DETERMINATION OF THE ELASTIC CONSTANTS OF MONOCLINIC CRYSTALS FROM THE STUDY OF DIFFUSE X-RAY REFLECTIONS

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ABSTRACT Theoretical relationships connecting diffusely scattered X-ray intensities from monoclinic class of crystals with its elastic constants have been derived by a proper choice of reflecting planes and lattice wave normals. Methods of evaluation of all the thirteen elastic constants from quantitative measurements of thermal diffuse scattering of X-rays have been described.

INTRODUCTION

The elastic constants of the monoclinic class of crystals have not been determined up to the present by the quantitative study of thermal diffuse scattering of X-rays. Since a large number of crystals, specially the organic ones, belong to the monoclinic class, it is of interest to see how best the X-ray method could be applied in this case. Crystals of higher symmetry have got fewer number of elastic constants and they were determined quite satisfactorily from the study of diffuse X-ray reflection by Wooster *et al* (Wooster, 1962), Chakraborty and Sen (1958) and others (Srivastava and Chakraborty, 1962; Joshi and Kashyap, 1964). In the case of monoclinic crystals which involve 13 elastic constants, a given measurement of diffuse intensity depends in general on a number of elastic constants and hence reduces considerably the accuracy of evaluation of any individual constant. However the reciprocal lattice nodes and wave vectors have been carefully chosen only for those *K*-values which are associated with minimum number of elastic constants and they are given in Table I and II.

THEORY

According to the classical theory of elasticity (Voigt, 1910) the elastic constants, C_{11}, C_{12} etc. in the monoclinic system of crystals are given by the matrix

$$\begin{matrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ & C_{22} & C_{23} & 0 & 0 & C_{26} \\ & & C_{33} & 0 & 0 & C_{36} \\ & & & C_{44} & C_{45} & 0 \\ & & & & C_{55} & 0 \\ & & & & & C_{66} \end{matrix}$$

where the frame of reference is the three orthogonal elastic axes in the crystal. The X and Z elastic axes concide respectively with the c and b crystallographic axes, and the Y elastic axis completes the righthanded orthogonal axial system, thus making an acute angle with the axis of the monoclinic lattice.

The intensity of the first order thermal diffuse reflection in a direction from an element of reciprocal space has been found to be proportional to

$$K[f_1 f_2 f_3]_{hkl} = g_1^2(A^{-1})_{11}+g_2^2(A^{-1})_{22}+g_3^2(A^{-1})_{33}+2g_1g_2(A^{-1})_{12} +2g_2g_3(A^{-1})_{23}+2g_3g_1(A^{-1})_{31}$$

where f_1, f_2, f_3 are the direction cosines of the thermal wave vector and g_1, g_2, g_3 are the direction cosines of the reciprocal lattice vector corresponding to the point hkl with respect to the elastic axes of the crystal, and $(A^{-1})_{11}$ etc. are the elements of matrix inverse to the matrix A which is given by

$$\begin{pmatrix} A_{11} \\ A_{22} \\ A_{33} \\ A_{12} \\ A_{13} \\ A_{23} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{66} & C_{55} & 0 & 0 & 2C_{16} \\ C_{66} & C_{22} & C_{44} & 0 & 0 & 2C_{26} \\ C_{55} & C_{44} & C_{33} & 0 & 0 & 2C_{45} \\ C_{16} & C_{26} & C_{45} & 0 & 0 & (C_{12}+C_{66}) \\ 0 & 0 & 0 & (C_{36}+C_{45}) & (C_{13}+C_{55}) & 0 \\ 0 & 0 & 0 & (C_{23}+C_{44}) & (C_{36}+C_{45}) & 0 \end{pmatrix} \begin{pmatrix} f_1^2 \\ f_2^2 \\ f_3^2 \\ f_2f_3 \\ f_3f_1 \\ f_1f_2 \end{pmatrix}$$

It is evident from Table I that the elastic constants C_{55}, C_{44} and C_{33} can be determined independently from the observed values of $K[100]_{oko}$, $K[010]_{oko}$ and $K[001]_{oko}$. By substituting the values of C_{55} and C_{44} in the expression for $K[001]_{hoo}$, $K[001]_{ool}$ and $K[001]_{hol}$, C_{45} can be evaluated. The constants, C_{44}, C_{45} and C_{55}, when substituted in $K[001]_{hko}$, would aslo give C_{33}. From $K[100]_{hoo}$, $K[100]_{hol}$ and $K(100]_{ool}$ three first degree equations in terms of C_{11}, C_{16} and C_{66} can be obtained, and by solving them the constants can be found as follows :

$$C_{11} = K[100]_{hoo} \begin{vmatrix} g_1^2 & -2g_1g_2 \\ \sin^2\beta & 2\sin\beta\cos\beta \end{vmatrix} \Big/ \Delta$$

$$C_{66} = \begin{vmatrix} g_1^2 & -2g_1g_2 \\ \sin^2\beta & 2\sin\beta\cos\beta \end{vmatrix} \begin{vmatrix} -2g_1g_2 & g_2^2-K[100]_{hol} \\ 2\sin\beta\cos\beta & \cos^2\beta-K[100]_{ool} \end{vmatrix} \Big/ \Delta$$

$$C_{16} = \begin{vmatrix} g_1^2 & -2g_1g_2 \\ \sin^2\beta & 2\sin\beta\cos\beta \end{vmatrix} \begin{vmatrix} g_2^2-K[100]_{hol} & g_1^2 \\ \cos^2\beta-K[100]_{ool} & \sin^2\beta \end{vmatrix} \Big/ \Delta$$

TABLE I

K-values in the monoclinic system; β = monoclinic angle.

Direction Cosines of Wave Vectors	Indices of the planes using b axis as the unique axis, and direction cosines of the reciprocal lattice vector					
	$hkl \rightarrow$	hoo	oko	ool	hko	hol
$[f_1 f_2 f_3]$	$g_1, g_2, g_3 \rightarrow$	[010]	[001]	$[\sin\beta, -\cos\beta, 0]$	$[0, g_2, g_3]$	$[g_1, g_2, 0]$
[100]		$\frac{C_{11}}{C_{11}C_{66}-C^2_{16}}$	$\frac{1}{C_{55}}$	$\frac{C_{66}\sin^2\beta+C_{11}\cos^2\beta+2C_{16}\sin\beta\cos\beta}{C_{11}C_{66}-C^2_{16}}$	$\frac{g^2_2 C_{11}}{C_{11}C_{66}-C^2_{16}}+\frac{g_3^2}{C_{55}}$	$\frac{g_1^2 C_{66}+g_2^2 C_{11}-2g_1g_2C_{16}}{C_{11}C_{66}-C^2_{16}}$
[010]		$\frac{C_{66}}{C_{66}C_{22}-C^2_{26}}$	$\frac{1}{C_{44}}$	$\frac{C_{22}\sin^2\beta+C_{66}\cos^2\beta+2C_{26}\sin\beta\cos\beta}{C_{66}C_{22}-C^2_{26}}$	$\frac{g_2^2 C_{66}}{C_{66}C_{22}-C^2_{26}}+\frac{g_3^2}{C_{44}}$	$\frac{g_1^2 C_{22}+g_2^2 C_{66}-2g_1g_2C_{26}}{C_{66}C_{22}-C^2_{26}}$
[001]		$\frac{C_{55}}{C_{55}C_{44}-C^2_{45}}$	$\frac{1}{C_{33}}$	$\frac{C_{44}\sin^2\beta+C_{55}\cos^2\beta+2C_{45}\sin\beta\cos\beta}{C_{55}C_{44}-C^2_{45}}$	$\frac{g^2_2 C_{55}}{C_{55}C_{44}-C^2_{45}}+\frac{g_3^2}{C_{33}}$	$\frac{g^2_1 C_{44}+g^2_2 C_{55}-2g_1g_2C_{45}}{C_{55}C_{44}-C^2_{45}}$

where the frame of reference is the three orthogonal elastic axes in the crystal. The X and Z elastic axes concide respectively with the c and b crystallographic axes, and the Y elastic axis completes the righthanded orthogonal axial system, thus making an acute angle with the axis of the monoclinic lattice.

The intensity of the first order thermal diffuse reflection in a direction from an element of reciprocal space has been found to be proportional to

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where f_1, f_2, f_3 are the direction cosines of the thermal wave vector and g_1, g_2, g_3 are the direction cosines of the reciprocal lattice vector corresponding to the point hkl with respect to the elastic axes of the crystal, and $(A^{-1})_{11}$ etc. are the elements of matrix inverse to the matrix A which is given by

$$\begin{pmatrix} A_{11} \\ A_{22} \\ A_{33} \\ A_{12} \\ A_{13} \\ A_{23} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{66} & C_{55} & 0 & 0 & 2C_{16} \\ C_{66} & C_{22} & C_{44} & 0 & 0 & 2C_{26} \\ C_{55} & C_{44} & C_{33} & 0 & 0 & 2C_{45} \\ C_{16} & C_{26} & C_{45} & 0 & 0 & (C_{12}+C_{66}) \\ 0 & 0 & 0 & (C_{36}+C_{45}) & (C_{13}+C_{55}) & 0 \\ 0 & 0 & 0 & (C_{23}+C_{44}) & (C_{36}+C_{45}) & 0 \end{pmatrix} \begin{pmatrix} f_1^2 \\ f_2^2 \\ f_3^2 \\ f_2f_3 \\ f_3f_1 \\ f_1f_2 \end{pmatrix}$$

It is evident from Table I that the elastic constants C_{55}, C_{44} and C_{33} can be determined independently from the observed values of $K[100]_{oko}$, $K[010]_{oko}$ and $K[001]_{oko}$ By substituting the values of C_{55} and C_{44} in the expression for $K[001]_{hoo}$, $K[001]_{ool}$ and $K[001]_{hol}$, C_{45} can be evaluated. The constants, C_{44}, C_{45} and C_{55}, when substituted in $K[001]_{hko}$, would aslo give C_{33}. From $K[100]_{hoo}$, $K[100]_{hol}$ and $K(100]_{ool}$ three first degree equations in terms of C_{11}, C_{16} and C_{66} can be obtained, and by solving them the constants can be found as follows :

$$C_{11} = K[100]_{hoo} \begin{vmatrix} g_1^2 & -2g_1g_2 \\ \sin^2\beta & 2\sin\beta\cos\beta \end{vmatrix} \Big/ \Delta$$

$$C_{66} = \begin{vmatrix} g_1^2 & -2g_1g_2 \\ \sin^2\beta & 2\sin\beta\cos\beta \end{vmatrix} \begin{vmatrix} -2g_1g_2 & g_2^2 - K[100]_{hol} \\ 2\sin\beta\cos\beta & \cos^2\beta - K[100]_{ool} \end{vmatrix} \Big/ \Delta$$

$$C_{16} = \begin{vmatrix} g_1^2 & -2g_1g_2 \\ \sin^2\beta & 2\sin\beta\cos\beta \end{vmatrix} \begin{vmatrix} g_2^2 - K[100]_{hol} & g_1^2 \\ \cos^2\beta - K[100]_{ool} & \sin^2\beta \end{vmatrix} \Big/ \Delta$$

TABLE I

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Direction Cosines of Wave Vectors	Indices of the planes using *b* axis as the unique axis, and direction cosines of the reciprocal lattice vector					
	hkl→	*hoo*	*oko*	*ool*	*hko*	*hol*
$[f_1 f_2 f_3]$	g_1, g_2, g_3→	[010]	[001]	$[\sin\beta, -\cos\beta, 0]$	$[0, g_2, g_3]$	$[g_1, g_2, 0]$
[100]		$\frac{C_{11}}{C_{11}C_{66}-C^2_{16}}$	$\frac{1}{C_{55}}$	$\frac{C_{66}\sin^2\beta+C_{11}\cos^2\beta+2C_{16}\sin\beta\cos\beta}{C_{11}C_{66}-C^2_{16}}$	$\frac{g^2_2C_{11}}{C_{11}C_{66}-C^2_{16}}+\frac{g_3^2}{C_{55}}$	$\frac{g_1^2C_{66}+g_2^2C_{11}-2g_1g_2C_{16}}{C_{11}C_{66}-C^2_{16}}$
[010]		$\frac{C_{66}}{C_{66}C_{22}-C^2_{26}}$	$\frac{1}{C_{44}}$	$\frac{C_{22}\sin^2\beta+C_{66}\cos^2\beta+2C_{26}\sin\beta\cos\beta}{C_{66}C_{22}-C^2_{26}}$	$\frac{g_2^2C_{66}}{C_{66}C_{22}-C^2_{26}}+\frac{g_3^2}{C_{44}}$	$\frac{g_1^2C_{22}+g_2^2C_{66}-2g_1g_2C_{26}}{C_{66}C_{22}-C^2_{26}}$
[001]		$\frac{C_{55}}{C_{55}C_{44}-C^2_{45}}$	$\frac{1}{C_{33}}$	$\frac{C_{44}\sin^2\beta+C_{55}\cos^2\beta+2C_{45}\sin\beta\cos\beta}{C_{55}C_{44}-C^2_{45}}$	$\frac{g^2_2C_{55}}{C_{55}C_{44}-C^2_{45}}+\frac{g_3^2}{C_{33}}$	$\frac{g^2_1C_{44}+g^2_2C_{55}-2g_1g_2C_{45}}{C_{55}C_{44}-C^2_{45}}$

TABLE II

K-values in the monoclinic system

Direction Cosines of Wave Vectors $[f_1 f_2 f_3]$	$hkl \rightarrow$ $g_1 g_2 g_3 \rightarrow$	*hoo* [010]	*oko* [001]	*hol* $[g_1, g_2, 0]$
$\left[\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0\right]$		$\frac{2(C_{11}+C_{66}+2C_{16})}{\Delta_1}$	$\frac{2}{(C_{55}+C_{44}+2C_{45})}$	$\frac{2\{g_1^2(C_{66}+C_{22}+2C_{26})+g_2^2(C_{11}+C_{66}+2C_{16})+2g_1g_2(C_{16}+C_{26}+C_{12}+C_{66})\}}{\Delta_1}$
$\left[0\ \frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\right]$		$\frac{2\{(C_{66}+C_{55})(C_{44}+C_{33})-(C_{36}+C_{45})^2\}}{\Delta_2}$	$\frac{2\{(C_{66}+C_{55})(C_{22}+C_{44})-(C_{26}+C_{45})^2\}}{\Delta_2}$	$\frac{2\{g_1^2(C_{22}+C_{44})(C_{44}+C_{33})-(C_{23}+C_{44})^2-g_2^2(C_{66}+C_{55})(C_{44}+C_{33})-(C_{36}+C_{45})^2-g_1g_2(C_{36}+C_{45})(C_{23}+C_{44})-(C_{26}+C_{45})(C_{44}+C_{33})\}}{\Delta_2}$
$\left[\frac{1}{\sqrt{2}}\ 0\ \frac{1}{\sqrt{2}}\right]$		$\frac{2\{(C_{11}+C_{55})(C_{55}+C_{33})-(C_{13}+C_{55})^2\}}{\Delta_3}$	$\frac{2\{(C_{11}+C_{55})(C_{66}+C_{44})-(C_{16}+C_{45})^2\}}{\Delta_3}$	$\frac{2[g_1^2\{(C_{66}+C_{44})(C_{55}+C_{33})-(C_{36}+C_{45})^2\}+g_2^2\{(C_{11}+C_{55})(C_{55}+C_{33})-(C_{13}+C_{55})^2\}+2g_1g_2\{(C_{13}+C_{55})(C_{36}+C_{45})-(C_{16}+C_{45})(C_{55}+C_{33})\}]}{\Delta_3}$

$\Delta_1 = \{(C_{11}+C_{66}+2C_{16})(C_{66}+C_{22}+2C_{26})-(C_{16}+C_{26}+C_{12}+C_{66})^2\}$

$\Delta_2 = \{(C_{66}+C_{55})(C_{22}+C_{44})(C_{44}+C_{33})-(C_{66}+C_{55})(C_{23}+C_{44})^2-(C_{26}+C_{45})^2(C_{44}+C_{33})-2(C_{26}+C_{45})(C_{36}+C_{45})(C_{23}+C_{44})-(C_{36}+C_{45})^2(C_{22}+C_{44})\}$

$\Delta_3 = \{(C_{11}+C_{55})(C_{66}+C_{44})(C_{55}+C_{33})-(C_{11}+C_{55})(C_{36}+C_{45})^2-(C_{16}+C_{45})^2(C_{55}+C_{33})+2(C_{16}+C_{45})(C_{13}+C_{55})(C_{36}+C_{45})-(C_{13}+C_{55})^2(C_{66}+C_{44})\}$

where

$$\Delta = K[100]_{hoo}\ \begin{array}{cccc} 2g_1g_2 & g_2^2 - K[100]_{hol} & g_1^2 & -2g_1g_2 \\ 2\sin\beta\cos\beta & \cos^2\beta - K[100]_{ool} & \sin^2\beta & 2\sin\beta\cos\beta \end{array}$$

$$\begin{array}{cc} g_2^2\ K[100]_{hol} & g_1^2 \\ \cos^2\beta - K[100]_{ool} & \sin^2\beta \end{array}$$

Having obtained the value of C_{66}, the constans C_{22} and C_{26} can be easily evaluated with the help of $K[010]_{hol}$, $K(010]_{ool}$ and $K[010]_{hoo}$ as follows :

$$C_{22} = \frac{C_{66}(g_1g_2\,K[010]_{hoo} + \sin\beta\cos\beta\,K[010]_{hol})}{g_1\sin\beta\,K[010]_{hoo}(g_1\cos\beta + g_2\sin\beta)} \quad \frac{C_{66}\,g_2\cos\beta}{g_1\sin\beta}$$

$$C_{26} \quad \frac{C_{66}(g_1^2K[010]_{ool} - \sin^2\beta\ K[010]_{hol})}{2\sin\beta\,g_1\,K[010]_{hoo}(g_2\sin\beta + g_1\cos\beta)} \quad \frac{C_{66}(g_1\cos\beta - g_2\sin\beta)}{2g_1\sin\beta}$$

These two constants can also be determined from the two equations derived by associating $K[010]_{ool}$ with $K[010]_{hko}$ and $K[010]_{hol}$ with $K[010]_{hko}$. The value of C_{12} is derivable from the relation,

$$\frac{K\left[\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0\right]_{hol}}{K\left[\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0\right]_{hoo}} = \frac{\{g^2_1(C_{66} + C_{22} + 2C_{26}) + g_2^2(C_{11} + C_{66} + 2C_{16}) - 2g_1g_2(C_{16} + C_{26} + C_{12} + C_{66})\}}{(C_{11} + C_{66} + 2C_{16})}$$

if all the other constants in it are known earlier.

This can also be obtained by linking $K\left[\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0\right]_{hoo}$ with $K\left[-\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0\right]_{oko}$ or $K\left[\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0\right]_{oko}$ with $K\left[\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0\right]_{ool}$. From the ratio of $K\left[0\ \frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\right]_{hoo}$ and $K\left[0\ \frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\right]_{oko}$ we obtain the relation,

$$\frac{K\left[0\ \frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\right]_{hoo}}{K\left[0\ \frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\right]_{oko}} = \frac{(C_{66} + C_{55})(C_{44} + C_{33}) - (C_{36} + C_{45})^2}{(C_{66} + C_{55})(C_{22} + C_{44}) - (C_{26} + C_{45})^2}$$

and when the known values of C_{66}, C_{44}, C_{45}, C_{26} and C_{55} are substituted, a second degree equation giving two values of C_{36} is obtained. Similarly, dividing $K\left[0 \ \frac{1}{\sqrt{2}} \ \frac{1}{\sqrt{2}}\right]_{hol}$ by $K\left[0 \ -\frac{1}{\sqrt{2}} \ \frac{1}{\sqrt{2}}\right]_{oko}$ two values of C_{23} are available.

Therefore, the above two constants can be determined uniquely by comparing the value of Δ_2, as obtained from $K\left[0 \ \frac{1}{\sqrt{2}} \ -\frac{1}{\sqrt{2}}\right]_{oko}$ with that calculated from its general expression using different combinations of the possible values of C_{36} and C_{23}. The only constant that is left now is C_{13} and this can be ascertained from the common value of the two pairs of values obtained by solving the two independent second degree equation in C_{13} derived from the ratios

$$K\left[\frac{1}{\sqrt{2}} \ 0 \ \frac{1}{\sqrt{2}}\right]_{hol} \quad \text{and} \quad K\left[\frac{1}{\sqrt{2}} \ 0 \ \frac{1}{\sqrt{2}}\right]_{hoo}$$

$$K\left[\frac{1}{\sqrt{2}} \ 0 \ \frac{1}{\sqrt{2}}\right]_{oko} \qquad K\left[\frac{1}{\sqrt{2}} \ 0 \ \frac{1}{\sqrt{2}}\right]_{oko}$$

the expressions for which can be obtained from Table II.

The accurate determination of the elastic constants from the study of diffuse X-ray reflections, specially when the photographic technique is applied, is limited by the errors involved in the measurements of intensities. In the present case maximum accuracy is attainable only in the evaluation of C_{44} and C_{55}. The measurement of $K(001)_{oko}$, which involves same direction cosines for the wave vector as well as the reciprocal lattice vector, is not likely to provide an accurate value of C_{33}. Inaccuracy in the estimation of each of the other constants depends on the number of predetermined elastic constants required for its computation. The method of evaluation of all the 13 elastic constants discussed above is being utilised for finding the constants of a few crystals.

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