CLEAVAGE IN PYRITE AND COBALTITE

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Abstract

When spheres are fabricated from single crystals and the crystals are "mechanically etched" by grinding with a coarse abrasive in the process of sphere fabrication, every crystallographic plane in the crystal is subjected to the same amount of force. This technique produces a sphere whose surface is entirely covered with minute cleavage steps. By employing optical light figure techniques, the planes which cleave can be identified and their relative degree of cleavability ascertained.

The essence of this method is that every plane which is part of the bounding sphere is subjected to identical cleavage forces for identical times such that every plane is allowed to develop and exhibit its natural cleavage properties. The use of other techniques employed by previous authors has failed to define specific cleavage planes which this study has revealed for pyrite.

This study demonstrates that cleavage in pyrite and cobaltite occurs parallel to $\{100\}$, $\{021\}$, $\{111\}$, and $\{110\}$ in order of decreasing rank respectively. The $\{311\}$ cleavage reported by Frenzel and Bloss (1967) for pyrite is shown to be non-existent. Both natural and synthetic crystals of pyrite and cobaltite were studied, and in all cases, the cleavage properties were found to be identical.

In addition to the demonstration of cleavage by light figures, resolution of cleavage in pyrite and cobaltite has been enhanced by surface replication for electron microscopy.

It is shown by reference to the pyrite structure that the $\{021\}$ form cleaves as opposed to its complementary noncleavage form $\{012\}$. The $\{001\}$ and $\{021\}$ cleavages are inextricably related. The cleavages that occur in pyrite are predictable in terms of the geometry of the structure and by the direction and strength of the bonds.

The relative importance of a crystal form as estimated from its size, frequency of occurrence, and presence as a cleavage form is well demonstrated in pyrite. The rank of cleavage and rank of forms which occur in pyrite are almost identical.

A detailed morphological study of pyrite from diverse geologic environments has shown that of the two complementary merohedral forms $\{021\}$ and $\{012\}$, the $\{021\}$ form is overwhelmingly more important in occurrence than $\{012\}$, the former being a cleavage plane, and the latter, a non-cleavage plane.

Introduction

In the past few years, at least two separate studies have been carried out on the determination of cleavage in pyrite. In 1960, Wolff and Broder examined a large series of minerals including pyrite. They produced "mechanical etch" pits by grinding single crystals with a coarse abrasive and investigated the cleavage effects by the light figure method. They observed the following macrocleavage planes to exist in pyrite, $\{001\}$, $\{011\}$, $\{111\}$, and $\{012\}$. The choice of indexing the pyritohedron form

was arbitrary. No attempt was actually made to differentiate between the two complementary merohedral forms {021} and {012}.

In 1967, Frenzel and Bloss performed a separate study on cleavage in pyrite using a guillotine-like device to produce cleavage along predetermined planes. This method was first described by Tertsch (1930). They also examined the effects of preferred orientation on X-ray diffractometer intensities as a means of determining cleavage. They reported cleavage to occur parallel to {001} and, to a lesser extent, along {311}. They did not verify the existence of cleavage along {110} and {111} reported by Palache *et al.* (1944, p. 284).

In this study, cleavage in pyrite and cobaltite is examined by means of light figure development on coarsely abraded single crystals. The use of preferred orientation effects on X-ray diffractometer intensities is also investigated.

DEVELOPMENT OF CLEAVAGE BY SPHERE FABRICATION

Examination of cleavage in single crystals is most effective when every crystallographic plane in the crystal is subjected to the same amount of force. This is best carried out when spheres are fabricated from single crystals by abrasion using a coarse grinding medium.

Spheres are conveniently produced by grinding single crystals with a wet slurry consisting of a 150 mesh abrasive on the end of a vertical brass pipe, the diameter of which is approximately 3/4 that of the resultant sphere. The pipe is made to rotate at a moderate speed and the crystal is simultaneously rotated about another axis (normal to the axis of rotation of the pipe). By this method, the use of coarse grinding abrasive particles of 240 mesh or larger produces "mechanical etching" on the crystal surface. In the process of forming the sphere, the coarse particles cleave or chip minute pieces from the crystal surface, producing a spherical form covered with minute cleavage steps. By employing optical light figure techniques, (Wolff and Broder, 1960) the planes which cleave can be identified and their relative degree of cleavability ascertained.

The essence of this method is that every plane P_i of the crystal which is part of the bounding sphere is subject to a normal force F_i for a time T_i. All planes of the crystal ΣP_i are, therefore, exposed to identical cleavage forces for identical times such that every plane P_i is able to develop its appropriate cleavage properties. This method, therefore, offers the best known technique by which an unspecified plane P_i may be allowed to develop and exhibit its natural cleavage properties.

The apparatus necessary for the study of light figures consists of a light source, a collimating system, a screen, and a crystal mounting device. The collimated light beam is directed through a hole in the screen and finally is made to impinge on the surface of the abraded crystal sphere. The reflected beams bouncing off the crystal are intercepted by the screen, thus producing the light figure.

A light figure is therefore generated by the reflection of light from the surface of the abraded sphere which contains intermingled sets of many parallel mirror-like faces. Each parallel set reflects a light beam in a different direction. If a screen is placed in the path of the reflected beams, each produces a spot where the light is intercepted and all the spots taken together form the pattern of a light figure.

The crystal is mounted on a goniometer head which, in turn, is mounted on a Wolfe two-circle goniometer (Wolfe, 1948), which, by virtue of its physical design and accuracy of construction, is ideal for light figure studies.

Identification of the crystallographic planes producing the light figure spots can be established by the direct measurement of interplanar angles between light figure spots using the two-circle goniometer, and by the symmetry observed in the light figure itself.

If further verification for the identification of a spot is necessary, it can be achieved by rotating the arcs of the goniometer head until the crystallographic axis representing the spot in question is brought to coincidence with the axis of the goniometer head. The goniometer head is then transferred to an X-ray diffractometer by means of a crystal orienting device (Mariano, 1965). By automatic scanning, at some definite 2θ angle for the wavelength used, the Bragg requirement is fulfilled and the corresponding spacing of the plane normal to the axis in question is revealed, thus identifying the indices of the light figure spot.

CLEAVAGE IN PYRITE AS DETERMINED BY LIGHT FIGURES

The actual examination of cleavage in pyrite was carried out by fabricating spheres from single crystals of varied geologic environments. They include pyrite from Rio Marina, Elba; Ambasaguas, Spain; Haverhill, Massachusetts; Bingham, Utah; Chino, New Mexico; and Leadville, Colorado. The resulting macrocleavage and microcleavage as revealed by light figures was identical for pyrite from each of the above localities.

It was found that the dominant cleavage in pyrite occurs in the $\{001\}$ form (the more dominant cleavage being manifested by the higher intensity of the spot in the light figure). The second strongest cleavage is the $\{021\}$ followed by weaker $\{111\}$ and finally a very weak $\{110\}$ cleavage. These macrocleavages are demonstrated in the light figures shown in Figure 1.

In addition to the macrocleavage, microcleavage zones were also observed in all cases. "Microcleavage refers to the separation of a crystal parallel to crystallographic directions or zones which represent important atomic arrays" (Wolff and Broder, 1960). Where two or more microcleavage zones intersect, macrocleavage occurs.

The full array of cleavage in pyrite as produced by light figure studies is shown in the stereographic projection of Figure 2.

The original cleavage studies performed by Wolff and Broder provide an excellent approach to the absolute identification of cleavage in minerals. The results obtained on the cleavage in pyrite in this study serves as a verification of the work by Wolff and Broder. We have in addition identified the cleavage pyritohedron in pyrite as the $\{021\}$ form as opposed to the $\{012\}$.

As pointed out by Donnay and Harker (1937), according to space group requirements, the forms $\{0kl\}$ must satisfy the condition $k = 2n$ (International Tables for X-Ray Crystallography, 1962, Space Group
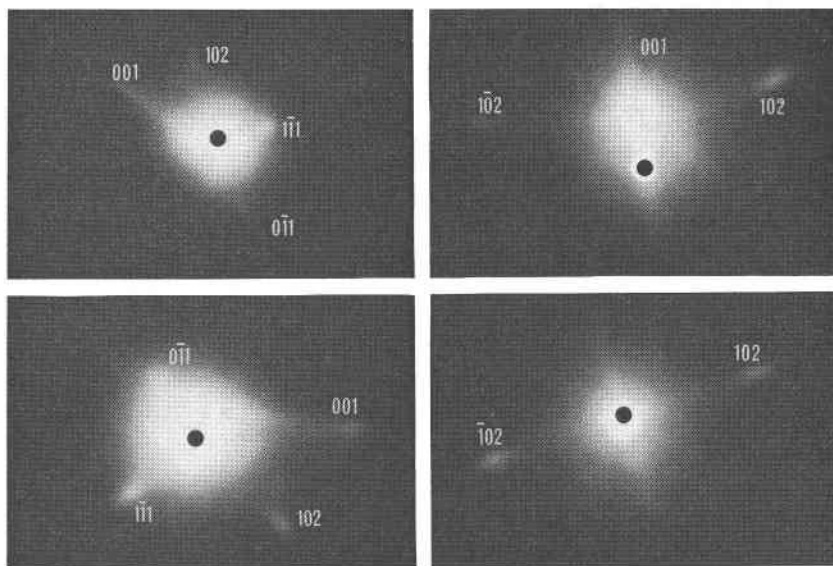
FIG. 1. Light figures of an abraded pyrite sphere. The four cleavages of pyrite are mani-
fested by the light figure pattern. Since the light figure spots represent reflections from
crystallographic planes, the indices of the spots are identified by symmetry relations, and
the measurement of interplanar angles. Further verification is made by X-ray diffraction.
The light figure shown in the upper right photograph is an offset duplicate of the light
figure in the lower right photograph. The offset photograph is necessary to remove the (001)
reflection from coincidence with the incident light beam.

No. 205). Space group X-ray extinction rules can therefore be used to
separate complementary pyritohedra—for instance {021}, {042} and
{063} are all allowable reflections and indeed this is the cleavage pyrito-
hedron in pyrite; whereas the {012} and {036} are not allowable reflec-
tions. In the non-cleavage pyritohedron, {024}, where $k = 2n$, is the only
permissible X-ray reflection.

It is most interesting to note here that the cleavage pyritohedron {021}
is also the most dominant of the complementary merohedral forms in
pyrite. In addition, synthetic pyrites assume the pyritohedron form
{021} as opposed to {012}.

A preferential etch which unambiguously differentiates the {021} from
{012} is illustrated in Figure 3. This etchant serves as a rapid means of
ascertaining the indices of the complimentary pyritohedra.

Further verification of the cleavage in pyrite was established by elec-
tron microscopy. The planes (021), (012), and (113) were physically de-
fined in pyrite single crystals such that each fabricated plane was within
± 1′ of arc deviation from representing the true crystallographic plane.

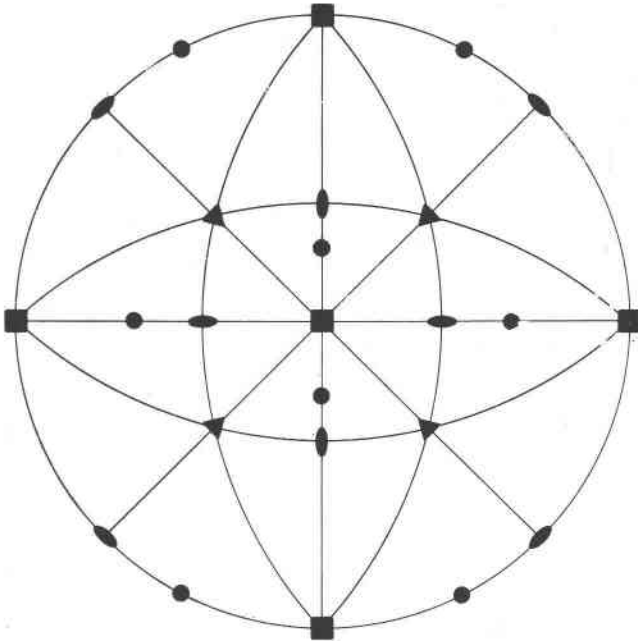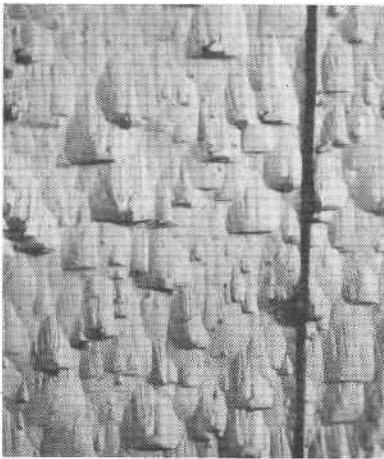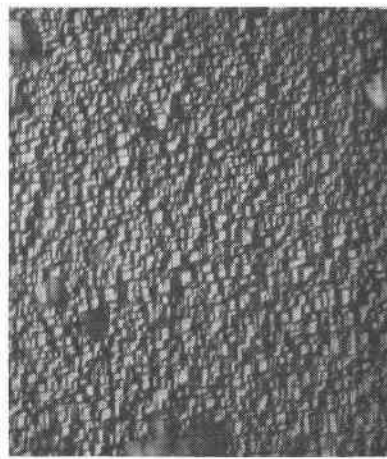Fig. 2. Stereographic projection illustrating macrocleavage planes (00I), (10$2$), (111), (110) and microcleavage zones [010], [$\bar{1}$01], [0$\bar{1}$1], [$\bar{1}$10] in pyrite.

a   350X   b   700X

Fig. 3. Pyrite crystal from Ambasaguas, Spain, etched in aqua regia. (a) cleavage pyritohedron (021); (b) non-cleavage pyritohedron (012).
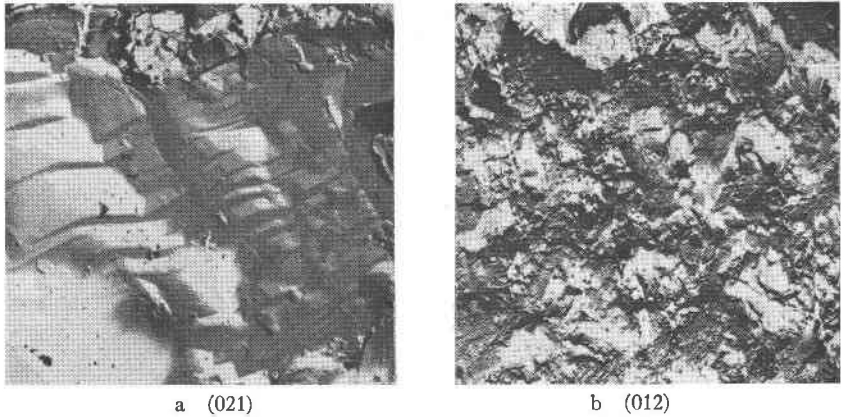
a   (021)   b   (012)

FIG. 4. Electron micrographs of surface replicas illustrating the (021) and (012) planes in pyrite after grinding with 15 μ abrasive. Magnification 10,000X. The electron micrographs reveal cleavage parallel to (021) and the absence of cleavage parallel to (012).

The defined planes were then abraded with a 15μ diamond paste and a surface replication of each plane was produced. The replicas were examined by electron microscopy at magnifications of 10,000 x. The (021) plane revealed excellent cleavage surfaces while the (012) and (113) gave only a continuous surface of irregular features.

The comparison of the (021) and (012) electron micrographs are shown in Figure 4.

The Effect of Preferred Orientation on the X-ray Intensities of Pyrite

Preferred orientation analyses were performed on pyrite and cobaltite powders varying in size range from -177μ to -37μ. The powders were prepared in the manner described by Frenzel and Bloss in order to maximize the effects of preferred orientation. The resulting intensities observed in diffractometer scans were seen to be almost random. Pyrite intensities are compared in Table I with theoretical intensities for pyrite calculated using the intensity program developed by Smith (1963). The calculated intensities are seen to be in reasonably good agreement with the experimental intensities given by Swanson et al. (1955).

The resulting intensities for scans C and D (identified in Table I) are seen to show an essentially random variation.

In the case of multiple cleavage, or even cleavage from the cube form alone, step cleavage can develop ridges or corners on the surface of the cleaved crystal. The existence of ridges and corners can enable a crystal particle to assume a more stable resting surface than the actual cleavage

Table I

Intensity Values for Pyrite Powders

	{111}	{200}	{210}	{211}	{220}	{311}
A	33.09%	95.58	54.98	45.77	51.39	100
B	36	84	66	52	40	100
C	10	100	10	50	10	50
D	9	100	14	10	40	9
E	40	100	100	50	40	65
F	29	100	64	37	42	35
G	18	39	95	26	51	100

A	Theoretical intensities
B	N.B.S. values Swanson et al. (experimental)

C	Callowhee, North Carolina pyrite - $177\mu + 149\mu$ *
D	" " " " $149\mu + 74\mu$
E	" " " " $74\mu + 44\mu$
F	" " " " $44\mu + 37\mu$
G	" " " " $- 37\mu$

* Experimentally measured for preferred
orientation effects.

plane itself, and this leads to the erroneous interpretation of an apparent cleavage plane. In the special case when the cleavage is characterized by one continuous plane, ridges and corners may not necessarily be developed.

In general, the effect of preferred orientation on diffractometer intensities due to cleavage is pronounced only on uniaxial or biaxial crystals with cleavage forms of low point group multiplicity. Crystals with excellent basal cleavage, i.e., alunite {001}, topax {001}, mica {001}, brucite {001}, etc. or such minerals as heulandite with {010} cleavage

can be expected to show large effects in measured X-ray intensities due to preferred orientation. However, when the point group multiplicity is high, the preferred orientation effects should be, inversely, small. This is not necessarily true in the case of eminent octahedral or dodecahedral cleavage, as exhibited in diamond, fluorite, and sphalerite. However, these minerals yield continuous cleavage planes that are immediately obvious even in casual hand-specimen observation. The mineral pyrite does not produce continuous cleavage surfaces. In fact, as will be shown, from a structural standpoint the cleavage due to the separation of bonds in pyrite results from a complex zig-zag path through the structure.

The four well-defined cleavages of pyrite may occur in combinations, and indeed, as described below, the {021} and {011} cleavages cannot occur independently. For this reason, particles of broken pyrite crystals will tend to have stepped surfaces. If many of the particles lie on ridges and corners, then the cleavage planes will tend not to parallel the powder slide and the preferred orientation effect of cleavage will be less visible.

On the other hand, the existence of prominent ridges and corners may actually lead to a second kind of preferred orientation. Planes which lie parallel to the lines of intersection of two good cleavages may have a higher probability of being parallel to the slide when particles lie on the ridges formed by these intersections. The planes whose intensities are enhanced may not themselves be cleavage planes, and then we have what can be called the preferred orientation of a noncleavage plane.

In pyrite the two most prominent cleavages are {100} and {021}. These two cleavages invariably occur together and produce ridges parallel to their intersections. The stepped cleavage pattern will prejudice the orientation of the pyrite particles in favor of planes which lie in the zones defined by the intersection of {100} and {021}.

We can thus understand for example why the measured intensities of {211} and {321} in the Callowhee pyrite sample (Figure 5) are much greater than one would expect by comparison with their calculated intensities. On the calculated scale, both {321} and {222} have intensities equal to 16 when {311} is chosen as 100. On the experimentally measured scale the intensity of {321} is more than 100 percent greater when scaled to the value of {311}. Furthermore, the measured intensity of {321} is more than two and a half times the intensity of {222}. The {222} planes represent a cleavage plane, whereas the {321} planes do not represent a cleavage. The very small enhancement of {321} by its coincidence with {123} (calculated intensity of 5) has been accounted for in the calculations. Thus, we have examples of the preferred orientation of noncleavage planes, and the enhancement of their intensities is a strong indication of the development of step cleavage patterns.
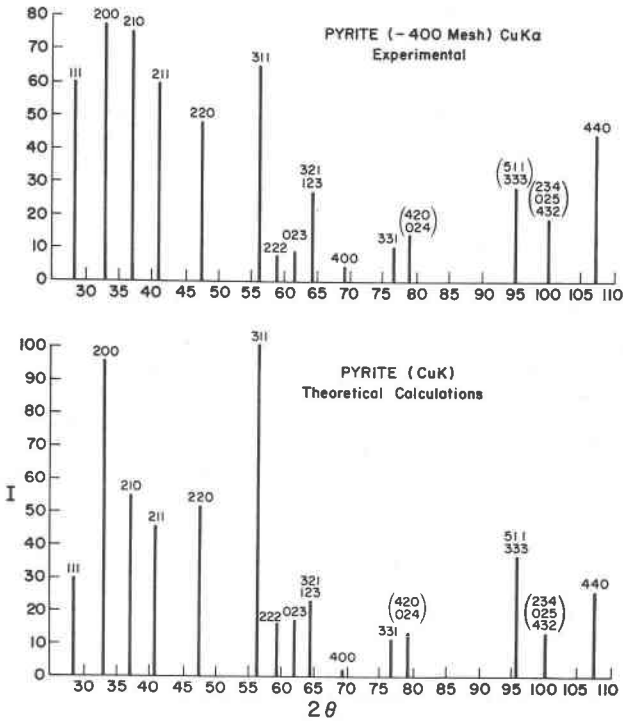
FIG. 5. A comparison of experimental and calculated powder diffraction intensities of pyrite.

Aside from the effects of preferred orientation, point group multiplicity, and coincidence of *d*-values, all powder diffraction intensities are sensitive to the range of particle size in the examined powder (Klug and Alexander, 1954). It has been shown that for particles ranging from 5 to 40 μ, the mean deviation of observed intensities is ± 10 percent, and for 15–50μ it is ± 18 percent.

In crystals that do not have eminent cleavage, X-ray reflection-intensities measured with powder samples, may be affected as much or more by variables of sample preparation, point group multiplicity, and *d*-value coincidence as by the result of preferred orientation. We therefore conclude, on the basis of these considerations, that X-ray intensity measurements on powder samples cannot be used as a reliable means of determining cleavage in crystals.

RELATIONSHIP OF CLEAVAGE TO STRUCTURE IN PYRITE

The fact that mechanical strain and cleavage in crystals are inherently dependent upon atomic arrangement has long been known. Where

the anisotropic character of a crystal is obvious, as in chain structures and layer structures, the relation of cleavage to structure is easily seen. In many crystals plastic deformation may occur, and the sum of all strain phenomena that ultimately leads to cleavage or fracture may be complex. Nevertheless, it is often possible to show a simple relation between crystal structure and cleavage. If one considers the relative strengths of bonds between atoms in pyrite, then the relationship of the cleavage to the structure of this mineral can be geometrically demonstrated.

There is a close resemblance of the pyrite structure to that of sodium chloride if one imagines that the Na ions are replaced by Fe and the Cl ions by S_2 groups. Throughout a pyrite crystal, however, the bonding is predominantly covalent. The S_2 groups form dumbbell-shaped units which lie along non-intersecting threefold axes. These sulphur dumbbells have a remarkably short S-S distance of about 2.10 Å. This separation is considerably less than the diameter of a sulphur ion, and is indicative of strong covalent bonding between the sulfur atoms of the S_2 groups. Undoubtedly, these S_2 groups or dumbbels are the strongest units of the pyrite structure. The second most important linkage in pyrite is formed by the iron-sulphur bonds. Each iron is octahedrally coordinated by sulphur atoms forming $d^2\ sp^3$ hybrid bonds. On the other hand, each sulphur is coordinated to only three irons on one side, and then to one sulphur on the other side to form an S_2 dumbbell. The Fe-S bonds are of equal strength.

Two obvious requirements for cleavage in pyrite are:

(1) The strongest bonds should not be broken.

(2) The least possible number of bonds per unit area should be broken. This requires that the S_2 dumbbells be left intact and the least number of Fe-S bonds be broken.

Two not so obvious requirements appear to be:

(3) The cleavage direction should be nearly normal to the resolved direction of the broken bonds.

(4) The repeat distance of a zigzag path necessary to produce a continued surface should be small. These repeats are indicative of the length of the path, and the number of bonds broken per mesh area of the lattice plane.

It is readily seen that the {001} and {111} planes fulfill the first requirement. The {001} planes separate mixed layers of S_2 dumbbells and Fe atoms. The {111} planes separate layers of S_2 groups from layers of Fe atoms. Thus both these cleavages require only the breaking of Fe-S bonds. The {111} cleavage, however, requires the breaking of many more bonds per unit area. This is easily visualized since only one Fe-S

bond per sulphur atom in {001} need be broken as compared to two and a half Fe-S bonds per sulphur atom in {111}. Thus {001} is a more predominant cleavage than {111}.

If the {001} direction is closely examined with requirement (3) in mind, then the {001} cleavage direction becomes a crinkled plane as illustrated in Figure 6. This figure shows that the {001} planes can be approximated by complementary {021} planes, which lie more nearly at right angles to the Fe-S bonds. Each {001} plane then becomes a crinkled surface whose ridges lie in the direction of the pyrite striations. We may think of the cube cleavage as actually consisting of alternating cleavage steps, one sulphur dumbbell wide, of the pyritohedron {021} planes.

An example of the development of the {021} cleavage in pyrite is given in Figure 7. This cleavage cannot occur as a continuous plane but must be represented by a zigzag path (in three dimensions). For this reason, the {021} cleavage requires the breaking of more bonds than the {001}, and this is in keeping with its lesser importance.

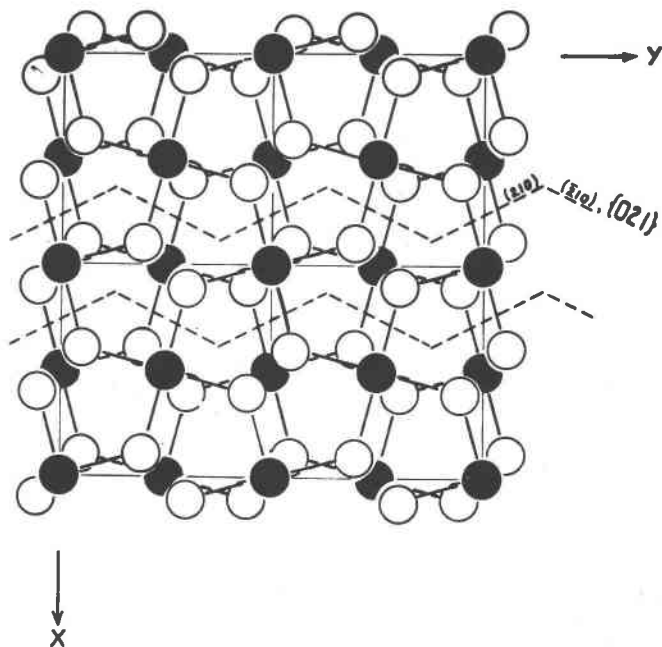Figure 8 shows the traces of {011} and {012} planes in pyrite. It is seen

FIG. 6. Projection of the pyrite structure on (001) illustrating the approximation of the cubic cleavage by the phritohedron {021}. Sulphur atoms are open circles, and iron atoms are black.
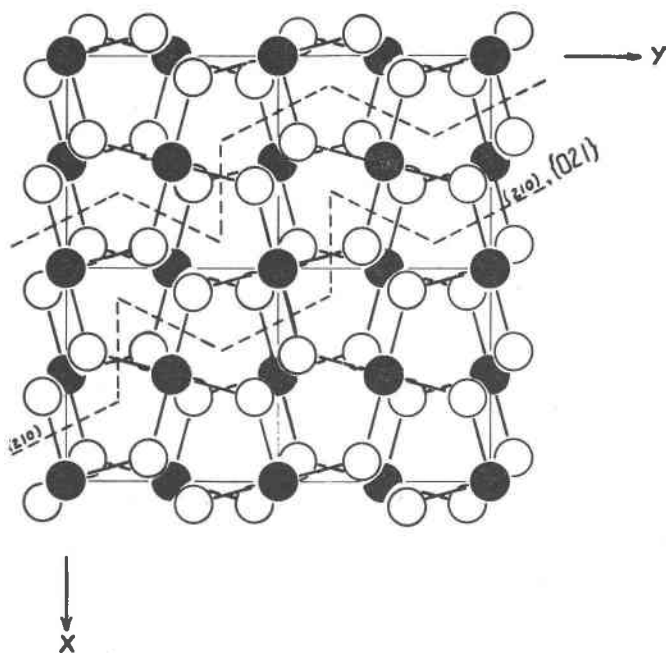
FIG. 7. Projection of the pyrite structure on (001) showing the cleavage scheme for the pyritohedron {021}.

that {012} does not conform well to requirements (1), (3), and (4). If the atoms were drawn closer to scale, the tendency of the {021} to break the S_2 groups would be more easily seen. The large repeat of the {012} scheme, as compared to that of {011} which is the poorest pyrite cleavage, is also obvious in Figure 8. Repeat schemes of planes pertinent to this discussion are graphically illustrated in Figure 9. The poor conformity of {012} to the cleavage requirements explains why it does not occur. The longer repeat path of {011} as compared to {021} requires the breaking of more bonds, and is consistent with the fact that the pyritohedron cleavage is more common.

The close relationship of the {001} and {021} planes shows why these cleavages do not occur separately, but are invariably found together. The fact that the cube is actually a pyritohedron on the scale of an S_2 group explains why these two forms are found together. Since the time the pyrite structure became known, people realized that the orientation of the S_2 groups conformed to the external morphology, including striations. The relation of the pyrite structure to both cleavage and external morphology has now been further elucidated in terms of the directions and strengths of bonding.
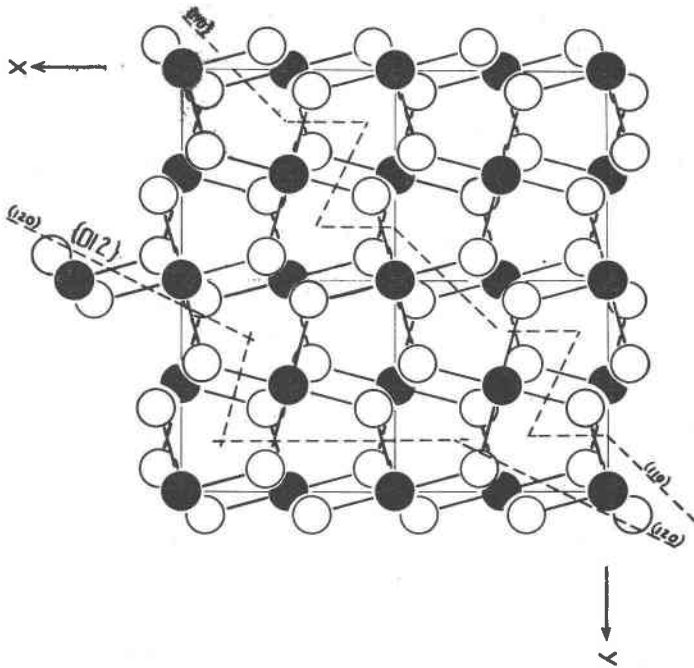
FIG. 8. Projection of the pyrite structure on (001) showing traces of the {110} cleavage plane and the (120) non-cleavage plane.

COBALTITE

The disordered, high temperature variety of cobaltite (CoAsS) has the pyrite structure, whereas the orthorhombic, low temperature kind differs from the isometric variety only in its ordered arrangement of As and S atoms. If one considers that cleavage in pyrite is determined by the strucutral arrangement of atoms and the relative strength and direction of bonds, then one may expect to find these same cleavages in cobaltite, and perhaps also in other base metal analogues of the pyrite structure.

Light figures were obtained with fabricated spheres of natural cobaltite from Tunaberg, Sweden, and artificial cobaltite, which was synthesized by Mikkelsen and Wold (1971) in silica tubes with the elements as starting materials. The light figures revealed that cobaltite has cleavages identical to pyrite in form, rank, and number. Electron microscopy of surface replicas further supports this claim.

As with pyrite, the dominant natural occurring pyritohedron form of cobaltite is also identical to the cleavage pyritohedron, which is {021} as opposed to {012}.
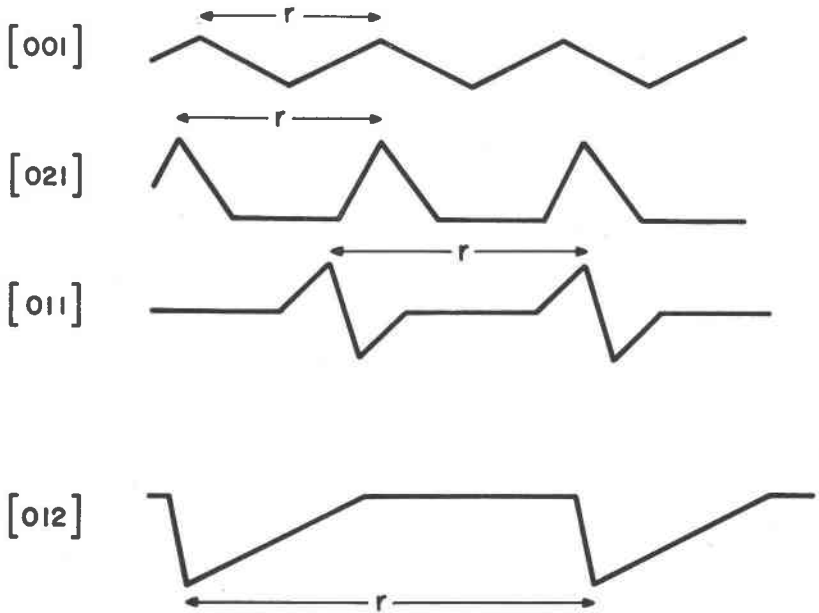
Fig. 9. Repeat patterns for specified zones in pyrite. (Each zone direction is coincident with (r) in the respective pattern.) The patterns are derived from Figures 6, 7 and 8, and they conform to the cleavage requirements described in the text. The repeat lengths (r) for the cleavages {001}, {021}, and {011} are relatively short as compared to the longer repeat length of the non-cleavage {012} pattern. The {111} cleavage does not require a zig-zag path, but it does require the breaking of more bonds per unit area than the {021} cleavage.

CONCLUSIONS

Light figure examination of abraded spheres demonstrates that pyrite and cobaltite cleave parallel to {001}, {021}, {111}, and {110} in decreasing order of rank respectively.

In addition to the demonstration of cleavage by light figures, resolution of cleavage in pyrite and cobaltite has been enhanced by surface replication for electron microscopy.

The {311} cleavage reported by Frenzel and Bloss is shown to be nonexistent. Since preferred orientation is only one of many variables affecting powder diffraction intensities, reliance upon the powder method in determing cleavage must be discouraged.

It can be shown by reference to the pyrite structure that the {021} form cleaves as opposed to its complementary noncleavage form {012}. The {001} and {021} cleavages are inextricably related. The cleavages that occur in pyrite are demonstrated by the geometry of the structure and by the direction and strength of the bonds.

The relative importance of a crystal form as estimated from its size, frequency of occurrence and presence as a cleavage form is well demonstrated in pyrite. The rank of cleavage and rank of forms which occur in pyrite are almost identical.

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