

Elastic anisotropy in minerals

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SUMMARY. Silicate minerals show several correlations between structure type and elastic constants. Stiffness coefficients are generally larger in the direction of Si-O bonding. A simple mechanical analogy in which atomic bonds are simulated by springs connected in series and parallel is used to estimate the size and anisotropy of the elastic moduli and their pressure derivatives.

STRUCTURE-PROPERTY relationships are of considerable interest to mineralogists when the concepts are of general applicability and are not overly complex. The atomistic explanation of optical birefringence in minerals (Bragg, 1924) is a good example. Regarding mechanical properties, most mineralogy texts relate hardness, cleavage, and plasticity to crystal structure, but few discuss elasticity despite its importance in geophysics. The elastic constants of minerals are important in rock mechanics and in seismic-wave velocities.

From previous work it appears that packing density is the primary variable affecting the elastic moduli of oxide compounds. Birch (1961*a*, 1961*b*) showed that most common minerals have about the same mean atomic weight (molecular weight divided by the number of atoms in the chemical formula), and that longitudinal sound velocity is roughly proportional to density. Shear velocities also increase with rock density (Simmons, 1964). Anderson and Nafe (1965) plotted bulk modulus (reciprocal volume compressibility) against volume per ion pair, demonstrating that most oxide data follow the same relation. Bulk modulus is inversely proportional to volume, regardless of whether the volume change is caused by pressure, compositional variation, temperature, porosity, or phase changes. As might be expected, bulk modulus increases with density because short-range repulsive forces make it increasingly difficult to compress the solid as the atoms move closer together.

Structure-stiffness correlation. All solids change shape under forces. Under small stress, the strain ϵ is related to the stress σ by Hooke's law, $(\sigma) = (c)(\epsilon)$. The elastic stiffness coefficients (c) constitute a fourth-rank tensor in which the number of independent coefficients depends on symmetry (Nye, 1957). In contracted matrix notation $\sigma_i = c_{ij} \epsilon_j$ where $i, j = 1, 2, 3$ refer to longitudinal stresses and strains along axes X_1, X_2, X_3 , respectively. For shearing motions about each of the axes, $i, j = 4, 5, 6$. The discussion that follows will be concerned with the relative values of c_{11}, c_{22} , and

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c_{33} , the coefficients relating change in length along a principal direction to a parallel component of stress.

The stiffness coefficients for silicate minerals presented in table I show a correlation between elastic anisotropy and structure type. All silicates contain (SiO_4) tetrahedra and, depending on how the tetrahedra are linked together, can be classified as framework, layer, chain, or ring silicates.

TABLE I. *Longitudinal stiffness constants expressed in megabars* (Hearmon, 1966)

<i>Framework silicates</i>		
α -quartz	SiO_2	$c_{11} = c_{22} = 0.9, c_{33} = 1.1$
silica glass	SiO_2	$c_{11} = c_{22} = c_{33} = 0.8$
<i>Single chain silicates</i> (pyroxenes)		
aegirine	$\text{NaFeSi}_2\text{O}_6$	$c_{11} = 1.9, c_{22} = 1.8, c_{33} = 2.3$
augite	$(\text{Ca, Mg, Fe})\text{SiO}_3$	$c_{11} = 1.8, c_{22} = 1.5, c_{33} = 2.2$
diopside	$\text{CaMgSi}_2\text{O}_6$	$c_{11} = 2.0, c_{22} = 1.8, c_{33} = 2.4$
<i>Double chain silicates</i> (amphiboles)		
hornblende	$(\text{Ca, Na, K})_{2-3}(\text{Mg, Fe, Al})_3(\text{Si, Al})_8\text{O}_{22}(\text{OH})_2$	$c_{11} = 1.2, c_{22} = 1.8, c_{33} = 2.0$
<i>Ring silicates</i>		
beryl	$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$	$c_{11} = c_{22} = 3.1, c_{33} = 2.8$
tourmaline	$(\text{Na, Ca})(\text{Li, Mg, Al})_3(\text{Al, Fe, Mn})_6(\text{OH})_4(\text{BO}_3)_3\text{Si}_6\text{O}_{18}$	$c_{11} = c_{22} = 2.7, c_{33} = 1.6$
<i>Layer silicates</i>		
biotite	$\text{K}(\text{Mg, Fe})_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	$c_{11} = c_{22} = 1.9, c_{33} = 0.5$
muscovite	$\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	$c_{11} = c_{22} = 1.8, c_{33} = 0.6$
phlogopite	$\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	$c_{11} = c_{22} = 1.8, c_{33} = 0.5$

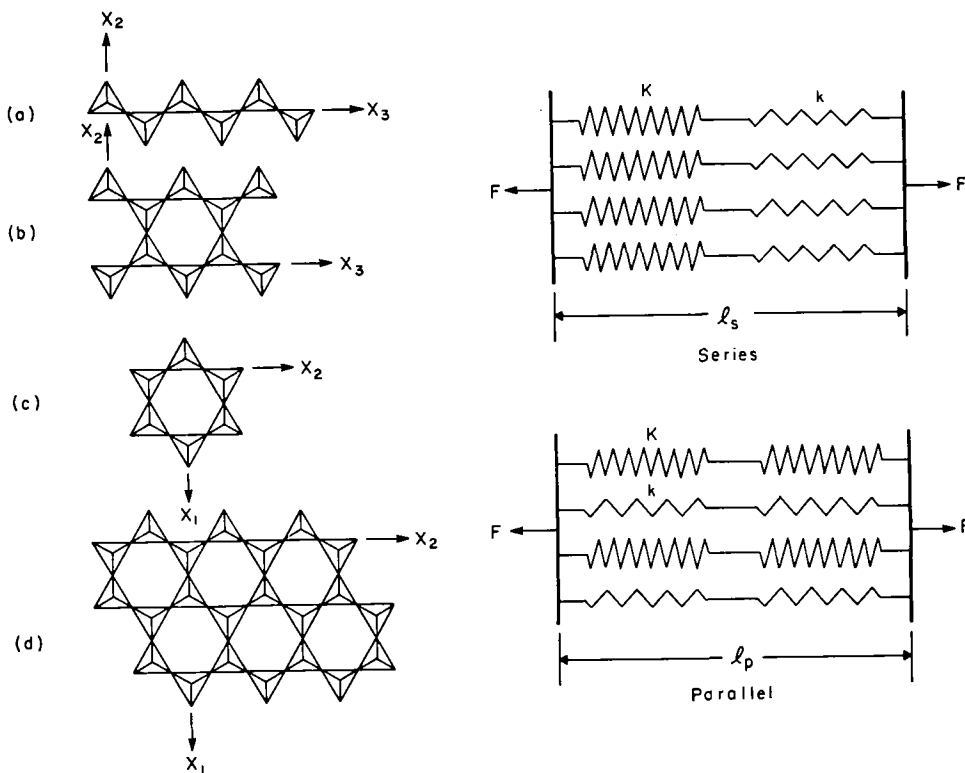
In framework silicates such as quartz and silica glass, the tetrahedra form three-dimensional networks. Since the bonding is nearly isotropic, there is no cleavage and little anisotropy in hardness or elasticity. Compare the longitudinal elastic moduli given in table I. When corrected for density ($\rho = 2.65 \text{ g cm}^{-3}$ for quartz and 2.2 g cm^{-3} for silica glass) the stiffness constants are nearly identical for the two forms of SiO_2 , substantiating the relation between bulk modulus and volume (Anderson and Nafe, 1965).

The influence of crystal structure becomes more obvious in the chain silicates. Pyroxenes contain SiO_3 single chains, and amphiboles Si_4O_{11} double chains as shown in fig. 1. Elastic coefficients in table I are referred to the measurement directions denoted by arrows in fig. 1. Bonding is stronger along the chain direction giving rise to pronounced cleavage. We also expect the crystal to be stiffer in this direction, resulting in larger moduli. Experiment confirms this suggestion; the stiffness parallel to the chain (c_{33}) is the largest in pyroxenes and amphiboles. We also note that c_{22} has increased considerably in hornblende, possibly because of the increase of chain width in this direction.

Beryl and tourmaline, two ring silicates, show a similar correlation between stiffness and structure. Both contain Si_6O_{18} rings as illustrated schematically in fig. 1. We expect strong bonding and greater stiffness in the plane of the ring, hence c_{33} should

be smaller than c_{11} and c_{22} as observed. Beryl is not very anisotropic because of the strong Be-O and Al-O bonds connecting the rings.

When Si_6O_{18} rings adjoin one another, the tetrahedral layer found in micas is formed. The cleavage and stiffness anisotropy become very obvious in layer silicates, where c_{11} and c_{22} are three times larger than c_{33} . This is the maximum elastic anisotropy observed, for reasons that are explained later.



FIGS. 1 and 2: FIG. 1 (left). Arrangements of SiO_4 tetrahedra in silicates. (a) Single chain silicates. (b) Double chain silicates. (c) Ring silicates. (d) Layer silicates. FIG. 2 (right). Series and parallel connections of springs used to represent atomic bonds. Strong bonds have large force constants K , while weak bonds are easily stretched and have smaller constants k .

Mechanical analogue. In the lattice theory of elastic coefficients, stiffness coefficients are related to atomic force constants by determining the energy associated with various strain components. The calculation is cumbersome for a monatomic simple cubic lattice (Kittel, 1953), and would be overwhelming for most mineral structures. To avoid mathematical complexity and gain further physical insight regarding the causes of elastic anisotropy, we make use of a simple mechanical system.

The analogy used to describe elastic anisotropy is one in which two mechanical springs represent atomic bonds with force constants k and K . Tables of force constants

(Wilson, Decius, and Cross, 1955) derived from infrared vibrational spectra show that typical values are within an order of magnitude of 10^5 dynes/cm ($1 \text{ md}/\text{\AA}$). In general the strongest bonds have the largest force constants because deep potential wells have larger second derivatives when well shapes are similar. Thus, for example, it is found that the stretching-force constants for C—C, C=C, and C≡C are about 5, 10, and $16 \text{ md}/\text{\AA}$, respectively.

To explain the elastic properties of solids containing both strong and weak bonds, consider the spring systems illustrated in fig. 2. When strong and weak springs are connected in series, most of the elastic energy is stored in the weak springs, while in the parallel connection the strong spring contains most of the energy. Let K and k be the force constants of two bonds arranged in series and parallel positions, as shown. This is a schematic representation of the bonding in mica. In muscovite Si—O and K—O bonds are in series for tensile stresses applied perpendicular to the sheet and in parallel when the applied forces lie in the plane. In pyroxenes, the parallel connection applies to measurements along the silicate chains, and series connections to the two perpendicular directions.

Analysing the series arrangement for an applied tensile force F gives

$$F = \sigma A_s = n_s K u_K + n_s k u_k = c_s A_s u_s / l_s,$$

where σ is the stress acting on a surface of cross sectional area A_s containing n_s chains, u_s/l_s is the resulting strain in the series (s) connection whose overall stiffness is c_s . u_K and u_k are the displacements of the springs with force constants K and k . An identical force applied to the parallel arrangement gives an analogous expression, $F = \sigma A_p = n_p K u_K + n_p k u_k = c_p A_p u_p / l_p$.

For the series connection both springs experience the same force so that their restoring forces are equal, $u_K K = u_k k$. The total displacement $u_s = u_k + u_K$, giving $u_k = u_s / (1 + k/K)$ and $u_K = u_s / (1 + K/k)$, and

$$c_s = \frac{n_s l_s}{A_s} \left(\frac{2kK}{k+K} \right) \quad (1)$$

In solving the parallel chain system, it is obvious that the displacements of the different springs are equal and that $u_p = 2u_k = 2u_K$. Substitution in the force equation gives the elastic constant

$$c_p = \frac{n_p l_p}{A_p} \left(\frac{k+K}{2} \right) \quad (2)$$

Note that c_s and c_p are unequal, even when all the springs are identical ($k = K$). The elastic coefficients depend on bond lengths through l and on the number of chains per unit area in different directions.

To determine the effects of strong and weak bonding on the elastic constants, assume that the geometric factors are about equal so that $n_p l_p / A_p = n_s l_s / A_s$, giving the ratio $c_s / c_p = 4kK / (k+K)^2$. In fig. 3, the quantity c_s / c_p is plotted as a function of K/k to illustrate the effects of mixed bonding. When $K/k = 1$, all bonds have the same force constant, and the elastic constants are of course the same for series and parallel connection, so that $c_s / c_p = 1$. At the other extreme $c_s / c_p \rightarrow 0$ as $K/k \rightarrow \infty$, but the

approach to zero is very slow. For $K/k = 2$, $c_s = 0.9c_p$ and even for $K/k = 10$, $c_s = 0.3c_p$. Since force constants for various chemical bonds are all within an order

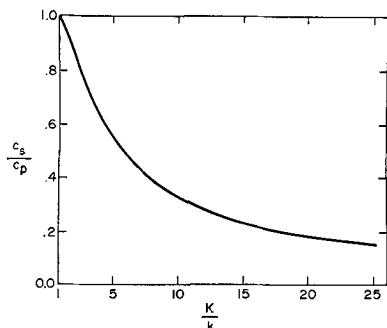


FIG. 3. Stiffness anisotropy for series and parallel connections plotted as a function of spring constant ratio K/k . The series connection is far more pliant when $K \gg k$.

of magnitude of one another, the expected maximum elastic anisotropy is about 3:1 as observed in muscovite (table I). In all cases $c_p > c_s$ as observed experimentally.

It would be useful to predict the magnitude of the observed stiffness coefficients (table I) as well as their anisotropy. For chains identical in size, number, and force constants, equations (1) and (2) reduce to

$$c_p = c_s = \frac{nl}{A}k \quad (3)$$

n , l , and A can be evaluated from the crystal structure, but k cannot. Typical values for k are 0.1 to 1.0 millidynes/Å for bending force constants and 1–10 md/Å for stretching constants.

Both types of deformation come into play in minerals. When an SiO_4 tetrahedron is stressed, for instance, both stretching and bending will take place. Si–O force constants (Matossi, 1949) are fairly typical with stretching constants 4 to 5 md/Å and bending constants 0.6 to 0.9 md/Å, while those involving Al are 10 to 20 % smaller (Hidalgo and Serratosa, 1956). A careful analysis would be required to determine the correct force constant to use in (3), but in any case all the atomic force constants have not been determined by spectroscopic data. When an average value $k \approx 1$ md/Å is substituted in (3), elastic stiffness coefficients of the right magnitude are obtained. Taking $l \approx 3$ Å, $n/A \approx 1/l^2 \approx 0.1$ Å⁻² gives $c \approx 3 \times 10^{12}$ dynes/cm² = 3 megabars, comparable to the experimental values (table I).

Pressure dependence of the elastic stiffness

The pressure derivatives of the elastic coefficients of minerals determine changes in seismic wave velocities deep within the earth, and are strong indicators of the onset of phase transformation. Elastic stiffness coefficients and their initial pressure derivatives for four minerals are listed in table II.

Using the spring model just described, three observations are to be rationalized: The pressure derivatives are all about one to ten megabar/megabar (dimensionless). Large stiffnesses usually show greater pressure derivatives than small ones: if $c_{11} > c_{22}$, then $\partial c_{11}/\partial P > \partial c_{22}/\partial P$. Pressure derivatives of the stiffnesses are positive in dense-packed structures but in open structures are occasionally negative. Quartz and beryl each have one negative derivative but the close-packed corundum and forsterite structures show none.

To estimate the pressure dependence of the elastic stiffness we again make the approximation that $n/A \sim 1/l^2$, then $c = k/l$, and

$$\Delta c/\Delta P = (1/l)(\Delta k/\Delta P) - (k/l^2)(\Delta l/\Delta P).$$

Assuming an isotropic solid, $\Delta P \sim (\Delta l)(c/l)$ so that

$$\frac{\Delta c}{\Delta P} \approx \frac{1}{c} \frac{\Delta k}{\Delta l} - \frac{k}{lc}. \quad (4)$$

A rough value for $\Delta k/\Delta l$ can be obtained by examining how k varies with interatomic distance. Short strong bonds have larger stiffnesses than long bonds. The bond stiffness

TABLE II. Comparison of elastic stiffnesses and their initial pressure derivatives for four minerals. Adiabatic stiffnesses c_{ij} are expressed in megabars, and the pressure derivatives $\partial c_{ij}/\partial P$ are dimensionless

<i>ij</i>	Beryl Yoon, 1971		Quartz McSkimin, Andreatch and Thurston, 1965		Corundum Gieske and Barsch 1968		Forsterite Graham and Barsch, 1969	
	c_{ij}	$\frac{\partial c_{ij}}{\partial P}$	c_{ij}	$\frac{\partial c_{ij}}{\partial P}$	c_{ij}	$\frac{\partial c_{ij}}{\partial P}$	c_{ij}	$\frac{\partial c_{ij}}{\partial P}$
11 } 22 }	3.09	4.5	0.87	3.3	4.98	6.2	3.29	8.3
33	2.83	3.4	1.06	10.8	5.02	5.0	2.01	5.9
44 } 55 }	0.66	-0.2	0.58	2.7	1.47	2.2	2.36	6.2
66	0.90	0.3	0.40	-2.7	1.68	1.5	0.67	2.1
12	1.29	3.9	0.07	8.7	1.63	3.3	0.81	1.7
13 } 23 }	1.19	3.3	0.12	6.0	1.17	3.7	0.07	4.3
14	—	—	0.18	1.9	-0.23	0.1	0.07	3.5

for Si-O is about 10 % larger than that for Al-O, and the bond length is about 10 % shorter. Therefore $\Delta k/\Delta l$ is roughly 1 md/Å². Substituting this value in (4) along with $c = 3 \times 10^{12}$ dyne/cm², $k = 1$ md/Å and $l = 3$ Å gives $\Delta c/\Delta P \approx 2$ (dimensionless), the right order of magnitude.

To explain the second observation consider the anisotropic structure in fig. 4a. The structure contains tightly bonded atoms in the X_1 direction and very loose bonding along X_2 . From arguments previously presented $c_{11} > c_{22}$. Now consider their pressure derivatives. From eq. (3) the change in stiffness with pressure is related to the change in the number of chains per unit area n/A , their repeat distance l , and bond stiffness k :

$$\frac{\Delta c}{\Delta P} = lk \frac{\Delta(n/A)}{\Delta P} + \frac{nk}{A} \frac{\Delta l}{\Delta P} + \frac{nl}{A} \frac{\Delta k}{\Delta P} \quad (5)$$

Under pressure the structure will compress mainly along X_2 because of the weak bonding in that direction, giving the exaggerated deformation in fig. 4b.

For the X_1 direction there will be little change in l_1 and k_1 so that

$$(\Delta c_{11}/\Delta P) \approx l_1 k_1 \Delta(n/A)/\Delta P.$$

The number of chains per unit area increases rapidly with pressure because of the big reduction in l_2 , decreasing A and increasing n/A . Therefore c_{11} increases rapidly with pressure.

For direction X_2 , there is little change in n/A with pressure because l_1 hardly changes. Therefore $\Delta c_{22}/\Delta P \approx (n/A)(k_2 \Delta l_2/\Delta P + l_2 \Delta k_2/\Delta P)$. The length and spring constant are inversely related to one another so that the increase in spring constant is partially offset by change in length. Hence c_{22} will not increase rapidly with pressure.

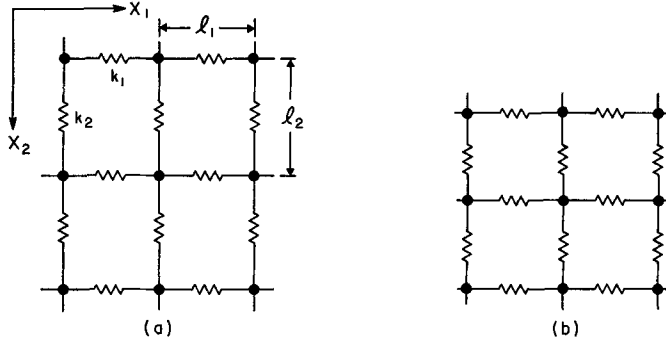


FIG. 4. Anisotropic model at low (a) and high (b) pressures.

The third observation regarding the pressure dependence is the occurrence of negative derivatives in open structures like beryl and quartz. When a close-packed structure is compressed, the atoms move closer together but this need not be true in an open structure where rotations can take place. To determine the effect on the elastic constants, consider equation (5) describing the pressure dependence of the stiffness. The new feature here is the pressure dependence of the stiffness k . If we are considering the stiffness along X_1 , for example, k_1 may decrease with P because at high pressure a stress along X_1 produces a bending rather than a stretching motion. The stiffness coefficients for bending are considerably smaller than for stretching. Thus rotation can lead to negative pressure-dependence of shearing stiffness coefficients.

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