The Biaxial Modulus of Single Crystal Cubic Thin Films under an Equibiaxial Strain

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Abstract

Formulae for the biaxial moduli and their principal values for (*hkl*) surface orientations of single crystal cubic thin films subjected to a state of equibiaxial strain when bonded to an isotropic substrate or cubic substrate with which it has a cube-cube orientation relationship are given. The assumption is made in this analysis that the single crystal film is thin enough that the traction-free surface leads to zero shear stresses throughout the film in suitably chosen coordinate systems. Expressions for the shear strains and the out-of-plane normal strain for (*hkl*) orientations are also given. It is shown that the stationary points of the biaxial modulus always lie on {*hhl*} orientations. Formulae for these stationary points are derived. The assumption of zero shear stresses throughout the film in suitably chosen coordinate systems produces values of the principal biaxial moduli that are in general different from those obtained in prior work where the assumption of zero shear strains throughout the film in suitably chosen coordinate systems was made.

Keywords: Anisotropy; Biaxial moduli; Cubic crystals; Elasticity; Thin films

1. Introduction

A state of equibiaxial strain is developed in thin films during or after the deposition process [1,2]. The stresses produced in the film/substrate due to the biaxial state of strain depend upon their biaxial moduli. These stresses can lead to curvature and delamination of the film [1,2]. Further information on the biaxial modulus of films and coatings can be found in [3] and references therein. For many practical applications, the film and the substrate are both polycrystalline. Random polycrystals can be assumed to be isotropic and the average elastic constants can be used for calculations. Textured or single crystalline films/substrates are also of importance and low index orientations such as (001), (111) and (110) are commonly used. Films/substrates with high index orientations - (*hhl*) or (*hkl*) - offer different combinations of physical properties [4–9] which cannot be obtained from the standard orientations. Single crystal silicon wafers with surface orientations such as (310, (511), (531) and (731) are sold commercially as substrates [10,11]. For such ‘exotic’ orientations, and even for the more common, and more conventional, (001), (111) and (110) substrate orientations, the anisotropy of the elastic properties needs to be considered in the calculation of residual stresses from curvature measurements [12] and in the design of microelectromechanical systems (MEMS) [13]. The biaxial modulus when either the film or the substrate is an (*hkl*) oriented cubic single crystal was derived and analyzed by Knowles [3], assuming that the shear strains were zero in suitably chosen coordinate systems. If the film is assumed to be thin, the shear stresses and tensile stresses acting normal to the film can also be considered zero throughout the film since the normal stresses on the free surfaces are zero. In such a situation, shear strains will exist for all (*hkl*) orientations other than {001}, {111} and {110} [14] and the biaxial modulus is also expected to be different from that under the assumption of zero shear strains made in [3]. The main objective of the current study is to analyze the expression for the biaxial modulus in cubic thin films, assuming zero stresses normal to the film plane.

The present study is organized as follows. The direction cosine matrix for the transformation from the crystal coordinate system to the film coordinate system and equations for the stresses and strains, with the assumptions of zero normal stresses and equibiaxial strain within the film plane, are given in Section 2. The expressions for the biaxial moduli, principal biaxial moduli and the corresponding axes for a (*hkl*) cubic plane are established in Section 3. Calculations of the extreme values of the biaxial moduli are shown in Section 4. The normal strain along the thickness direction and the shear strains that result from the assumptions of equibiaxial strain and zero normal stresses are given in Section 5. The transition of the biaxial modulus from a shear stress free assumption to a shear strain free assumption is discussed in

Section 6. The results of the current study are further discussed in Section 7 and the conclusions are given in Section 8.

2. Stresses and Strains in Thin Films under Equibiaxial Strains

For linear elastic solids, Hooke's law relates the strains (ε_i) and stresses (σ_i) through [15,16]

$$\begin{aligned} \sigma_i &= c_{ij}\varepsilon_j \\ \varepsilon_i &= s_{ij}\sigma_j \end{aligned} \tag{1}$$

where *i* and *j* take all the values from 1–3 and the sum is taken over repeated indices. The stiffness and compliance constants are denoted by c_{ij} and s_{ij} respectively. The contracted Voigt notation [15,16] is used for the stiffness and compliance constants, and for the stresses and strains.

A right-handed orthonormal system, *X*, is defined such that the x_3^X axis is along the normal to the film plane and the x_1^X axis is along the meridional tangent. The meridional tangent to the plane (*hkl*) is the direction of intersection of (*hkl*) and the meridional plane (i.e., the plane containing the directions [*hkl*] and [001]). Another right-handed orthonormal system, *F*, is defined by rotating the *X* frame about the x_3^X axis by an angle ψ . By varying ψ from $0° - 360°$, the stresses, strains, and elastic properties along each of the directions within the film plane can be calculated by transforming them to the *F* frame. The unit normal to the film plane normal can be expressed in terms of the azimuth (θ) and elevation (ϕ) angles with respect to the crystal coordinate system. θ is the angle between x_1 and the projection of the film plane normal on the $x_1 - x_2$ plane, and ϕ is the angle between the film plane normal and the x_3 axis. The direction cosines (n_1, n_2, n_3) of a plane defined by its normal (θ, ϕ) are

$$\begin{aligned} n_1 &= \cos\theta\sin\phi \\ n_2 &= \sin\theta\sin\phi \\ n_3 &= \cos\phi \end{aligned} \tag{2}$$

For all values of θ, $\phi = 0°$ corresponds to the (001) plane. For all the other cubic planes, the plane normal (θ,ϕ) can be obtained from the Miller indices (*hkl*) as

$$\begin{aligned} \theta &= \tan^{-1}\left(\frac{k}{h}\right) \\ \phi &= \cos^{-1}\left(\frac{l}{\sqrt{h^2+k^2+l^2}}\right) \end{aligned} \tag{3}$$

The assumption that the film is thin implies zero normal stresses which gives

$$\sigma_3^F = \sigma_4^F = \sigma_5^F = 0 \tag{4}$$

Under a state of equibiaxial strain, $\varepsilon_1^F = \varepsilon_2^F = \varepsilon_{||}$. If the strain state is equibiaxial throughout the film plane, $\varepsilon_6^F = 0$. For the most general symmetry of the film plane, Hooke's law can be written in the form

$$\begin{pmatrix} \sigma_1^F \\ \sigma_2^F \\ 0 \\ 0 \\ 0 \\ \sigma_6^F \end{pmatrix} = \begin{pmatrix} c_{11}^F & c_{12}^F & c_{13}^F & c_{14}^F & c_{15}^F & c_{16}^F \\ c_{12}^F & c_{22}^F & c_{23}^F & c_{24}^F & c_{25}^F & c_{26}^F \\ c_{13}^F & c_{23}^F & c_{33}^F & c_{34}^F & c_{35}^F & c_{36}^F \\ c_{14}^F & c_{24}^F & c_{34}^F & c_{44}^F & c_{45}^F & c_{46}^F \\ c_{15}^F & c_{25}^F & c_{35}^F & c_{45}^F & c_{55}^F & c_{56}^F \\ c_{16}^F & c_{26}^F & c_{36}^F & c_{46}^F & c_{56}^F & c_{66}^F \end{pmatrix} \begin{pmatrix} \varepsilon_{||} \\ \varepsilon_{||} \\ \varepsilon_3^F \\ \varepsilon_4^F \\ \varepsilon_5^F \\ 0 \end{pmatrix}. \tag{5}$$

The direction cosine matrix for the transformation from the crystal coordinate system to the *X* coordinate system is

$$\left[a^{CX}\right] = \begin{pmatrix} \cos\theta\cos\phi & \sin\theta\cos\phi & -\sin\phi \\ -\sin\theta & \cos\theta & 0 \\ \cos\theta\sin\phi & \sin\theta\sin\phi & \cos\phi \end{pmatrix} \tag{6}$$

If the x_1^X and x_2^X axes are rotated within the film plane by an angle ψ, the direction cosine matrix for the transformation from the *X* frame to the *F* frame is

$$[a^{XF}] = \begin{pmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{7}$$

The direction cosine matrix for the overall transformation from the crystal frame to the *F* frame, given by the product of the two matrices, is

$$[a]=\left[a^{XF}\right]\left[a^{CF}\right]$$
$$=\begin{pmatrix} -\sin\theta\sin\psi+\cos\theta\cos\phi\cos\psi & \cos\theta\sin\psi+\sin\theta\cos\phi\cos\psi & -\sin\phi\cos\psi \\ -\sin\theta\cos\psi-\cos\theta\cos\phi\sin\psi & \cos\theta\cos\psi-\sin\theta\cos\phi\sin\psi & \sin\phi\sin\psi \\ \cos\theta\sin\phi & \sin\theta\sin\phi & \cos\phi \end{pmatrix}. \tag{8}$$

This has also been described in Ref. [14]. The stiffness and compliance constants transform according to the rule for fourth-order tensors as

$$c_{ijkl}^{F}=a_{ip}a_{jq}a_{kr}a_{ls}c_{pqrs},\ s_{ijkl}^{F}=a_{ip}a_{jq}a_{kr}a_{ls}s_{pqrs} \tag{9}$$

The relationship between transformed stiffness and compliance constants described as fourth-order tensors and in the contracted Voigt notation can be found in Refs. [3] and [4].

3. Expression for the Biaxial Modulus and the Principal Biaxial Moduli

The biaxial modulus (*M*) along the direction x_1^F on the film plane (i.e., on the ($x_1^F-x_2^F$) plane) is given by

$$M=\frac{\sigma_1^F}{\varepsilon_1^F}=c_{11}^F+c_{12}^F+\frac{c_{13}^F\varepsilon_3^F+c_{14}^F\varepsilon_4^F+c_{15}^F\varepsilon_5^F}{\varepsilon_{\|}} \tag{10}$$

3.1 {*hkl*} Interface Orientations

Using Eqs. (8), (9) and (10), *M* on a general plane in cubic thin films can be expressed as

$$M_{\{hkl\}}=b_1+b_2\sin 2\psi+b_3\sin^2\psi \tag{11}$$

where

$$b_1=\frac{2c_{44}l_1\left(4c_{44}^2+52c_{44}l_2+5l_2^2-H\left(l_3+2\left(-4l_2\cos 2\phi+H\cos 4\phi\right)\sin^2 2\theta\right)\right)}{m_1-H\left(m_2\cos 4\phi+\cos 4\theta\left(m_3+m_4\cos 4\phi\right)+m_5\cos 2\phi\right)}, \tag{11.a}$$

$$b_2=\frac{-c_{44}l_1H\cos\phi\left(l_2-H\cos 2\phi\right)\sin 4\theta\sin^2\phi}{y_1\cos^6\phi+y_2\cos^4\phi\sin^2\phi+\left(y_3+y_4\right)\cos^2\phi\sin^4\phi+c_{44}\left(y_5+y_6\right)\sin^6\phi}, \tag{11.b}$$

$$b_3 = \frac{-2c_{44} l_1 H\left(z_1 + z_2 \cos 2\phi + 6H \cos 4\phi \sin^2 2\theta\right)\sin^2 \phi}{m_1 - H\left(m_2 \cos 4\phi + \cos 4\theta\left(m_3 + m_4 \cos 4\phi\right) + m_5 \cos 2\phi\right)}, \tag{11.c}$$

$$l_1 = c_{11} + 2c_{12}, \tag{11.d}$$

$$l_2 = c_{11} - c_{12}, \tag{11.e}$$

$$l_3 = \left(-5c_{11} + 5c_{12} + 2c_{44}\right)\cos 4\theta, \tag{11.f}$$

$$m_1 = 4\left(21c_{11} - 8c_{12}\right)c_{44}^2 + 4c_{44}^3 + \left(19c_{11} + 13c_{12}\right)c_{44} l_2 + l_1 l_2^2, \tag{11.g}$$

$$m_2 = -c_{11}^2 + 2c_{12}^2 - 9c_{12}c_{44} + 2c_{44}^2 - c_{11}\left(c_{12} + 13c_{44}\right), \tag{11.h}$$

$$m_3 = -c_{11}^2 - c_{11}c_{12} + 2c_{12}^2 - \left(5c_{11} + c_{12}\right)c_{44} + 2c_{44}^2, \tag{11.i}$$

$$m_4 = c_{11}^2 + c_{11}c_{12} - 2c_{12}^2 - 3c_{11}c_{44} - 7c_{12}c_{44} - 2c_{44}^2, \tag{11.j}$$

$$m_5 = 2\left(m_6 - H\left(c_{44} + l_1\right)\cos 4\phi\right)\sin^2 2\theta, \tag{11.k}$$

$$m_6 = -c_{11}^2 + 2c_{12}^2 - 3c_{12}c_{44} + 2c_{44}^2 - c_{11}\left(c_{12} + 7c_{44}\right) \tag{11.l}$$

and

$$H = 2c_{44} + c_{12} - c_{11} \tag{11.m}$$

is the anisotropy parameter defined by Hirth and Lothe [17].

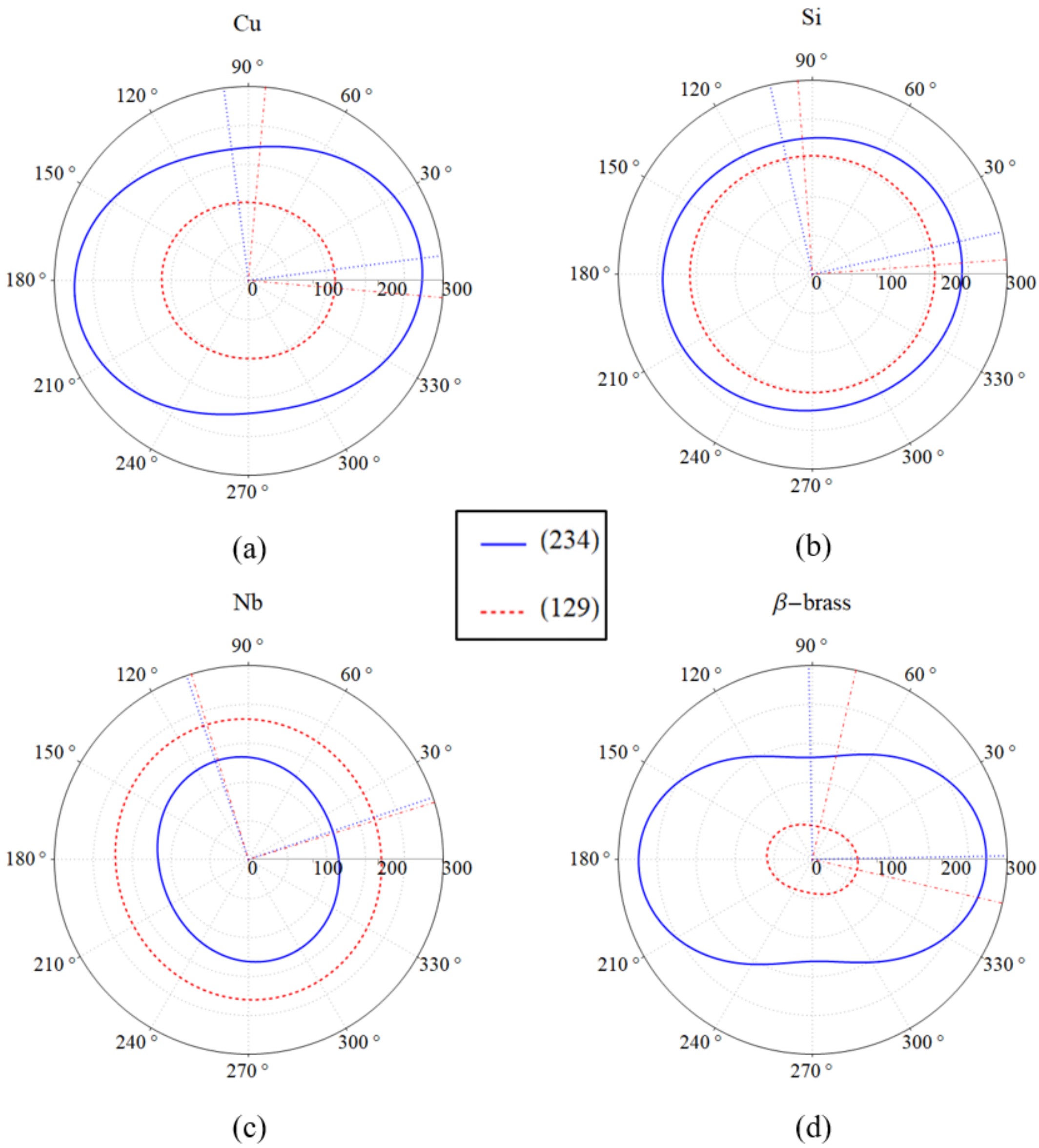

Figure 1 The biaxial modulus on the (234) and (129) planes in (a) Cu, (b) Si, (c) Nb and (d) β-brass. The variations of M (in GPa) with the angle ψ from the meridional tangent are shown. The principal stress axes on (234) and (129) are marked with blue dotted lines and red dot-dashed lines respectively.

Along the principal stress directions within the film plane, $\sigma_6^F = 0$. The principal biaxial moduli are also the extrema of $M_{\{hkl\}}$. The orientations of the principal stress axes are obtained by solving either

$$\sigma_6^F = \left(c_{16}^F + c_{26}^F\right)\varepsilon_{\|} + c_{36}^F\varepsilon_3^F + c_{46}^F\varepsilon_4^F + c_{56}^F\varepsilon_5^F = 0 \tag{12}$$

Table 1 The principal stress axes and the corresponding principal biaxial moduli for the (234) and (129) planes in Cu, Si, Nb and β-brass

	ψ_1	M_1 (GPa)	η_1	ψ_2	M_2 (GPa)	η_2
(234)						
Cu	7.30°	269	$[0.3030\ 0.6835\ \overline{0.6641}]$	97.30	204	$[\overline{0.8777}\ 0.4717\ 0.0851]$
Si	12.60°	232	$[0.2205\ 0.7242\ \overline{0.6534}]$	102.60°	209	$[\overline{0.9020}\ 0.4065\ 0.1461]$
Nb	18.58°	137	$[0.1254\ 0.7626\ \overline{0.6346}]$	108.58°	160	$[\overline{0.9200}\ 0.3288\ 0.2133]$
β-brass	1.06°	268	$[0.39652\ 0.6282\ \overline{0.6694}]$	91.06°	157	$[\overline{0.8396}\ 0.5431\ 0.0124]$
(129)						
	ψ_1	M_1 (GPa)	η_1	ψ_2	M_2 (GPa)	η_2
Cu	–5.05°	134	$[0.5111\ 0.8253\ \overline{0.2402}]$	84.95°	121	$[\overline{0.8527}\ 0.5219\ \overline{0.0212}]$
Si	4.30°	189	$[0.3658\ 0.8991\ \overline{0.2404}]$	94.30°	183	$[\overline{0.9244}\ 0.3810\ 0.0181]$
Nb	17.07°	204	$[0.1523\ 0.9610\ \overline{0.2305}]$	107.07°	218	$[\overline{0.9824}\ 0.1727\ 0.0708]$
β-brass	–12.97°	70.8	$[0.6237\ 0.7455\ \overline{0.2350}]$	77.03°	51.3	$[\overline{0.7742}\ 0.6306\ \overline{0.0541}]$

or equivalently

$$\frac{\partial M_{\{hkl\}}}{\partial \psi} = 0 \tag{13}$$

which gives

$$\psi_1 = -\frac{1}{2}\tan^{-1}\left(2\frac{b_2}{b_3}\right)$$
$$= \frac{1}{2}\tan^{-1}\left(\frac{\sin 4\theta\cos\phi\left(c_{44}\cos 2\phi-(c_{11}-c_{12})\cos^2\phi\right)}{4c_{44}\sin^2\theta\cos^2\theta(3\cos^4\phi-\cos^2\phi)+2(c_{11}-c_{12})\left(\cos^2\phi-\sin^2\theta\cos^2\theta(1+3\cos^4\phi)\right)}\right)$$

(14)

and

$$\psi_2 = \psi_1 + 90° \tag{15}$$

The corresponding principal biaxial moduli are

$$M_1 = b_1 - \frac{b_3}{2}\left(-1+\sqrt{1+\frac{4b_2^2}{b_3^2}}\right) \tag{16}$$

$$M_2 = b_1 + \frac{b_3}{2}\left(1+\sqrt{1+\frac{4b_2^2}{b_3^2}}\right) \tag{17}$$

It is to be noted that both M_1 and M_2 are discontinuous if $b_2 \neq 0$ and $b_3 = 0$ as the inverse tangent function (used in Eqs. (14) and (15)) is discontinuous. For planes of the type (*hhl*) and (0*kl*), $b_2 = 0$ and the principal biaxial moduli given by Eqs. (16) and (17) are continuous. Eqs. (16) and (17) reproduced in terms of the s_{ij} constants are shown in Appendix A.

The anisotropy of cubic materials is generally quantified using the Zener anisotropy ratio, *A*, defined as

$$A = \frac{2c_{44}}{c_{11}-c_{12}} \tag{18}$$

If $A=1$, the elastic properties are isotropic. The deviation from 1 indicates the extent of anisotropy.

For general (*hkl*) planes, we take (234) and (129) as examples. The variation of the biaxial moduli within the (234) and (129) planes of copper ($A=3.23$), silicon ($A=1.56$), niobium $(A = 0.50)$ and β-brass ($A = 8.50$) are shown in Figures 1a–d. The stiffness constants obtained by inverting the compliance constants reported in Ref. [18] were used for Cu, Si and Nb. For β-brass, the stiffness values were those from Table III of Ref. [19]. The principal stress axes and the corresponding principal biaxial moduli are shown in Table 1. It is observed that the biaxial moduli and their loci vary with the crystal and the orientation of the film plane under consideration. The choice of film plane has a lesser effect on the magnitudes of *M* in Si and Nb, whereas Cu and β-brass exhibit greater extents of anisotropy. As expected from Eq. (14), the orientations of the principal stress axes also vary with the material and the orientation of the film plane. The principal biaxial moduli are noticeably higher on the (234) plane than on the (129) plane for Cu, Si and β-brass, for each of which $A > 1$, while the reverse is true for Nb, for which $A < 1$.

3.2 {001} Interface Orientations

For the {001} orientations, $b_2 = b_3 = 0$ in Eq. (11) and the biaxial modulus is given by

$$M_{\{001\}} = c_{11} + c_{12} - \frac{2c_{12}^2}{c_{11}} = \frac{1}{s_{11} + s_{12}} \tag{19}$$

This result was previously derived in Ref. [12]. *M* is isotropic in the plane and its value does not depend on c_{44}. The biaxial moduli on the (001) plane of Cu, Si, Nb, and β-brass are shown in Fig. 2a. Nb has the highest $M_{\{001\}}$ (234 GPa), followed by Si (179 GPa), Cu (115 GPa) and β-brass (52 GPa).

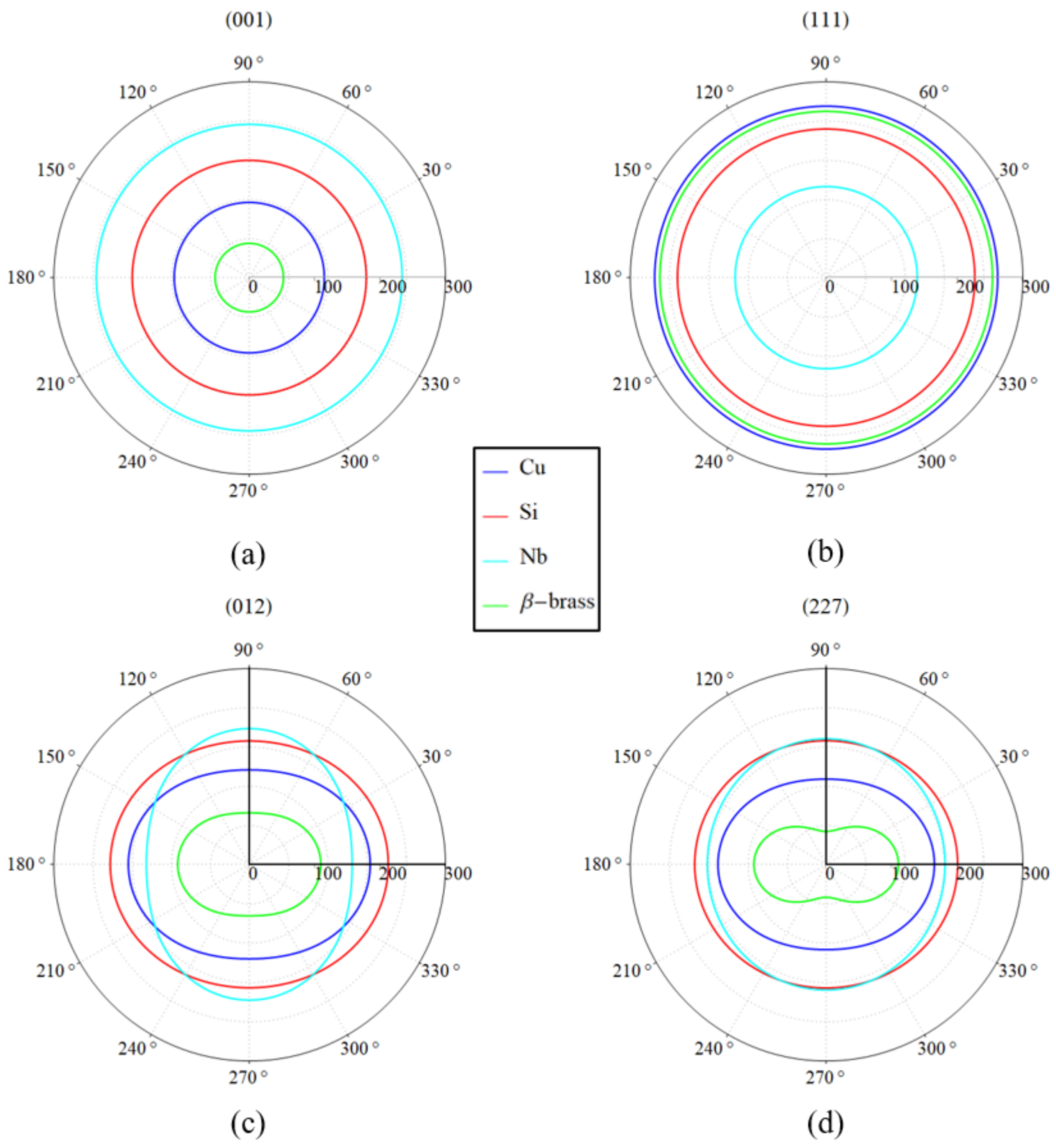

Figure 2 The variations of M with ψ on the (a) (001), (b) (111), (c) (012) and (d) (227) planes of Cu, Si, Nb and β-brass. The black lines at $\psi = 0°$ and $\psi = 90°$ correspond to the principal stress axes. The principal stress axes for (012) are $[02\bar{1}]$ and $[00\bar{1}]$. For the (227) plane, they are $[77\bar{4}]$ and $[\bar{1}10]$.

3.3 {111} Interface Orientations

Evaluating Eq. (11) using $\theta = 45°$ and $\phi = \cos^{-1}\left(1/\sqrt{3}\right)$ gives $b_2 = b_3 = 0$ which shows that the biaxial modulus is isotropic on the $\{111\}$ planes. The value of M, which was also previously reported in Ref. [12], is given by

$$M_{\{111\}} = \frac{6(c_{11} + 2c_{12})c_{44}}{c_{11} + 2c_{12} + 4c_{44}} = \frac{6}{4s_{11} + 8s_{12} + s_{44}} \tag{20}$$

The biaxial moduli on the (111) plane of Cu, Si, Nb, and *β*-brass are shown in Fig. 2b. The highest $M_{\{111\}}$ is observed on Cu (262 GPa), followed by *β*-brass (254 GPa), Si (227 GPa) and Nb (139 GPa).

3.4 {0*kl*} Interface Orientations

The normals to all the planes of the type (0*kl*) have their azimuthal angles $\theta = 90°$. When $\theta = 90°$, $b_2 = 0$ and

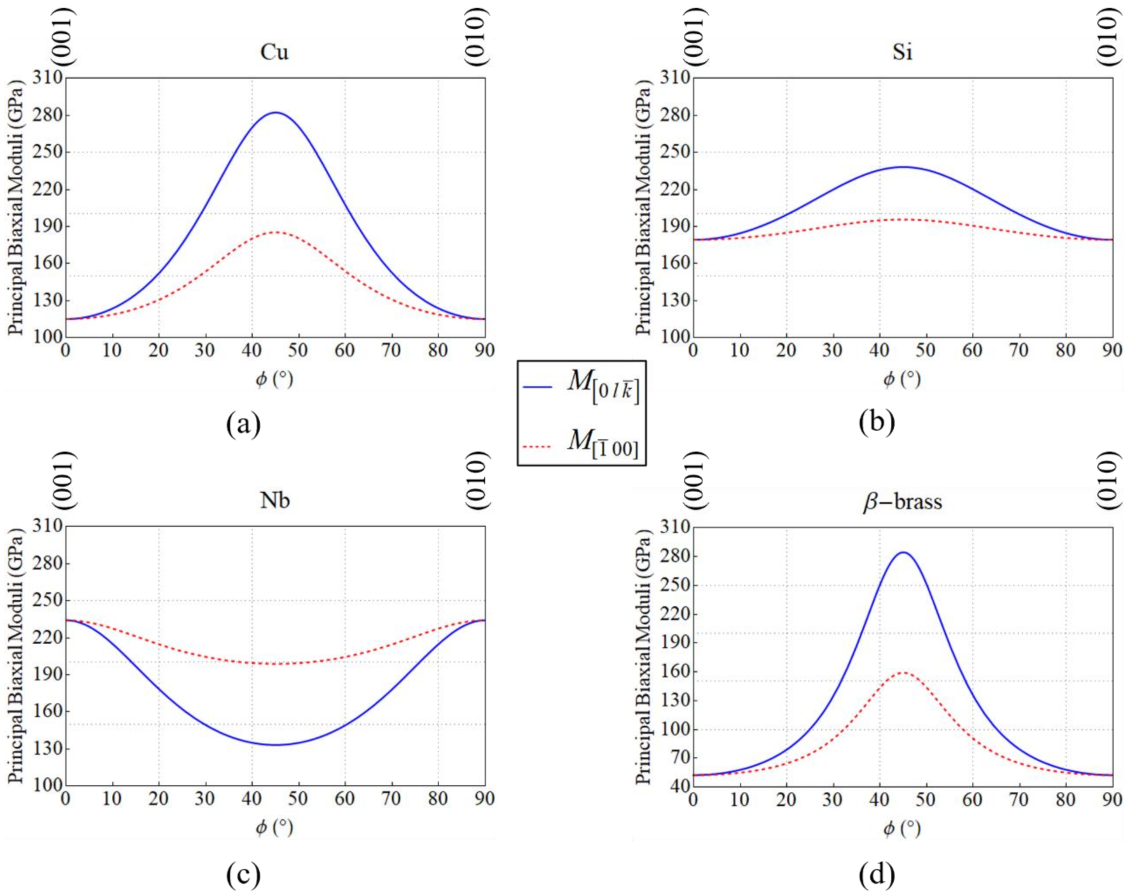

Figure 3 The variations of the principal biaxial moduli on planes of the type (0*kl*) in Cu, Si, Nb and *β*-brass as a function of the angle between the plane normal and [001].

$$b_1 = -\frac{8c_{44}(c_{11}-c_{12})(c_{11}+2c_{12})}{-c_{11}^2 - 6c_{11}c_{44} + c_{12}(c_{12}+2c_{44}) - H(c_{11}+c_{12})\cos 4\phi}$$
$$b_3 = \frac{2(c_{11}-c_{12})(c_{11}+2c_{12})H\sin^2 2\phi}{-c_{11}^2 - 6c_{11}c_{44} + c_{12}(c_{12}+2c_{44}) - H(c_{11}+c_{12})\cos 4\phi} \tag{21}$$

For such planes, Eq. (11) simplifies to

$$M_{\{0kl\}} = b_{11} + b_{13}\sin^2\psi \tag{22}$$

The other planes related to (0*kl*) by symmetry will also have the same value of *M*. The orientations of the principal axes obtained using Eqs. (14) and (15) are $\psi = 0°$ and $90°$ respectively. The corresponding principal stress directions for a plane of type (0*kl*) are $[0l\bar{k}]$ and $[\bar{1}00]$. The corresponding principal biaxial moduli, given by Eqs. (16) and (17), are

$$M_1 = M_{(0kl)[0l\bar{k}]} = b_1$$
$$M_2 = M_{(0kl)[\bar{1}00]} = b_1 + b_3 \tag{23}$$

The biaxial moduli on the (012) plane of Cu, Si, Nb, and β-brass are shown in Fig. 2c. As expected, the principal stress axes are along $\psi = 0°$ and $90°$. For Cu, Si and β-brass, $M_{(012)[02\bar{1}]}$ is greater than $M_{(012)[\bar{1}00]}$, while $M_{(012)[\bar{1}00]}$ is greater for Nb. $M_{(012)[02\bar{1}]}$ and $M_{(012)[\bar{1}00]}$ for Cu, Si, Nb and β-brass are 185 and 145 GPa, 213 and 189 GPa, 158 and 207 GPa, and 110 and 79 GPa respectively.

The principal biaxial moduli of Cu, Si, Nb and β-brass as a function of ϕ, the angle between the plane normal and [001] are shown in Figs. 3a–d. $\phi = 0°$, $45°$ and $90°$ correspond to the (001), (011) and (010) planes, respectively. Both the principal moduli show a similar change as ϕ is varied. The plots are symmetric around $\phi = 45°$ as (011) is a mirror plane. The maximum difference between the principal biaxial moduli is observed on (011) for all the four materials. The crests are observed at $45°$ for Cu, Si and β-brass (materials with $A > 1$), while Nb ($A < 1$) has a depression at $45°$. The difference between the principal biaxial moduli on the (011) and the (001) planes can be estimated using Eqs. (16), (17) and (19):

$$M_{(011)[01\bar{1}]} - M_{(001)} = \left(\frac{c_{11} + 2c_{12}}{c_{11}\left(c_{11} + c_{12} + 2c_{44}\right)} \right) c_{12} H$$
$$M_{(011)[\bar{1}00]} - M_{(001)} = \frac{\left(c_{11} + c_{12}\right)\left(c_{11} + 2c_{12}\right)}{c_{11}\left(c_{11} + c_{12} + 2c_{44}\right)} H \tag{24}$$

The thermodynamic stability of cubic crystals [15] requires that $c_{44} > 0$, $c_{11} > |c_{12}|$, and $c_{11} + 2c_{12} > 0$. Therefore, the fractions enclosed in parentheses in both the equations are always positive. $M_{(011)[\bar{1}00]} - M_{(001)}$ will have the same sign as *H*. The sign of $M_{(011)[01\bar{1}]} - M_{(001)}$ depends on the sign of the product $c_{12}H$. For a vast majority of real cubic crystals, c_{12} is positive and hence the sign of the product depends on that of *H*. Based on the stiffness values reported in Ref. [18], the c_{12} of barium is –0.38 GPa and *H* is 12 GPa. Therefore, $M_{(001)}$ of Ba is greater than $M_{(011)[01\bar{1}]}$ but lower than $M_{(011)[\bar{1}00]}$. UBe_{13}, GeTe-SnTe with 20 mol% GeTe, $Sm_{1-x}Y_xS$ (x = 0.3, 0.25, 0.42 and 0.424) and SmB_6 are other cubic crystals with a negative c_{12}.

3.5 {*hhl*} Interface Orientations

For the planes of the type (*hhl*), $\theta = 45°$ and Eq. (11) is again of the form

$$M_{\{hhl\}} = b_1 + b_3 \sin^2 \psi \tag{25}$$

where

$$b_1 = -\frac{4c_{44}\left(c_{11} + 2c_{12}\right)\left(3c_{11} - 3c_{12} + 2c_{44} - H\cos 2\phi\right)}{\left(2c_{12} - 3c_{44}\right)\left(c_{12} + 2c_{44}\right) - c_{11}\left(c_{11} + c_{12} + 11c_{44}\right) - H\left(-4c_{44}\cos 2\phi + \left(c_{11} + 2c_{12} + c_{44}\right)\cos 4\phi\right)}$$
$$b_3 = \frac{4c_{44}H\left(c_{11} + 2c_{12}\right)\left(1 + 3\cos 2\phi\right)\sin^2\phi}{\left(2c_{12} - 3c_{44}\right)\left(c_{12} + 2c_{44}\right) - c_{11}\left(c_{11} + c_{12} + 11c_{44}\right) - H\left(-4c_{44}\cos 2\phi + \left(c_{11} + 2c_{12} + c_{44}\right)\cos 4\phi\right)} \tag{26}$$

As for {0*kl*} planes, the principal stress axes are along $\psi = 0°$ and $90°$. The corresponding principal biaxial moduli are

$$M_1 = M_{(hhl)[ll\overline{2h}]} = b_1$$
$$M_2 = M_{(hhl)[\bar{1}10]} = b_1 + b_3 \tag{27}$$

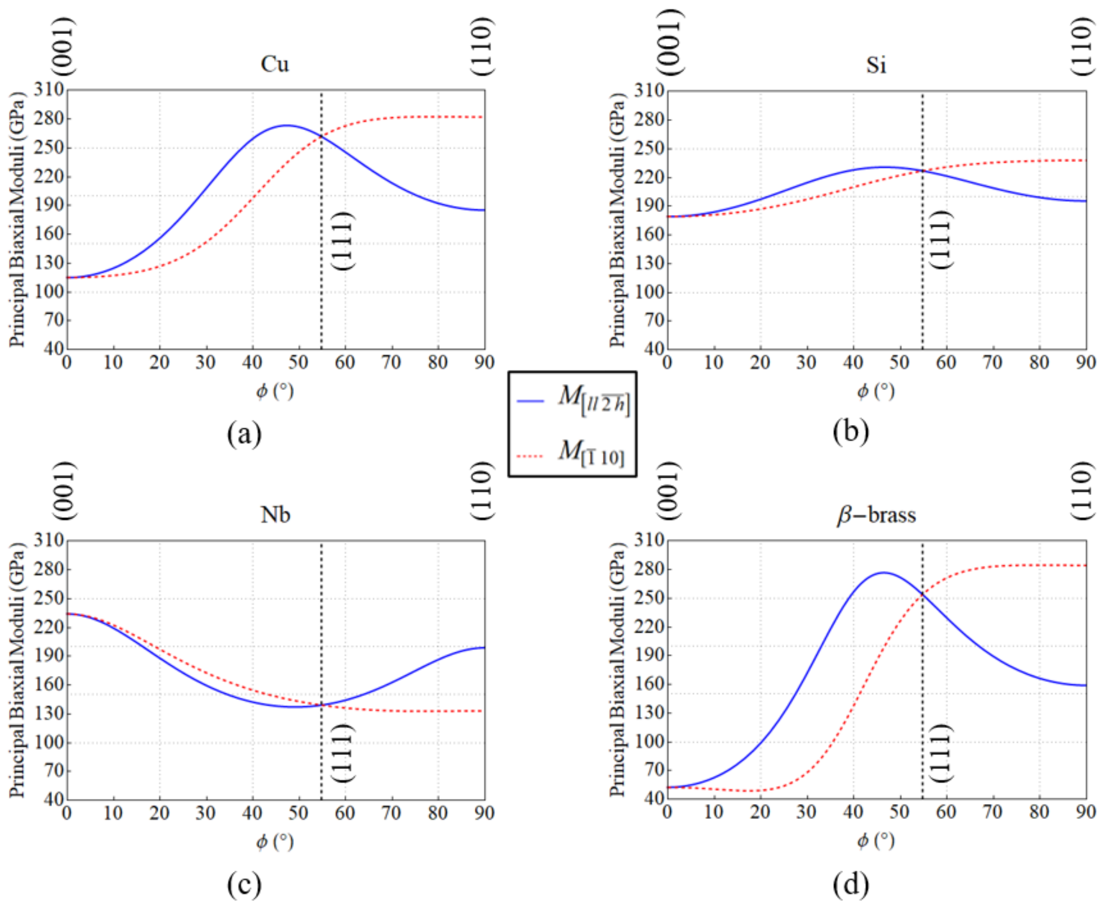

Figure 4 The variation of the principal biaxial moduli on planes of the type (*hhl*) in Cu, Si, Nb and *β*-brass as a function of the angle between the plane normal and [001].

The biaxial moduli on the (227) plane of Cu, Si, Nb, and *β*-brass are shown in Fig. 2d. The principal stress axes are along $\psi = 0°$ and $90°$. $M_{(227)[77\bar{4}]}$ and $M_{(227)[\bar{1}10]}$ for Cu, Si, Nb and *β*-brass are 165 and 130 GPa, 201 and 189 GPa, 182 and 192 GPa, and 110 and 50 GPa respectively.

The principal biaxial moduli of Cu, Si, Nb, and *β*-brass on (*hhl*) planes as a function of ϕ are shown in Figs. 4a-d. In all cubic materials, $M_{(hhl)[ll\bar{2}h]}$ and $M_{(hhl)[\bar{1}10]}$ coincide at $54.74°$ (i.e., $\cos^{-1}(1/\sqrt{3})$) . This corresponds to the (111) plane where *M* is isotropic.

It is shown in Appendix B that the global extrema of the biaxial modulus always lie on planes of the type $\{hhl\}$. Further analysis of the principal biaxial moduli on planes of the type $\{hhl\}$ is shown in Section 4.

4. Global Extrema of the Biaxial Modulus

The principal biaxial moduli (Eqs. (16) and (17)) give the extrema of the biaxial moduli on each plane. The stationary points of the principal biaxial moduli are examined to obtain the global extrema. The stationary points of *M* can be obtained by solving

$$\frac{\partial}{\partial\phi}\left(\frac{\partial M_1}{\partial\theta}\right)=0=\frac{\partial}{\partial\phi}\left(\frac{\partial M_2}{\partial\theta}\right) \tag{28}$$

In Appendix C, it is shown that the only stationary points of the type {0*kl*} are {001}, {011} and {010}. As these planes are also of the type {*hhl*} in cubic crystals, the stationary points on (*hhl*) planes alone are considered here.

For (*hhl*) planes, $\theta = 45°$, substituting this in Eq. (16) gives

$$M_1 = a\,\frac{b+8H\cos 2\phi - 3H\cos 4\phi}{c-4c_{44}H\cos 2\phi + d\cos 4\phi} \tag{29}$$

where

$$a = -c_{44}(c_{11}+2c_{12}), \tag{29.a}$$

$$b = 11H - 32c_{44}, \tag{29.b}$$

$$c = c_{11}^2 - (2c_{12}-3c_{44})(c_{12}+2c_{44}) + c_{11}(c_{12}+11c_{44}), \tag{29.c}$$

and

$$d = (c_{11}+2c_{12}+c_{44})H. \tag{29.d}$$

The stationary values obtained by solving $dM_1 / d\phi = 0$ are

1. $\phi = 0°$, the {001} planes,

2. $\phi = 90°$, the {110} planes, and

3. the solutions to the biquadratic equation

$$p + q\cos^2\phi + r\cos^4\phi = 0 \tag{30}$$

where

$$p = 64(c_{11} + 2c_{12})(c_{11} - 3c_{12} + 2c_{44})c_{44}^2 H, \tag{30.a}$$

$$q = 128(c_{11} + 2c_{12})(c_{11} + 5c_{12} - 2c_{44})c_{44}^2 H, \tag{30.b}$$

and

$$r = -64(c_{11} + 2c_{12})(2c_{11} + 4c_{12} - c_{44})c_{44} H^2. \tag{30.c}$$

Therefore, the solutions will be real when

$$0 \le \frac{-q \pm \sqrt{q^2 - 4pr}}{2r} \le 1. \tag{31}$$

The stationary points of M_1 (on planes other than {001} and {110}) will be on (*hhl*) planes inclined to the (001) plane by angles of

$$\begin{aligned} \phi_{11} &= \cos^{-1}\left(\sqrt{\frac{-q + \sqrt{q^2 - 4pr}}{2r}}\right) \\ \phi_{12} &= \cos^{-1}\left(\sqrt{\frac{-q - \sqrt{q^2 - 4pr}}{2r}}\right). \end{aligned} \tag{32}$$

Substituting $\theta = 45°$ in Eq. (17) gives

$$M_2 = g\,\frac{h - H\cos 2\phi}{c - 4c_{44}H\cos 2\phi + d\cos 4\phi} \tag{33}$$

where

$$g = -4a, \tag{33.a}$$

and

$$h = 8c_{44} - 3H. \tag{33.b}$$

The stationary values obtained by solving $dM_2 / d\phi = 0$ are

1. $\phi = 0°$, the {001} planes,

2. $\phi = 90°$, the {110} planes, and

3. the solutions to the biquadratic equation

$$u + v\cos^2\phi + w\cos^4\phi = 0 \tag{34}$$

where

$$u = -64(c_{11} + 2c_{12})(c_{11}^2 - 2c_{12}^2 + c_{12}c_{44} + 2c_{44}^2 + c_{11}(c_{12} + 3c_{44}))c_{44}H, \tag{34.a}$$

$$v = 128(c_{11} + 2c_{12})(c_{11} + 2c_{12} + c_{44})(4c_{44} - H)c_{44}H, \tag{34.b}$$

and

$$w = -64(c_{11} + 2c_{12})(c_{11} + 2c_{12} + c_{44})c_{44}H^2. \tag{34.c}$$

For the solutions to Eq. (34) to be real, they must satisfy both the inequalities

$$0 \le \frac{-v + \sqrt{v^2 - 4uw}}{2w} \le 1 \tag{35}$$

$$0 \le \frac{-v - \sqrt{v^2 - 4uw}}{2w} \le 1 \tag{36}$$

After simplification, it turns out that the necessary and sufficient conditions required to satisfy Eqs. (35) and (36) are $H \ge 0$ and $H \le 0$ respectively. Therefore, the principal biaxial modulus M_2 will always have one stationary point other than the ones on {001} and {110} at

$$\begin{aligned} \phi_{21} &= \cos^{-1}\left(\sqrt{\frac{-v + \sqrt{v^2 - 4uw}}{2w}}\right), \text{ if } H > 0 \\ \phi_{22} &= \cos^{-1}\left(\sqrt{\frac{-v - \sqrt{v^2 - 4uw}}{2w}}\right), \text{ if } H < 0 \end{aligned} \tag{37}$$

In short, the principal biaxial moduli of an anisotropic (with $H \neq 0$) cubic thin film will have stationary points on at least three distinct planes: {001}, {110} and {*hhl*} inclined to (001) by either ϕ_{21} or ϕ_{22} depending upon the sign of *H*. A maximum of two more planes with stationary points may be present based on the two conditions in Eq. (31). The global extrema are to be selected from the stationary points. The stationary points, global extrema and the corresponding orientations of a few cubic materials are shown in Table 2.

Table 2 Stationary points of the biaxial moduli in Cu, Si, Nb and Li. The global maxima are shown in bold, and the minima are underlined. The normals to the planes with the stationary points are of the form $(\theta = 45°, \phi_{ij})$, where ϕ_{ij} are given by Eqs. (32) and (37). The stiffness values were obtained by inverting the compliance constants reported in Ref. [18].

Material	**Cu**	**Si**	**Nb**	**Li**
$\boldsymbol{H}$ **(GPa)**	103	56	–56	17
$\boldsymbol{M_{\{001\}}}$ **(GPa)**	<u>115</u>	<u>179</u>	**234**	5.85
$\boldsymbol{M_{1\,\{110\}}}$ **(GPa)**	282	**238**	133	31.9
$\boldsymbol{M_{2\,\{110\}}}$ **(GPa)**	185	196	199	17.8
$\boldsymbol{M_1(\phi_{11})}$ **(GPa)**	**283**	-	-	**31.9**
$\boldsymbol{M_1(\phi_{12})}$ **(GPa)**	-	-	<u>133</u>	<u>5.36</u>
$\boldsymbol{M_2(\phi_{21})}$ **(GPa)**	274	231	-	31.0
$\boldsymbol{M_2(\phi_{22})}$ **(GPa)**	-	-	137	-
$\boldsymbol{\phi_{11}}$	78.47°	-	-	82.35°
$\boldsymbol{\phi_{12}}$	-	-	76.89°	18.08°
$\boldsymbol{\phi_{21}}$	47.30°	46.60°	-	46.16°
$\boldsymbol{\phi_{22}}$	-	-	49.10°	-

5. Expressions for the Strains ε_3^F, ε_4^F and ε_5^F

The third, fourth and fifth lines of Eq. (5) are solved to obtain ε_3^F, ε_4^F and ε_5^F. The out-of-plane strain is given by

$$\varepsilon_3^F = \frac{e_{31}}{e_3}\varepsilon_{||}, \tag{38}$$

where

$$\begin{aligned} e_{31} = \frac{1}{128}(-(H(\cos 4\theta(\cos 4\phi(-2c_{11}^2 - 2c_{11}c_{12} + 7c_{11}c_{44} + 4c_{12}^2 + 13c_{12}c_{44} - 2c_{44}^2) \\ +2c_{11}^2 + 2c_{11}c_{12} + c_{11}c_{44} - 4c_{12}^2 + 11c_{12}c_{44} + 2c_{44}^2) \\ +2\sin^2 2\theta \cos 2\phi(2c_{11}^2 + H\cos 4\phi(2c_{11} + 4c_{12} - c_{44}) + 2c_{11}c_{12} + 3c_{11}c_{44} - 4c_{12}^2 + 17c_{12}c_{44} + 2c_{44}^2) \\ +\cos 4\phi(2c_{11}^2 + 2c_{11}c_{12} + 9c_{11}c_{44} - 4c_{12}^2 + 35c_{12}c_{44} + 2c_{44}^2))) \\ +8c_{44}^2(4c_{11} - 17c_{12}) - c_{44}(c_{11} - c_{12})(13c_{11} + 51c_{12}) - 2(c_{11} - c_{12})^2(c_{11} + 2c_{12}) + 4c_{44}^3) \end{aligned} \tag{38.a}$$

and

$$\begin{aligned} e_3 = c_{11}c_{44}^2\cos^6\phi + c_{44}(c_{11}^2 + c_{11}c_{44} - c_{12}(c_{12} + 2c_{44}))\cos^4\phi\sin^2\phi \\ +\frac{1}{8}((c_{11} - c_{12})^2(c_{11} + 2c_{12}) + 6c_{11}(c_{11} - c_{12})c_{44} + 6(c_{11} - c_{12})c_{44}^2 + 4c_{44}^3 \\ +(c_{11}^2 + c_{11}c_{12} - 2(c_{12} + c_{44})^2)H\cos 4\theta)\cos^2\phi\sin^4\phi \\ +\frac{1}{8}c_{44}(c_{11}^2 + 6c_{11}c_{44} - c_{12}(c_{12} + 2c_{44}) + (c_{11} + c_{12})H\cos 4\theta)\sin^6\phi. \end{aligned} \tag{38.b}$$

Since both e_{31} and e_3 are independent of ψ, ε_3^F for a given film plane depends only on the magnitude of the equibiaxial strain, $\varepsilon_{||}$. For a state of equibiaxial strain on planes of the type (0*kl*) and (*hhl*) in Cu and Nb, the resulting ε_3^F (in terms of $\varepsilon_{||}$) are plotted against ϕ in Figs. 5a and b, respectively. The values of $\varepsilon_3^F/\varepsilon_{||}$ on (0*kl*) type planes are symmetric about (011) when the film plane is varied from (001) to (011). This is expected as (011) is a mirror plane. Cu has a peak while Nb has a depression at (011). For the (*hhl*) type planes, Cu has a peak at (111), whereas Nb has a depression. The stationary points for both Cu and Nb are at {001}, {111} and {110}. The maximum (most negative) values of $\varepsilon_3^F/\varepsilon_{||}$ for both Cu and Nb are approximately –1.45. However, the maximum for Cu is on {001}, and that for Nb is on {111}. The minimum (least negative) values for Cu and Nb are –0.74 on {111} and –1.07 on {001} respectively.

The shear strains ε_4^F and ε_5^F are

$$\varepsilon_4^F = \frac{e_1 \cos\psi + e_2 \sin\psi}{e_3} \varepsilon_{\|} \tag{39}$$

$$\varepsilon_5^F = \frac{e_1 \sin\psi - e_2 \cos\psi}{e_3} \varepsilon_{\|} \tag{40}$$

where

$$e_1 = \frac{H}{8}(c_{11} + 2c_{12})(c_{11} - c_{12} - H\cos 2\phi)\sin 4\theta \sin^3\phi, \tag{41}$$

and

$$e_2 = -\frac{H}{64}(c_{11} + 2c_{12})((8c_{44} + H + 3H\cos 4\phi)\sin^2 2\theta \sin 2\phi + (14c_{44} - H + (2c_{44} + H)\cos 4\theta)\sin 4\phi). \tag{42}$$

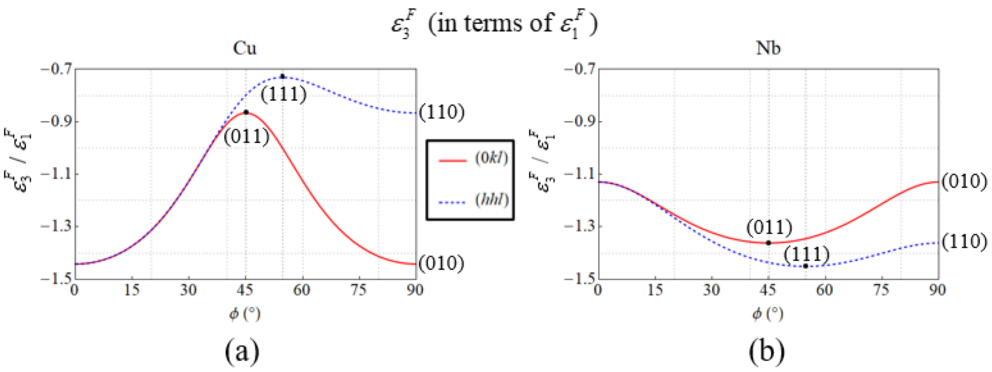

Figure 5 The out-of-plane normal strain ε_3^F (in terms of the in-plane equibiaxial strain ε_1^F) in (a) Cu and (b) Nb on planes of the type (*hhl*) and (0*kl*) plotted against the angle between the plane and (001).

The shear strains ε_4^F and ε_5^F are dependent on ψ. The strains ε_3^F, ε_4^F and ε_5^F (in units of $\varepsilon_{\|}$) calculated for different planes in Cu are shown in Figs. 6a–d. As expected, the normal strain ε_3^F is a constant within the plane, and the shear strains ε_4^F and ε_5^F vary sinusoidally with a phase difference of 90° between them. The shear strains have their extreme values along the principal stress directions on the $\{0kl\}$ and $\{hhl\}$ type planes. On a general (hkl) type plane, the orientations of the extrema depend upon the stiffness constants. The shear strains in Nb are lower than those in Cu on all the three planes considered here. The normal strains are higher for Nb on the (231) and (012) planes while they are approximately equal on the (227) plane.

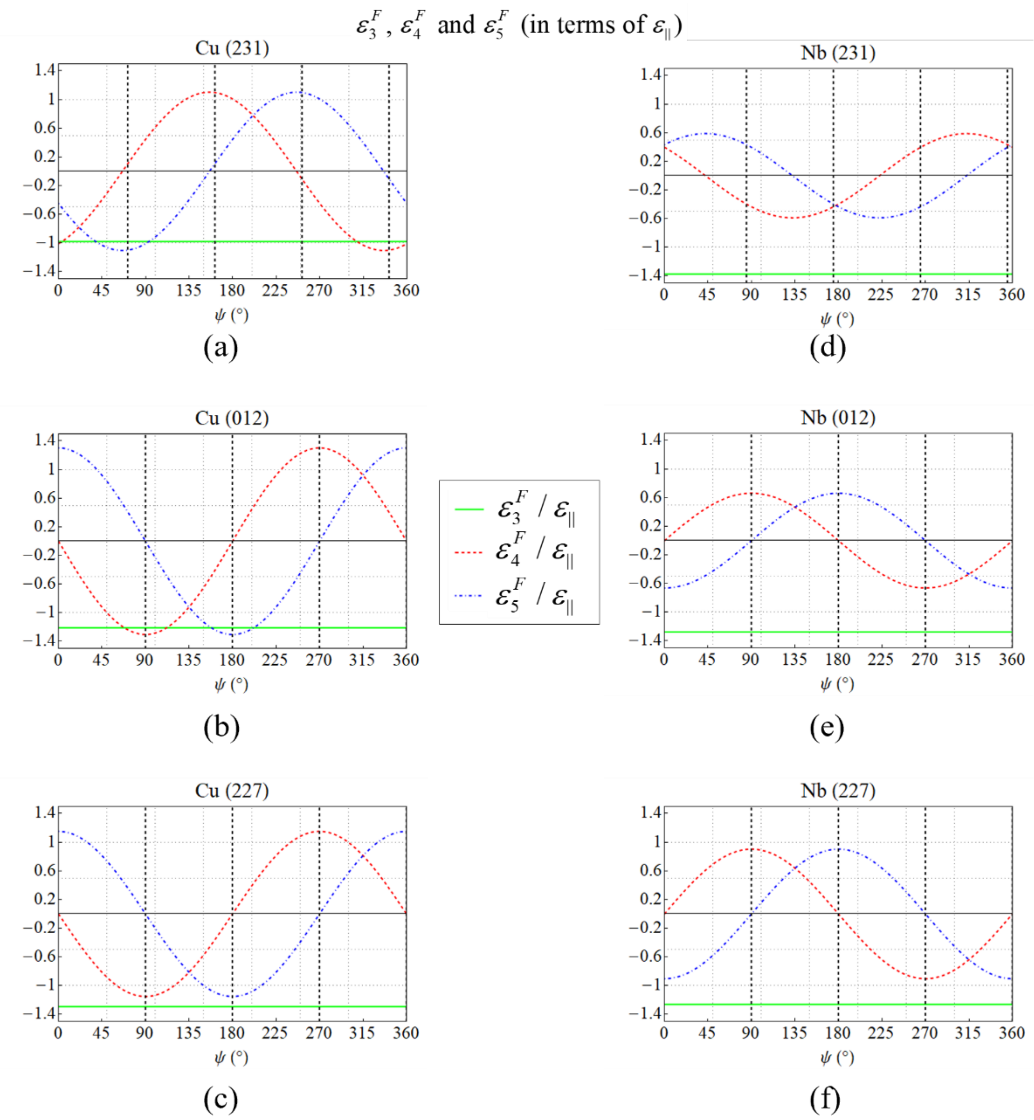

Figure 6 The variations of the strains ε_3^F, ε_4^F and ε_5^F per unit $\varepsilon_{||}$ within the: (231), (012) and (227) planes of (a–c) Cu, and (d–f) Nb. The principal stress axes are indicated with vertical dashed lines.

5.1 Planes without Shear Strains

Both the shear strains will vanish only when $e_1 = e_2 = 0$ in Eqs. (41) and (42). The following solutions are obtained:

1. $\{\theta = 0°, \phi = 0°, \pm 90°, 180°\}$ and $\{\theta = \pm 90°,\ \phi = \pm 90°\}$, which are the {100} planes.
2. $\{\theta = \pm 45°,\ \phi = \pm\cos^{-1}\left(1/\sqrt{3}\right)\}$, the {111} planes.
3. $\{\theta = \pm 45°,\ \phi = \pm 90°\}$, $\{\theta = 0°,\ \phi = \pm 45°\}$ and $\{\theta = \pm 90°,\ \phi = \pm 45°\}$. These are the {110} planes.

There are two more sets of solutions to $e_1 = e_2 = 0$ which are dependent on the c_{ij} values. However, the solutions do not have real values if the criteria for the thermodynamic stability of cubic crystals are satisfied. Therefore, under a state of equibiaxial strain in the film plane, only the {100}, {111} and {110} planes can have zero shear strains in cubic thin films.

6. Comparison of the Biaxial Moduli under the Assumptions of Zero Shear Strains and Zero Normal Stresses

The biaxial modulus (M_σ) subjected to an equibiaxial strain under the assumption of zero shear strains in the film was studied by Knowles [3]. M_σ is given by Eq. (5) of [3]:

$$M_\sigma = c_{11}^F + c_{12}^F - c_{13}^F\left(\frac{c_{13}^F + c_{23}^F}{c_{33}^F}\right). \tag{43}$$

Under such conditions, internal residual shear stresses are present on all planes other than {001}, {111} and {110}. In the current study, where it is assumed that the shear stresses normal to the film are zero, the same planes are found to have zero shear strains. Therefore, the expression for the biaxial modulus subjected to an equibiaxial strain using the thin-film assumption (zero shear stresses normal to the film plane) shown in Eq. (10) of the present study reduces to Eq. (5) of Ref. [3] for the {110}, {001} and {111} planes.

For planes other than {110}, {001} and {111}, it is important to assess the consequences of the initial assumptions of the states of stresses and strains in the film on the biaxial modulus. The principal biaxial moduli on the planes of type (0*kl*) and (*hhl*) subjected to equibiaxial strain are calculated by varying the boundary conditions from a shear stress-free state to a shear strain-free state. For (0*kl*) and (*hhl*) interfaces, we have the general boundary conditions

$$\begin{aligned} \varepsilon_1^F &= \varepsilon_2^F = \varepsilon_{\|} \\ \varepsilon_6^F &= 0 \\ \sigma_3^F &= 0 \\ \sigma_6^F &= 0 \end{aligned} \qquad (44)$$

and we can have either $\sigma_4^F = 0$ and $\sigma_5^F = 0$ for traction-free conditions or $\varepsilon_4^F = 0$ and $\varepsilon_5^F = 0$ for conditions where there are internal residual shear stresses.

For (0*kl*) interfaces, $\theta = 90°$ and since one of the principal stress axes is along $\psi = 90°$, we have, in general, the matrix equation

$$\begin{pmatrix} \sigma_1^F \\ \sigma_2^F \\ 0 \\ 0 \\ \sigma_5^F \\ 0 \end{pmatrix} = \begin{pmatrix} c_{11}^F & c_{12}^F & c_{13}^F & 0 & c_{15}^F & 0 \\ c_{12}^F & c_{22}^F & c_{23}^F & 0 & 0 & 0 \\ c_{13}^F & c_{23}^F & c_{33}^F & 0 & c_{35}^F & 0 \\ 0 & 0 & 0 & c_{44}^F & 0 & 0 \\ c_{15}^F & 0 & c_{35}^F & 0 & c_{55}^F & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66}^F \end{pmatrix} \begin{pmatrix} \varepsilon_{\|} \\ \varepsilon_{\|} \\ \varepsilon_3^F \\ 0 \\ \varepsilon_5^F \\ 0 \end{pmatrix} \qquad (45)$$

where terms calculated or required to be zero are shown.

For (*hhl*) interfaces, with $\theta = 45°$ and a principal stress axis along $\psi = 0°$, we have in general the matrix equation

$$\begin{pmatrix} \sigma_1^F \\ \sigma_2^F \\ 0 \\ 0 \\ \sigma_5^F \\ 0 \end{pmatrix} = \begin{pmatrix} c_{11}^F & c_{12}^F & c_{13}^F & 0 & c_{15}^F & 0 \\ c_{12}^F & c_{22}^F & c_{23}^F & 0 & c_{25}^F & 0 \\ c_{13}^F & c_{23}^F & c_{33}^F & 0 & c_{35}^F & 0 \\ 0 & 0 & 0 & c_{44}^F & 0 & c_{46}^F \\ c_{15}^F & c_{25}^F & c_{35}^F & 0 & c_{55}^F & 0 \\ 0 & 0 & 0 & c_{46}^F & 0 & c_{66}^F \end{pmatrix} \begin{pmatrix} \varepsilon_{\|} \\ \varepsilon_{\|} \\ \varepsilon_3^F \\ 0 \\ \varepsilon_5^F \\ 0 \end{pmatrix} \tag{46}$$

where the terms calculated or required to be zero are shown.

The fourth and sixth rows of Eqs. (45) and (46) are clearly satisfied as equations. The third and fifth rows can be rearranged in the most general form

$$\begin{pmatrix} c_{33}^F & c_{35}^F \\ c_{35}^F & c_{55}^F \end{pmatrix} \begin{pmatrix} \varepsilon_3^F \\ \varepsilon_5^F \end{pmatrix} = \begin{pmatrix} -(c_{13}^F + c_{23}^F)\varepsilon_{\|} \\ -(c_{15}^F + c_{25}^F)\varepsilon_{\|} + \sigma_5^F \end{pmatrix} \tag{47}$$

and so

$$\begin{pmatrix} \varepsilon_3^F \\ \varepsilon_5^F \end{pmatrix} = \frac{1}{\det} \begin{pmatrix} c_{55}^F & -c_{35}^F \\ -c_{35}^F & c_{33}^F \end{pmatrix} \begin{pmatrix} -(c_{13}^F + c_{23}^F)\varepsilon_{\|} \\ -(c_{15}^F + c_{25}^F)\varepsilon_{\|} + \sigma_5^F \end{pmatrix} \tag{48}$$

where

$$\det = c_{33}^F c_{55}^F - \left(c_{35}^F\right)^2 \tag{49}$$

If we define the strains $\left(\varepsilon_3^F\right)_0$ and $\left(\varepsilon_5^F\right)_0$ as the strains which arise when $\sigma_5^F = 0$, we have:

$$\begin{aligned} \left(\varepsilon_3^F\right)_{\sigma_5^F = 0} &= \left(\frac{-(c_{13}^F + c_{23}^F)c_{55}^F + (c_{15}^F + c_{25}^F)c_{35}^F}{\det} \right) \varepsilon_{\|} \\ \left(\varepsilon_5^F\right)_{\sigma_5^F = 0} &= \left(\frac{(c_{13}^F + c_{23}^F)c_{35}^F - (c_{15}^F + c_{25}^F)c_{33}^F}{\det} \right) \varepsilon_{\|} \end{aligned} \tag{50}$$

If the shear strain $\varepsilon_5^F = 0$, we have from the third line of Eq. (45) (as well as Eq. (46))

$$\varepsilon_3^F = -\left(\frac{c_{13}^F + c_{23}^F}{c_{33}^F} \right) \varepsilon_{\|} . \tag{51}$$

The shear stress $\left(\sigma_5^F\right)_0$ at which $\varepsilon_5^F = 0$ is

$$\left(\sigma_5^F\right)_0 = c_{15}^F\varepsilon + c_{25}^F\varepsilon + c_{35}^F\varepsilon_3^F = \left(c_{15}^F + c_{25}^F - \frac{c_{35}^F(c_{13}^F + c_{23}^F)}{c_{33}^F}\right)\varepsilon_{\|}$$
$$= -\frac{\det}{c_{33}^F}\left(\varepsilon_5^F\right)_0 . \tag{52}$$

If we assume that the level of residual shear stress in the film is a fraction α of that at which $\varepsilon_5^F = 0$,

$$\sigma_5^F = \alpha\left(\sigma_5^F\right)_0 = -\alpha\frac{\det}{c_{33}^F}\left(\varepsilon_5^F\right)_0 \text{ with } 0 \le \alpha \le 1. \tag{53}$$

whence in Eq. (45),

$$\begin{aligned}\frac{\varepsilon_3^F}{\varepsilon_{\|}} &= \frac{\left(\varepsilon_3^F\right)_0}{\varepsilon_{\|}} - \frac{\alpha c_{35}^F}{\det}\frac{\left(\sigma_5^F\right)_0}{\varepsilon_{\|}} \equiv \frac{\left(\varepsilon_3^F\right)_0}{\varepsilon_{\|}} + \alpha\frac{c_{35}^F}{c_{33}^F}\frac{\left(\varepsilon_5^F\right)_0}{\varepsilon_{\|}}\\ \frac{\varepsilon_5^F}{\varepsilon_{\|}} &= \frac{\left(\varepsilon_5^F\right)_0}{\varepsilon_{\|}} + \frac{\alpha c_{33}^F}{\det}\frac{\left(\sigma_5^F\right)_0}{\varepsilon_{\|}} \equiv \frac{\left(\varepsilon_5^F\right)_0}{\varepsilon_{\|}} - \alpha\frac{c_{33}^F}{c_{33}^F}\frac{\left(\varepsilon_5^F\right)_0}{\varepsilon_{\|}} \equiv (1-\alpha)\frac{\left(\varepsilon_5^F\right)_0}{\varepsilon_{\|}}\end{aligned} \tag{54}$$

Since $\varepsilon_4^F = \varepsilon_6^F = 0$, we then have for both {*hhl*} and {0*kl*} interfaces,

$$\sigma_1^F = c_{11}^F\varepsilon_{\|} + c_{12}^F\varepsilon_{\|} + c_{13}^F\varepsilon_3^F + c_{15}^F\varepsilon_5^F . \tag{55}$$

Now, from Eqs. (54) and (55),

$$\begin{aligned}M_1 = \frac{\sigma_1^F}{\varepsilon_{\|}} &= c_{11}^F\varepsilon_{\|} + c_{12}^F\varepsilon_{\|} + c_{13}^F\varepsilon_3^F + c_{15}^F\varepsilon_5^F\\ &= c_{11}^F + c_{12}^F + c_{13}^F\frac{\left(\varepsilon_3^F\right)_0}{\varepsilon_{\|}} + \left(\alpha\frac{c_{35}^F c_{13}^F}{c_{33}^F} + (1-\alpha)c_{15}^F\right)\frac{\left(\varepsilon_5^F\right)_0}{\varepsilon_{\|}}\end{aligned} \tag{56}$$

so that as we alter α from zero (traction-free boundary conditions) to one (zero residual shear strains boundary conditions), M_1 is a linear function of α.

For {0*kl*} planes, the second line of Eq. (45) gives

$$\sigma_2^F = c_{12}^F\varepsilon_{\|} + c_{22}^F\varepsilon_{\|} + c_{23}^F\varepsilon_3^F \tag{57}$$

and for {*hhl*} planes, from the second line of Eq. (46), we have

$$\sigma_2^F = c_{12}^F \varepsilon_{||} + c_{22}^F \varepsilon_{||} + c_{23}^F \varepsilon_3^F + c_{25}^F \varepsilon_5^F . \tag{58}$$

Therefore, in general, for $\{hhl\}$ and $\{0kl\}$ planes,

$$M_2 = \frac{\sigma_2^F}{\varepsilon_{||}} = c_{12}^F + c_{22}^F + c_{23}^F \frac{\left(\varepsilon_3^F\right)_0}{\varepsilon} + \left(\alpha \frac{c_{35}^F c_{23}^F}{c_{33}^F} + (1-\alpha) c_{25}^F\right) \frac{\left(\varepsilon_5^F\right)_0}{\varepsilon} . \tag{59}$$

and so M_2 is also a linear function of α.

The magnitudes of the principal biaxial moduli on the (012) planes of Cu and Nb with a transition from residual shear stress free to residual shear strain free boundary conditions are shown in Fig. 7.

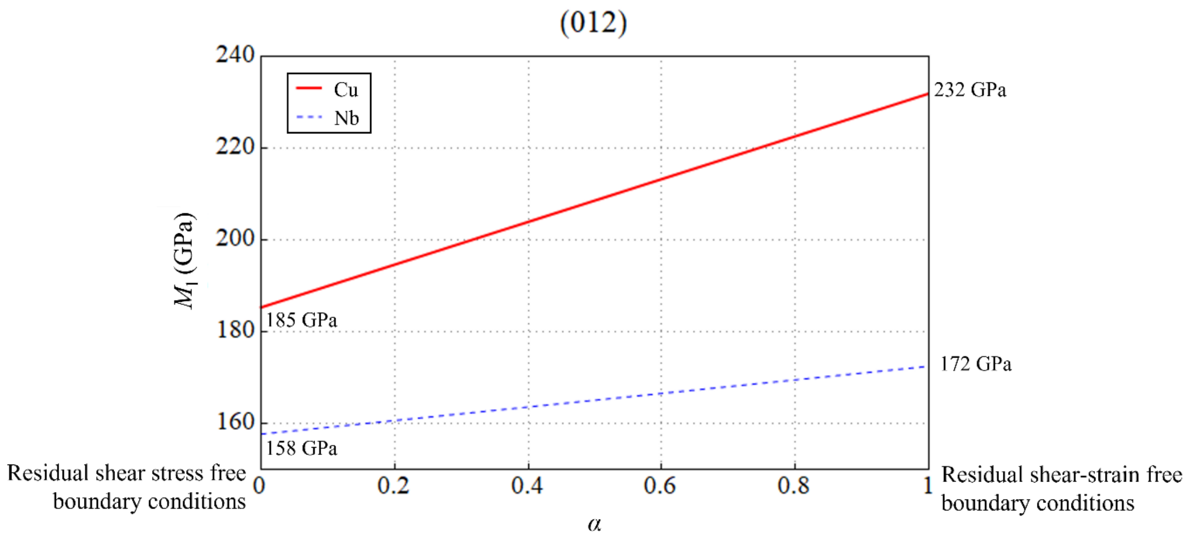

Figure 7 The principal biaxial modulus M_1 plotted against α for the (012) planes of Cu and Nb.

7. Discussion

The expressions for the biaxial moduli of cubic thin films along directions that lie on a general (*hkl*) plane have been derived. For a given film material, the magnitude of *M* depends on the direction considered as well as the orientation of the film plane. On the $\{111\}$ and $\{001\}$ planes, *M* is independent of the direction within the plane. Expressions for the principal stress directions on planes other than $\{111\}$ and $\{001\}$ are obtained by equating either the shear stress

σ_6^F or $\partial M / \partial \psi$ to zero. The corresponding values of the principal biaxial moduli are the extrema on the given plane. The principal axes always lie along $\psi = 0°$ and $90°$ for planes of the type {0*kl*} and {*hhl*}.

The stationary points of the biaxial modulus are found to lie on planes of the type {*hhl*}. The global extrema are determined from the stationary values of the two principal biaxial moduli. Both M_1 and M_2 have stationary values on {110} and $M_1 = M_2$ on {001}. M_1 can have a maximum of two more stationary values depending upon the number of real solutions to Eqs. (30) and (32). Additionally, M_2 will always have exactly one stationary value on a plane of type {*hhl*} given by Eq. (37). In total, cubic thin films can have a minimum of four and a maximum of six (symmetry-wise distinct) stationary points. The global extrema of 90 cubic materials have been calculated using Eq. (38) for 90 cubic materials using the values of the elastic constants reported in Refs. [6], [7] and [9]. Out of the 90 cubic materials investigated, the global extrema for most of the known cubic materials are on {001} and {110}, and both the extrema are found to lie on planes other than {001} and {110} in ten materials.

When the thin film assumption is made, the stresses that act normal to the film plane are zero. The expression for the out-of-plane normal strain ε_3^F generated under a state of equibiaxial strain in the film plane is derived (Eq. (38)). In each of the 90 cubic materials investigated, based on the compliance values reported in Refs. [18], [19] and [20], the stationary points are observed on {001}, {111} and {110} planes. In addition, the extrema always appeared on the {111} and {001} planes. Except for Ba, $\varepsilon_3^F / \varepsilon_{||}$ is negative for all the investigated materials. This implies that a normal compressive strain is produced in almost all cubic materials when the in-plane equibiaxial strain is tensile in nature and vice versa. Magnitudes greater than unity are observed in 61 out of the 90 materials considered here. This means that the normal strains generated are often greater in magnitude than the in-plane strain.

The expressions derived for the shear strains ε_4^F and ε_5^F are shown in Eqs. (39) and (40). As both shear strains are functions of ψ, their magnitudes depend on the direction of measurement within the film plane. The thin film assumption of zero normal stresses results in out-of-plane shear strains for all orientations of the film plane except {001}, {111} and {110}. Therefore, the expression for the biaxial modulus differs from that derived by Knowles [3] under the assumption of zero shear strains. The high magnitudes of elastic strains predicted by calculations are not likely to be observed experimentally as they will be relaxed plastically.

An important aspect that has not been considered in the calculated quantities is the uncertainty. The results calculated in this study are the biaxial moduli, its principal values and the corresponding orientations, stationary values and global extrema and the strains ε_3^F, ε_4^F and ε_5^F. As they are all based on the reported values of stiffness/compliance constants, the propagation of the errors in the elastic constants to the calculated values are considered in detail in Appendix D.

The fraction of surface atoms with broken bonds relative to the atoms in the bulk increases with a decrease in film thickness. For extremely thin films, it is known that the relaxation of the surfaces atoms and the redistribution of charges cause changes to the crystal structure and the elastic properties [21,22]. However, in the current study, the surface effects have not been considered and the results here are more relevant for films with thicknesses in the micrometre range than for those with nanometre thicknesses

8. Conclusions

The assumption of zero normal stresses on the film plane results in shear strains acting normal to the film plane. The biaxial moduli of a given cubic film subjected to an equibiaxial strain for general {0*kl*}, {*hhl*} and {*hkl*} interface orientations are found to be influenced by such boundary conditions as well. The planes on which global extrema of *M* occur using the boundary conditions assumed in Ref. [3] and the current study are found to be different, although the extrema in both the cases occur on planes of the type {*hhl*}. Likewise, the values of the principal biaxial moduli and the principal stress directions also depend on the assumed boundary conditions.

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Appendix A

Formulae for the Principal Biaxial Moduli in a Plane (*hkl*) in Terms of s_{ij}

When the x_1^F and x_2^F axes are oriented along the principal axes under a state of equibiaxial strain and traction-free boundary conditions, the strains in the film are

$$\begin{pmatrix} \varepsilon_{\|} \\ \varepsilon_{\|} \\ \varepsilon_3^F \\ \varepsilon_4^F \\ \varepsilon_5^F \\ 0 \end{pmatrix} = \begin{pmatrix} s_{11}^F & s_{12}^F & s_{13}^F & s_{14}^F & s_{15}^F & s_{16}^F \\ s_{12}^F & s_{22}^F & s_{23}^F & s_{24}^F & s_{25}^F & s_{26}^F \\ s_{13}^F & s_{23}^F & s_{33}^F & s_{34}^F & s_{35}^F & s_{36}^F \\ s_{14}^F & s_{24}^F & s_{34}^F & s_{44}^F & s_{45}^F & s_{46}^F \\ s_{15}^F & s_{25}^F & s_{35}^F & s_{45}^F & s_{55}^F & s_{56}^F \\ s_{16}^F & s_{26}^F & s_{36}^F & s_{46}^F & s_{56}^F & s_{66}^F \end{pmatrix} \begin{pmatrix} \sigma_1^F \\ \sigma_2^F \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{A.1}$$

where s_{ij}^F are the contracted Voigt notations [15,16] for the s_{ijkl}^F given by Eq. (9) and the orientations of the principal axes are the solutions to the equation

$$\tan 2\psi = \frac{\sin 4\theta \cos\phi\left((s_{11}-s_{12})\cos 2\phi - s_{44}\cos^2\phi\right)}{4(s_{11}-s_{12})\sin^2\theta\cos^2\theta(3\cos^4\phi-\cos^2\phi)+2s_{44}\left(\cos^2\phi-\sin^2\theta\cos^2\theta(1+3\cos^4\phi)\right)}. \tag{A.2}$$

The principal biaxial moduli are given by

$$M_1 = \frac{s_{22}^F - s_{12}^F}{s_{11}^F s_{22}^F - (s_{12}^F)^2} = \frac{s_{11} - s_{12} - (n_1 + n_2 \sin 4\psi + n_3 \cos 4\psi)J - (n_4 \sin 2\psi - n_5 \cos 2\psi)J}{s_{11}^2 - s_{12}^2 - d_1 s_{11} J - d_2 s_{12} J + d_3 J^2} \tag{A.3}$$

and

$$M_2 = \frac{s_{11}^F - s_{12}^F}{s_{11}^F s_{22}^F - (s_{12}^F)^2} = \frac{s_{11} - s_{12} - (n_1 + n_2 \sin 4\psi + n_3 \cos 4\psi)J + (n_4 \sin 2\psi - n_5 \cos 2\psi)J}{s_{11}^2 - s_{12}^2 - d_1 s_{11} J - d_2 s_{12} J + d_3 J^2} \tag{A.4}$$

where

$$J = s_{11} - s_{12} - \frac{s_{44}}{2} \tag{A.4.a}$$

is the anisotropy parameter defined by Hirth and Lothe [17],

$$\begin{aligned}
n_1 &= \frac{1}{2}\left(\sin^2\theta\cos^2\theta\sin^4\phi + \sin^2\phi\cos^2\phi + 1\right),\\
n_2 &= \frac{1}{4}\sin 4\theta\cos\phi(1+\cos^2\phi),\\
n_3 &= \frac{1}{2}\left(\sin^2\theta\cos^2\theta(1+6\cos^2\phi+\cos^4\phi) + \sin^2\phi\cos^2\phi - 1\right),\\
n_4 &= \frac{1}{4}\sin 4\theta\cos\phi\sin^2\phi,\\
n_5 &= -\sin^2\theta\cos^2\theta\sin^2\phi(1+\cos^2\phi) + \sin^2\phi\cos^2\phi,
\end{aligned} \tag{A.4.b}$$

$$\begin{aligned}
d_1 &= (3n_1 - 1) + n_2 \sin 4\psi + n_3 \cos 4\psi,\\
d_2 &= (1 - n_1) + n_2 \sin 4\psi + n_3 \cos 4\psi,\\
d_3 &= \frac{1}{2}\sin^2\theta\cos^2\theta\sin^4\phi(3\cos^2\phi + 1) + \frac{1}{2}\sin^2\phi\cos^2\phi\\
&\quad + \sin 2\theta\cos 2\theta\sin^2\phi\cos^3\phi\sin 4\psi\\
&\quad + \frac{1}{2}\left(\sin^2\theta\cos^2\theta\sin^2\phi(3\cos^4\phi + 6\cos^2\phi - 1) - \sin^2\phi\cos^2\phi\right)\cos 4\psi.
\end{aligned} \tag{A.4.c}$$

Principal moduli on (0*kl*) planes

Substituting $\theta = 90^\circ$ in Eqs. (A.3) and (A.4), we get

$$M_1 = \frac{4(s_{11} - s_{12})}{4(s_{11}^2 - s_{12}^2) - s_{11}J + s_{11}J\cos 4\phi} \tag{A.5}$$

$$M_2 = \frac{4(s_{11}-s_{12}) - J + J\cos 4\phi}{4(s_{11}^2-s_{12}^2) - s_{11}J + s_{11}J\cos 4\phi}. \tag{A.6}$$

Principal moduli on (*hhl*) planes

Substituting $\theta = 45^\circ$ in Eqs. (A.3) and (A.4), we get

$$M_1 = \frac{s_{11}-s_{12}-\frac{J}{2}(1+\cos^2\phi)}{s_{11}^2-s_{12}^2-s_{11}J\left(\frac{1}{2}+2\cos^2\phi-\frac{3}{2}\cos^4\phi\right)-s_{12}J\cos^2\phi+J^2(\cos^2\phi-\cos^4\phi)} \tag{A.7}$$

$$M_2 = \frac{s_{11}-s_{12}-\frac{J}{2}(5\cos^2\phi-3\cos^4\phi)}{s_{11}^2-s_{12}^2-s_{11}J\left(\frac{1}{2}+2\cos^2\phi-\frac{3}{2}\cos^4\phi\right)-s_{12}J\cos^2\phi+J^2(\cos^2\phi-\cos^4\phi)}. \tag{A.8}$$

Appendix B

Stationary Points of the Principal Biaxial Moduli

The two principal moduli within a plane are defined by the equations

$$M_1 = \frac{\sigma_1^F}{\varepsilon_{||}} = \frac{s_{22}^F - s_{12}^F}{s_{11}^F s_{22}^F - (s_{12}^F)^2} \tag{B.1}$$

and

$$M_2 = \frac{\sigma_2^F}{\varepsilon_{||}} = \frac{s_{11}^F - s_{12}^F}{s_{11}^F s_{22}^F - (s_{12}^F)^2} \tag{B.2}$$

Following the formalism used in Appendix B of Ref. [3] which makes extensive use of the analysis of Ref. [23], the conditions under which M_1 and M_2 have stationary values can be specified.

The condition derived by Norris [23] for a stationary value to be obtained of an engineering modulus *f* for a triclinic material is that a vector $\mathbf{d}^{(f)} = 0$ at a stationary point of *f* for a suitable vector $\mathbf{d}^{(f)}$ independent of the three-dimensional vector $\mathbf{q} = q_1\mathbf{e}_1^F + q_2\mathbf{e}_2^F + q_3\mathbf{e}_3^F$, defined in the formalism here relative to the orthonormal set of axes x_1^F, x_2^F and x_3^F, in which the unit vectors along these three axes are $\mathbf{e}_1^F$, $\mathbf{e}_2^F$ and $\mathbf{e}_3^F$, respectively, about which the rotation takes place. This then leads to three conditions for stationary values of *f*, one from each component of $\mathbf{d}^{(f)}$ along the axes x_1^F, x_2^F and x_3^F respectively. The analysis requires differentiation of *f* with respect to θ for a general **q**, evaluated at $\theta = 0°$; this in turn requires differentiation of the s_{ij}^F in Eq. (5) with respect to θ for a general **q**, also evaluated at $\theta = 0°$.

The vector $\mathbf{d}^{(f)}$ is defined by the condition

$$\frac{\partial f(\mathbf{q})}{\partial \theta} = \mathbf{d}^{(f)} \cdot \mathbf{q}. \tag{B.3}$$

It follows from Section 3 of Ref. [23], that

$$\begin{aligned} \frac{\partial s_{11}^F(\mathbf{q})}{\partial \theta} &= 4s_{15}^F q_2 - 4s_{16}^F q_3 \\ \frac{\partial s_{22}^F(\mathbf{q})}{\partial \theta} &= -4s_{24}^F q_1 + 4s_{26}^F q_3 \\ \frac{\partial s_{12}^F(\mathbf{q})}{\partial \theta} &= -2s_{14}^F q_1 + 2s_{15}^F q_2 + 2\left(s_{16}^F - s_{26}^F\right) q_3 \end{aligned} \tag{B.4}$$

where the s_{ij}^F are the values at $\theta = 0°$, i.e., the values with respect to the x_1^F, x_2^F and x_3^F orthonormal set of axes.

Differentiating M_1 and M_2 with respect to the s_{ij}^F, we have

$$\begin{aligned}
\frac{\partial M_1}{\partial s_{11}^F} &= \frac{s_{12}^F s_{22}^F - \left(s_{22}^F\right)^2}{\left(s_{11}^F s_{22}^F - \left(s_{12}^F\right)^2\right)^2} \\
\frac{\partial M_1}{\partial s_{22}^F} &= \frac{s_{11}^F s_{12}^F - \left(s_{12}^F\right)^2}{\left(s_{11}^F s_{22}^F - \left(s_{12}^F\right)^2\right)^2} \\
\frac{\partial M_1}{\partial s_{12}^F} &= \frac{2 s_{12}^F s_{22}^F - s_{11}^F s_{22}^F - \left(s_{12}^F\right)^2}{\left(s_{11}^F s_{22}^F - \left(s_{12}^F\right)^2\right)^2}
\end{aligned} \tag{B.5}$$

and

$$\begin{aligned}
\frac{\partial M_2}{\partial s_{11}^F} &= \frac{s_{12}^F s_{22}^F - \left(s_{12}^F\right)^2}{\left(s_{11}^F s_{22}^F - \left(s_{12}^F\right)^2\right)^2} \\
\frac{\partial M_2}{\partial s_{22}^F} &= \frac{s_{11}^F s_{12}^F - \left(s_{11}^F\right)^2}{\left(s_{11}^F s_{22}^F - \left(s_{12}^F\right)^2\right)^2} \\
\frac{\partial M_2}{\partial s_{12}^F} &= \frac{2 s_{11}^F s_{12}^F - s_{11}^F s_{22}^F - \left(s_{12}^F\right)^2}{\left(s_{11}^F s_{22}^F - \left(s_{12}^F\right)^2\right)^2}
\end{aligned} \tag{B.6}$$

Hence, it follows that

$$\begin{aligned}
\mathbf{d}^{(M_1)} = \frac{-2}{\left(s_{11}^F s_{22}^F - (s_{12}^F)^2\right)^2} \Big[& \left(2\left(s_{11}^F s_{12}^F - (s_{12}^F)^2\right) s_{24}^F + \left(2 s_{12}^F s_{22}^F - s_{11}^F s_{22}^F - (s_{12}^F)^2\right) s_{14}^F\right) \mathbf{e}_1^F \\
& - \left(2\left(s_{12}^F s_{22}^F - (s_{22}^F)^2\right) s_{15}^F + \left(2 s_{12}^F s_{22}^F - s_{11}^F s_{22}^F - (s_{12}^F)^2\right) s_{25}^F\right) \mathbf{e}_2^F \\
& - \left(-2\left(s_{12}^F s_{22}^F - (s_{22}^F)^2\right) s_{16}^F + 2\left(s_{11}^F s_{12}^F - (s_{12}^F)^2\right) s_{26}^F + \left(2 s_{12}^F s_{22}^F - s_{11}^F s_{22}^F - (s_{12}^F)^2\right)\left(s_{16}^F - s_{26}^F\right)\right) \mathbf{e}_3^F \Big]
\end{aligned} \tag{B.7}$$

$$\begin{aligned}
\mathbf{d}^{(M_2)} = \frac{-2}{(s_{11}^F s_{22}^F - (s_{12}^F)^2)^2} \Big[& \left(2\left(s_{11}^F s_{12}^F - (s_{11}^F)^2\right) s_{24}^F + \left(2 s_{11}^F s_{12}^F - s_{11}^F s_{22}^F - (s_{12}^F)^2\right) s_{14}^F\right) \mathbf{e}_1^F \\
& - \left(2(s_{12}^F s_{22}^F - (s_{12}^F)^2) s_{15}^F + \left(2 s_{11}^F s_{12}^F - s_{11}^F s_{22}^F - (s_{12}^F)^2\right) s_{25}^F\right) \mathbf{e}_2^F \\
& - \left(-2\left(s_{12}^F s_{22}^F - (s_{12}^F)^2\right) s_{16}^F + 2\left(s_{11}^F s_{12}^F - (s_{11}^F)^2\right) s_{26}^F + \left(2 s_{11}^F s_{12}^F - s_{11}^F s_{22}^F - \left(s_{12}^F\right)^2\right)\left(s_{16}^F - s_{26}^F\right)\right) \mathbf{e}_3^F \Big]
\end{aligned} \tag{B.8}$$

The three conditions for the stationary values of M_1 and M_2 are that each of the coefficients of $\mathbf{e}_1^F$, $\mathbf{e}_2^F$ and $\mathbf{e}_3^F$ in equations (B.7) and (B.8) respectively are zero.

The coefficients of $\mathbf{e}_3^F$

These coefficients are of particular interest. In equation (13), the condition that this coefficient is zero becomes for M_1 the condition:

$$\frac{2}{\left(s_{11}^F s_{22}^F - (s_{12}^F)^2\right)^2}\left(\left(2(s_{22}^F)^2 - s_{11}^F s_{22}^F - (s_{12}^F)^2\right)s_{16}^F + \left(2s_{11}^F s_{12}^F + s_{11}^F s_{22}^F - 2s_{12}^F s_{22}^F - (s_{12}^F)^2\right)s_{26}^F\right) = 0 \tag{B.9}$$

The sixth row of Eq. (A.1) gives

$$s_{22}^F s_{16}^F + s_{11}^F s_{26}^F - s_{12}^F (s_{16}^F + s_{26}^F) = 0\,. \tag{B.10}$$

From the first two rows in Eq. (A.1), we have:

$$\begin{bmatrix} \sigma_1^F \\ \sigma_2^F \end{bmatrix} = \frac{\varepsilon}{s_{11}^F s_{22}^F - (s_{12}^F)^2}\begin{bmatrix} s_{22}^F - s_{12}^F \\ s_{11}^F - s_{12}^F \end{bmatrix}. \tag{B.11}$$

Hence, the sixth row of Eq. (A.1) reduces to the condition

$$\left((s_{22}^F)^2 - (s_{12}^F)^2\right)s_{16}^F + \left(s_{11}^F s_{12}^F + s_{11}^F s_{22}^F - s_{12}^F s_{22}^F - (s_{12}^F)^2\right)s_{26}^F = 0\,. \tag{B.12}$$

Using Eq. (B.12) in Eq. (B.9) gives

$$\frac{s_{11}^F - s_{22}^F}{\left(s_{11}^F s_{22}^F - (s_{12}^F)^2\right)^2}\left(s_{12}^F s_{26}^F - s_{22}^F s_{16}^F\right) = 0 \tag{B.13}$$

which has the two solutions

$$\text{(i) } s_{11}^F = s_{22}^F \quad \text{and (ii) } s_{12}^F s_{26}^F = s_{22}^F s_{16}^F \tag{B.14}$$

The first of these conditions is satisfied when the film plane is parallel to the {001} and {111} planes.

Making use of equation (B.10) and since $s_{11}^F s_{22}^F - (s_{12}^F)^2 > 0$ as a consequence of the Born stability criteria, the second condition becomes

$$s_{16}^F = s_{26}^F = 0 \qquad \text{(B.15)}$$

This single condition precludes general (*hkl*) interfaces as being locations of stationary values of M_1 because it is evident from the algebra defining principal axes for the biaxial moduli that for such interfaces $s_{16}^F \neq 0$ and $s_{26}^F \neq 0$. This then leaves {0*kl*} and {*hhl*} interfaces as the only locations of stationary values of M_1.

In Eq. (B.8), the condition that this coefficient is zero becomes for M_2 the condition:

$$\left(2s_{11}^F s_{12}^F + (s_{12}^F)^2 - s_{11}^F s_{22}^F - 2s_{12}^F s_{22}^F\right) s_{16}^F + \left((s_{12}^F)^2 + s_{11}^F s_{22}^F - 2(s_{11}^F)^2\right) s_{26}^F = 0 \qquad \text{(B.16)}$$

Using Eq. (B.12), Eq. (B.16) simplifies to:

$$\frac{s_{11}^F - s_{22}^F}{\left(s_{11}^F s_{22}^F - (s_{12}^F)^2\right)^2}\left(s_{12}^F s_{16}^F - s_{11}^F s_{26}^F\right) = 0 \qquad \text{(B.17)}$$

which has the two solutions

$$\text{(i) } s_{11}^F = s_{22}^F \text{ and (ii) } s_{12}^F s_{16}^F = s_{11}^F s_{26}^F \qquad \text{(B.18)}$$

As for M_1, the first of these conditions is satisfied for M_2 for the {001} and {111} planes. Making use of Eq. (B.12), the second condition again becomes

$$s_{16}^F = s_{26}^F = 0. \qquad \text{(B.19)}$$

It can be shown that the coefficients of $\mathbf{e}_1^F$ and $\mathbf{e}_2^F$ in Eqs. (B.7) and (B.8) are also zero for planes of the type {*hhl*} and {0*kl*} confirming that the stationary points, and hence, the global extrema of the biaxial modulus, lie only along such interfaces.

Appendix C

Stationary Points of the Principal Biaxial Moduli on (0*kl*) Planes

The principal biaxial moduli on (0*kl*) planes given by Eq. (22) are

$$
\begin{aligned}
M_1 &= -\frac{8c_{44}(c_{11}-c_{12})(c_{11}+2c_{12})}{-c_{11}^2-6c_{11}c_{44}+c_{12}(c_{12}+2c_{44})-H(c_{11}+c_{12})\cos 4\phi} \\
M_2 &= \frac{2(c_{11}-c_{12})(c_{11}+2c_{12})(-4c_{44}+H\sin^2 2\phi)}{-c_{11}^2-6c_{11}c_{44}+c_{12}(c_{12}+2c_{44})-H(c_{11}+c_{12})\cos 4\phi}
\end{aligned}
\tag{C.1}
$$

The stationary points of M_1 are the solutions to

$$
\frac{dM_1}{d\phi} = \frac{32\left(c_{11}^2-c_{12}^2\right)\left(c_{11}+2c_{12}\right)c_{44}H\sin 4\phi}{\left(c_{11}^2+6c_{11}c_{44}-c_{12}\left(c_{12}+2c_{44}\right)+\left(c_{11}+c_{12}\right)H\cos 4\phi\right)^2} = 0 \tag{C.2}
$$

As the Born stability criteria requires $c_{11} > 0$, $c_{11} > |c_{12}|$, $(c_{11}+2c_{12}) > 0$ and $c_{44} > 0$, the only solutions other than the case of complete isotropy ($H = 0$) are $\phi = 0^\circ$, 45° and 90° which correspond to the planes (001), (011) and (010) respectively.

Similarly, the stationary points of M_2 are the solutions to

$$
\frac{dM_2}{d\phi} = \frac{32\left(c_{11}-c_{12}\right)\left(c_{11}+2c_{12}\right)c_{12}c_{44}H\sin 4\phi}{\left(c_{11}^2+6c_{11}c_{44}-c_{12}\left(c_{12}+2c_{44}\right)+\left(c_{11}+c_{12}\right)H\cos 4\phi\right)^2} = 0 \tag{C.3}
$$

which are again $\phi = 0^\circ$, 45° and 90°. The other solutions $c_{12} = 0$ and $H = 0$ will mean that M_2 is the same on all (0*kl*) planes. In Appendix B, it is shown that the stationary points of the principal biaxial moduli are always on (*hhl*) and (0*kl*) planes, which are now further restricted to lie only on planes of the type (*hhl*).

Appendix D

Uncertainty in the Calculated Values of the Biaxial Moduli

Compliance constants (s_{ij}) reported in Ref. [18] are inverted to obtain the stiffness constants (c_{ij}).

For cubic materials,

$$c_{11} = \frac{s_{11}+s_{12}}{\left(s_{11}-s_{12}\right)\left(s_{11}+2s_{12}\right)}$$
$$c_{12} = \frac{-s_{12}}{\left(s_{11}-s_{12}\right)\left(s_{11}+2s_{12}\right)} \tag{D.1}$$
$$c_{44} = \frac{1}{s_{44}}$$

The most probable error in the calculation of stiffness constants is

$$\Delta c_{ij} = \sqrt{\left(\frac{\partial c_{ij}}{\partial s_{11}}\Delta s_{11}\right)^2 + \left(\frac{\partial c_{ij}}{\partial s_{12}}\Delta s_{12}\right)^2 + \left(\frac{\partial c_{ij}}{\partial s_{44}}\Delta s_{44}\right)^2} \tag{D.2}$$

Similarly, the most probable errors in the values of the principal biaxial moduli are given by

$$\Delta M_i = \sqrt{\left(\frac{\partial M_i}{\partial c_{11}}\Delta c_{11}\right)^2 + \left(\frac{\partial M_i}{\partial c_{12}}\Delta c_{12}\right)^2 + \left(\frac{\partial M_i}{\partial c_{44}}\Delta c_{44}\right)^2} \,. \tag{D.3}$$

where M_i are given by Eqs. (16) and (17).

Example: Copper

The compliances (in $(\mathrm{TPa})^{-1}$) of copper reported in Ref. [18] are $s_{11} = 15.0$, $s_{12} = -6.3$ and $s_{44} = 13.3$. The reported standard deviations of s_{ij} are $\sigma(s_{11}) = \pm 0.2\ (\mathrm{TPa})^{-1}$, $\sigma(s_{12}) = \pm 0.06\ (\mathrm{TPa})^{-1}$ and $\sigma(s_{44}) = \pm 0.09\ (\mathrm{TPa})^{-1}$. The standard errors are obtained by dividing by $\sqrt{n}$, where n is the number of datasets:

$$\Delta s_{ij} = \frac{\sigma(s_{ij})}{\sqrt{n}} \,. \tag{D.4}$$

For the reported values of Cu, $n = 10$, and using Eq. (D.2), we have

$\Delta c_{11} = \pm 4$ GPa,

$\Delta c_{12} = \pm 4$ GPa,

and

$\Delta c_{44} = \pm 0.2$ GPa .

The calculated principal biaxial moduli and the estimated errors on different planes in Cu obtained from Eq. (D.3) are

$M_{\{001\}} = 110 \pm 12$ GPa ,

$M_{\{111\}} = 262 \pm 3$ GPa ,

and

$M_1 = 185 \pm 5$ GPa and $M_2 = 282 \pm 3$ GPa on (110).

The stationary values of the biaxial modulus of Cu are 114.94, 282.36, 185.26 and 282.59 and 273.47 GPa. Assuming that the uncertainty is ± 5 GPa for each of these, the global maximum cannot be ascertained since 282.36 and 282.59 are both 282 ± 5 GPa . Based on the s_{ij} values reported in Ref. [18], the global minimum is 110 ± 12 GPa on {001} and the global maximum is 282 ± 5 GPa which is either $M_{(110)[0l\bar{k}]}$ or M along $\psi = 0°$ on {*hhl*} with $\phi = 78.47°$.

Uncertainty in the *M* values calculated using the reported values of c_{ij} and standard deviations

For copper the c_{ij} values reported in Ref. [18] are

$c_{11} = 169$ GPa,

$c_{12} = 122$ GPa,

$c_{44} = 75.3$ GPa.

The reported standard deviations are

$\sigma(c_{11}) = \pm 1.5$ GPa,

$\sigma(c_{12}) = \pm 1.8$ GPa,

$\sigma(c_{44}) = \pm 0.6$ GPa.

Substituting these values in Eq. (D.4) with $n = 10$ gives the standard errors, which can now be used in Eq. (D.3) to get

$M_{\{001\}} = 115 \pm 2$ GPa ,

$M_{\{111\}} = 261 \pm 2$ GPa ,

$M_{1\{110\}} = 185 \pm 0.6$ GPa,

and

$M_{2\{110\}} = 282 \pm 0.6$ GPa.

The errors are almost an order of magnitude lower than that when the s_{ij} were used. Still the locations of the global maximum of the biaxial modulus of Cu cannot be ascertained. Therefore the locations of the global maximum and minimum of Cu will require more accurate measurements of the elastic constants.

Similarly, the values of all the quantities (biaxial moduli, orientation of principal stress axes, and the strains $\varepsilon_3^F, \varepsilon_4^F$ and ε_5^F) calculated using the equations derived in this study will have errors that depend on the uncertainty in the determination of the elastic constants. The uncertainty in the results also depends on the orientation of the interface. The specific example of Cu shows that the location of the maximum biaxial modulus cannot be ascertained. The analysis also shows that the errors in the results obtained using the c_{ij} formalism is lower when the reported c_{ij} values are used. The inversion of the reported s_{ij} matrix to obtain the c_{ij} values increases the uncertainty of the final results.

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List of Figure Captions

Figure 1 The biaxial modulus on the (234) and (129) planes in (a) Cu, (b) Si, (c) Nb and (d) β-brass. The variations of M (in GPa) with the angle ψ from the meridional tangent are shown. The principal stress axes on (234) and (129) are marked with blue dotted lines and red dot-dashed lines respectively.

Figure 2 The variations of M with ψ on the (a) (001), (b) (111), (c) (012) and (d) (227) planes of Cu, Si, Nb and β-brass. The black lines at $\psi = 0°$ and $\psi = 90°$ correspond to the principal stress axes. The principal stress axes for (012) are $[02\bar{1}]$ and $[00\bar{1}]$. For the (227) plane, they are $[77\bar{4}]$ and $[\bar{1}10]$.

Figure 3 The variations of the principal biaxial moduli on planes of the type (0*kl*) in Cu, Si, Nb and β-brass as a function of the angle between the plane normal and [001].

Figure 4 The variation of the principal biaxial moduli on planes of the type (*hhl*) in Cu, Si, Nb and β-brass as a function of the angle between the plane normal and [001].

Figure 5 The out-of-plane normal strain ε_3^F (in terms of the in-plane equibiaxial strain ε_1^F) in (a) Cu and (b) Nb on planes of the type (*hhl*) and (0*kl*) plotted against the angle between the plane and (001).

Figure 6 The variations of the strains ε_3^F, ε_4^F and ε_5^F per unit $\varepsilon_{\parallel}$ within the: (231), (012) and (227) planes of (a–c) Cu, and (d–f) Nb. The principal stress axes are indicated with vertical dashed lines.

Figure 7 The principal biaxial modulus M_1 plotted against α for the (012) planes of Cu and Nb.

List of Table Captions

Table 1 The principal stress axes and the corresponding principal biaxial moduli for the (234) and (129) planes in Cu, Si, Nb and β-brass

Table 2 Stationary points of the biaxial moduli in Cu, Si, Nb and Li. The global maxima are shown in bold, and the minima are underlined. The normals to the planes with the stationary points are of the form $(\theta = 45°, \phi_{ij})$, where ϕ_{ij} are given by Eqs. (29) and (34). The stiffness values were obtained by inverting the compliance constants reported in Ref. [6].