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Extreme values of the shear modulus for hexagonal crystals

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ABSTRACT

In this paper, the variability of the shear modulus of hexagonal crystals was studied. Analytic expressions for the extreme values of the shear modulus were obtained. Numerical analysis of the extrema for hexagonal crystals was given on the basis of experimental data from the Landolt-Börnstein handbook. The greatest difference between the maximum and minimum values of the shear modulus was found for a layered crystal - graphite. A large difference between maximum and minimum is also characteristic for molybdenum disulphide. Classification scheme is proposed for the extreme values of shear modulus for hexagonal crystals as function of two dimensionless parameters.

The variability of Young's modulus, Poisson's ratio and shear modulus for hexagonal crystals was investigated in [1–7]. Cadmium and thallium crystals were analyzed in [1]. At the same time, the results related to cadmium contain an error associated with an incorrect recalculation of the compliance coefficients. Corrected results show that cadmium cannot have negative Poisson's ratio ν ($0.1<\nu<0.7$). Useful formulas for Young's modulus, shear modulus and Poisson's ratio were obtained in [2] by analyzing the tensor structure of the elasticity characteristics of crystals for various crystalline systems, hexagonal, in particular. Three extreme values of Young's modulus were obtained using method of Lagrange's multipliers in [3]. Extreme values of Poisson's ratio were investigated in [4]. Poisson's ratios were also studied in [5,6]. Average Poisson's ratio for hexagonal crystals was studied in [7]. Below we analyze the variability of the shear modulus of hexagonal crystals using the experimental data on the elastic constants collected in Landolt-Börnstein handbook [8].

The shear modulus $G(\mathbf{n},\mathbf{m})$ in linear elasticity is determined by two unit vectors $\mathbf{n}$ and $\mathbf{m}$ [9] and tensor compliance coefficients s_{ijkl}

$$G^{-1}(\mathbf{n},\mathbf{m}) = 4s_{ijkl}n_i m_j n_k m_l. \tag{1}$$

Here $\mathbf{n}$ is the unit vector of the normal to the slip plane, $\mathbf{m}$ is the unit vector of the slip direction. Matrix compliance coefficients s_{mn} are often used instead of the tensor compliance coefficients s_{ijkl} [10]. Hexagonal crystals are characterized by the five independent compliances $s_{11}, s_{33}, s_{44}, s_{12}, s_{13}$ that have the following thermodynamic limitations $s_{11}>0$, $s_{33}>0$, $s_{44}>0$, $1>s_{12}/s_{11}>2s_{13}^2/(s_{33}s_{11})-1$. Three Euler's angles φ, θ, ψ are conveniently used instead of the vector parameterization $\mathbf{n}$, $\mathbf{m}$ of the crystal orientation. The formula for shear modulus of hexagonal crystals (1) can be written with the use of these angles in the form [11]

$$\begin{gathered}\frac{1}{s_{44}G(\theta,\psi)} = 1+\left(\Pi_3\sin^2\psi+4\Pi_{03}\cos^2\theta\cos^2\psi\right)\sin^2\theta,\\ \Pi_{03}\equiv\frac{\delta}{s_{44}},\quad \Pi_3\equiv\frac{2s_{11}-2s_{12}-s_{44}}{s_{44}},\\ \delta\equiv s_{11}+s_{33}-2s_{13}-s_{44}.\end{gathered} \tag{2}$$

The dependence of the shear modulus is a periodic function of two angular variables θ, ψ (the shear modulus does not depend on the angle φ) with periods $T_\theta=T_\psi=\pi$. The dimensionless parameters Π_{03}, Π_3 and the dimensional parameter δ are characteristics of the anisotropy degree of hexagonal crystals. The restriction on the dimensionless parameter $\Pi_3>-1$ follows from the positivity of the compliance coefficients $s_{44}>0$ and $s_{66}=2s_{11}-2s_{12}>0$.

Let us analyze the extreme values of the shear modulus. Expression (2) for the shear modulus of hexagonal crystals depends on two Euler's angles θ, ψ. The necessary conditions for extrema (the attainment of maxima or minima) of the shear modulus consist in the fulfillment of the stationary conditions

$$\frac{\partial G(\theta,\psi)}{\partial\psi}=0,\quad \frac{\partial G(\theta,\psi)}{\partial\theta}=0.$$

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These conditions give the following system of equations for the stationary values of the angles θ, ψ [12]

$$\begin{cases} \sin^2\theta\ \sin 2\psi\ \left(\Pi_3 - 4\Pi_{03}\cos^2\theta\right) = 0 \\ \sin 2\theta\ \left(\Pi_3\sin^2\psi + 4\Pi_{03}\ \cos 2\theta\cos^2\psi\right) = 0 \end{cases} \quad (3)$$

The solutions of the first equation are $\theta = 0$; $\psi = 0$ or $\psi = \pi/2$ and $\cos^2\theta = \Pi_3/(4\Pi_{03})$. Substitution of these solutions into the second equation of system (3) allows to find several stationary points: $\theta = 0$ at any ψ; $\psi = 0$ and $\theta = \pi/4$; $\psi = 0$ and $\theta = \pi/2$; $\psi = 0$ and $\theta = 3\pi/4$; $\psi = \pi/2$ and $\theta = \pi/2$; $\psi = \psi_0$ and $\theta = \theta_0$ at the conditions $0 \le \cos^2\psi_0 = \Pi_3/(4\Pi_{03} - \Pi_3) \le 1$, $0 \le \cos^2\theta_0 = \Pi_3/(4\Pi_{03}) \le 1$. Four stationary values of the shear modulus correspond to these stationary points. The value of the shear modulus

$$G_1 = \frac{1}{s_{44}} \quad (4)$$

is attained at $\theta = 0$ and any angles ψ and at $\theta = \pi/2$, $\psi = 0$. This is possible for the slip plane (001) and the sliding directions $\mathbf{m} = (\cos(\varphi+\psi), \sin(\varphi+\psi), 0)^T$ and $\mathbf{n} = (\sin\varphi, -\cos\varphi, 0)^T$, $\mathbf{m} = (\cos\varphi, \sin\varphi, 0)^T$. The angle φ is the rotation angle of the crystallographic coordinate system in the (001) plane, i.e. in the isotropy plane. Another value of the shear modulus

$$G_2 = \frac{1}{s_{44}(1+\Pi_3)} = \frac{1}{s_{66}} \quad (5)$$

is attained at $\theta = \psi = \pi/2$, which corresponds to unit vectors $\mathbf{n} = (\sin\varphi, -\cos\varphi, 0)^T$, $\mathbf{m} = (0,0,1)^T$. The third value

$$G_3 = \frac{1}{s_{44}(1+\Pi_{03})} = \frac{1}{s_{11}+s_{33}-2s_{13}} \quad (6)$$

is attained at $\theta = \pi/4$, $\psi = 0$ and $\theta = 3\pi/4$, $\psi = 0$, which corresponds to the vectors $\mathbf{n} = \left(\sqrt{2}/2\ \sin\varphi, -\sqrt{2}/2\ \cos\varphi, \sqrt{2}/2\right)^T$, $\mathbf{m} = (\cos\varphi, \sin\varphi, 0)^T$. Finally, the inverse value of the shear modulus

$$G_4^{-1} = s_{44}\left(1 + \Pi_3 - \frac{\Pi_3^2}{4\Pi_{03}}\right) \quad (7)$$

is possible at stationary points θ_0, ψ_0 at the conditions $0 \le \cos^2\theta_0 = 0.25\Pi_3/\Pi_{03} \le 1$, $0 \le \cos^2\psi_0 = \Pi_3/(4\Pi_{03} - \Pi_3) \le 1$.

Let us further investigate the values G_1, G_2, G_3, G_4 from the viewpoint of the fulfillment of a sufficient condition for the extremum of a function of two variables. If denoted by A, B, C the second derivatives of the shear modulus at the indicated stationary points

$$A = \frac{\partial^2 G}{\partial\theta^2}, \quad B = \frac{\partial^2 G}{\partial\theta\partial\psi}, \quad C = \frac{\partial^2 G}{\partial\psi^2}$$

and consider their combination

$$D = AC - B^2,$$

then at $D > 0$ extrema of the shear modulus are attained at the corresponding stationary point (maximum at $A < 0$ and minimum at $A > 0$). In the case $D < 0$ there are no extrema in a stationary point. An additional analysis is required at $D = 0$ [12].

In the case of a stationary point $\theta = \pi/2$, $\psi = 0$ we have $G = G_1$ and

$$D = \frac{16\Pi_{03}\Pi_3}{s_{44}}, \quad A = -\frac{8\Pi_{03}}{s_{44}}. \quad (8)$$

Then, according to the sufficient condition for the extremum of the function of two variables accounting for the positivity of the compliance coefficient s_{44}, the value of the shear modulus G_1 will be extreme if $\Pi_3 > 0$, $\Pi_{03} > 0$ or $\Pi_3 < 0$, $\Pi_{03} < 0$. The value G_1 corresponds to the maximum at $\Pi_{03} > 0$ ($A < 0$), and this value is minimum at $\Pi_{03} < 0$ ($A > 0$).

In the case of a stationary point $\theta = 0$ with any ψ we have $G = G_1$, the combination D vanishes and

$$A = -\frac{2\left(4\Pi_{03}\cos^2\psi + \Pi_3\sin^2\psi\right)}{s_{44}}. \quad (9)$$

Due to $D = 0$ an additional analysis is required for each concrete crystal.

In the case of a stationary point $\theta = \psi = \pi/2$ we have $G = G_2$ and

$$D = \frac{4\Pi_3^2}{s_{44}^2(1+\Pi_3)^4} > 0, \quad A = \frac{2\Pi_3}{s_{44}(1+\Pi_3)^2}. \quad (10)$$

The value G_2 will always be extreme because of the positive D. At $\Pi_3 > 0$ the value A is also positive and the value G_2 is minimal for the shear modulus. At $\Pi_3 < 0$ rightfully $A < 0$ and the discussed value is the maximum.

In the case of stationary points $\theta = \pi/4$, $\psi = 0$ and $\theta = 3\pi/4$, $\psi = 0$ we have $G = G_3$ and

$$D = \frac{8\Pi_{03}(2\Pi_{03} - \Pi_3)}{s_{44}^2(1+\Pi_{03})^4}, \quad A = \frac{8\Pi_{03}}{s_{44}(1+\Pi_{03})^2}. \quad (11)$$

The value G_3 will be an extremum at $\Pi_{03}(2\Pi_{03} - \Pi_3) > 0$ by virtue of the positivity D. At $\Pi_{03} > 0$ the second derivative A is positive and value G_3 is minimum, and $\Pi_{03} < 0$ ($A < 0$) this value is maximum.

Table 1
Extreme values of the shear moduli for some hexagonal crystals and the values of the angles θ_0, ψ_0 (in degree) at which the value G_4 is attained, as well as the values of the dimensionless parameters Π_3 and Π_{03}. Global extremes are indicated in bold type.

Crystals	Π_{03}	Π_3	$\Pi_{03}(2\Pi_{03} - \Pi_3)$	G_1, GPa	G_2, GPa	G_3, GPa	G_4, GPa	θ_0	ψ_0
Be	0.04	0.21	−0.005	**162**	**134**	156	–	–	–
Cd	0.23	−0.49	0.21	18.8	**36.8**	**15.3**	–	–	–
CdSe	−0.32	−0.08	0.17	**13.4**	14.53	**19.6**	14.46	75.5	75.0
Co	−0.24	0.06	0.13	70.9	**66.8**	**93.6**	–	–	–
GaN	−0.60	−0.71	0.29	**24.1**	**83.1**	59.7	48.1	56.9	49.4
GaSe	−0.54	−0.73	0.18	**10.2**	**37.9**	21.9	19.6	54.2	43.9
C (graphite)	−0.88	−0.99	0.69	**4**	**439**	34.3	13.9	58.0	51.4
MnAs	0.36	1.14	−0.15	**34.5**	**16.1**	25.4	–	–	–
MoS_2	−0.40	−0.87	−0.03	**18.6**	**146**	30.8	–	–	–
C_7H_{12}	1.22	3.33	−1.09	**0.91**	**0.21**	0.41	–	–	–
SiC	−0.29	−0.17	0.12	**169**	204	**237**	198	67.2	65.2
Ti	−0.06	0.34	0.03	46.5	**34.7**	**49.5**	–	–	–
TiB_2	1.21	0.79	1.96	**250**	140	**113**	151	66.2	63.8
Zn	0.97	−0.40	2.28	39.5	**65.6**	**20.0**	–	–	–