

Cleavage surface energy of selenite

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Abstract

The specific surface energy of selenite was measured by basal plane cleavage as a function of temperature and pressure. No significant difference was found in the specific surface energy of selenite in 1 atm of air (358 ergs/cm²) and at 10⁻⁶ Torr (352 ergs/cm²). A slight difference was observed between the specific surface energy at the lower temperature of -35°C (384 ergs/cm²) and at the higher temperature of 65°C (360 ergs/cm²). The specific surface energy is nearly independent of atmospheric and temperature effects within the range of temperatures and pressures studied.

Introduction

Environmental effects upon the cleavage surface energy of selenite (CaSO₄·2H₂O) are the subject of this research. Energy required for basal plane cleavage is assumed to be expended on the breaking of highly localized hydrogen bonds between lamella (Fig. 1).

Previous studies on graphite (Bryant *et al.*, 1964), muscovite (Obriemoff, 1930; Deryagin and Metsik, 1959; Bryant *et al.*, 1963), phlogopite (Gutshall *et al.*, 1970), and talc (Ward and Phillips, 1971) assumed either ionic or van der Waals bonding as primary sources of inter-layer adhesion. In these studies, the environment was found to have a large effect on the cleavage surface energy. In materials with principally ionic bonding between the layers, e.g. muscovite, cleavage surface energy is at a maximum in a vacuum and considerably lower in air or a few Torr partial pressure of water vapor.

The authors have correlated experimental measurements of the specific cleavage energy (Gutshall *et al.*, 1970) to theoretical calculations (Ward and Phillips, 1971; Phillips *et al.*, 1969). This dual approach has led to insights into the applicability of several approximations used in models of bonding in lamellar crystals, in particular, the use of the Born model, the rigid lattice approximation (Tosi, 1964), and the role of image charges in the cleavage energy of muscovite (Morris and Phillips, in preparation). Selenite (Fig. 1) affords an unusually good material for extending the study into hydrogen bonding, hence the studies reported here.

Cleavage of selenite

The specific surface energy of selenite was determined by measuring the energy required to cleave a

known surface area of the sample. A complete description of the experimental techniques has been published (Bryant *et al.*, 1963), therefore only a brief review of the experiment is presented. The test system consists of a glass sample chamber attached to a vacuum system (Fig. 2). The force used to cleave the sample is applied by a calibrated quartz fiber and bellows assembly. Photographs taken from the side and top of the sample chamber record all the necessary data for the cleavage energy determination.

The study of selenite required the system to be modified for temperature control of the sample. The sample was mounted on a copper rod which extended through the wall of the vacuum system (Fig. 2). The sample temperature was regulated by controlling the temperature of the copper rod. The end of the rod external to the vacuum system was placed in a temperature bath. The sample temperature was measured by a thermocouple embedded in the copper rod just below the sample.

The samples of selenite were rectangular plates 0.5 mm by 10 mm by 50 mm. After preparation, each sample was visually inspected for defects. One face of the sample was glued to the copper rod with Eastman 910 Adhesive. The other face was coated with cellophane tape, and a hook was attached to one end of the sample (Fig. 2). Backing with cellophane tape was necessary to prevent secondary cleavage plane fracture during the test.

Selenite cleavage is subject to noticeable microscopic pinning and stepping. Qualitative studies were made of sample surfaces from the cleavage experiments by using standard replication techniques and an electron microscope. In the successful cleavage experiments stepping was low, and contributions to the final results were believed to be less than the errors in instrument calibration, i.e., less than 5 per-

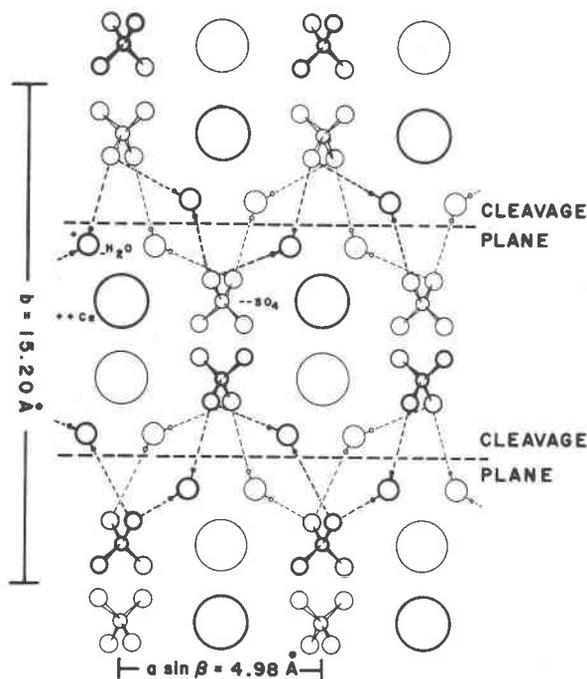


FIG. 1. The structure of selenite projected on to the plane perpendicular to the z axis of the I unit cell. The layers are composed of SO_4^{2-} and Ca^{2+} ions with H_2O molecules on their (010) surfaces. The heavy broken line indicates the cleavage plane passing through O-H-O bonds.

cent in the specific surface energy, which is well within the coefficient of variation of the data.

Table 1 summarizes the data on selenite, and Table 2 summarizes previous experiments and calculations on other minerals and one synthetic material.

Assuming that all of the work expended in cleaving goes into the breaking of highly localized individual H-bonds, the experimental result of 358 ergs/cm² predicts a cohesive energy of the H-bond of 8.4 kcal/mole. Compared to the cohesive energies of

other H-bonded systems, the values found here are quite consistent. For example ice has an O-H...O bonding energy of 3.5 kcal/mole, solid phenol 4.2 kcal/mole (Hamilton and Ibers, 1968), and 4.5 kcal/mole in water (Pauling, 1960). The O-H...F bond is 13 kcal/mole between F and ligated water molecules (Pauling, 1960).

Discussion

Selenite showed no measured environmental effects, the specific surface energy measured in air, 358 ergs/cm² being approximately the same as that measured in vacuum, 352 ergs/cm². Thus the experiments show air and the accompanying water vapor to constitute a non-interactive environment.

The data in Table 1 show that a temperature range of from -35°C to 65°C has little effect on the cleavage surface energy of selenite. Although the lower temperature data are slightly larger (than the higher temperature values), it is felt that this is not significant. Thermal effects upon the chamber could well account for the difference.

These experiments show the mean value of all specific surface energy measurements to be 363 ergs/cm² for selenite, a value within the range found in previous experiments for muscovite and phlogopite in air. A proposed model for the molecular mechanism responsible for lowering the specific surface energy of muscovite by water vapor was given by Phillips (Phillips *et al.*, 1969) and recently modified (Trott *et al.*, in preparation). The model suggests that water molecules, having a permanent dipole moment, are attracted by a very strong inhomogeneous electric field at the crack tip. The coordination of H_2O with potassium ions between the mica sheets is responsible for a delocalization of charge; and via hydrogen bonding

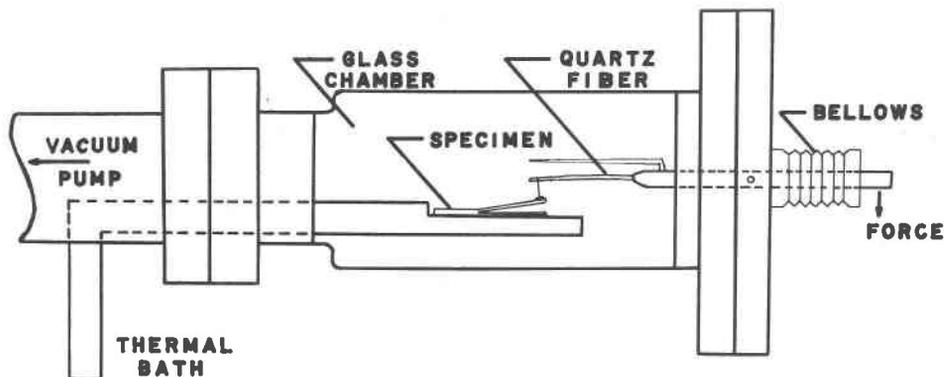


FIG. 2. Schematic diagram of test chamber used for cleavage measurements.

TABLE 1. Mean specific surface energy values measured for selenite with changing temperature and pressure

Temperature (degrees °C)	Pressure (Torr)	SSE* (ergs/cm ²)	IBE** (ergs/cm ²)
25	760	358	716
-35	10 ⁻⁶	384	768
25	10 ⁻⁵	352	704
65	10 ⁻⁵	360	720

*The values are averaged over 10 measurements with a coefficient of variation of less than 5%.

**Interlayer Binding Energy (IBE) is twice the Specific Surface Energy (SSE).

to the silicate sheet, the ionic unit is neutralized. Although the experiments presented here do not prove the hydrogen bonds replace ionic bonds, they do lend support to the proposed model (Trott *et al.*, in preparation).

During the cleavage of selenite, care was taken to

conduct the tests before dehydration of the selenite samples changed the interlayer binding. Exposure to a vacuum at room temperatures for a few hours will dehydrate the selenite specimen to the point where there are large increases in the specific surface energy. If left for several hours in the vacuum chamber the transparent selenite becomes milk-white in appearance (CaSO₄·½ H₂O, bassanite; CaSO₄, anhydrite). In order to be aware of the temperature-dehydration profile of our samples, a small crystal was placed in a mass spectrometer (a double-focus, high-resolution, Varian SM-1B). As the sample was subjected to increasing temperature, a marked increase in the 17 and 18 mass peaks was repeatedly observed near 51°C.

Times for cleavage at elevated temperatures were kept in the neighborhood of a minute, with little observed change in specific surface energy. Statistical thermodynamic studies are being conducted to understand the molecular mechanism initiating the dehydration of CaSO₄·2H₂O.

TABLE 2. Specific surface energy values measured in various environments

Mineral	Environment	Pressure (Torr)	Specific Surface Energy (ergs/cm ²)	Source (Ref)
<u>Phlogopite</u>				
Exp.				
	Air	760	350	Gutshall <i>et al.</i> , 1970
	Vacuum	10 ⁻⁷	6,060	" "
	Ammonia	1-5	2,420	Gutshall <i>et al.</i> , 1971
	Carbon Monoxide	1-5	2,260	" "
	Oxygen	1-5	4,920	" "
	Calc. Vacuum		5,780	Morris and Phillips 1975
<u>Muscovite</u>				
Exp.				
	Air	760	300	Bryant <i>et al.</i> , 1963
	H ₂ O	1-10	300	" "
	Vacuum	10 ⁻¹³	5,125	" "
	He	760	5,125	" "
	Nitrogen N ₂	760	5,125	" "
	Argon Ar	760	5,125	" "
	Calc. Vacuum		5,780	Morris and Phillips, 1975
<u>Talc</u>				
	Calc. Vacuum		490	Ward and Phillips, 1971
<u>Margarite</u>				
	Exp. Vacuum	10 ⁻⁷	11,500	Gutshall <i>et al.</i> , 1971
	Calc. Vacuum		11,560	Phillips <i>et al.</i> , 1969
<u>Graphite</u>				
	Exp. Vacuum	10 ⁻¹³	1,750	Bryant <i>et al.</i> , 1964
	Air	1-5	300	" "
	H ₂ O	1-5	300	" "
	Calc. Vacuum		2,500	" "

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