SOME DIRECT MEASUREMENTS OF THE SURFACE ENERGY OF QUARTZ AND ORTHOCLASE

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Abstract

Specific surface energy, γ, of quartz and orthoclase was determined by the Obreimoff-Gilman method, in which the work of cleaving a single crystal is measured. The γ of quartz ranges from about 400 ergs/cm² for $(10\bar{1}1)$ and $(\bar{1}011)$ to about 1000 ergs/cm² for $(10\bar{1}0)$ and $(11\bar{2}0)$. The γ measured for orthoclase is about 7800 ergs/cm². The γ was calculated from elastic constants for a number of common minerals. The range is from 200 to 2000 ergs/cm².

Introduction

The surface energy of a solid may be defined as the work required to produce a certain amount of new surface. In a rough way it is a measure of the density and strength of broken atomic bonds at a surface. In a number of geologic problems the surface energy of minerals may be extremely important. For example, surface energy may partly determine brittle strength of rocks. The best cleavage of minerals may be the plane of minimum surface energy (Gilman, 1959). Surface energy may control development of certain textural features of igneous and metamorphic rocks. Certain methods of mineral separation depend upon surface energies of minerals.

In spite of this, few measurements of surface energy of minerals have been made. One reason is that surface energy per unit of surface area ("specific surface energy") is a very small quantity. It is difficult to design an experiment in which new surface is produced and in which one can easily identify surface energy among the usually much larger quantities of energy which go into heat or into producing plastic flow or chemical changes. Obreimoff (1930) was one of the first to succeed in doing this; he measured directly the specific surface energy of mica. Gilman (1960) recently improved Obreimoff's method, adapting it to a wide variety of crystals. Gilman measured the specific surface energies of a number of substances in the NaCl structure type, as well as calcite, fluorite and others.

In the present study Gilman's method is applied to two materials of considerable geologic interest. The first, orthoclase, has good cleavage and Gilman's method is directly applicable. The second, quartz, has very poor cleavage and additional experimental techniques had to be developed before Gilman's method could be used. The experiments were done at room temperature. Gilman's experiments were carried out at
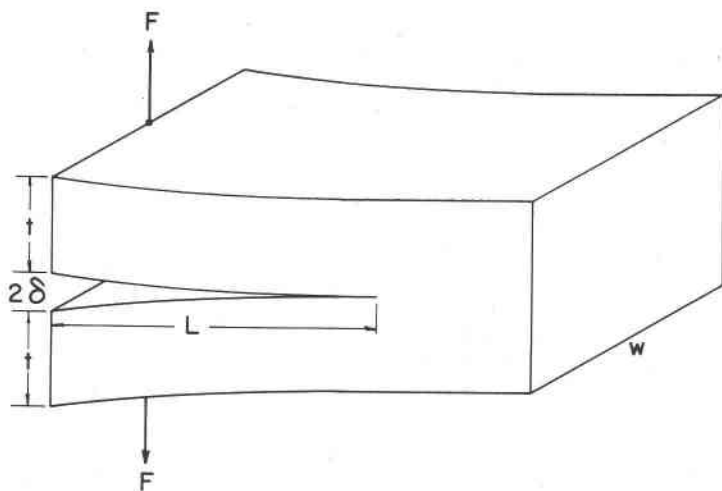
Fig. 1. Partially cleaved bar of single crystal

temperatures down to $-196°$ C. to avoid plastic flow of his materials.

Following description of the experiments below, all known measured surface energies of minerals are tabulated. These are compared with surface energies calculated from elastic constants.

For a review of the general subject of surface energy and its measurement the reader is referred to Gilman (1960) and Partington (1952).

THEORY

General

In the method used here a single flat crack is introduced into a crystal and then the work required to cause the crack to enlarge is measured. From an energy balance equation, evaluated as the crack starts to grow, one obtains the surface energy per unit area of crack surface.

The starting material is a single crystal cut to the shape of a rectangular bar. A long flat crack is introduced into the bar. For crystals with good cleavage this is a cleavage crack; for noncrystalline materials or materials with poor cleavage the crack may have any orientation. The bar is next gripped at the split end and pulled in such a way that the crack extends. In Fig. 1 the bar is shown at the instant the crack starts to enlarge under the action of the force, F. The displacement of the split ends, 2δ, is grossly exaggerated.

For this system Gilman (1960, p. 2211) showed that specific surface energy, γ, of the crack surface is

$$\gamma = 6F^2L^2/Ew^2t^3 \tag{1}$$

in which F is the force just needed to cause the crack to enlarge, E is Young's modulus in the direction of crack growth, and L, w and t are bar dimensions (Fig. 1).

One difficulty with Gilman's analysis is that elastic energy due to stress concentration near the crack tip was apparently not considered in determination of the total elastic energy in the system shown in Fig. 1. It is necessary to see how big a contribution this makes before Eq. (1) can be used.

Crack tip energy

The elastic energy, U', stored in the region near the tip of the crack must be determined. Consider a bar containing a crack several units of t long with the tip of the crack sufficiently far away from the uncracked end so that the stress distribution at the crack tip is unaffected by the free surface. The bar is separated, for analysis, into three parts (Fig. 2), with the surface of separation an arbitrary distance c' from the crack tip. The forces, F, and moments M on the cut end are shown schematically. The thickness of the bar normal to the diagram is w.

Normal stresses, which act in a direction parallel with the plane of the crack will have little influence on the stress at the crack tip and therefore on the strain energy associated with the crack tip. Only the shearing stress resulting in the shear force F will be significant. Unfortunately the exact stress distribution at the crack tip arising from
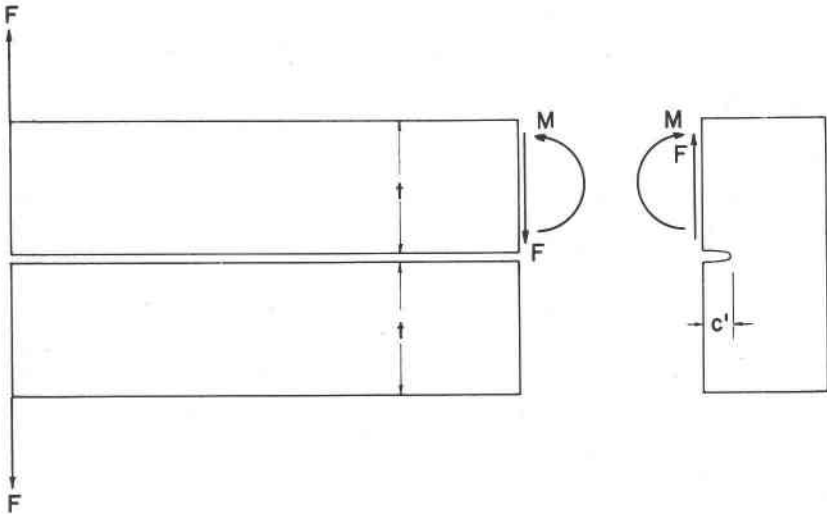

Fig. 2. Analysis of stress in partially cleaved bar. Stresses omitted in lower half of bar for simplicity.

such shear loads is not available from the literature. An approximation to the loading which yields the correct order of magnitude for the strain energy at the crack tip is made by assuming that the transverse load F can be replaced by a pressure p acting on the crack surface, where

$$p = F/c'w.$$

Then the strain energy will be approximately (Orowan, 1949, p. 193)

$$U' = (c')^2 p^2 w/E = F^2/Ew.$$

But for a system in which the force, F, remains constant as the crack grows, then

$$dU'/dL = 0,$$

and there is thus no contribution from crack tip energy as the crack starts to grow. Equation (1) is thus valid. For a system in which δ rather than F is held constant, there is a contribution but it is small and can be neglected for the range of bar sizes used in the experiments here.

EXPERIMENTS

Preparation of material

Bars were cut from blocks of clear Brazilian quartz and from two large single crystals of orthoclase from pegmatites. Quartz was etched in concentrated HF for 3 hours, feldspar for 1 hour following sawing, rough polishing and the special treatment given quartz to produce the desired starting configuration (Fig. 1). Quartz bars containing Dauphiné twins, as revealed by the etching, were discarded.

A special technique was developed to form a large single crack in the quartz bars in any desired direction. First a small hole was drilled through the bar at the center of one of the large faces (Fig. 3a). The axis of the hole lay in the plane whose surface energy was desired. Next the bar was compressed between steel plates (Fig. 3b). This produced tension at two points on the surface of the hole and a crack formed. Further compression caused it to grow until it was about half as long as the bar. One end of the crack was next drawn out to the end of the bar by placing lead between that end of the bar and the steel plate (Fig. 3c). This gave a single straight crack in the desired plane, which was the starting configuration.

The starting configuration in feldspar was easily attained. A wedge with an included angle of 30° was pressed against one end of the etched bar while the other end was gripped in a clamp. The long axis of the wedge was held parallel with the trace of the (001) cleavage on the end of the bar. A cleavage crack was initiated by carefully pressing the wedge against the bar in a small vice.
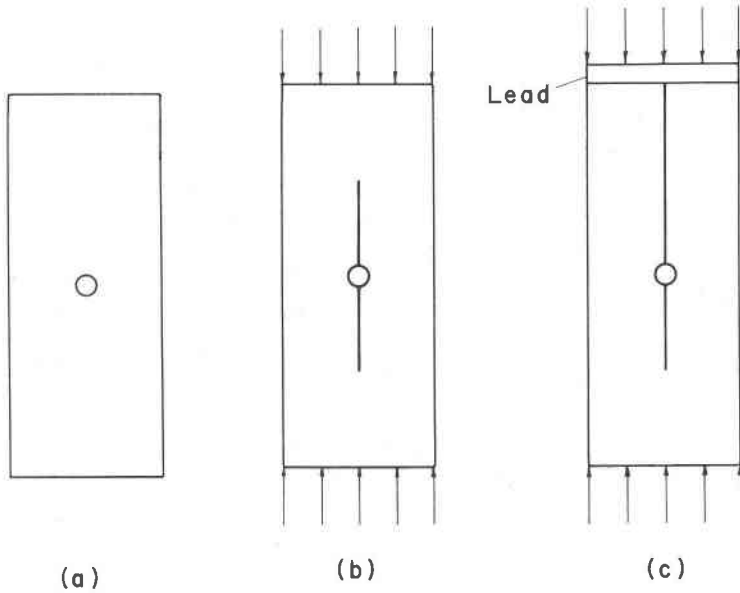
Fig. 3. Method of introducing single crack into bar of quartz. Not to scale.

After the above preparation, the bars of quartz or orthoclase were immediately gripped and cleaved.

Measurements

The split ends of the bars were pulled by pivoted grips in a direction normal to the long dimension of the bars (in the direction of the forces, F, in Fig. 1). Force was applied by hand through a screw at the rate of about 20 g/sec. Force was measured by a load cell and plotted *vs.* time on an XY recorder.

Dimensions of the bars were measured by vernier calipers to 0.02 mm. Length of the crack, L, could be obtained precisely because a sharp step forms when the crack stops. This marks the point of farthest advance of the crack at the stage shown in Fig. 3(c), and is observed after the bar is finally split in two.

Force and dimensions are shown in Table 1 together with calculated γ. Probable experimental error of γ is about 20 per cent, due principally to uncertainty in t. The two halves of the cleaved bar are rarely of equal thickness and the average t must be used.

The quartz bars were cut so that surface energy of a number of common faces could be measured. The longest dimension of the bars was in all cases in the same plane as the *c*-axis. Young's modulus of the quartz

bars was computed from elastic constants (Birch *et al.*, 1942, p. 68) using standard formulae (Nye, 1957, p. 145). The feldspar bars were cut so that the surface to be measured was the (001) cleavage; the long axis of the bars was approximately parallel with the *b*-axis. The values of Young's modulus of quartz and felsdpar are given in Table 1 in megabars (1 megabar equals 10^{12} dynes/cm²).

The surfaces of the cracks produced in quartz were mirror smooth and probably did not deviate more than a few degrees from the desired plane. As a crack was extended it did in some cases curve out of the plane in which it was initiated. As this always happened gradually, it could be safely assumed that one was measuring the γ of the plane having the original crack orientation.

With feldspar it was much less certain that one was producing a single

TABLE 1. MEASUREMENTS OF SURFACES ENERGY

Mineral	Face	E/mb	F/g	t/cm	w/cm	L/cm	γ/ergs	cm⁻²
Quartz	(11$\bar{2}$0)	1.03	2650	0.77	0.84	2.43		760
Quartz	(10$\bar{1}$1)	0.91	780	0.68	0.62	2.90	280	
		0.91	1690	0.66	1.00	2.52	420	
		0.91	1760	0.66	1.01	2.31	370	
		0.91	2530	0.62	0.81	1.45	570	
Ave.								410
Quartz	($\bar{1}$011)[1]	0.91	2680	0.64	1.29	2.05	460	
		1.25	3320	0.61	1.36	2.05	530	
Ave.								500
Quartz	(10$\bar{1}$0)	1.03	3100	0.65	1.30	2.62	830	
		1.03	4040	0.62	1.36	2.27	1110	
		1.03	5400	0.65	1.52	1.91	980	
		1.03	5720	0.71	1.00	1.49	1180	
Ave.								1030
Orthoclase	(001)[2]	0.83	3950	0.35	0.94	1.43	6000	
		0.83	4000	0.48	1.20	2.80	5680	
		0.83	7000	0.59	1.13	2.43	7980	
		0.83	7500	0.57	1.00	2.00	8800	
		0.83	7700	0.65	1.11	3.00	11300	
		0.83	9040	0.63	1.03	1.75	6850	
Ave.								7770

[1] This bar was twinned, with the twin boundary just inside the point of farthest advance of the crack before pulling. The crack propagated from a region of (10$\bar{1}$1) into a region of ($\bar{1}$011). The measured γ was that of ($\bar{1}$011) although E must be that of (10$\bar{1}$1).

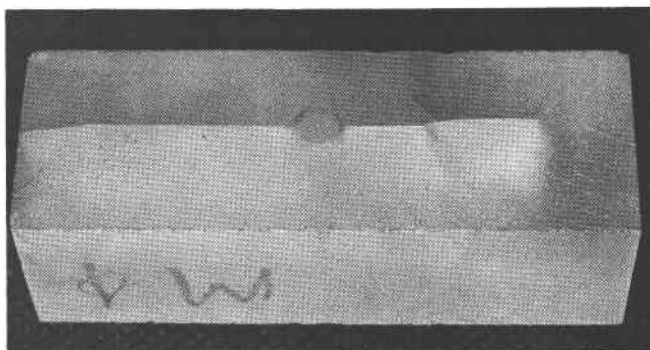[2] This bar of orthoclase was from one crystal, all the other bars from another crystal.

Fig. 4. Partially cleaved bar of quartz. Apart from zigzag side crack bar was suitable for measurement of γ. Longest dimension of bar is 1 inch.

cleavage plane. Before pulling, a cleavage crack often appeared to be made up of short segments in slightly different planes offset from one another and joined by short bridging cracks. After cleaving the bars small flakes and splinters always covered the surface. It appeared that cracks must be propagating not on one but on several cleavage planes.

Certain crack orientations in quartz could only be produced with great difficulty. This was particularly true with $(\bar{1}011)$; reliable measurements on only 2 or the original 8 bars were made. About half of the $(10\bar{1}1)$ and $(10\bar{1}0)$ bars gave reliable data. By comparison, 8 out of 10 feldspar bars gave reliable data. Most of the difficulty with quartz stems from the method of producing the crack. It is difficult to draw the crack out at one end of the bar, while keeping it well inside the other end, and without developing side cracks. Diameter of the hole may be important; an optimum diameter-width ratio is about $\frac{1}{4}$. Much of the loss occurred here before this ratio was discovered. A typical quartz bar, usable except for a side crack, is shown in Fig. 4.

DISCUSSION

Estimate of γ from elastic constants

A rough estimate of γ can be obtained from the elastic constants of a crystal if one makes the assumption that the force acting across any surface, such as a cleavage plane, may be represented by a sine function. The force is taken to be zero when the atoms across the plane have their normal separation, and to die out again at a distance equal to the atomic radius of these atoms. From this simple theory an expression for γ is found to be (Gilman, 1960, p. 2216):

$$\gamma = Ea^2/d_0\pi^2 \qquad (2)$$

in which E is Young's modulus normal to the plane in question and a is the atomic radius of atoms lying in the cleavage plane. The quantity d_0 is the spacing of cleavage planes; it may be less than or equal to unit cell dimensions. For example, calcite has a single $(10\bar{1}1)$ cleavage plane per unit cell, so that d_0 here is the crystallographic d-spacing of $(10\bar{1}1)$. Aragonite, on the other hand has two (010) cleavage planes per unit cell, so that here d_0 is equal to half the crystallographic d-spacing of (010).

To calculate γ for some plane in a crystal, then, one has to know E, which is readily obtainable from measured elastic constants, and a and d_0 which are obtainable from cell constants after some consideration of the crystal structure. In Table 2 γ is given for common minerals for which elastic constants are available. The plane is either the best cleavage of the mineral, or, for minerals with essentially no cleavage, a low index face. The source of the crystallographic data was standard works such as Strukturbericht, the elastic data, Birch *et al.* (1942) and Verma (1960).

In the calculation of γ for quartz a number of assumptions had to be made about cleavage in quartz. Fairbairn's analysis (1939) which includes Niggli's illumination diagrams of the bonding in quartz served as the basis of these assumptions.

To obtain d_0 of, say, $(10\bar{1}1)$ one has to determine the number of cleavage planes per unit cell parallel to $(10\bar{1}1)$. Cleavage planes are assumed to cut the least number of first order Si-O bonds. It is further assumed to be immaterial whether the bonds cut belong to the same or to different tetrahedra, or whether the resulting surface is neutral or not. On this basis there are 3 cleavage planes per unit cell for $(10\bar{1}1)$ and $(\bar{1}011)$, and 4 for $(10\bar{1}0)$.

Discussion

Although the theory leading to Eq. (2) gives at best a rough estimate of γ for most minerals and particularly for silicates, it probably gives results correct to an order of magnitude. It is therefore of interest to compare predictions of this theory with measurements. Measurements available from the present work, and from Gilman and others are given in Table 2.

Agreement in Table 2 between measured and predicted γ for halite, periclase and even calcite and fluorite is seen to be good. This observation combined with good agreement for LiF, BaF_2, Si and Fe (3% Si) reported by Gilman (1960, p. 2217) suggests that, except for silicates, Eq. (2) gives a result which in general will not be off by more than a factor of about 2. Even the results for quartz reported here agree with the simple theoretical prediction to within a factor of 2. One can therefore make certain generalizations based on the calculated results in Table 2.

TABLE 2. SUMMARY OF MEASURED AND CALCULATED γ

Mineral	Face	d_0/Å	a/Å	E/mb	γ/ergs cm^{-2} calc.	meas.	
Graphite[1]	(0001)	—	—	—	119		Good, et al., (1958)
Calcite[2]	(10Ī1)	3.90	1.20	0.52	190		
						230	Gilman (1960)
Aragonite	(010)	4.00	1.20	0.75	270		
Halite	(100)	2.80	1.40	0.44	310	330	Gilman (1960)
Sphalerite	(110)	—	—	—	360		Gilman (1959)
Fosterite[3]	(010)	5.10	1.05	1.70	370		
Muscovite	(001)	—	—	—	—	375	Obreimoff (1930)
Fluorite	(111)	4.10	1.56	0.92	540	450	Gilman (1960)
Barite	(001)	3.55	1.35	0.94	480		
Quartz[4]	(10Ī1)	1.10	0.80	1.3	760	410	
	(Ī011)	1.10	0.80	0.77	450	500	
	(10Ī0)	1.06	0.80	0.79	480	1030	
Galena	(100)	—	—	—	625		Gilman (1959)
Hematite	(0001)	2.30	1.00	2.25	980		
Glass	—	—	—	—	—	1214	Berdennikov (1933)
	—	—	—	—	—	540	Griffith (1921)
Periclase	(100)	2.10	1.05	2.50	1310	1200	Gilman (1960)
Rutile	(110)	1.20	1.00	1.70	1420		
Pyrite	(100)	5.40	1.50	3.70	1550		
Spinel[5]	(111)	2.35	1.05	3.80	1780		
Orthoclase[6]	(001)	3.6	0.83	1.0	200	7770	

[1] This estimate is based on a theory of interfacial energy and heats of immersion of graphite in organic liquids (Good et al., 1958).

[2] Cleavage is assumed to leave the carbonate units intact. Gilman (1960, p. 2217) calculated γ to be 380 ergs/cm^2 due to his choice of a different value of E perpendicular to (10Ī1).

[3] Silica tetrahedra are assumed to remain intact during cleavage and a is taken as the average of the Mg and O radii.

[4] The distance a is taken as half the Si-O distance in low quartz (Machatschki, 1936).

[5] Cleavage is assumed to sever Mg-O bonds and a is taken as the average of the Mg and O radii.

[6] E was determined from linear compressibility (Birch et al., 1942, p. 58) assuming that Poisson's ratio is 0.27. The distance a is taken as half the Si-O distance (Bailey and Taylor 1955).

Specific surface energy of the common minerals, omitting feldspar for the moment, ranges from about 100 to 2000 ergs/cm^2. In general the harder minerals have higher γ, although there are a number of exceptions. The variation of γ in a single material (quartz) may be quite large with respect to differences in γ among minerals.

Gilman has suggested (1959) that relative ease of cleavage parallel to

various planes in a mineral is determined by γ of these planes. This seems to be borne out by the present results of quartz. γ of $(10\bar{1}1)$ and $(\bar{1}011)$ is lower than that of $(10\bar{1}0)$ and $(11\bar{2}0)$. According to nearly all investigators the best cleavage in quartz is $(10\bar{1}1)$, the next best is $(\bar{1}011)$ with very poor cleavage parallel to $(10\bar{1}0)$, $(11\bar{2}0)$ and other faces. Probable experimental error is so great that no significance should be attached to the difference reported here between γ of $(10\bar{1}1)$ and $(\bar{1}011)$.

The value of γ reported here for quartz differs markedly from that obtained by Schellinger (1952) by a calorimetric method. For crushed material he obtained 107,000 ergs/cm² for quartz, 60,000 ergs/cm² for pyrite, 32,000 ergs/cm² for calcite and 26,000 ergs/cm² for halite. He thought that his results were several orders of magnitudes too high but offered no explanation. In his method granulated material was crushed in a ball mill, the whole being immersed in a calorimeter. Knowing the work done on the material, the heat evolved and from measurements of surface area, an energy balance equation gave specific surface energy of the material. Surface area of the crushed material was obtained by the BET adsorption method (using CO_2 at $-78.5°$ C.) and also by air permeability. The most likely source of the discrepancy in his results is the surface area measurement. Inability of the gas to completely penetrate the innumerable fissures in the crushed material would give a low figure for new surface area produced and hence an apparent specific surface energy which was too high. Rough agreement of the present results for quartz with γ of glass measured by other methods and with γ obtained by various theoretical arguments suggests that the lower values reported here for quartz are more nearly correct than those obtained by calorimetric measurments.

The γ reported for orthoclase is probably quite different from that which would be obtained for a perfect single crystal. The frayed splintery cleavage surfaces produced suggest that cleavage of natural orthoclase is more complicated than the simple model assumed in the derivation of Eq. (1). The poor reproducibility of the measurements and the big difference between the measured γ and that of other hard minerals (Table 2) also suggest the influence of factors not included in the theory. These factors may include plastic flow near the crack tip, or more likely, a blocking effect on crack propagation by submicroscopic domains of soda-rich feldspar. Either factor would increase apparent specific surface energy. That both crystals gave values between 5000 and 10,000 ergs/cm² may have some significance where γ of ordinary feldspar rather than that of more perfect material is desired. For this reason the data are included.

Extension to other minerals

Additional elastic constants are needed to enlarge the list of surface energies of the common minerals given in Table 2, whether these are calculated or measured surface energies. For the measurement of γ, the minimum requirement is Young's modulus parallel to the plane of interest.

Calculation of surface energy using Eq. (2) has little meaning for silicates and it is proably not worthwhile to continue in this direction unless a more realistic theory can be developed.

To measure γ in serveral directions a mineral must have essentially no cleavage. Few minerals resemble quartz in this respect. This is unfortunate, for it would be of considerable interest to test Gilman's hypothesis further, that cleavage planes are planes of minimum surface energy. This has been tested for the first time here with quartz, and seems to be borne out.

Summary and Conclusions

Specific surface energy, γ, of quartz and orthoclase has been determined by the Obreimoff-Gilman method, in which one measures the work of cleaving a single crystal. The principal difficulty to be overcome was the introduction of a single flat crack into a crystal of quartz. Once this was accomplished, γ could be measured in any desired direction. It was measured in $(10\bar{1}1)$, $(\bar{1}011)$, $(10\bar{1}0)$ and $(11\bar{2}0)$ where it ranged from 400 to 1000 ergs/cm^2. The rhombohedra, parallel to which quartz cleaves most easily, have the lowest γ. This supports Gilman's suggestion that cleavage planes in crystals are planes of low γ.

Specific energy of orthoclase was about 7800 ergs/cm^2, a figure which is undoubtedly too high, by perhaps as much as an order of magnitude. The cleavage process in natural orthoclase may be complicated by factors such as plastic flow or a blocking effect on crack propagation by submicroscopic domains of soda-rich feldspar.

The γ of a number of common minerals was calculated from elastic constants. γ ranges from 200 to 2000 ergs/cm^2.

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REFERENCES

BAILEY, S. W. AND W. H. TAYLOR (1955), The structure of triclinic potassium feldspar. *Acta Cryst.* **8,** 621–632.

BERDENNIKOV, W. P. (1933), Messung der Oberflächenspannung von festen Körpern. *Phys. Zeit. Sowjetunion* **4,** 397–419.

BIRCH, F., H. F. SCHAIRER AND H. C. SPICER, (1942), Handbook of Physical Constants. *Geol. Soc. Am. Spec. Paper* **36,**

FAIRBAIRN, H. W. (1939), Correlation of quartz deformation with its crystal structure. *Am. Mineral.* **24,** 351–368.

GILMAN, J. J. (1959), Cleavage, ductility and fracture in crystals. In Fracture, John Wiley & Sons N.Y., 193–224.

———— (1960), Direct measurement of the surface energies of crystals. *Jour. Appl. Phys.* **31,** 2208–2218.

GOOD, R. J., L. A. GIRIFALCO AND G. KRAUS, (1958), A theory for estimation of interfacial angles, Part II. *Jour. Phys. Chem.* **62,** 1418–1421.

GRIFFITH, A. A. (1921), The phenomenon of rupture and flow in solids. *Phil. Trans. Roy. Soc. London* **221,** 163–197.

MACHATSCHKI, F. (1936), Die Kristallstruktur von Tiefquarz SiO_2 und Aluminiumorthoarsenate $AlAsO_4$. *Zeit. Krist.* **94,** 222–230.

NYE, J. F. (1957), Physical Properties of Crystals. Clarendon Press, Oxford.

OBREIMOFF, J. W. (1930), The splitting strength of mica. *Proc. Roy. Soc. London, A,* **127,** 290–297.

OROWAN, E. (1949), Fracture and strength of solids. *Rept. Prog. Phys.* **12,** 185–232.

PARTINGTON, J. R. (1952), An Advanced Treatise on Physical Chemistry. Vol. 3, Longmanns, Green, London, p. 342.

SCHELLINGER, A. K. (1952), Solid surface energy and calorimetric determination of surface energy relationships for some common minerals. *Min. Eng.* **4,** 369–374.

VERMA, R. K. (1960), Elasticity of some high-density crystals. *Jour. Geophys. Res.* **65,** 757–766.