

plastic wrap are quite similar. For each, the 110 peak falls somewhat above the line joining the tops of the 002 and 006 peaks. For our alternative method using the aluminum sample-holder (Fig. 1C), the 110 peak falls somewhat below this reference line indicating that some degree of preferred orientation has returned, perhaps because of fragmentation of some of the aggregates as they were packed into the holder. For the normal and smear mount preparations (Figs. 1D and E) the relative height of the 110 peak decreases markedly in respect to the basal peaks, thereby betraying considerable increase in the preferred orientation.

The effect of our technique on needle-shaped cleavage fragments was investigated using a synthetic  $K_2Pb_4Si_8O_{21}$  with tetragonal symmetry which exhibits perfect  $\{110\}$  cleavage (Gibbs et al., 1962). Note that the  $hk0$  reflections are enhanced, relative to other peaks, by the preferred orientation present in the normal aluminum sample holder mount (Fig. 2A) but considerably suppressed by our grain aggregate mounting technique (Fig. 2B).

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THE EFFECT OF SURFACE PROPERTIES ON REFRACTIVE INDEX  
DETERMINATION BY THE BREWSTER ANGLE METHOD

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The relationship between the refractive index of a substance and the angle at which light reflected from a polished surface of the substance

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undergoes maximum polarization has been known for many years. The angle at which this occurs is known as the Brewster angle after D. Brewster who first pointed out (1815) that the index of refraction is equal to the tangent of the angle of maximum polarization. Although the subject has been treated in numerous textbooks on optics, *e.g.*, Born and Wolf (1964), the method has not received much serious attention from mineralogists as a method of determining refractive index. Recently, however, H. Schumann (1963, 1965) published several papers in which the measurement of refractive indices by this method is described, using a modified one-circle goniometer.

The authors adapted a two-circle optical goniometer for this purpose. The light source was modified to give a light beam with less than ten minutes divergence in the plane of incidence. A continuous-band interference filter, with a band width of about 300 Å, was used as monochromator, and a polarizer was introduced to polarize the incident light parallel to the plane of incidence. The light beam illuminated an area on the sample of about 2 mm by 6 mm. The mean angle of incidence could be measured to within one minute of arc. The intensity of the reflected beam was measured by a photomultiplier tube mounted on the telescope of the goniometer and the values obtained were used to form a smoothed graph of intensity versus angle of incidence, from which the point of minimum intensity was obtained. A reproducibility of less than  $\pm 3$  minutes was obtained in measuring the Brewster angle in this way, which, for the refractive index in the sphalerite range, corresponds to an accuracy of about  $\pm 0.0006$  in the refractive index measurement.

The refractive indices of a number of transparent minerals were determined, and the values obtained were generally in good agreement with refractive indices determined by the immersion method. Sphalerite, however, was a notable exception. Values significantly lower than the textbook values were obtained in every case. After investigating many possible sources of error, it became evident that the apparent refractive index of the surface of polished sphalerite is actually lower than that of the mineral in bulk. The sphalerite specimens used in this work were light yellow crystals from Santander, Spain, and contained the following impurities: Fe 0.0004 percent, Cd 0.085 percent, Mn 0.01 percent.

The degree of perfection of the polish was found to influence the determinations strongly. However, even with the best polishing methods, including the combined polishing-etching method recommended by Cameron and van Rensburg (1965), which left no discernible scratches, the apparent refractive index was still appreciably lower than that of sphalerite measured by bulk methods. (It is also noteworthy that Schumann's

(1965) refractive index of sphalerite, determined by the Brewster angle method, is also much lower than the generally accepted value (2.326 *vs* 2.364), although he did not draw attention to this fact.) Furthermore, the apparent refractive index of the same polished surface was found to decrease over a period of days. The relevant figures for Santander sphalerite, obtained with light of wavelength of 6000 Å, are as follows:

Remarks	Apparent Refractive Index
Fresh polish (Cameron-van Rensburg method)	2.346
Same surface, three days later	2.337
Same surface, eleven days later	2.330
Refractive index of sphalerite measured by bulk method (Bond, 1965)	2.364

Further aging did not appreciably reduce the refractive index below 2.330. Tests on other polished samples of sphalerite gave similar results.

The decreasing refractive index with time indicates a progressive change in the surface of the sample. The most likely explanation for the low values is that of surface oxidation. The refractive indices of zinc oxide (ZnO) in sodium light ( $\lambda = 5890$  Å), are  $n_o = 2.013$  and  $n_e = 2.029$ , which are much lower than that of sphalerite. On breaking zinc-sulphur bonds in the air, as is done on cleaving or polishing a sample in air, it is reasonable to expect that a layer of zinc oxide will be immediately formed at the surface, particularly since zinc oxide has a much higher heat of formation than zinc sulphide. The build-up of the oxide layer appears to continue for some days, after which the process appears to be arrested. Old cleavage surfaces gave approximately the same results as old polished surfaces, which indicates that the aging process does not depend only on the polishing procedure.

No tests were conducted on other sulphide minerals, because most sulphides are opaque, and their bulk refractive index cannot be accurately determined for comparison with the Brewster angle results. Furthermore, high absorption coefficients, which characterize most sulphides, have an appreciable influence on the Brewster angle. However, the experience with sphalerite indicates that the Brewster angle method of determining refractive indices cannot safely be used for minerals such as sulphides, whose surfaces are liable to undergo rapid oxidation. Even visual inspection of the surface does not appear to be adequate for the detection of significant amounts of surface oxidation, since the sphalerite

used for the experiments did not show any perceptible change under the ore microscope.

In conclusion, therefore, it is recommended that extreme caution be exercised in interpreting the results of refractive index measurements made on sulphides and related minerals by the Brewster angle method.

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A MICRO METHOD FOR DETERMINATION OF CATION EXCHANGE CAPACITY OF CLAYS BY INFRARED SPECTROSCOPY<sup>1</sup>

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Most of the many methods devised for the determination of the cation exchange capacity (c.e.c.) of clays require substantial amounts of material and involve laborious chemical analyses of either the solutions or the clay material itself. For example, a common method for determining c.e.c. involves saturation of a material with  $\text{NH}_4^+$ , followed by a chemical analysis to determine the amount of  $\text{NH}_4^+$  retained on the sample. Presented herewith is a technique which has application in c.e.c. determinations and which obviates or greatly decreases the necessity for chemical analyses and requires a very small amount of material.

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