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OPTICAL ANISOTROPY IN PYRITE

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ABSTRACT

Polished surfaces of pyrite reflect light in a manner different from that predicted by accepted theories of crystal optics, although the behaviour is qualitatively compatible with crystal symmetry. The effects may be an expression of surface deformation induced by polishing.

INTRODUCTION

Reflection anisotropy in pyrite has generally been regarded as anomalous, although Stanton (1955, 1957) showed it to be a characteristic feature of the mineral.

A detailed study has been made of the geometry of anisotropic effects in pyrite to discover whether it is compatible with crystal symmetry. The results have been analysed in terms of classical reflection theory and the geometry compared with that of crystals of lower symmetry.

The results have considerable significance in the field of ore-mineral identification by quantitative optical methods. As yet, little is known of reflectivity variation in differently oriented crystal sections and of the effect of polishing. Only careful qualitative and quantitative studies will rectify these deficiencies.

SYMMETRY OF PYRITE

The space group of pyrite is $T_h^6 = Pa3$.

Despite occasional indications to the contrary (*cf.* Miers, Hartley and Dick, 1898; Pöschl, 1911; Smolař, 1913; Smith, 1942) the morphology and etch patterns of pyrite generally exhibit symmetry of class *m*3 in the cubic system; this is verified by X-ray investigations (Bragg, 1913).

An important feature of this symmetry class is that there are no tetrad symmetry axes. The normals to octahedral faces are triad axes, and the normals to cube faces are diad axes only, as frequently shown by the presence of a single set of striations on each cube face of a pyrite crystal. In general, striations on the (001) face are parallel to the a_1-axis [100] (Fig. 1).

THEORY OF REFLECTION FROM CRYSTAL SURFACES

The following summary of experimental facts has been more exhaustively reviewed by Hallimond (1953) and Cameron (1961).

When normally incident, plane polarized light is reflected from a polished surface, the intensity of the light is invariably decreased; the *reflectivity* of the surface is defined as the ratio of the intensity of the reflected light to that of the incident light.

For a polished surface of an anisotropic crystal, the incident light will also generally undergo a rotation of the polarization azimuth, and a degree of ellipticity will be induced in the vibration. The light will be reflected *without* change of polarization state or azimuth only if it is initially polarized parallel to a *direction of uniradial reflection* within the surface. In general, there are two such directions at right angles, corresponding to the direction of maximum reflectivity and the direction of minimum reflectivity for the surface concerned. Normally incident light which is not polarized parallel to either of these directions will be rotated upon reflection *towards the direction of maximum reflectivity.*

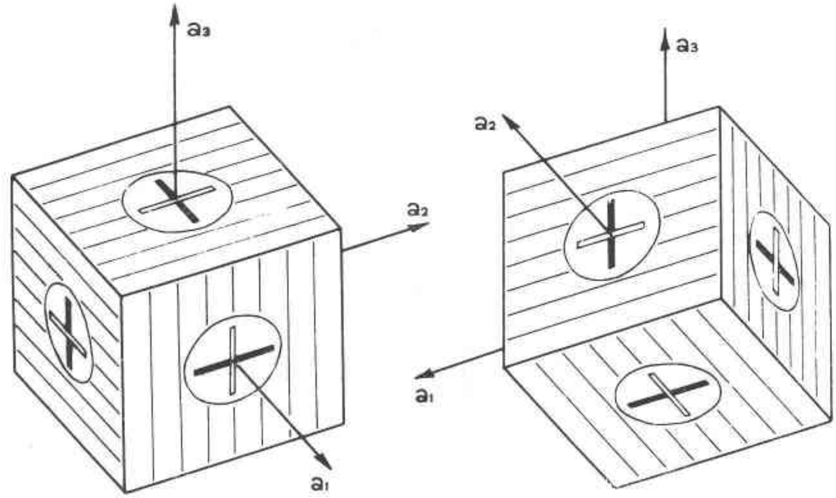

FIG. 1. Directions of uniradial reflection on a normally striated pyrite cube. Full bar: maximum reflectivity for red. Open bar: minimum reflectivity for red.

When the reflected ray is elliptically polarized, its apparent polarization azimuth is the major axis of the vibration ellipse. Although the ellipticity modifies the observed effects, the polarization azimuth will still be rotated in the sense indicated above, unless ellipticity effects are far greater than any yet measured for ore minerals.

The amount of rotation is dependent upon the wavelength of the incident ray, so that incident white light is resolved into component wavelengths, each one having a different polarization azimuth. This effect is known as *dispersion of the apparent angle of rotation* (DA_r). In general, just one color will be extinguished (or nearly extinguished) for a given setting of the analyser when this effect is studied with a reflecting microscope. The *polarization color* then observed consists essentially of a mixture of the remaining colors; the intensity of each being a complex function of the incident light composition, reflectivity variation with wavelength, and final polarization azimuth (relative to the analyser). The general effect is that of a color complementary to that which has been extinguished.

Cissarz (1931) studied surfaces in the zones [100], [010], [001] of the orthorhombic mineral stibnite. One uniradial direction in such surfaces is parallel to the zone axis, and for each zone, this direction has a constant reflectivity value. The value for the other uniradial direction varies continuously with the position of the surface in the zone.

The two uniradial reflectivities are equal for just one surface in each quadrant of the zone [100]. The normals to these surfaces are the *axes of reflection isotropy.*

Berek (1931b) published a theoretical treatment of these results, which incorporated Cissarz's conclusion that for all surfaces within a principal zone, the reflectivity parallel to the zone axis is a constant. This result was predicted by Drude (1887), Voigt (1908) and others in theoretical discussions of pleochroic crystals.

REFLECTION OPTICS OF PYRITE

Polarization effects in pyrite were studied in some detail by Stanton (1955, 1957) and summarized as follows: (1) Optical anisotropy is a general feature of pyrite. Polarization colors are pink and blue-grey. They are somewhat variable from crystal to crystal, but are not affected by heating to 572°C in an inert atmosphere. The colors are not apparent in surfaces which have been harshly ground before polishing, (2) Surfaces parallel to the faces {100}, {110} and {210} are all anisotropic. In each case, maximum polarization colors are observed when the crystallographic axis within the surface concerned is at 45° to the polarization plane of the incident light, and (3) No anisotropy is apparent in sections cut parallel to octahedral faces {111}.

Klemm (1961) studied a large number of very carefully polished sections of pyrite and concluded that anisotropy is a widespread, but by no means universal, property of pyrite. Klemm concluded that the anisotropy is probably a manifestation of crystal lattice distortion caused by impurities. Pyrite produced from very pure reagents at the Washington Geophysical Laboratory, however, shows normal reflection anisotropy (R. L. Stanton, pers. comm.).

Cameron and Green (1950) studied the conoscopic optics of pyrite. They state that slight rotation of the analyser from the crossed position causes the polarization cross in white light to break into isogyres having red fringes on the convex side and blue fringes on the concave side. This effect is attributed by Cameron and Green to dispersion of the reflection rotation, *i.e.* to an effect of varying angle of incidence of the conoscopic light.

APPARATUS AND TECHNIQUES

The studies presented here attempt to establish the geometry of reflection anisotropism in different crystals of pyrite, and to discover whether the optical anisotropism has a similar nature wherever it occurs. Differences in *strength* of anisotropism from crystal to crystal were not investigated.

Observations were made with a Cooke, Troughton and Simms "Metalore" reflecting microsope fitted with a Wright ocular. A tungsten-filament lamp with condenser lens was used with red or blue glass filters fitted to this lamp for most of the monochromatic work. Some observations were made using a sodium vapor lamp but these were few, as pyrite is almost isotropic for yellow light.

The directions of maximum and minimum reflectivity were identified by determining the sense of rotation of light reflected from the surface in the 45° position. Many sections of pyrite show only very weak polarization effects, and determination of the rotation was greatly facilitated by use of a Nakamura accessory plate in the slotted ocular. The two halves of this plate have the effect of equal, small rotations of the analyser in respectively clockwise and counterclockwise directions. For monochromatic light the two halves are equally illuminated when the analyser is set at the extinction position. If the polars are precisely crossed and rotation has occurred, one or other of the halves (depending on the sense of rotation) will be distinctly brighter than its fellow. Thus if the microscope is set up for orthoscopic examination, the polars precisely crossed and the Nakamura plate inserted, the uniradial directions and the sense of rotation at the 45° position can be readily determined. Used similarly with white light, the plate gives a sensitive test for the presence of dispersion of the apparent angle of rotation.

Conoscopic observations were made in the manner described by Cameron and Green (1950).

Because of the small rotation angles involved, observations were almost completely qualitative. However, this has not hindered analysis of the results in terms of optical geometry.

MATERIAL STUDIED

Because of the qualitative nature of the measurements, sections were cut in only three or four orientations on most specimens. Since the symmetry of pyrite is high, this is equivalent to a study of well over thirty differently oriented surfaces in each crystal, which is sufficient for verification of the general form of the optical geometry. One crystal was studied in many sections to verify certain predicted relations, and to establish the compatibility of anisotropic effects with crystal symmetry.

Specimens from Uralla, Leadville, Peelwood and Captain's Flat (all in N.S.W.) were studied in sections as described. These specimens vary in habit: Captain's Flat specimens were simple cubes, Peelwood material consisted of striated cubes with small octahedral faces, and Leadville and Uralla crystals were cube-pyritohedron combinations.

RESULTS

Orthoscopic examination. The results of Stanton (1955, 1957) have been verified for pyrite crystals of various habit and origin from several localities in New South Wales. These results may be restated as follows:

1. Carefully polished sections of pyrite generally exhibit polarization effects.
2. If a surface parallels a principal crystallographic axis, this will be one of the directions of uniradial reflection.
3. For octahedral faces there is no discernible dispersion of the apparent angle of rotation ($DA_r = 0$); indeed, such surfaces are apparently quite isotropic.

The following additional information, summarized diagrammatically in Figures 1 and 2, was gained from supplementary studies:

4. DA_r is essentially zero for surfaces parallel to negative pentagonal dodecahedral faces $\{120\}$, and for surfaces in the zone sectors between any such face and the two adjacent octahedral faces. However, the exact position of surfaces for which $DA_r = 0$ could not be determined with the apparatus used.

5. For surfaces in the principal crystallographic zones, the following relations hold for red light:
   (a) In surfaces parallel to cube and $\{210\}$ faces, the uniradial direction of maximum reflectivity is perpendicular to the natural striations on these faces (Fig. 1).
   (b) For surfaces in the major sectors between negative pentagonal

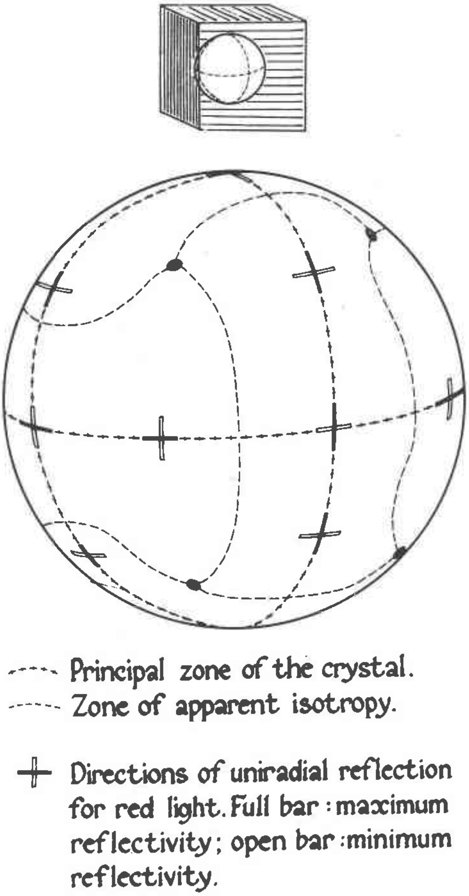

FIG. 2. Optical relations in pyrite, shown in spherical projection. (Uniradial reflection directions are shown for surfaces parallel to faces of cube and rhombic dodecohedron forms.)

dodecahedral faces in the principal zones, the uniradial direction of maximum reflectivity is parallel to the zone axis. For surfaces in the minor sectors, it is perpendicular to the zone axis (Fig. 2).

6. Rotation of blue light is opposite in sense to that of red light for all sections showing sufficient anisotropy for satisfactory determination of these properties. Thus the uniradial direction of maximum reflectivity for blue corresponds to the direction of minimum reflectivity for red. No dispersion of the axes of apparent isotropy in the principal sections could be detected.

7. The qualitative relations shown in Figures 1 and 2 are fully compatible, geometrically, with morphological crystal symmetry.
8. No anisotropy was observed in sodium light (5890 Å). Because of the low sensitivity of the apparatus, this means only that pyrite shows *less marked* anisotropic effects in yellow light than in light from the red and blue portions of the spectrum.

Conoscopic examination. The conoscopic figures for pyrite which are described by Cameron and Green (1950) are fully explained by them in terms of dispersion of the reflection rotation. However, by using quite strongly anisotropic pyrite and small rotations of the analyser, rather different results may be obtained.

In such cases, if slight clockwise rotation of the analyser produces an effect similar to that described by Cameron and Green, then the disposition of the color fringes may be *reversed* by either (1.) uncrossing the analyser in a *counter*-clockwise sense, or (2.) rotating the specimen through 90° on the microscope stage. If *both* operations are carried out, the original color distribution will be restored.

These effects can be explained only by a dispersion of apparent angles of rotation with red and blue light rotated in opposite senses. The effect is explained diagrammatically in Figure 3.

COMPARISON WITH PREVIOUS CONCEPTS

Optical symmetry axes. It has been found by experiment that if a polished surface of pyrite parallels a crystal axis, that axis will always be parallel to a direction of uniradial reflection in the surface. This is one of the special properties used by Berek (1931a) and others to define optical symmetry axes in crystals of lower symmetry. The laws of crystal optics require the reflectivity parallel to such symmetry axes to be constant. *This does not apply for pyrite.*

For red light, the direction [001] (see Fig. 1) is the direction of minimum reflectivity on (100), but of maximum reflectivity on (010). Assuming that the actual reflectivity values are identical on each cube face (as is required by crystal symmetry), the reflectivity of direction [001] must be less on (100) than on (010). That is, *the uniradial reflectivity parallel to a crystallographic axis is not constant.*

The low degree of anisotropy in pyrite shows that the variation in reflectivity with which we are dealing is not great. It is only the high symmetry which permits ready recognition of the departure from constancy. The fact remains that pyrite does not obey the normal laws of crystal optics; it follows that consideration of conventional elements of optical geometry must be of a purely comparative nature.

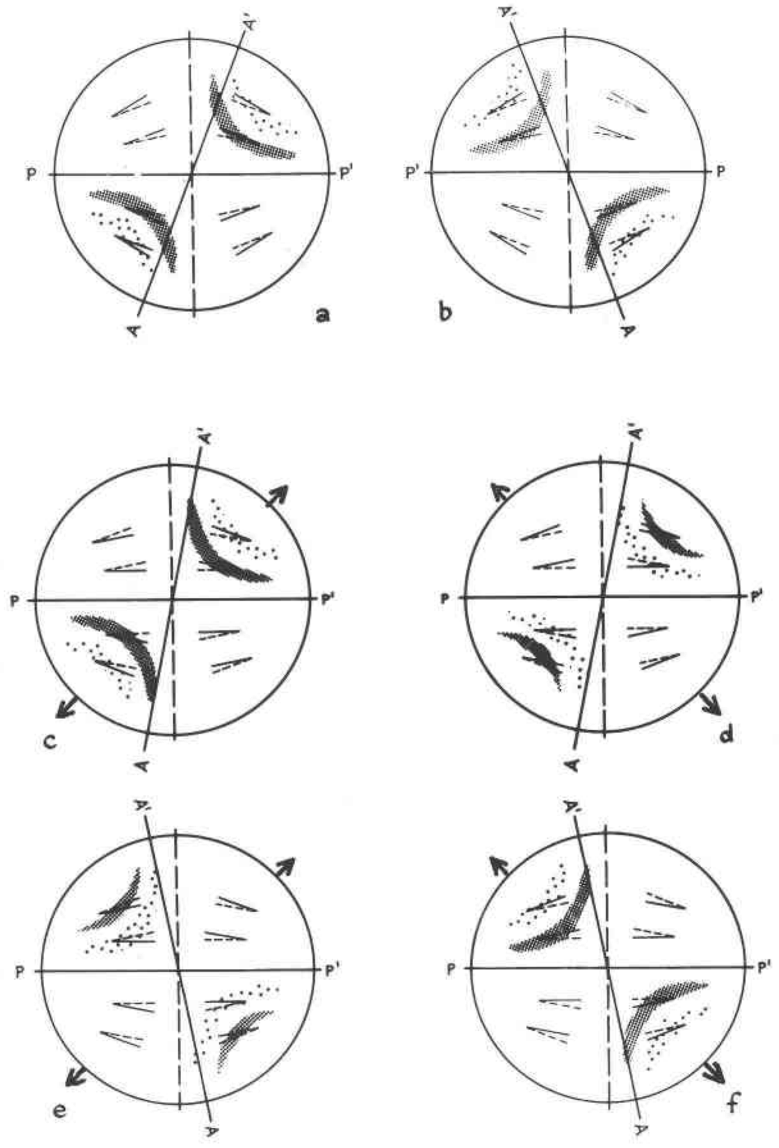

FIG. 3. Diagrammatic explanation of conoscopic figures for pyrite.

(a), (b):—Isotropic mineral; colour fringes caused by dispersion of the reflection rotation.

(c)–(f):—Pyrite; colour fringes caused by dispersion of the apparent angle of rotation. (Arrows indicate uniradial direction of maximum reflectivity for red.)

Close stippling:—Red fringe (i.e. blue extinction).
Open stippling:—Blue fringe (i.e. red extinction).
PP′, AA′:—Plane of polarization of polarizer, analyser respectively.
/:—Plane of polarization of reflected blue ray.
⋰:—Plane of polarization of reflected red ray.

Axes of reflection isotropy. For red light, the direction [001] is the direction of minimum reflectivity on faces (100) and (110), but of maximum reflectivity on (010). It may be assumed that the uniradial reflectivities change their values continuously with change of surface orientation, as Cissarz (1931) found to be the case with stibnite. Therefore there exists a surface lying between (110) and (010) in the zone [001] such that the reflectivity for direction [001] is neither greater nor less than the other uniradial reflectivity, and the surface appears isotropic in red light. In fact, surfaces parallel to $\{120\}$ show no observable anisotropy in either red or blue light.

There are two important distinctions between these surfaces and the corresponding planes (normal to axes of reflection isotropy) in orthorhombic stibnite. First, when Cissarz studied surfaces in the principal zone in stibnite, only one uniradial reflectivity varied, while the other remained constant; in pyrite, both reflectivities vary. Secondly, the planes in stibnite occur as a pair within just one principal crystallographic zone; in pyrite, there are three such pairs, corresponding to the three identical principal zones.

Because of this second distinction, pyrite cannot be considered as either "positive" or "negative" in the sense defined by Berek (1931b).

Windungsachsen. In translucent (moderately absorbent) crystals of lower symmetry, there exist just four special transmission directions for which all rays of light behave identically, as regards both velocity and absorption; these were defined by Voigt (1908) as Windungsachsen (gyroid or rotation axes).

Surfaces normal to the Windungsachsen reflect light without change of polarization state, and with reflectivity independent of azimuth (Berek, 1931a).

In other words, such sections behave isotropically in normally incident light; and there is no pair of special directions (either principal vibration directions or directions of uniradial reflection) associated with them.

In translucent crystals of lower symmetry, these two conditions apply *only* to planes normal to the Windungsachsen.

The results described in the present paper suggest that these conditions are satisfied by surfaces in pyrite parallel to the octahedra. As far as is known, such surfaces behave isotropically; and if optical relationships are truly compatible with crystal symmetry (as present results suggest) then there cannot exist a *pair* of special directions normal to a triad symmetry axis.

There are four Windungsachsen in crystals of lower symmetry; there are four normals to the octahedra in pyrite. Moreover, relative to each principal plane, these normals may be considered as two pairs, each pair being symmetrically disposed about that plane. This is precisely the arrangement observed relative to the single optic plane in crystals of lower symmetry.

Despite these similarities, however, the normals to the octahedra should be considered at best comparable with, and certainly not equivalent to, Windungsachsen; first because there is no evidence that these are the *only* directions in pyrite satisfying the conditions outlined above; and secondly because, since pyrite does not obey normal laws of optics, the significance of these directions is probably different from that in lower-symmetry crystals.

SUMMARY OF THE EXPERIMENTAL RESULTS

1. In general, when a polished surface of pyrite reflects plane polarized, normally incident light, the plane of polarization undergoes a slight rotation. The sense of rotation for blue light is opposite to that for red light.
2. When pyrite is studied in white light, this dispersion of the apparent angle of rotation causes polarization colors in orthoscopic examination, and fringed isogyres in conoscopic examination.
3. The geometry of the reflection anisotropy in pyrite is qualitatively compatible with the morphologic symmetry of the mineral.
4. In a pyrite surface parallel to a principal crystallographic axis, the axis direction is a direction of uniradial reflection. However, the reflectivity value of this direction is *not* a constant for all such surfaces.

THE DISCREPANCY BETWEEN THEORY AND OBSERVATION

The fact that the reflection anisotropy of pyrite is not compatible with accepted theories of crystal optics is proven by the variation in reflectivity for directions parallel to crystal axes. Previous work (*e.g.*, Berek, 1931b) would indicate that this reflectivity should be constant. Indeed, complete optical isotropy is indicated for any isometric crystal.

The explanation of the discrepancy may be that we are concerned here only with *polished surfaces* of an opaque material. Klemm (1961) found that perfect crystal faces of pyrite do not exhibit polarization effects. Cissarz (1931) found that the reflectivity values of *polished* cleavage surfaces in stibnite are almost 20 percent lower than corresponding values measured on *unpolished* cleavage surfaces. Observed anisotropy in pyrite may therefore be a result of polishing, and not inherent in the actual crystal lattice.

If this were so, the effects observed might well be compatible with crystal symmetry, yet still be outside the scope of conventional theories of optical geometry.

CAUSE OF THE ANISOTROPY

Four possible causes of anisotropic effects may be considered.

1. Internal strains, perhaps set up during crystallization, might be responsible. Optical geometry would require such strains to be at once compatible with crystal symmetry, and homogeneous throughout the crystal; the lattice symmetry would be unaltered, and the problem would remain as before.

2. Oriented inclusions of some other mineral of lower crystal symmetry might be present. Such inclusions, if present, must be quite uniform, since pyrite polarization colors are always similar. Inclusions have not been detected in X-ray investigations, while trace-element content in pyrite varies greatly (*e.g.*, Fischer and Hiller, 1956); hence this explanation seems unlikely.

3. Directional hardness effects are well-known in cubic crystals (*e.g.*, Giardini, 1958), and these might give rise to submicroscopic, oriented pits, scratches, or ridges in polished surfaces. However, Stanton (1957) has shown that such irregularities are not responsible for pyrite anisotropy.

4. The most probable explanation of anisotropy in pyrite is that reflection takes place within a sort of Beilby layer of crystal-lattice distortion at the crystal surface. This layer is visualized, not as a zone of flow, but as a very thin skin having a nonisometric crystalline structure partially controlled by the orientation of the underlying lattice. The suggested layer, being extremely thin, might be caused by even the gentlest polishing, and indeed may be destroyed by harsh grinding. The optical geometry observed as a result of such surface deformation would necessarily conform with crystal symmetry, while individual polished surfaces would behave anisotropically, like polished sections of lower-symmetry crystals.

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REFERENCES

BEREK, M. (1931a) Elementare Einführung in die Optik absorbierender Kristalle und in die Methodik ihrer Bestimmung im reflektierten Licht. *Centralbl. Mineral.*, 1931, **A**, 198–209.

——— (1931b) Die singulären optischen Richtungen (Windungsachsen) in beliebig stark absorbierenden Kristallen rhombischer Symmetrie. *Z. Kristallogr.*, **80,** 18–36.

Bragg, W. L. (1913) The analysis of crystals by the X-ray spectrometer. *Roy. Soc. London Proc.*, **A89,** 468–489.

Cameron, E. N. (1961) *Ore Microscopy*. John Wiley and Sons, New York.

——— and L. H. Green (1950) Polarization figures and rotation properties in reflected light and their application to the identification of ore minerals. *Econ. Geol.*, **45,** 719–754.

Cissarz, A. (1931) Optsiche Messungen an Antimonglanz. *Neues Jahrb. Mineral.*, **64A,** 137–162.

Drude, P. (1887) Ueber die Gesetze der Reflexion und Brechung des Lichtes an der Grenze absorbierender Krystalle. *Ann. Phys.*, **32,** 584–625.

Fischer, M. and J. E. Hiller (1956) Über den thermoelektrischen Effekt des Pyrits. *Neues Jahrb. Mineral.*, Abh. **89,** 281–301.

Giardini, A. A. (1958) A study of the directional hardness in silicon. *Amer. Mineral.*, **43,** 957–969.

Hallimond, A. F. (1953) *The Polarizing Microscope*, 2nd. ed., Cooke, Troughton and Simms, Ltd., York, England.

Klemm, D. D. (1961) (P. Ramdohr, personal communication).

Miers, H., E. G. T. Hartley and A. Dick (1898) A tetartohedral (?) crystal of pyrites. *Mineral. Mag.*, **12,** 112–113.

Pöschl, V. (1911) Beiträge zur Kenntnis der Minerale der Pyrit- und Markasitgruppe. *Z. Kristallogr.*, **48,** 572–618.

Smith, F. G. (1942) Variation in the properties of pyrite. *Amer. Mineral.*, **27,** 1–9.

Smolař, G. (1913) Ein skelettkristal von Přibramer Pyrit. *Z. Kristallogr.*, **52,** 501–505.

Stanton, R. L. (1955) The anisotropism of pyrite. *Austral. J. Sci.*, **18,** 98–99.

——— (1957) Studies of polished surfaces of pyrite, and some implications. *Can. Mineral.*, **6,** 87–118.

Voigt, W. (1908) Über singuläre Richtungen in pleochroitischen Kristallen. *Ann. Phys.*, **27,** 1002–1022.

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