volume is usually of a far from analytic form and almost certainly requires a numerical integration for its evaluation. However, it has been suggested that for some directions of measurement, certain functions which play an important part in the determination of the second-order contribution can be simplified without approximation, while in others, some approximation is made (Prasad & Wooster, 1956). This was made use of in the method previously reported (Lucas, 1968). The present paper includes a

method for simplification, without such an approximation, in the more commonly used crystallographic directions and for general reflexions.

**The relationship between observed and theoretically calculated thermal diffuse scattering intensity**

The observed intensity of diffuse scattering,  $I'_d(\text{obs})$ , close to a reciprocal lattice point, after background scattering has been deducted and higher than second-order effects neglected, may be approximated (Lucas, 1968) to

$$I'_d(\text{obs}) = G \left( K[ABC]_{hkl} \cdot \frac{1}{R^2} + HK'[ABC]_{hkl} \cdot \frac{1}{R} \right) \quad (1)$$

where

$$G = I_0 \left[ \frac{e^2}{mc^2} \right]^2 \frac{kT\Omega|F_T|^2 q^2 P}{2\mu\tau^2}$$

and

$$H = \frac{1}{2}\pi^3 kTq^2.$$

$I'_d(\text{obs})$  is the total diffuse intensity observed, less background,

$I_0$  is the intensity per unit area of cross-section of the direct beam,

$e$  is the electronic charge,

$m$  is the mass of the electron,

$c$  is the velocity of light,

*crystallographic directions and special-type reflexions*

$\bar{1}10$	$10\bar{1}$	$0\bar{1}1$	$111$	$\bar{1}\bar{1}\bar{1}$	$1\bar{1}\bar{1}$	$1\bar{1}\bar{1}$
$\frac{2}{\left(\frac{s_3}{s_4} + \frac{s_4}{s_3}\right)}$	$\frac{2}{\left(\frac{s_3}{s_4} + \frac{s_4}{s_3}\right)}$	0	$\frac{2}{\left(\frac{s_5}{s_6^{(1)}} + \frac{s_6^{(1)}}{s_5}\right)}$	$\frac{2}{\left(\frac{s_5}{s_6^{(1)}} + \frac{s_6^{(1)}}{s_5}\right)}$	$\frac{2}{\left(\frac{s_5}{s_6^{(1)}} + \frac{s_6^{(1)}}{s_5}\right)}$	$\frac{2}{\left(\frac{s_5}{s_6^{(1)}} + \frac{s_6^{(1)}}{s_5}\right)}$
$\frac{2}{\left(\frac{s_3}{s_4} + \frac{s_4}{s_3}\right)}$	0	$\frac{2}{\left(\frac{s_3}{s_4} + \frac{s_4}{s_3}\right)}$	$\frac{2}{\left(\frac{s_5}{s_6^{(1)}} + \frac{s_6^{(1)}}{s_5}\right)}$	$\frac{2}{\left(\frac{s_5}{s_6^{(1)}} + \frac{s_6^{(1)}}{s_5}\right)}$	$\frac{2}{\left(\frac{s_5}{s_6^{(1)}} + \frac{s_6^{(1)}}{s_5}\right)}$	$\frac{2}{\left(\frac{s_5}{s_6^{(1)}} + \frac{s_6^{(1)}}{s_5}\right)}$
0	$\frac{2}{\left(\frac{s_3}{s_4} + \frac{s_4}{s_3}\right)}$	$\frac{2}{\left(\frac{s_3}{s_4} + \frac{s_4}{s_3}\right)}$	$\frac{2}{\left(\frac{s_5}{s_6^{(1)}} + \frac{s_6^{(1)}}{s_5}\right)}$	$\frac{2}{\left(\frac{s_5}{s_6^{(1)}} + \frac{s_6^{(1)}}{s_5}\right)}$	$\frac{2}{\left(\frac{s_5}{s_6^{(1)}} + \frac{s_6^{(1)}}{s_5}\right)}$	$\frac{2}{\left(\frac{s_5}{s_6^{(1)}} + \frac{s_6^{(1)}}{s_5}\right)}$
0	$\frac{2(1+s_4/s_2+s_4/s_3)}{\left(\frac{s_2}{s_3} + \frac{s_3}{s_2} + \frac{s_4}{s_2} \cdot \frac{s_4}{s_3}\right)}$	$\frac{2(1+s_4/s_2+s_4/s_3)}{\left(\frac{s_2}{s_3} + \frac{s_3}{s_2} + \frac{s_4}{s_2} \cdot \frac{s_4}{s_3}\right)}$	$\frac{2}{\left(\frac{s_5^{(1)}}{s_6} + \frac{s_6}{s_5^{(1)}}\right)}$	0	0	$\frac{2}{\left(\frac{s_5^{(1)}}{s_6} + \frac{s_6}{s_5^{(1)}}\right)}$
$\frac{2(1+s_4/s_2+s_4/s_3)}{\left(\frac{s_2}{s_3} + \frac{s_3}{s_2} + \frac{s_4}{s_2} \cdot \frac{s_4}{s_3}\right)}$	$\frac{2(1+s_4/s_2+s_4/s_3)}{\left(\frac{s_2}{s_3} + \frac{s_3}{s_2} + \frac{s_4}{s_2} \cdot \frac{s_4}{s_3}\right)}$	0	$\frac{2}{\left(\frac{s_5^{(1)}}{s_6} + \frac{s_6}{s_5^{(1)}}\right)}$	$\frac{2}{\left(\frac{s_5^{(1)}}{s_6} + \frac{s_6}{s_5^{(1)}}\right)}$	0	0
$\frac{2(1+s_4/s_2+s_4/s_3)}{\left(\frac{s_2}{s_3} + \frac{s_3}{s_2} + \frac{s_4}{s_2} \cdot \frac{s_4}{s_3}\right)}$	0	$\frac{2(1+s_4/s_2+s_4/s_3)}{\left(\frac{s_2}{s_3} + \frac{s_3}{s_2} + \frac{s_4}{s_2} \cdot \frac{s_4}{s_3}\right)}$	$\frac{2}{\left(\frac{s_5^{(1)}}{s_6} + \frac{s_6}{s_5^{(1)}}\right)}$	0	$\frac{2}{\left(\frac{s_5^{(1)}}{s_6} + \frac{s_6}{s_5^{(1)}}\right)}$	0
$\frac{2}{\left(\frac{s_2}{s_3^{(1)}} + \frac{s_3^{(1)}}{s_2}\right)}$	$\frac{2}{\left(\frac{s_2}{s_3^{(1)}} + \frac{s_3^{(1)}}{s_2}\right)}$	$\frac{2}{\left(\frac{s_2}{s_3^{(1)}} + \frac{s_3^{(1)}}{s_2}\right)}$	0	$\frac{2}{\left(\frac{s_5}{s_6^{(2)}} + \frac{s_6^{(2)}}{s_5}\right)}$	$\frac{2}{\left(\frac{s_5}{s_6^{(2)}} + \frac{s_6^{(2)}}{s_5}\right)}$	$\frac{2}{\left(\frac{s_5}{s_6^{(2)}} + \frac{s_6^{(2)}}{s_5}\right)}$

$k$  is the Boltzmann constant,  
 $T$  is the absolute temperature,  
 $\tau$  is the volume of the unit cell,  
 $|F_T|$  is the structure amplitude at temperature  $T$ ,  
 $q$  is the distance of the lattice point from the origin in reciprocal lattice space,  
 $R$  is the distance in reciprocal space from the point of observation to the nearest lattice point,  
 $\Omega$  is the solid angle subtended by the detector aperture at the crystal,  
 $P$  is the polarization factor,  
 $\mu$  is the linear absorption coefficient of the crystal,

and

$$K'[ABC]_{hkl} = \sum_{\alpha=1}^3 \frac{\cos^4(q, \xi_{\alpha})}{\rho^2 V_{\alpha}^4},$$

$\rho$  is the crystal density.  
 $\xi_{\alpha}$  ( $\alpha = 1, 2, 3$ ) are the amplitudes of the three acoustical waves having wave vector  $\mathbf{R}$  and  
 $V_{\alpha}$  ( $\alpha = 1, 2, 3$ ) are their corresponding velocities.

For some directions  $K'[ABC]_{hkl} = (K[ABC]_{hkl})^2$  exactly, while for others this is subject to a certain deviation. In general the relationship may be expressed as follows:

$$K[ABC]_{hkl} = \sum_{\alpha=1}^3 \frac{\cos^2(q, \xi_{\alpha})}{\rho V_{\alpha}^2} \qquad K'[ABC]_{hkl} = \frac{(K[ABC]_{hkl})^2}{1 + \Delta} \qquad (2)$$

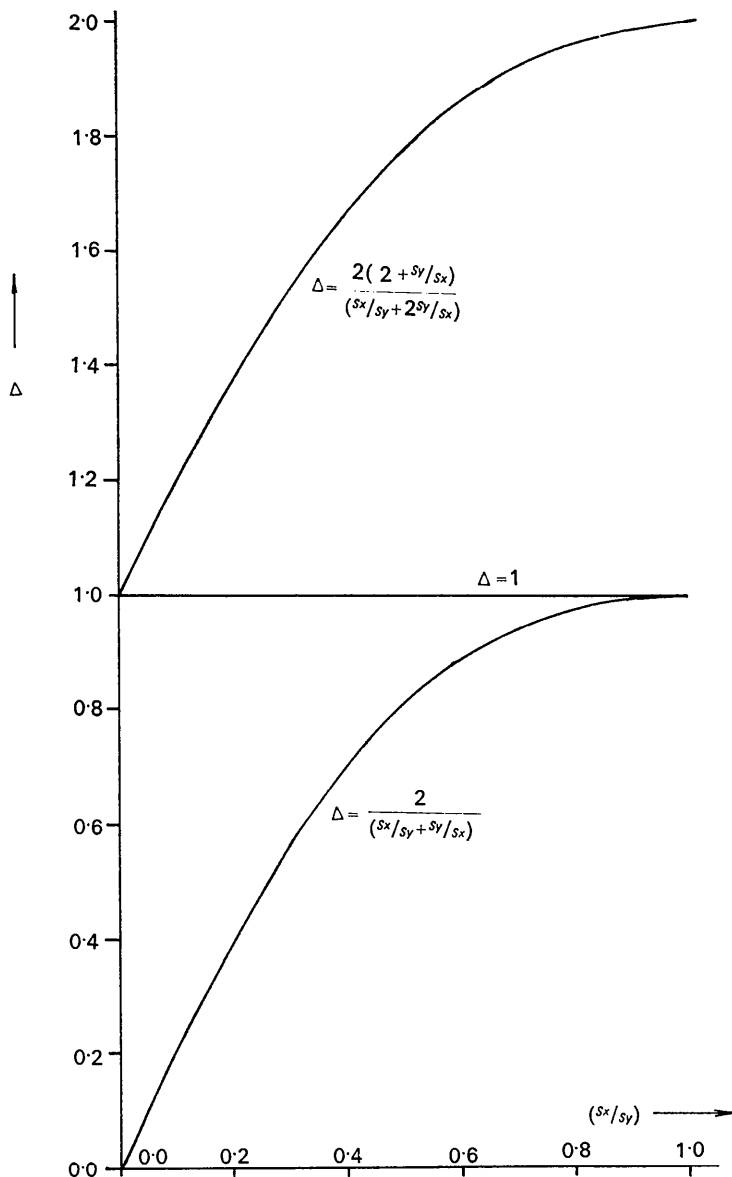


Fig.1.  $\Delta$  values as a function of  $s_x/s_y$ .

Equation (1) may then be written:

$$I'_d(\text{obs}) = G \left( K[ABC]_{hkl} \cdot \frac{1}{R^2} + H'(K[ABC]_{hkl})^2 \cdot \frac{1}{R} \right)$$

where

$$H' = \frac{H}{1 + \Delta}.$$

The least-squares method now requires that:

$$\Sigma \left[ GH'(K[ABC]_{hkl})^2 \frac{1}{R_i} + GK[ABC]_{hkl} \cdot \frac{1}{R_i^2} - I'_{d_i}(\text{obs}) \right]^2$$

should be a minimum.

**General expressions for  $\Delta$  along the major crystallographic directions for cubic crystals**

Expressions for  $K[ABC]_{hkl}$  and  $K'[ABC]_{hkl}$  in terms of  $P, Q, R$  ( $= \frac{h, k, l}{\sqrt{h^2 + k^2 + l^2}}$ ) are given by Ramachandran & Wooster (1951) for the major crystallographic directions. Substitution into equation (2) gives the following values for  $\Delta$ :

$$[100], \Delta = \frac{2[(P^2Q^2 + P^2R^2)s_1s_2 + Q^2R^2s_2^2]}{P^4s_1^2 + (Q^4 + R^4)s_2^2}$$

$$[010], \Delta = \frac{2[(Q^2R^2 + Q^2P^2)s_1s_2 + R^2P^2s_2^2]}{Q^4s_1^2 + (R^4 + P^4)s_2^2}$$

$$[001], \Delta = \frac{2[(R^2P^2 + R^2Q^2)s_1s_2 + P^2Q^2s_2^2]}{R^4s_1^2 + (P^4 + Q^4)s_2^2}$$

$$[110], \Delta = \frac{2[(P + Q)^2(P - Q)^2s_3s_4 + (P + Q)^2R^2s_2s_4 + (P - Q)^2R^2s_2s_3]}{(P + Q)^4s_4^2 + (P - Q)^4s_3^2 + R^4s_2^2}$$

$$[101], \Delta = \frac{2[(R + P)^2(R - P)^2s_3s_4 + (R + P)^2Q^2s_2s_4 + (R - P)^2Q^2s_2s_3]}{(R + P)^4s_4^2 + (R - P)^4s_3^2 + Q^4s_2^2}$$

$$[011], \Delta = \frac{2[(Q + R)^2(Q - R)^2s_3s_4 + (Q + R)^2P^2s_2s_4 + (Q - R)^2P^2s_2s_3]}{(Q + R)^4s_4^2 + (Q - R)^4s_3^2 + P^4s_2^2}$$

$$[\bar{1}10], \Delta = \frac{2[(P - Q)^2(P + Q)^2s_3s_4 + (P - Q)^2R^2s_2s_4 + (P + Q)^2R^2s_2s_3]}{(P - Q)^4s_4^2 + (P + Q)^4s_3^2 + R^4s_2^2}$$

$$[10\bar{1}], \Delta = \frac{2[(R - P)^2(R + P)^2s_3s_4 + (R - P)^2Q^2s_2s_4 + (R + P)^2Q^2s_2s_3]}{(R - P)^4s_4^2 + (R + P)^4s_3^2 + Q^4s_2^2}$$

$$[0\bar{1}1], \Delta = \frac{2[(Q - R)^2(Q + R)^2s_3s_4 + (Q - R)^2P^2s_2s_4 + (Q + R)^2P^2s_2s_3]}{(Q - R)^4s_4^2 + (Q + R)^4s_3^2 + P^4s_2^2}$$

$$[111], \Delta = \frac{4(P + Q + R)^2(1 - PQ - QR - RP)s_5s_6}{(P + Q + R)^4s_3^2 + 4(1 - PQ - QR - RP)^2s_2^2}$$

$$[\bar{1}\bar{1}1], \Delta = \frac{4(-P + Q + R)^2(1 + PQ - QR + RP)s_5s_6}{(-P + Q + R)^4s_3^2 + 4(1 + PQ - QR + RP)^2s_2^2}$$

$$[1\bar{1}\bar{1}], \Delta = \frac{4(P - Q + R)^2(1 + PQ + QR - RP)s_5s_6}{(P - Q + R)^4s_3^2 + 4(1 + PQ + QR - RP)^2s_2^2}$$

$$[11\bar{1}], \Delta = \frac{4(P + Q - R)^2(1 - PQ + QR + RP)s_5s_6}{(P + Q - R)^4s_3^2 + 4(1 - PQ + QR + RP)^2s_2^2}$$

(3)

where

$$s_1 = 1/c_{11}$$

$$s_3 = 1/(c_{11} - c_{12})$$

$$s_5 = 1/(c_{11} + 2c_{12} + 4c_{44})$$

$$s_2 = 1/c_{44}$$

$$s_4 = 1/(c_{11} + c_{12} + 2c_{44})$$

$$s_6 = 1/(c_{11} - c_{12} + c_{44}).$$

For certain special-type reflexions, these formulae have simplified forms and are given in Table 1.

$$\left[ \begin{array}{l} s_3^{(1)} = 4s_3 \quad : \quad s_4^{(1)} = 4s_4 \\ s_5^{(1)} = 2s_5 \quad : \quad s_6^{(1)} = 2s_6 \quad : \quad s_6^{(2)} = 8s_6 \end{array} \right].$$

The expressions are of the following general type:

$$0, 1, \frac{2(2 + s_2/s_1)}{(s_1/s_2 + 2s_2/s_1)}, \frac{2}{(s_x/s_y + s_y/s_x)}, \frac{2(1 + s_4/s_2 + s_4/s_3)}{(s_2/s_3 + s_3/s_2 + s_4/s_2 \cdot s_4/s_3)}.$$

These are represented in graphical form in Figs. 1 and 2 (over the  $s$ -ratio ranges:  $0 \rightarrow 1$ ).

**Discussion**

The present work derives expressions, for cubic crystals, of the relationship between  $K'[ABC]_{hkl}$  and

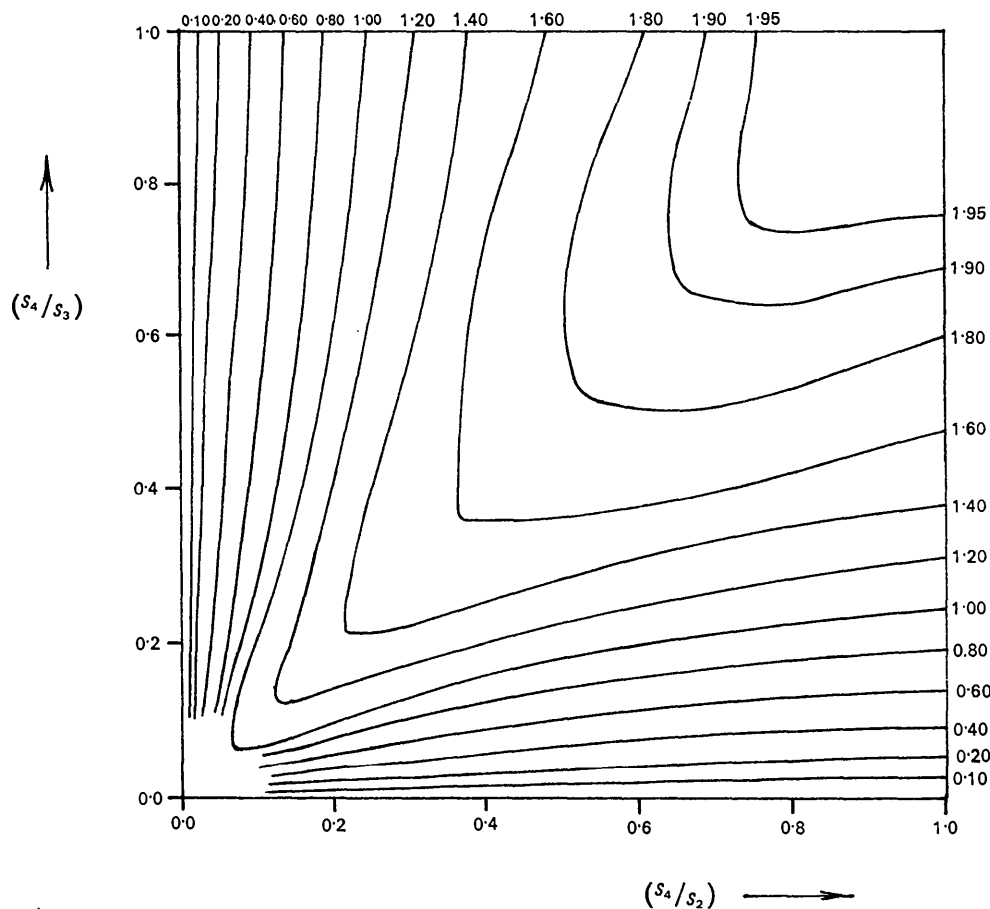


Fig. 2.  $\Delta$  values as a function of  $s_4/s_3$  and  $s_4/s_2$  for  $\Delta = \frac{2(1 + s_4/s_2 + s_4/s_3)}{(s_2/s_3 + s_3/s_2 + s_4/s_2 \cdot s_4/s_3)}$

$K[ABC]_{hkl}$  for any reciprocal lattice point and for the major crystallographic directions. It is shown that incorporation of the results into the refinement equation may be achieved by a simple modification. The expressions for  $\Delta$  are shown to be of a form common to many directions and lattice points. The variation of the  $\Delta$ -values has been given numerically and may be read from one of the graphs included by calculation of the appropriate  $s$ -ratios from approximate elastic constants. This value is then used to correct the constant,  $H$ , in equation (2), the refinement procedure continuing in the previously described manner. An alternative is to include the set of equations (3) in the

refinement program, select and calculate the appropriate  $\Delta$  value by specifying  $[ABC]$ ,  $(hkl)$  and approximate elastic constant values with the input data. The value for  $\Delta$  could then be updated for each cycle with the new values of the elastic constants.

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