The lattice strains in a specimen (hexagonal system) compressed nonhydrostatically in an opposed anvil high pressure setup

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A general expression has been derived for the lattice strain which corresponds to the measurement by x-ray diffraction method on a specimen (hexagonal system) compressed nonhydrostatically in an opposed anvil high pressure setup. The expressions relevant to the different diffraction geometries used in high pressure experiments with opposed anvils emerge as the special cases of this equation. The effect of the deviatoric stress component on the lattice parameters derived from the interplanar spacings measured at high pressure is discussed.

I. INTRODUCTION

The stress state in a solid specimen compressed in an opposed anvil setup deviates from the hydrostatic condition. The effect of nonhydrostaticity on the strains measured by x-ray diffraction methods has been examined by many investigators. A discussion of the earlier work can be found in a recent article,^{1,2} wherein it is shown that the lattice strain, which corresponds to the x-ray diffraction measurement, can be calculated only if the anisotropic elasticity theory (AET) is used. The strain in a direction $[hkl]$ calculated using isotropic elasticity theory (IET) corresponds to the macroscopic strain which in general differs from the x-ray measured lattice strain in the same direction. For the cubic system, the ratio of the lattice strain to the macroscopic strain, both along $[hkl]$, depends on (hkl) and the elastic anisotropy factor $2(S_{11} - S_{12})/S_{44}$. The distinction between the two strains vanishes only if the crystallites constituting the specimen are elastically isotropic.

In this article we use AET to derive, for the first time, a general expression for the lattice strain produced by the deviatoric stress component in a specimen belonging to hexagonal system compressed nonhydrostatically in an opposed anvil high pressure setup. The expressions for the various diffraction geometries used in practice emerge as special cases of this equation. The expression has been derived also for the changes in the lattice parameters caused by the deviatoric stress component. The use of these equations in analyzing the high pressure x-ray diffraction data has been discussed.

II. BACKGROUND INFORMATION

A. Diffraction geometry

As discussed earlier,^{1,2} the diffraction geometries used in high pressure work fall under the following three categories:

(1) Parallel geometry (PLG): This describes the diffraction geometry of a diamond anvil cell (DAC). The direction of the incident x-ray beam coincides with the direction of the applied load. The angle between the diffracting plane normal and the direction of the applied load equals $(\pi/2 - \theta)$, where θ is the Bragg angle.

(2) Perpendicular geometry (PDG): This describes the diffraction geometry of tungsten carbide anvil setup. In this case, $\psi = \pm \pi/2$.

(3) Scott - Weaver - Takahashi - Bassett - Kinsland (SWEATBAK) geometry: This describes the diffraction geometry when DAC is used in the PDG mode.^{3,4} The complete diffraction rings can be recorded on a flat film placed normal to the incident x-ray beam. The diffraction ring diameters, parallel and perpendicular to the load axis are of interest, and for these $\psi = \pm \theta$ and $\psi = \pm \pi/2$, respectively.

B. The stress state

The stress state at the center of the specimen compressed between the anvils will be described with respect to a mutually perpendicular right handed system of coordinates x_i ($i = 1, 2, 3$), x_3 being Perpendicular to the anvil face. The origin of coordinates lies midway between the parallel anvil faces on the line passing through the center of and normal to the anvil face. We follow the convention⁵ used in single crystal elasticity theory. As discussed earlier,⁶ the stress at the center of the specimen is given by

$$\sigma_{ij} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{11} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix} \quad (1a)$$

$$= \begin{pmatrix} \sigma_p & 0 & 0 \\ 0 & \sigma_p & 0 \\ 0 & 0 & \sigma_p \end{pmatrix} + \begin{pmatrix} -t/3 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & -t/3 & 0 \end{pmatrix} \quad (1b)$$

$$= \sigma_p + d_{ij}, \quad (1c)$$

where d_{ij} is the deviatoric stress component, σ_p is the mean normal stress, and t is the uniaxial stress component (USC). σ_p and t are given by

$$\sigma_p = (2\sigma_{11} + \sigma_{33})/3 = (\sigma_{11} + t/3) \quad (1d)$$

$$t = (\sigma_{33} - \sigma_{11}).$$

The maximum shear or von Mises criterion gives

$$t = \sigma_y = 2\tau_y, \quad (2)$$

where σ_y and τ_y denote, respectively, the yield and shear strengths of the specimen material. There exists a radial stress gradient^{1,2,6-8} in the specimen causing σ_p and t to vary with the distance from the center. Even though the incident

FIG. 1. The relative orientations of the three sets of axes.

x-ray beam illuminates a small volume around the center, magnitudes of σ_p and t vary within this volume. In the following discussion we assume average values of σ_p and t over the specimen region illuminated by the incident x-ray beam.

C. Choice of axes

Let us consider a crystallite in the specimen with its plane (hkl) contributing to the intensity at the point of observation. This plane (ABC) referred to the x_i'' axes is shown in Fig. 1. The x_1'' and x_3'' axes coincide with the crystallographic axes a and c of the hexagonal system and x_2'' is chosen perpendicular to both x_1'' and x_3'' to form a right handed system of coordinates. Another orthogonal set of axes x_i' is chosen such that x_1' and x_3' are along $O'A$ and OO' (normal to the plane ABC), respectively. x_2' is in the plane ABC . The orientations of x_i' axes with respect to x_i'' axes are shown in Fig. 1. All the crystallites whose orientations can be obtained by rotating the crystallite about OO' contribute to the intensity at the point of observation. These crystallites are termed the φ group of crystallites.

III. EQUATION FOR LATTICE STRAIN

We first derive the expressions for the lattice strains in a polycrystalline specimen under a stress state given by Eq. (1) under the assumptions of stress continuity (Reuss limit⁹) and strain continuity (Voigt limit¹⁰) across the grain boundaries. We then obtain the strain in an actual case as a combination of the strains calculated under the two limits. The expressions for the lattice strains for the hexagonal system have been derived earlier¹¹ in the context of x-ray elastic constants. Here, we derive the expressions in a self-contained manner, which include the various geometries used in the high pressure x-ray diffraction work.

The strain component due to d_{ij} in the presence of σ_p can be calculated by considering d_{ij} acting on the specimen which is already under a hydrostatic pressure σ_p . As the load between the anvils is increased σ_p increases and the resulting strain can be large; these strains are described best by a stan-

dard equation of state. The d_{ij} also increase with increasing σ_p , but remain small as compared with σ_p . For some materials, the d_{ij} components may reach a few gigapascals (GP) at a σ_p of hundreds of gigapascals. However, since such materials have large elastic moduli which further increase with increasing σ_p , the strains due to d_{ij} are small. Thus, the use of linear elasticity theory in calculating strains due to d is justified. The x-ray diffraction technique measures interplanar spacings, and therefore, the strain calculated from the measurement at high pressure and 1 atm corresponds to the elastic strain component ϵ'_{33} along x_3' . In the next two sections ϵ'_{33} produced by d_{ij} is calculated under the Reuss and Voigt limits.

A. Reuss limit

We follow essentially the same scheme as used earlier¹ to derive the expression for ϵ'_{33} arising from d_{ij}' . The first step is to transform d_{ij} to d_{ij}'' by two successive transformations:

$$d_{ij}' = a_{ik} a_{jl} d_{kl}, \quad (3)$$

$$d_{ij}'' = b_{ik} b_{jl} d_{kl}', \quad (4)$$

The single and double prime indicate that the quantity is referred to the x_i' and x_i'' axes, respectively. The matrices a_{ij} and b_{ij} are given by

$$a_{ij} = \begin{bmatrix} x_j & x_1 & x_2 & x_3 \\ x_i' & \cos \varphi \cos \psi & -\sin \varphi & \cos \varphi \sin \psi \\ x_1' & \sin \varphi \cos \psi & \cos \varphi & \sin \varphi \sin \psi \\ x_2' & -\sin \psi & 0 & \cos \psi \end{bmatrix} \quad (5)$$

and

$$b_{ij} = \begin{bmatrix} x_j' & x_1' & x_2' & x_3' \\ x_i'' & \frac{N}{M} & 0 & \frac{\sqrt{3}ch}{M} \\ x_1'' & \frac{-\sqrt{3}c^2h(h+2k)}{MN} & \frac{\sqrt{3}al}{N} & \frac{c(h+2k)}{M} \\ x_2'' & \frac{-\sqrt{3}c^2h(h+2k)}{MN} & \frac{\sqrt{3}al}{N} & \frac{c(h+2k)}{M} \end{bmatrix},$$

where

$$M^2 = 4c^2(h^2 + hk + k^2) + 3a^2l^2,$$

$$N^2 = c^2(h+2k)^2 + 3a^2l^2.$$

(hkl) are the Miller indices, and a and c the lattice parameters of the hexagonal cell. On carrying out transformations (3) and (4), and averaging over the φ group of crystallites

such that $\langle \sin^2 \varphi \rangle = \langle \cos^2 \varphi \rangle = 1/2$ and $\langle \sin \varphi \rangle = \langle \cos \varphi \rangle = 0$ for a completely random orientation of the crystallites in the specimen we get

$$\begin{aligned} d''_{11} &= \left[\frac{1}{2} - \frac{9c^2 h^2}{2M^2} \right] E, \\ d''_{22} &= \left[\frac{1}{2} - \frac{3c^2(h+2k)^2}{2M^2} \right] E, \\ d''_{33} &= \left[\frac{1}{2} - \frac{9a^2 l^2}{2M^2} \right] E, \\ d''_{23} &= \left[-\frac{3\sqrt{3}acl(h+2k)}{2M^2} \right] E, \\ d''_{13} &= \left[-\frac{9achl}{2M^2} \right] E, \\ d''_{12} &= \left[\frac{-3\sqrt{3}c^2 h(h+2k)}{2M^2} \right] E \end{aligned} \quad (7)$$

where

$$E = \left(\frac{t}{3} \right) (1 - 3 \cos^2 \psi),$$

The resulting strain ϵ''_{ij} is given by

$$\epsilon''_{ij} = S_{ijkl} d''_{kl}, \quad (8)$$

where S_{ijkl} are the elastic compliances in tensor notation. The strain component ϵ'_{33} is given by

$$\epsilon'_{33} = \epsilon''_{ij} l_i l_j, \quad (9)$$

where l_i represent the direction cosines of the angles x'_3 makes with x_i . On carrying out steps (8) and (9) we get

$$\epsilon'_{33} = \epsilon_d^R(hkl) = -\frac{t}{3} (1 - 3 \cos^2 \psi) / (2G_R^x),$$

where

$$\begin{aligned} (G_R^x)^{-1} &= [S_{11}(1-B)(2-3B) - S_{12}(1-B) \\ &\quad - S_{13}(1-2B)(1-3B) - S_{33}B(1-3B) \\ &\quad + 3S_{44}B(1-B)] \end{aligned} \quad (10)$$

and

and S_{mn} are elastic compliances in two-suffix notation⁵ at a pressure σ_p . $\epsilon_d^R(hkl)$ represents the strain produced by the deviatoric stress component under the Reuss limit. G_R^x is the shear modulus under the Reuss limit appropriate to the x-ray measurement. It may be noted that G_R^x is different from the Reuss shear modulus G_R for the bulk specimen

B. Voigt limit

The expression for ϵ'_{33} under the Voigt limit can be derived by writing the expression for ϵ'_{33} for an elastically isotropic case, and substituting for the elastic constants the Voigt-average values. This gives

$$\epsilon_d^V = -\frac{t}{3} (1 - 3 \cos^2 \psi) / (2G_V), \quad (1)$$

where G_V is the shear modulus under the Voigt limit given by

$$(2G_V)^{-1} = X_1/X_2, \quad (1)$$

where

$$\begin{aligned} X_1 &= 15S_0S_{44}(S_{11} - S_{12}), \\ X_2 &= S_{44}(S_{11} - S_{12})[2(S_{11} + S_{12}) + 4.5S_{13} + S_{33}] \\ &\quad + 6S_0[S_{44} + 2(S_{11} - S_{12})], \\ S_0 &= S_{33}(S_{11} + S_{12}) - 2S_{13}^2. \end{aligned}$$

The elastic compliances are at a pressure σ_p . If we assume that the actual stress-strain state in a polycrystalline specimen lies in between those described by the Reuss and Voigt limits, then the lattice strain produced by d_{ij} is given by

$$\Delta \epsilon(hkl) = -\left(\frac{t}{3} \right) (1 - 3 \cos^2 \psi) / [2\langle G \rangle], \quad (1)$$

where

$$\langle G \rangle = \alpha G_R^x + (1 - \alpha)G_V$$

and α is a fraction. Obviously $\alpha=1$ and $\alpha=0$ correspond to the Reuss and Voigt limits, respectively. The value of α to be used in an actual case, as discussed in Sec. IV A, is 0.5.

C. Measured strain

The strain $\Delta \epsilon(hkl)$ produced by d_{ij} in the presence of large σ_p is calculated [Eq. (13)] by considering d_{ij} acting on the specimen under a hydrostatic pressure σ_p . In terms of the measured d spacings, $\Delta \epsilon(hkl)$ is given by

$$\Delta \epsilon(hkl) = [d_{p+d}(hkl) - d_p(hkl)] / d_p(hkl). \quad (1)$$

The subscripts $(p+d)$ and p refer to the measurements under nonhydrostatic pressure ($\sigma_p + d_{ij}$) and at a hydrostatic pressure σ_p , respectively. The total strain measured under nonhydrostatic pressure is given by

$$\epsilon(hkl) = [d_{p+d}(hkl) - d_0(hkl)] / d_0(hkl), \quad (1)$$

where $d_0(hkl)$ is the spacings at 1 atm. It is seen from Eqs. (14) and (15) that

$$\epsilon(hkl) = \epsilon_p(hkl) + [1 + \epsilon_p(hkl)] \Delta \epsilon(hkl), \quad (1)$$

where

$$\epsilon_p(hkl) = [d_p(hkl) - d_0(hkl)] / d_0(hkl). \quad (1)$$

In practice the unit cell volume u at various pressures is determined from the measurements at high pressures of the spacings, and the volume strains are calculated. Analogous to the linear (one dimensional) strains defined in Eqs. (14) and (15), the following volume strains can be defined:

$$\Delta \epsilon(v) = (v_{p+d} - v_p) / v_p, \quad (1)$$

$$\epsilon(v) = (v_{p+d} - v_0) / v_0, \quad (1)$$

$$\epsilon_p(v) = (v_p - v_0) / v_0. \quad (1)$$

$$\mathbf{A} \tilde{\epsilon}(v) = \epsilon(v) - \epsilon_p(v) = [1 + \epsilon_p(v)] \Delta \epsilon(v). \quad (21)$$

IV. DISCUSSION

A. General

In an earlier work¹ the lattice strain in a real situation was expressed as a linear combination of the strains calculated under the Reuss and Voigt limits. Equation (13) in this work makes use of the average of G_R^x and G_V , which amounts to expressing the inverse of the strain in a real situation as the average of the inverse of the strains calculated under the Reuss and Voigt limits. The two averaging procedures are identical if $G_R^x = G_V$, a case of complete elastic isotropy (see the next section), and give comparable results if (G_R^x/G_V) does not deviate from unity appreciably. In the range $0.5 < (G_R^x/G_V) < 2$, which covers most real materials, the two calculations differ by less than 11%. A comparison of the two averaging procedures with a rigorous calculation of the strain in a real situation^{12,13} indicates that the average of G_R^x and G_V ($\alpha=0.5$) provides a better description of strain in a real situation than the linear combination of the strains under the Reuss and Voigt limits when (G_R^x/G_V) deviates from unity considerably, for example, in the case of zinc for which (G_R^x/G_V) can reach 0.3.

B. Elastic isotropy

A hexagonal system is elastically isotropic if the following conditions are satisfied:

$$S_{11} = S_{33}, \quad (22a)$$

$$S_{44} = 2(S_{11} - S_{13}), \quad (22b)$$

$$S_{12} = S_{13}. \quad (22c)$$

It can be shown that the linear compressibility of a hexagonal system is isotropic if only the first and the last of the above three conditions are satisfied. Thus, the isotropic linear compressibility of a hexagonal system is not a sufficient condition for the complete elastic isotropy.

Under the conditions of complete elastic isotropy, Eq. (13) reduces to

$$\Delta \epsilon_{\text{iso}} = -\frac{t}{3} (1 - 3 \cos^2 \psi) / (2G). \quad (23)$$

Under the conditions of isotropy, $G_V = G_R = (S_{44})^{-1}$. Since G_V and G_R represent, respectively, the upper and the lower bounds¹⁴ of the shear modulus G of the polycrystalline specimen containing randomly oriented crystallites $G = G_V = G_R$. In terms of the bulk modulus and the Poisson's ratio of the specimen material

$$\Delta \epsilon_{\text{iso}} = -\frac{t}{3} (1 - 3 \cos^2 \psi) \left\{ \frac{1}{3K} \right\} \left\{ \frac{1}{1 - 2\nu} \right\},$$

where K is the bulk modulus.

C. Lattice parameters

The lattice parameters a_{p+d} and c_{p+d} determined from the interplanar spacings measured at nonhydrostatic high pressure include the contributions from the deviatoric stress component and the hydrostatic pressure component. The changes in the lattice parameters produced by d_{ij} are given by

$$(\Delta a)_d = a_{p+d} - a_p \quad (25a)$$

and

$$(\Delta c)_d = c_{p+d} - c_p. \quad (25b)$$

The suffixes $(p+d)$ and p indicate, respectively, nonhydrostatic and hydrostatic pressure conditions. For (hkl) -type reflections it can be shown that

$$d_{p+d}^{-2}(hkl) = \frac{1}{3} \frac{H^2}{a_p^2}$$

and

$$d_p^{-2}(hkl) = \frac{4}{3} \frac{H^2}{a_p^2}, \quad (26b)$$

where

$$H^2 = (h^2 + hk + k^2)$$

On combining Eqs. (14), (25a), (26a), and (26b), we get

$$\left(\frac{\Delta a}{a_p} \right)_d = \Delta \epsilon(hkl) = -\frac{t}{3} (1 - 3 \cos^2 \psi) / [\langle 2G \rangle_{hkl}], \quad (27a)$$

where

$$\langle G \rangle_{hkl} = \frac{1}{2} [(2S_{11} - S_{12} - S_{13})^{-1} + G_V].$$

By considering $(00l)$ -type reflections and following a similar approach as given above we get

$$\left(\frac{\Delta c}{c_p} \right)_d = \Delta \epsilon(00l) = -\frac{t}{3} (1 - 3 \cos^2 \psi) / [\langle 2G \rangle_{00l}], \quad (27b)$$

where

$$\langle G \rangle_{00l} = \frac{1}{2} [(S_{33} - S_{13})^{-1} + G_V].$$

For $\cos \psi \leq 1/\sqrt{3}$, both $(\Delta a/a_p)_d$ and $(\Delta c/c_p)_d$ are positive quantities because a compressive t is negative by convention, and S_{11} and S_{33} are positive, and S_{12} and S_{13} are negative. Thus, $a_{p+d} > a_p$ and $c_{p+d} > c_p$. It may be noted that $\Delta \epsilon(hkl)$ for nonzero indices depends on (hkl) . When the lattice parameters are obtained by least squares fit to the measured d spacings, the part of $\Delta \epsilon(hkl)$ for nonzero indices gets absorbed in a and c , and the remaining part appears as the scatter in the fit. The numerical values of a_{p+d} and c_{p+d} slightly depend on the type and number of reflections used in the calculation. For this reason, the values of $(\Delta a/a_p)_d$ and $(\Delta c/c_p)_d$ as obtained from Eq. (25a) and Eq. (25b), respectively, will differ slightly from the corresponding values obtained from Eq. (27a) and Eq. (27b). For an isotropic case Eqs. (27a) and (27b) reduce to

TABLE I. A comparison of the $(\Delta a/a_p)_d$, $(\Delta c/c_p)_d$, and $\Delta \epsilon(v)$ values for rhenium and cadmium using various equations.

Specimen material	$(\Delta a/a_p)_d$	$(\Delta c/c_p)_d$	$\Delta \epsilon(v)$
Rhenium	0.00 541 ^a	0.00 500 ^a	0.01 582 ^b
	0.00 548 ^c	0.00 487 ^d	0.01 580 ^b
	0.00 560 ^e	0.00 560 ^e	0.01 684 ^f
Cadmium	0.00 154 ^c	0.00 235 ^a	0.00 543 ^b
	0.00 144 ^c	0.00 287 ^d	0.00 575 ^b
	0.00 167 ^c	0.00 167 ^e	0.00 501 ^f

^aThe first six reflections have been used in the least squares fit.

^bCalculated from Eq. (29).

^cFrom Eq. (27a).

^dFrom Eq. (27b).

^eFrom Eq. (28).

^fFrom Eq. (30).

$$\left(\frac{\Delta a}{a_p}\right)_d = \left(\frac{\Delta c}{c_p}\right)_d = \Delta \epsilon_{\text{iso}} = -\frac{r}{3} (1 - 3 \cos^2 \psi)/(2G). \tag{28}$$

The volume strain produced by d_{ij} as defined by Eq. (18) is given by

$$\Delta \epsilon(v) = 2(\Delta a/a)_d + (\Delta c/c)_d, \tag{29}$$

which for the isotropic case reduces to

$$\Delta \epsilon(v) = -\left(\frac{r}{3}\right) (1 - 3 \cos^2 \psi)/(3/2G). \tag{30}$$

The results of Eqs. (27)–(30) were compared with those of the least squares fit taken as the benchmark. For this purpose, we used the computed d values which simulate the effects of the nonhydrostatic pressure. The d values under nonhydrostatic pressure are given by Eq. (14) which for convenience can be rearranged as follows:

$$d_{p+d}(hkl) = d_p(hkl)[1 + \Delta \epsilon(hkl)].$$

The d values were calculated for rhenium (moderate elastic anisotropy) and cadmium (large elastic anisotropy). The r values of -6 and -0.22 GPa for rhenium and cadmium, respectively, the elastic compliances at 1 atm, and $\alpha=0.5$ were used to compute the d values for all (hkl) values listed in Table II. These data correspond to the error-free measurement of the d values under nonhydrostatic pressure with 1 atm mean normal pressure. Since the purpose of this calculation was to compare the values of $(\Delta a/a_p)_d$, $(\Delta c/c_p)_d$ and $\Delta \epsilon(v)$ obtained from different equations, no attempt was made to simulate the errors measurement. The a_{p+d} and c_{p+d} values were calculated from the d_{p+d} values by the method of least squares. The $(\Delta a/a_p)_d$ and $(\Delta c/c_p)_d$ were calculated using Eqs. (25a) and (25b), respectively; the values at 1 atm for a_p and c_p are relevant in these calculations. These values along with those calculated using Eqs. (27) and (28) are given in Table I. It is seen that in the case of rhenium which exhibits moderate elastic anisotropy, the estimates from Eqs. (27) and (28) agree well with those obtained from the least squares fit. In the case of cadmium (with large elastic anisotropy), the estimates of $(\Delta a/a_p)_d$ and $(\Delta c/c_p)_d$ ob-

TABLE II. The R values with $\alpha=0.5$ for a few elements. Only reflection with intensity ≥ 5 are considered [intensity of (101) is taken as 100].

(hkl)	Cd	Co	Fe	Mg	Re	Ti	Zn	Zr
100	0.862	1.000	1.010	0.988	0.979	1.054	11.903	0.91
002	1.311	0.770	0.923	0.919	0.853	0.871	1.342	0.85
101	11.1171	1.037	1.018	1.015	1.028	1.029	0.852	1.02
112	0.995	1.016	0.997	1.014	1.027	0.969	0.962	1.02
110	0.862	1.000	1.010	0.988	0.979	1.054	0.903	0.97
103	1.117	0.959	0.975	0.991	0.987	0.043	1.111	0.96
112	0.883	1.040	1.013	1.018	1.034	1.022	0.855	1.03
201	0.859	1.016	1.012	0.999	0.999	1.047	0.880	0.99
211	0.860	1.010	1.011	0.995	1.0491	1.050	0.889	1.08
114	1.039	0.999	0.990	1.007	1.016	0.968	1.015	1.01
203	0.923	1.036	1.008	1.020	1.037	1.005	0.884	1.03

tained from Eq. (27) agree well with the corresponding values obtained from the least squares fit. Equations (28) and (30), which are based on IET, are not expected to be valid for the case of large elastic anisotropy. It is interesting to note, however, that the $\Delta \epsilon(v)$ calculated using the results of Eq. (30) agrees very well with the value, obtained by the least squares fit. The reason for this agreement is discussed in the next section.

D. AET versus IET

Equation (23) can be derived¹¹ also by assuming that the bulk specimen is elastically isotropic (as is the case of polycrystalline specimen containing randomly oriented crystallites) and using IET to calculate the strain produced by the deviatoric stress component d_{ij} . As discussed in an earlier article,¹² this strain corresponds to the strain in the bulk specimen, and in general, differs from the lattice strain $\Delta \epsilon(hkl)$. This distinction vanishes only if the crystallites constituting the specimen are elastically isotropic. Because of their simplicity, the equations derived by IET are often used to interpret the experimental data. A comparison of the strains calculated using AET and IET gives an idea of the errors introduced when equations based on IET are used for a material containing crystallites which are elastically anisotropic. Such a comparison is provided by the ratio R ,

$$R = \Delta \epsilon(hkl)/\Delta \epsilon_{\text{iso}} = 2G/[G_R + G_V]. \tag{31}$$

The R values for eight elemental solids crystallizing in a hexagonal system are listed in Table II for various (hkl) values. The elastic compliances¹⁶ and lattice parameters at 1 atm have been used in the calculations. For a given element R can be less or more than unity. This means that depending on (hkl) , the strain calculated using IET can be larger or smaller than the strain calculated using AET. Thus, when $\Delta \epsilon(v)$ is calculated by AET using a number of reflections, the differences between AET and IET tend to average out and as shown in the previous section, $\Delta \epsilon(v)$ calculated by IET agrees very well with the actual value even for the materials showing large elastic anisotropy. Further, for each element listed in Table II, the effect of anisotropy is maximum for (001)-type reflections. However, because of preferred orientation that develops during pressurization, (001)-type re-

FIG. 2. A typical p - v relation for a solid. (a) The volume strain $(v_p - v_0)/v_0$ vs pressure (σ_p) curve under a hydrostatic condition. (b) The volume strain $(v_{p+d} - v_0)/v_0$ vs pressure (σ_p) curve under a nonhydrostatic condition. The offset between (a) and (b) is exaggerated for clarity. K_0 is the bulk modulus at 1 atm.

Rections are often not observed. The anisotropy effect for other reflections is found to be small. Thus, the assumption of isotropy in the case of the elements listed in Table II does not introduce appreciable error.

E. Estimation of USC

The estimation of $USC(t)$ from the measurement of the d spacings under high pressure is of interest, as t characterizes the nonhydrostatic pressure condition and is related to the shear strength of the specimen material [Eq. (2)]. In this section a method of analyzing the x-ray diffraction data to derive t is discussed. This method combines the pressure-volume (p - v) relations measured under hydrostatic and nonhydrostatic pressure conditions. A typical p - v relation is shown in Fig. 2. The p - v curve under nonhydrostatic pressure ($\sigma_p + d_{ij}$) gives, at each pressure σ_p , a volume strain which is smaller than the corresponding volume strain under hydrostatic pressure σ_p . This is because $\Delta\tilde{\epsilon}(v)$, the contribution to the volume strain from d_{ij} , is positive for $\cos\psi \leq 1/\sqrt{3}$ while $\epsilon_p(v)$ is negative. It is to be noted that for the commonly used diffraction geometries for measuring the p - v relation, $\cos\psi \leq 1/\sqrt{3}$. If the ruby fluorescence technique is used to measure the pressure under a nonhydrostatic condition, then the measured pressure corresponds¹⁷ to σ_p . The pressure estimated by mixing a material (pressure marker) of known p - v relation with the specimen and measuring the volume strain, corresponds to σ_p only if the shear strength of the marker material is low as compared with that of the specimen material. However, if the shear strengths of the marker and specimen materials are comparable, then the estimated pressure is not simply related to σ_p . Assuming that the pressure measured in the experiments under the nonhydrostatic pressure conditions is σ_p , the difference between the volume strains,

$\Delta\tilde{\epsilon}(v)$, under nonhydrostatic and hydrostatic pressure conditions is given by Eq. (21). On combining Eqs. (21), (27a), (27b), and (29) we get

$$t = -\frac{3\Delta\tilde{\epsilon}(v)}{(1 - 3\langle\cos^2\psi\rangle)[1 + \epsilon_p(v)]} \times \left[\frac{2}{\langle 2G \rangle_{hkl}} + \frac{1}{\langle 2G \rangle_{00l}} \right]^{-1}, \quad (32)$$

$$t = -\frac{\Delta\tilde{\epsilon}(v)(3K)}{(1 - 3\langle\cos^2\psi\rangle)[1 + \epsilon_p(v)]} \left(\frac{1 - 2\nu}{1 + \nu} \right). \quad (33)$$

It may be noted that the elastic constants in Eqs. (32) and (33) are at a pressure σ_p . At a given pressure, the $\Delta\tilde{\epsilon}(v)$ can be obtained from the strain offset between the p - v relations under nonhydrostatic and hydrostatic pressure conditions. Often, it is not possible to measure the p - v relation under a hydrostatic condition in the megabar pressure range. In such cases, the p - v relation under the hydrostatic pressure condition can be computed using high precision measurements of the bulk modulus and its pressure derivative, and a suitable theoretical equation of state.²⁰ The use of Eq. (32) requires the elastic compliances at a pressure σ_p , which can be obtained if the elastic compliances, their pressure derivatives, and a suitable method of extrapolating these to high pressure are available. However, Eq. (33) derived under the condition of elastic isotropy requires K and ν at σ_p . K at high pressure can be obtained from the value of K and its pressure derivative at 1 atm, and a theoretical equation of state. The pressure dependence of ν is often small and a linear extrapolation to high pressure is adequate in most cases. As the assumption of elastic isotropy in a hexagonal system does not introduce appreciable error, Eq. (33) can be used conveniently in calculating t from measured $\Delta\tilde{\epsilon}(v)$.

The SWEATBAK geometry permits the recording of the complete diffraction ring on a flat film placed normal to the incident x-ray beam. The strains $\epsilon_{\theta}(hkl)$ and $\epsilon_{\perp}(hkl)$ can be calculated using Eq. (16) and the diffraction ring diameters measured parallel and perpendicular to the load axis, respectively. Using Eqs. (16) and (23) we get the following relation for the elastically isotropic case:

$$t = \frac{3K[\epsilon_{\theta}(hkl) - \epsilon_{\perp}(hkl)]}{[1 + \epsilon_p(hkl)]\cos^2\theta} \left(\frac{1 - 2\nu}{1 + \nu} \right). \quad (34)$$

F. Effect of preferred orientation

A completely random orientation of the crystallites in the specimen has been assumed in the present analysis such that $\langle\cos\varphi\rangle = \langle\sin\varphi\rangle = 0$ and $\langle\cos^2\varphi\rangle = \langle\sin^2\varphi\rangle = 1/2$. However, specimens of hexagonal close packed metals upon compression between the anvils are known to exhibit preferred ori-

entation (texture).²⁰ In such cases, the average values of the trigonometric functions will have to be evaluated using expressions given earlier.¹ This will require complete knowledge of the crystallite orientation distribution function in the region of the specimen illuminated by the x-ray beam during the high pressure experiments.

V. CONCLUSIONS

General expressions have been derived for the lattice strains in the specimen belonging to the hexagonal system compressed nonhydrostatically in an opposed anvil setup. The expressions for the various diffraction geometries used in high pressure work emerge as special cases of these equations. The use of these equations in practice to analyze the x-ray diffraction data requires knowledge of the elastic compliances at high pressures. Assumption of elastic isotropy of the crystallites comprising the specimen introduces considerable simplification in the equations. The strains calculated by AET and IET for any given (*hkl*) are found to differ by less than 15% for most elements in hexagonal system. Even for highly anisotropic materials such as cadmium, cobalt, and zinc, a large anisotropy effect is observed for only (001)-type reflections. The equations derived using IET can be used to analyze the diffraction data from hexagonal systems without introducing appreciable error.

¹A. K. Singh, J. Appl. Phys. **73**, 4278 (1993).
²A. K. Singh, I. Appl. Phys. **74**, 5920 (1993).
³J. S. Weaver, T. Takahashi, and W. A. Bassett, Eos Trans. Am. Geophys. Union **53**, 511 (1972).
⁴G. L. Kinsland and W. A. Bassett, Rev. Sci. Instrum. **41**, 130 (1976).
⁵J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, London, UK, 1960).
⁶C.-M. Sung, C. Goetze, and H. K. Mao, Rev. Sci. Instrum. **48**, 1386 (1977).
⁷H. Kimura, D. G. Ast, and W. A. Bassett, J. Appl. Phys. **53**, 3253 (1982).
⁸C. Mead and R. Jeanloz, J. Geophys. Res. **93**, 3261 (1991).
⁹A. Reuss, Z. Angew. Math. Mech. **9**, 49 (1929).
¹⁰W. Voigt, *Lehrbuch der Kristallphysik* (Teubner, Leipzig, 1928).
¹¹P. D. Evenschor, W. Frolich, and V. Hauk, Z. Metallk. **62**, 38 (1971).
¹²E. Kroner, Z. Phys. **151**, 504 (1958).
¹³P. D. Evenschor and V. Hauk, Z. Metallk. **63**, 798 (1972).
¹⁴R. Hill, Proc. Phys. Soc. (London) **A 65**, 349 (1952).
¹⁵A. L. Ruoff, H. Luo, H. Xia, and Y. K. Vohra, High Press. Res. **6**, 183 (1991).
¹⁶G. Simmons and H. Wang, *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook* (MIT, Cambridge, MA, 1971).
¹⁷It may be noted that under a nonhydrostatic condition, the pressure estimated from the shifts of the R lines depends slightly on the crystallographic orientation of the ruby chip with respect to the *x*₁ axes (Ref. 17). The pressure determined using the *R*₂ line is a better indicator of σ_p , as the response of the *R*₂ line to stress is less anisotropic (Refs. 17 and 18). However, the R lines are often not well resolved at high nonhydrostatic pressures.
¹⁸S. M. Sharma and Y. M. Gupta, in *Recent Trends in High Pressure Research*, edited by A. K. Singh (Oxford and IBH, New Delhi, 1992), p. 7.
¹⁹Y. M. Gupta and X. A. Shen, Appl. Phys. Lett. **58**, 583 (1991).
²⁰R. Jeanloz, B. K. Godwal, and C. Mcade, Nature **349**, 687 (1991).