Interpretation of the Lattice-strains Measured Under Non-hydrostatic Pressure

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The equations for the lattice strains produced by non-hydrostatic compression of the specimen are presented for all seven crystal systems in a form suitable for the analysis of experimental data. Examples of cubic (FeO and bcc iron) and hexagonal (hcp iron) systems are given to demonstrate that the analyses of the data give the estimates of single crystal elastic constants under high pressures. As the lattice strains can be measured at high pressures up to a few megabars using a diamond anvil cell, this approach offers an unique method of estimating the elastic constants at such high pressures. Further, this is the only method of estimating elastic constants of a phase stabilized under pressure. The article also discusses some other interesting specimen-material properties that can be derived at such high pressures.

[ Non-hydrostatic compression, Uniaxial stress component, Elastic constants, High pressure ]

1. Introduction

The fact that the stress state of the specimen compressed in an opposed anvil setup is non-hydrostatic was established in two early experiments. In a specially configured diffraction geometry, Scott-Weaver et al [1] passed the incident x-ray beam normal to the load direction in a diamond anvil cell, and recorded the diffraction pattern on a flat film placed normal to the incident beam. The diffraction ring which was circular to start with, showed a small distortion when the sample was loaded. In an independent study, Sato et al [2] observed that the volume strains measured in MgO, CaO, NaF and NaCl up to 15 GPa with a Bridgman opposed-anvil setup gave anomalous values of the bulk moduli and the pressure-derivatives when analyzed using standard equation of state (EOS). Both the observations could be explained by assuming that the stress component in the load direction was larger than the component perpendicular to it.

Singh and Kennedy [3] were the first to derive an expression, using anisotropic elasticity theory (AET), for the lattice strains in a specimen produced by non-hydrostatic stress state (NSS). The theory predicted that the lattice strain for cubic system is dependent on (hkl) in presence of NSS. This theory was verified experimentally and used in the interpretation of the data by a number of investigators [4-29]. The analysis of the diffraction data on NaCl using this theory gave interesting information on the uniaxial stress component [30]. It was possible to derive the values of \((S_{11}/S)\) and \((S_{11}-S_{12})/S\), where \(S=(S_{11}-S_{12}-S_{44}/2)\), from the analysis [31] of the compression data up to 1 GPa, which agreed very well with the corresponding values calculated from the \(S_{ij}\) -values and the pressure derivatives got by ultrasonic-velocity measurements. This may be regarded as the first attempt to derive information on single crystal elastic constants under high pressure by analyzing the x-ray diffraction data obtained under NSS. A treatment of the subject based on the isotropic elasticity theory (IET) was proposed by Ruoff [32]. This theory is of limited utility in analyzing the lattice strain data, as it does not explain all the experimental observations.

However, the model for NSS given in this paper is generally valid, and has been extensively used in subsequent works.

The derivations of the equations for lattice strains using AET recognize the fact that the crystallites constituting a polycrystalline specimen are, in general, elastically anisotropic. Further, of all the crystallites in the specimen, only those which are suitably oriented contribute to the diffracted intensity at the point of observation. The position of the recorded diffraction line, therefore, is an average taken over only such crystallites. The equation derived by Singh and Kennedy [3] was for the WC-anvil geometry wherein the incident x-ray beam passes normal to the load direction, and the point of observation lies in the plane containing the incident beam and is normal to the load direction. The commonly used diamond anvil cell geometry was treated separately [33]. Realizing the need of a general equation which included all possible diffraction geometries, equations for cubic [34-36], hexagonal [37], trigonal [38] and tetragonal [39], have been derived recently. Following the procedure given in these investigations [34-39], Uchida et al [40] derived the relevant equations for all the crystal systems.

In this article, we first discuss some recent developments in the experimental techniques [41, 42] which make it possible to use the theory to the fullest to obtain the information which could not be obtained from the analysis of the data got from the conventional diffraction geometry. The equations for a general diffraction geometry [34-40] are then expressed in a form which is suitable for the analysis of the data obtained using the new geometry.

2. New Diffraction Geometry

In the normal WC-anvil geometry with the point of observation in the plane perpendicular to the load axis, the diffracted intensity comes from the crystallites with the plane normal perpendicular to the load axis. Funamori et al [41] modified the Drickamer cell which permitted recording of the diffraction data in normal (horizontal) as well as vertical geometry (Fig.1). In the vertical-geometry, the diffracted
intensity at the point of observation arises from the crystallites with the plane-normals parallel to the load-axis.

Fig. 1. Schematic diagram of a modified Drickamer cell [41].

Using an x-ray transparent gasket (beryllium or amorphous boron) in a DAC, Mao et al [42] developed an experimental setup which permits recording of the diffraction data from a group of crystallites with the plane-normals oriented at an angle, \( \psi \), with the load-axis (Fig. 2). The angle, \( \psi \), can be varied between 0 and 2\( \pi \). The horizontal and vertical geometries [41] correspond to \( \psi = \pi/2 \) and \( \psi = 0 \) respectively.

Fig. 2. Setup to measure \( d \)-spacings as a function of \( \psi \) [42].

3. Lattice Strains under NSS

A. The Stress State:

Consider a solid specimen compressed without any pressure-transmitting medium, between flat and parallel faces of a pair of perfectly rigid anvils. When the load is so high that the specimen deforms plastically, and the stresses in the specimen far exceed the yield strength of the specimen material, stress state in the specimen-region at the center of the anvil-face develops symmetry about the load-direction (axial direction). Because of the finite shear strength of the specimen material, the axial stress component, \( \sigma_{33} \), is larger than the radial stress component. The stress tensor is given by,

\[
\sigma_y = \begin{bmatrix}
\sigma_{11} & 0 & 0 \\
0 & \sigma_{11} & 0 \\
0 & 0 & \sigma_{33}
\end{bmatrix}
\]

\[
\sigma_y = \begin{bmatrix}
\sigma_p & 0 & 0 \\
0 & \sigma_p & 0 \\
0 & 0 & \sigma_p
\end{bmatrix} + \begin{bmatrix}
-t/3 & 0 & 0 \\
0 & -t/3 & 0 \\
0 & 0 & 2t/3
\end{bmatrix}
\]

(1a)

The first and second terms represent the mean principal stress (equivalent hydrostatic pressure) and deviatoric stress component respectively. Further, \( t = (\sigma_{33} - \sigma_{11}) \) is the uniaxial stress component. The maximum shear stress or von Mises yield-criterion leads to the relation: \( t = (\sigma_{33} - \sigma_{11}) = 2\tau_y = \sigma_y \), where \( \tau_y \) and \( \sigma_y \) are respectively the shear strength and yield strength of the specimen material. Both, \( \tau_y \) and \( \sigma_y \), are pressure-dependent. The equivalent hydrostatic pressure is given by:

\[
\sigma_p = (\sigma_{11} + \sigma_{11} + \sigma_{33})/3 = (\sigma_{11} + t/3).
\]

(1b)

B. Equations for lattice strains:

The strain produced by NSS is a superposition of strains produced by \( \sigma_p \) and \( D_{ij} \). In magnitude, \( \sigma_p \) is much larger than \( D_{ij} \). The strain produced by \( \sigma_p \) can become very large, and is better analyzed using a standard equation of state. The strain produced by \( D_{ij} \) is small and adequately described by linear elasticity theory. In terms of the measured quantities, the strain produced by \( D_{ij} \) is given by,

\[
\varepsilon_d(hkl) = \frac{d_m(hkl) - d_p(hkl)}{d_p(hkl)}
\]

(2a)

where, \( d_m(hkl) \) is the measured inter-planar spacing under NSS, and \( d_p(hkl) \) is the spacing under a hydrostatic pressure \( \sigma_p \). \( (hkl) \) denote the Miller indices. The equations for the lattice strains derived earlier [34-40] can be rearranged to give the following relation:

\[
\varepsilon_d(hkl) = (1 - 3 \cos^2 \psi)Q(hkl)
\]

(2b)

where,

\[
Q(hkl) = (t/3)[\alpha(2G_R^X(hkl))^{-1} + (1-\alpha)(2G_Y)^{-1}]
\]

(2c)

where \( G_R^X(hkl) \) is the shear modulus calculated under Reuss (iso-stress) condition, the averaging being done over the group of crystallites which contribute to the diffracted intensity at the point of observation. \( G_Y \) is the shear modulus of...
polycrystalline aggregate with random orientation of crystallites calculated under iso-strain condition. The relative weightage of the iso-stress and iso-strain conditions in an actual case is decided by the factor \( \alpha \), which lies between 0 and 1. Eq.(2c) is written in this form for the sake of generality. Under high pressures, the iso-stress condition prevails, i.e., \( \alpha = 1 \).

On combining Eqs.(2a) and (2b) we get,

\[
d_m(hkl) = d_P(hkl)[1 + \left(1 - 3\cos^2 \psi \right)Q(hkl)]
\]  
(2d)

The equations derived earlier [34-40] can be rearranged to give the following relations for \( G_R^X(hkl) \),

**Cubic System :**

\[
[2G_R^X(hkl)]^{-1} = \frac{1}{2} \{ S_{11} - S_{12} - 3(S_{11} - S_{12} - S_{44}/2) \} \Gamma(hkl)
\]  
(3a)

where, \( \Gamma(hkl) = (h^2k^2 + k^2l^2 + l^2h^2) / (h^2 + k^2 + l^2)^2 \)

**Hexagonal System :**

\[
[2G_R^X(hkl)]_{hex} = \frac{1}{2} \{ -3(S_{11} - 6S_{13} + 3S_{33} - 3S_{44}) \}
\]  
(3b)

where, \( l_2^2 = 3a^2l^2 / M^2 \), \( M^2 = 4c^2(h^2 + hk + l^2) + 3a^2l^2 \)

and \( a \) and \( c \) are the lattice parameters of the hexagonal cell. It may be noted that \( l_2^2 \) is same as \( B \) in Ref. [37].

**Trigonal System :**

\[
[2G_R^X(hkl)]^{-1} = \frac{1}{2} \{ S_{11} - S_{12} - 3(S_{11} - S_{12} - 3S_{33} - 3S_{44}) \} \Gamma(hkl)
\]  
(3c)

where, \( l_1 = \sqrt{3}ch / M \), \( l_2 = c(h + 2k) / M \), \( l_3 = \sqrt{3}al / M \).

The expression for \( M \) is same as for the hexagonal system. The \( S_{ij} \)-terms are referred to hexagonal set of axes. For the trigonal classes, \( 3\bar{2}m \) and \( 3m \), \( S_{25} = 0. \)

**Tetragonal System :**

\[
[2G_R^X(hkl)]^{-1} = \frac{1}{2} \{ S_{11} - S_{12} - 3S_{11} + 3S_{12} + 3S_{44} \} \Gamma(hkl)
\]  
(3d)

where, \( l_1 = ch / M \), \( l_2 = ck / M \), \( l_3 = al / M \).

\[ M^2 = a^2l^2 + c^2(h^2 + k^2) \]

For classes, \( 4mm, 42m \) and \( 423 \), \( S_{16} = 0. \)

**Orthorhombic System :**

\[
[2G_R^X(hkl)]^{-1} = \frac{1}{2} \{ -S_{12} + S_{13} + S_{23} \} \Gamma(hkl)
\]  
(3e)

where, \( l_1 = h d(hkl) / a \), \( l_2 = k d(hkl) / b \) and \( l_3 = l d(hkl) / c \).

The interplanar spacing is denoted by \( d(hkl) \), \( a \), \( b \) and \( c \) are the unit cell dimensions.

**Monoclinic System :**

\[
[2G_R^X(hkl)]^{-1} = \frac{1}{2} \{ S_{11} - S_{12} - 3(S_{11} - S_{12} - S_{44}/2) \} \Gamma(hkl)
\]  
(3f)

where, \( l_1 = h d(hkl) / a \), \( l_2 = k d(hkl) / b \) and \( l_3 = l d(hkl) / c \). With monoclinic angle, \( \beta \), \( l_3 = (a - hc \cos \beta) d(hkl) / ac \sin \beta \).

**Triclinic System :**

\[
[2G_R^X(hkl)]^{-1} = \frac{1}{2} \{ S_{11} - S_{12} - 3(S_{11} - S_{12} - S_{44}/2) \} \Gamma(hkl)
\]  
(3g)

where, \( l_1 = h d(hkl) / a \), \( l_2 = k d(hkl) / b \) and \( l_3 = l d(hkl) / c \). With monoclinic angle, \( \beta \), \( l_3 = (a - hc \cos \beta) d(hkl) / ac \sin \beta \).

4. Analysis of the data

A. General :

Eqs.(2a)-(2d) are quite general and valid for all crystal systems. Eq.(2d) gives the \( \psi \)-dependence of the measured d-spacing of a reflection. The experimental verification of this became possible only recently when \( d_m(hkl) \) versus \( \psi \) data became available [42]. Fig.(3a) shows a comparison of the experimental data with the trend predicted by Eq.(2d). It is seen that Eq.(2d) describes the \( \psi \)-dependence of the measured...
d-spacings very well. Further, in accordance with Eq.(2d), the $d_m(hkl)$ versus $(1-3\cos^2\psi)$ was found to be a straight line for a large number of cases examined, which included cubic [Fig.(3b)], hexagonal and rhombohedral systems. The $R^2$-value in most cases varied between 1 and 0.98. The fit, however, tends to become poorer as the pressures reach the megabar range. The lowest $R^2$-value encountered among more than 100 reflections analyzed so far was 0.86.

![Graph of $d_m(111)$ versus $\psi$ data](image)

**Fig. 3.** (a) $d_m(111)$ versus $\psi$ data (open circles and squares). Trend predicted by Eq.(2d) is shown by continuous curve. (b) $d_m(111)$ versus $(1-3\cos^2\psi)$ plot.

**B. Strain due to $\sigma_P$:**

Eq. (2b) suggests that the strain produced by the deviatoric stress component is identically zero if $(1-3\cos^2\psi)=0$, i.e., $\psi = \cos^{-1}(1/\sqrt{3})$. The d-spacing measured under this condition exactly equals $d_P(hkl)$.

Equivalently, $d_P(hkl)$-values can be obtained from the intercept (on the $d$-axis) of the $d_m(hkl)$ versus $(1-3\cos^2\psi)$ plot. The method suggested by Funamori et al [41] gives the d-spacings at $\psi=0$ and $\psi=\pi/2$, and these two values can be used to calculate $d_P(hkl)$. Thus, the determination of $d_P(hkl)$ requires either measurement at $\psi = \cos^{-1}(1/\sqrt{3})$ or at least any two $\psi$-values. The measurements at a number of $\psi$-values are preferred to a single measurement at $\psi = \cos^{-1}(1/\sqrt{3})$ or at two $\psi$-values, as the effect of measurement-errors on $d_P(hkl)$ is minimized through the straight-line fit. It may be noted that $d_P(hkl)$ can not be extracted from data under NSS by any other method.

The lattice parameters calculated from $d_P(hkl)$-values show the features of compression under truly hydrostatic pressure. The lattice parameter, $a_P(hkl)$, of FeO(cubic) at 8.3 GPa calculated from $d_P(hkl)$-values are listed in Table 1. It is seen that $a_P(hkl)$-values calculated from different reflections show a small scatter about the mean value, which reflects the error of measurement rather than the effect of any departure from the hydrostatic nature of stress. The effect of NSS on the lattice parameter is seen from the scatter in $a(hkl)$-values (Table 1) calculated from $d_m(hkl)$ at $\psi = \pi/2$. These values very nearly correspond to the values obtained with a conventional DAC geometry. The standard deviation in this case is 6-times larger than the value for $a_P(hkl)$. The unit cell volume is overestimated (by 1.7 per cent, for data in Table 1) if the effect of NSS is ignored [2,43].

**Table 1.** A comparison of the standard deviations in $a_P(hkl)$ and $a(hkl)$ values for FeO at 8.3 GPa.

<table>
<thead>
<tr>
<th>$hkl$</th>
<th>$a_P(hkl)$ (Å)</th>
<th>$a(hkl)$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>4.2276</td>
<td>4.2577</td>
</tr>
<tr>
<td>200</td>
<td>4.2270</td>
<td>4.2384</td>
</tr>
<tr>
<td>220</td>
<td>4.2325</td>
<td>4.2607</td>
</tr>
<tr>
<td>311</td>
<td>4.2290</td>
<td>4.2489</td>
</tr>
<tr>
<td>222</td>
<td>4.2325</td>
<td>4.2757</td>
</tr>
<tr>
<td>400</td>
<td>4.2288</td>
<td>4.2404</td>
</tr>
<tr>
<td>Mean (Å) :</td>
<td>4.2296</td>
<td>4.2536</td>
</tr>
<tr>
<td>s. d. :</td>
<td>0.002</td>
<td>0.013</td>
</tr>
<tr>
<td>Cell volume (Å³) :</td>
<td>75.6655</td>
<td>76.9609</td>
</tr>
</tbody>
</table>

The data on h.c.p. iron and rhombohedral phase of FeO were also analyzed in this manner. The $d_P(hkl)$-values derived from the $d_m(hkl)$ versus $(1-3\cos^2\psi)$ plots agree very well with the respective values calculated from the lattice parameters $a$ and $c$ obtained from $d_P(hkl)$-values. The agreement is found to be much poorer when the calculations are repeated with $d_m(hkl)$-values at $\psi = \pi/2$, which correspond very nearly to the conventional DAC geometry.

**C. Analysis of $Q(hkl)$: Estimation of anisotropy factor for a cubic system**

The $Q(hkl)$-values obtained from the $d_m(hkl)$ versus $(1-3\cos^2\psi)$ plots contain important information on $S_{ij}$. In the case of cubic system, Eqs.(2c) and (3a) suggest that the $Q(hkl)$ versus $\Gamma(hkl)$ plot is a straight line[Fig.(4)]. The slope, $T$, and intercept, $I$, of this line are given by,

$$T = -(\alpha t / 3)[S_{11} - S_{12} - S_{44} / 2]$$

(4a)
and,
\[
\left( \frac{T}{I} \right) = -\frac{x}{(x-1)} + 5(\alpha^{-1} - 1)x / (x-1)(3x + 2)
\]  \hfill (4c)

Meng et al [46] used the IET to derive an equation relating \( t \) with aggregate bulk and shear moduli of the specimen material, and the difference between the real pressure and the pressure measured by x-ray method in presence of NSS. The use of IET is relevant in the derivation of this equation, as all quantities in this equation are aggregate properties, except the x-ray measured pressure. The use of a more rigorous approach based on AET on the lines discussed in this article gives an equation\[47\] which is essentially the same as of Meng et al [46], but contains a factor, \( f(hkl) \), (as a multiplier) which is function of anisotropy factors. It may be noted that the elastic anisotropy is determined by a single factor \( x \) for cubic system. For other systems, more than one factor is required to define elastic anisotropy. The resulting equation is given by,

\[
t = 6\langle f(hkl) \rangle \left\langle Q(hkl) \right\rangle G
\]  \hfill (5)

where, \( \langle f(hkl) \rangle \) and \( \langle Q(hkl) \rangle \) are respectively the averages of \( f(hkl) \) and \( Q(hkl) \)-values for all the measured \( (hkl) \). \( G \) denotes the shear modulus of the polycrystalline specimen-material. The \( Q(hkl) \)-values are derived from the experimental data. If a large number of reflections are used in the averaging, then \( \langle f(hkl) \rangle = 1 \). The \( S_{ij} \)-values were obtained from Eqs. (4a) and (4b), measured compressibility, and \( t \) values from Eq.(5) for FeO and b.c.c. iron. The resulting \( C_{ij} \)-values are given in Table 2. Also see ref. [48].

It is seen from Eqs. (2c), (2d) and (3b), that a plot of \( Q(hkl) \) versus \( \Gamma(hkl) \) is a parabola [Fig.(5)]. The three constants obtained from the parabolic fit through the data when equated to the corresponding terms in Eq. (3b) give three relations involving \( S_{ij} \) terms. Two more relations are obtained by equating the measured \( a \)- and \( c \)-axis compressibilities to respectively \( (S_{11} + S_{12} + S_{13}) \) and \( (S_{33} + 2S_{13}) \). The \( t \)-values can be obtained using Eq.(5). The \( S_{ij} \) values were obtained in this manner for h.c.p. iron. The resulting \( C_{ij} \)-values are given in Table 2. A detailed account of this analysis will appear elsewhere [49].
Table 2. The single crystal elastic constants of FeO, and b.c.c. and h.c.p. iron as estimated from the $d_m(hkl)$ versus $\psi$ data obtained under non-hydrostatic compression. The units are GPa and (GPa)$^{-1}$ for elastic constants and compressibility respectively. Numbers in parenthesis indicate standard errors.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>FeO (cubic)</th>
<th>b.c.c. iron</th>
<th>h.c.p. iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
<td>8.3</td>
<td>4.6</td>
<td>52</td>
</tr>
<tr>
<td>$c_{11}$</td>
<td>313 (44)</td>
<td>281 (11)</td>
<td>639 (55)</td>
</tr>
<tr>
<td>$c_{12}$</td>
<td>127 (22)</td>
<td>144 (7)</td>
<td>300 (55)</td>
</tr>
<tr>
<td>$c_{13}$</td>
<td>-</td>
<td>-</td>
<td>254 (41)</td>
</tr>
<tr>
<td>$c_{33}$</td>
<td>-</td>
<td>-</td>
<td>648 (83)</td>
</tr>
<tr>
<td>$c_{44}$</td>
<td>28 (7)</td>
<td>112 (35)</td>
<td>422 (23)</td>
</tr>
<tr>
<td>$t$</td>
<td>1.4 (0.2)</td>
<td>1.2 (0.1)</td>
<td>4.4 (0.2)</td>
</tr>
<tr>
<td>$[3K(P)]$</td>
<td>1.765$^a$</td>
<td>1.759$^b$</td>
<td>0.8467$^c$</td>
</tr>
<tr>
<td>$\chi(a)\times 10^3$</td>
<td>-</td>
<td>-</td>
<td>0.8217$^d$</td>
</tr>
<tr>
<td>$\chi(c)\times 10^3$</td>
<td>-</td>
<td>-</td>
<td>0.8967$^d$</td>
</tr>
</tbody>
</table>

$\chi(a)$, $\chi(c)$ - a- and c-axis compressibilities

a - ref. [44]  b - ref. [50]  c - ref. [51]

5. Conclusions:

The $\psi$ -dependence of the measured $d$-spacings predicted by Eq. (2b) is supported by the experimental data. The $d_p(hkl)$ -values derived from the $d_m(hkl)$ versus $\psi$ data exhibit the characteristics of true hydrostatic compression.

The expressions given in this article can be used to analyze the data under NSS to get the estimates of the single crystal elastic constants.

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