

# THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 27

JANUARY, 1942

No. 1

## VARIATION IN THE PROPERTIES OF PYRITE<sup>1</sup>

F. GORDON SMITH, *University of Toronto, Toronto, Canada.*

### ABSTRACT

Thirty-seven crystals of pyrite representing a wide range of habit, locality, and mode of occurrence, vary as follows: composition,  $\text{FeS}_{1.94}$  to  $\text{FeS}_{2.01}$  (10 analyses); specific gravity, 5.000 to 5.025 (10 crystals); optical anisotropism, none to strong; specific resistance at 20° C., in known and random directions, 0.014 to 256 ohms/cm. cube; temperature coefficient of resistance, -214 through zero to +26.5; thermo-electric potential against copper, strongly negative, through zero, to strongly positive, and often different in different parts of one crystal. Well developed lineage structure, with the "trunk" following a body-diagonal of the cube, is shown by one crystal.

These variations are explained mainly in terms of two variables: sulphur deficiency, giving Fe-atoms in S-positions and increasing the metallic character and conductivity; lineage structure giving interruptions of the crystal structure and reducing the conductivity. There is an indication that optically anisotropic pyrite is formed below 135° C. by regular arrangement of Fe-atoms in S-positions.

### INTRODUCTION

Pyrite is generally regarded as a mineral with unusually constant properties. One property, namely the electrical conductivity, is known, however, to differ greatly in different specimens. In a recent study (1940) this variation was confirmed but no satisfactory explanation was found. The present work represents a continuation of the previous study, using the same material as before and the same specimen numbers, together with some further crystals. To the observations previously recorded, further data on the specific electrical resistance are added, together with observations on the following properties which were previously not treated or only briefly mentioned: temperature coefficient of resistance; thermo-electric potential; composition; density; optical behaviour and heat-treatment in relation to atomic structure; secondary crystal structure; crystal habit, colour and lustre. The new observations illuminate the previously unsolved problem and suggest an explanation of the surprising variation in conductivity.

Pyrite was studied in this manner for two reasons: it is a typical ex-

<sup>1</sup> This work was carried out with the aid of a scholarship of the National Research Council of Canada; published with the permission of the Council.

ample of a crystalline compound with properties between metallic and homopolar; and since most of the ore minerals lie between these limits, many of the types of variation found in pyrite might be expected in the other ore minerals. Furthermore, since pyrite is so frequently found in ore deposits, the variation of its properties, combined with geological evidence, might lead to criteria for recognizing the conditions of deposition of the associated ores.

The author wishes to thank Professor M. A. Peacock for extensive assistance with many phases of this work. Thanks are also due to Professor L. Gilchrist for the loan of electrical equipment, to Professor H. G. Smith for criticism of the manuscript, to Dr. A. A. Brant for help with the electrical theory, to Professor L. J. Rogers for chemical analyses, to Professor F. E. Beamish for spectroscopic analyses, and to Professor E. S. Moore for laboratory facilities.

#### ELECTRICAL RESISTANCE AT CONSTANT TEMPERATURE

In the previous work (1940) the specific resistance ( $\rho$  ohms/cm. cube) was measured at room temperature on numerous right prisms cut in oriented and random directions from crystals of pyrite, using mercury electrodes. From prisms cut in various directions from one crystal it was found that the specific resistance along a unique body-diagonal of the cube was 20 times as great as the specific resistance along a direction at right angles to the unique direction. In different crystals the ratio of the greatest to least resistivity was about 10,000 to 1.

In the present work it was found that the resistance of some crystals of pyrite changes rapidly with temperature. It was therefore necessary to make a new set of measurements at constant temperature. This was done in the previously described manner, the temperature being held at  $20 \pm 1^\circ \text{C}$ . by enclosing the prisms in a tube in a water-bath.

One new crystal of pyrite was studied, namely No. 37, from Elba. It was a small pyritohedron, with fine striations perpendicular to the cube edges. The prism for electrical measurements was cut so that the edges were parallel to the crystallographic axes.

The new results for the specific resistance ( $\rho_{20^\circ}$ ) are given with the crystallographic direction of measurement in Table 3. As might be expected, the new values are similar to the old ones, but not exactly the same.

#### TEMPERATURE COEFFICIENT OF RESISTANCE

The temperature coefficient of resistance of a substance at  $t^\circ \text{C}$ . is defined as the rate of change of specific resistance with temperature, divided by the specific resistance at  $0^\circ \text{C}$ ., or

$$\alpha_t = \frac{1}{\rho_0} \frac{d\rho}{dt} \dots \dots \dots (1)$$

As is well known, the coefficient is positive for metallic substances; but it has often been reported negative for semi-metallic substances. Cases are known, for example, graphite, where the sign changes from negative at very low temperatures to positive at room temperature (Giauque, 1936).

Dean and Koster (1935) proved the variability of the sign of the temperature coefficient in the semi-metallic compound galena (PbS), and showed that there is a direct connection between the size of the solid aggregates making up the conductor and the sign of the coefficient. With small particle sizes the resistance was high and the coefficient was large and negative; but when the conductor was made up of a single crystal the resistance was smaller and the coefficient was small and positive. The theory put forward to explain this relation was that a compact single crystal of galena has a positive temperature coefficient similar to the metals; but if lattice discontinuities exist, some of the conducting electrons are bound at the interfaces, but can be released by thermal agitation. This effect of electron binding at lattice breaks has a greater effect on semi-conductors than on good conductors, as a larger percentage of the total number of conducting electrons is thus affected.

The temperature coefficient of resistance of pyrite has been reported to be positive for some crystals and negative for others (Mellor, 1935, pp. 215-216). Beckman (1912) found that the resistance increased with temperature as for metals, but that the relation between resistance and temperature was more accurately expressed by a formula:

$$\rho = \rho_0 e^{\alpha T}$$

where  $T$  is the absolute temperature. Koenigsberger and Reichenheim (1906) showed that the curve relating resistance and temperature reaches a minimum in the vicinity of 0° C. Since there is good evidence that the temperature coefficient of resistance is different in different specimens of pyrite, this coefficient was determined for most of the pyrite crystals used for resistance measurements.

From preliminary measurements it was found that the resistance of some of the pyrite crystals increased, and of others decreased, on heating. Prism 22, with the greatest specific resistance, was found to have a very large negative coefficient, and the complete relation between resistivity and temperature was found between 0° and 200° C.

The electrical contacts were of copper, electroplated to two opposite ends of the prism, with flexible copper cables soldered to the copper contacts. The prism was dried over phosphorus pentoxide for 7 days, quickly

dipped in varnish, and after this was dry, thickly coated with cellulose nitrate. A mercury thermometer and the pyrite prism were then sealed together in a small cement casing and immersed in a water bath for temperatures from 0° to 50° C. and in an oil bath from 50° to 200° C. The resistance at the various temperatures was found as before with a Megger resistance tester.

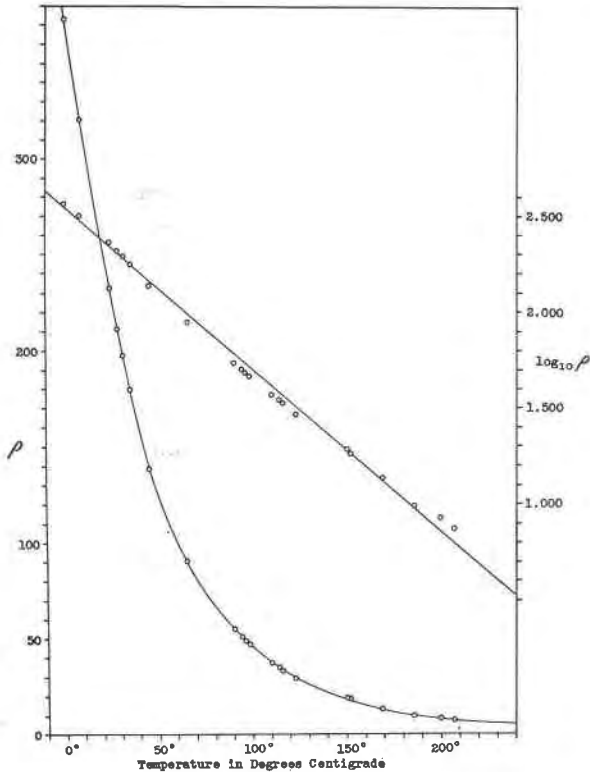


FIG. 1. Observed relation of specific resistance and logarithm of the specific resistance to temperature on pyrite crystal No. 22, with the largest negative temperature coefficient of resistance.

The data are shown in Fig. 1, with the specific resistance and the common logarithm of the specific resistance plotted against the temperature in degrees Centigrade. The relation is very nearly exponential, the equation for the entire 200° range being:

$$\rho = 71600e^{-0.0195T}$$

where  $\rho$  is the specific resistance and  $T$  is the temperature in °K.

The equation relating resistivity and temperature for the above crystal is of the form:

$$\rho = k \cdot e^{-\alpha T} \dots \dots \dots (2)$$

Assuming that this type of equation holds good for the other crystals, the value of the constant  $\alpha$  was found directly from the values of  $\rho$  at two temperatures using the relation:

$$\frac{\Delta \log \rho}{\Delta T} = -\alpha \dots \dots \dots (3)$$

The coefficient of resistance as usually defined, equation (1), does not remain constant over a large range of temperature for these crystals. However, the constant  $\alpha$  in equation (2) can be written:

$$-\alpha = \frac{1}{\rho} \cdot \frac{d\rho}{dt}$$

Therefore, at temperatures near 0° C., it is approximately equal to the ordinary coefficient, which can be treated as constant over any small range.

The specific resistance of each of the prisms of pyrite was found at 20° as described before, and at 100° when the tube containing the prism and its mercury contacts was suspended in a current of steam. The approximate temperature coefficient of resistance  $\alpha$ , calculated as above, is shown in Table 3. The coefficient for the majority of the specimens was negative, for a few it was sensibly zero, and for the rest it was positive. It was also different in the three directions of measurement in most of the prisms.

Using the best data in the *International Critical Tables*,  $\alpha$  and  $\rho_{20^\circ}$  were calculated for gold, silver, copper, lead, antimony, and bismuth, the results being as follows:

	Ag	Au	Cu	Pb	Sb	Bi
$\alpha \times 10^4$	35	25	38	30	34	32
$\rho_{20^\circ} \times 10^6$	1.65	2.44	1.69	22	41.7	128

It was assumed that these measurements were made on compact, ideal crystals. It will be noted that the coefficient is always positive, and about 1/273 for all the metals.

The early investigations suggested that there might be a relation between the coefficient  $\alpha$  and the specific resistance. On plotting  $\alpha$  against  $\log_{10} \rho_{20^\circ}$  it was found that smooth curves could be drawn through the

points representing the three directions of measurement on single prisms, and that these slope in the same general direction (Fig. 2). The higher the resistance, the more negative the coefficient. This is also apparent from the general distribution of all the points.

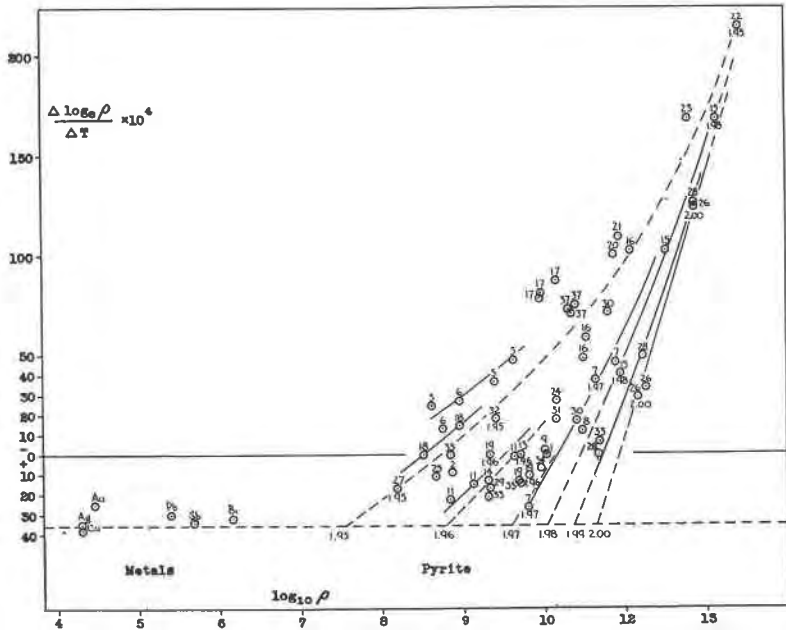


FIG. 2. Family of curves relating the approximate temperature coefficient of resistance to the logarithm of the specific resistance of specimens of pyrite numbered as in Table 3.

The equivalent points for Ag, Au, Cu, Pb, Sb, and Bi were also plotted, and it will be seen that these points lie very nearly on the straight line representing the constant value  $\alpha = 1/273$ . Some of the points for pyrite tend to approach this line, suggesting that the samples in question approach metallic behaviour.

According to the theory outlined above, these results are to be expected. A crystal with a high resistance and large negative thermal coefficient of resistance is one containing a large number of lattice discontinuities. The imperfections have some degree of regularity of position, since both the resistivity and the coefficient are different in different directions in most of the crystals of pyrite. The type of crystal imperfections and the reason for all the points in Fig. 2 not lying on one curve will be discussed later.

## THERMO-ELECTRIC POTENTIAL

When an electrical circuit contains two different conductors and one of the contacts between them is warmed, a current is set up in the circuit. The potential developed is dependent on the character of the two conductors and the difference in temperature at the cold and hot junctions. The sign convention is that a conductor *A* has a positive thermo-electric potential to another conductor *B*, if the resulting current flows from *B* to *A* at the hot junction.

The thermo-electric potential of pyrite has been reported to be positive, negative and both positive and negative on the same crystal (Mellor, 1935, p. 216). Rose (1870) believed that the positive or negative potential was directly related to the positive or negative crystal forms. This was criticized by Friedel (1874), but Tutton (1911, p. 168) again stated that the sign of the hemihedral forms present determined the sign of the potential.

There seems to be no theoretical basis for relating the crystal habit and thermo-electric potential. However, the potential must be very closely connected with the temperature coefficient of resistance, since this determines whether the density of conducting electrons increases or decreases on heating.

The thermo-electric potential difference against copper was determined qualitatively for most of the pyrite crystals in the following manner: a clean copper wire was connected to the pyrite by pressure with the hand, and the end of a heated copper wire was touched to any equivalent place on the pyrite. The deflection of a millivoltmeter connected to the two copper wires was observed when contact was made. Preliminary work showed that all the specimens with a large negative temperature coefficient of resistance had a positive thermo-electric potential difference against copper, but for those with large resistivities, the amount of the deflection was small. This is due to the very large internal resistance of the specimen being studied, when compared with the resistance of the instrument.

The direction and amount of the deflection was noted when contact was made with crystal faces and saw-cuts through the centre of the crystals. The potentials corresponding to the instrument deflections are shown in Table 3. In some cases considerable zoning parallel to the faces was observed. In nearly every crystal showing zoning, the potential near and on crystal faces was more positive than in the centre of the crystal.

From an examination of the data, the relation between thermo-electric potential and thermal coefficient of resistance is established. Those crystals of pyrite with positive, zero, and small negative coefficients had

negative potentials against copper, and those with large negative coefficients had positive potentials.

If the interpretation of the cause of negative thermal coefficient of resistance is correct, and also its relation to the thermo-electric potential, then most crystals of pyrite have a greater degree of secondary crystal imperfection near the faces than in the central part. That is, the larger the crystal has grown, the more imperfect the lattice continuity. This will be discussed more fully later.

#### COMPOSITION

Many recorded analyses of pyrite show a deficiency in sulphur. A summary of a few newer representative analyses mostly from Doelter (1926, p. 527) is given in Table 1.

TABLE 1. ANALYSES OF PYRITE

Spec. No.	1	2	3	4	5	6	7	8
Fe	47.10	46.84	47.00	46.49	46.20	46.66	47.28	46.51
S	52.97	51.97	52.50	53.49	52.81	53.06	52.89	53.26
Cu	—	tr.	—	—	—	—	—	—
SiO <sub>2</sub> or insol.	—	0.52	—	0.04	1.00	0.08	—	0.59
	100.07	99.33	99.50	100.02	100.01	99.80	100.17	100.36
Calc. to 100% Fe	47.07	47.40	47.24	46.50	46.66	46.79	47.25	46.62
S	52.93	52.60	52.76	53.50	53.34	53.21	52.75	53.38
FeS <sub>8</sub>	1.96	1.93	1.95	2.00	1.99	1.98	1.95	1.99

1—Miniera di Casall, Prov. Grosseto (Doelter, No. 21). 2—Parana, Brazil (Doelter, No. 24). 3—Elba (Doelter, No. 39). 4—Elba (Doelter, No. 40). 5—Rio Tinto, Spain (Doelter, No. 41). 6—Elba (Juza and Biltz, 1932, p. 274). 7—U. S. A. (Juza and Biltz, *loc. cit.*). 8—Central City Mine, Gilpin Co., Col. (Doelter, No. 25).

Harvey (1928) suggested that departure from the ideal formula might account for differences in the electrical properties of the ore minerals. However, no definite relation between any of the properties of pyrite and its composition seems to have been established.

Several crystals of pyrite were analyzed by the author. Small chips were taken in each case from the same part of the crystal from which the prism for electrical measurements was taken. The chips were ground in an agate mortar under alcohol and about 0.2 gm. was digested in a cold mixture of nitric acid, bromine and potassium bromide, followed by gentle heating. After removing silica by filtration, the iron was reprecipitated as hydroxide, filtered and ignited to oxide. The sulphur was precipitated as barium sulphate in a large volume of solution, filtered and



ignited. The ratio of sulphur to iron alone was determined, although most of the specimens contained silica which was not weighed. The results, quoted as the atomic ratio in  $\text{FeS}_n$ , are shown in Table 3.

Professor L. J. Rogers kindly analyzed several crystals of pyrite for iron and sulphur. Iron and sulphur were determined on separate portions of the pulverized material, the former by titration and the latter by precipitation as barium sulphate after fusion in a bomb with sodium carbonate and peroxide. The results are given in Table 2.

TABLE 2. ANALYSES OF PYRITE

Spec. No.	32	7	13	15	19	26
Fe	45.5	46.35	45.85	45.95	45.80	45.9
S	51.0	52.25	51.5	52.2	51.5	53.1
	96.5	98.60	97.35	98.15	97.30	99.0
Calc. to 100% Fe	47.2	47.0	47.1	46.8	47.1	46.3
S	52.8	53.0	52.9	53.2	52.9	53.7
$\text{FeS}_n$	1.95	1.97	1.96	1.98	1.96	2.01

The atomic ratio,  $\text{FeS}_n$ , is also shown in Table 3, the asterisk denoting the results of Professor Rogers' analyses.

The effect of impurities on the properties of pyrite is problematical. Head (1934) has postulated that the gold in auriferous pyrite occurs as sheets along lattice discontinuities, and if present, one would expect the gold to increase the conductivity. However, the best-conducting specimen, No. 27, was analyzed spectroscopically by Professor F. E. Beamish and he reported it very pure, with no gold, a minute trace of manganese ( $<0.0001\%$ ) and no other metals above  $0.0001\%$ . Tests were made for arsenic on No. 26 and No. 27 by Professor Rogers with negative results. A colorimetric test of No. 26 for nickel, using dimethylglyoxime, was negative.

The analyses show that pyrite may vary from  $\text{FeS}_{2.00}$  to  $\text{FeS}_{1.94}$  and still contain essentially nothing but iron and sulphur. When the formulas for the analyzed crystals were added to the points in Fig. 2, it became clearer why all the points did not lie on one line. While not without exception it appears that the points lie on a family of curves, one for each composition interval,  $\text{FeS}_{1.95}$ ,  $\text{FeS}_{1.96}$ , and so on. There are thus two variables controlling the electrical properties of pyrite. When the composition remains constant, the temperature coefficient becomes larger negative and the resistance increases as the number of lattice discontinuities increases. However, for any one degree of such secondary crystal

imperfection the resistance decreases as the crystal becomes more deficient in sulphur.

It must be kept in mind, however, that the series of curves in Fig. 2 are in the nature of a generalization, and no precision is claimed. The zoning observed in some crystals may be in part compositional,<sup>2</sup> and there was no real assurance that the electrical measurements were performed on material exactly the same as that analyzed.

#### DENSITY

The recorded density of pyrite (Doelter, 1926, p. 547) shows a range of 5.2 to 4.6. Kennigott found in 10 selected crystals that the density varied from 5.000 to 5.028. Allen, Grenshaw and Johnston gave the density of pure pyrite as 5.02, and pyrite from Elba, 5.027. The density calculated from the cell dimensions given by Peacock and Smith (1941) is 5.003 for  $\text{FeS}_{2.00}$  and 5.014 for  $\text{FeS}_{1.98}$ .

It was thought that density determinations on the pyrite crystals would show, independently of the electrical criteria, the degree of crystal imperfection. The difference between the calculated density ( $G_{\text{calc.}}$ ) and the measured density ( $G_{\text{meas.}}$ ) would thus be a means of calculating the amount of open space due to lattice discontinuities. Single crystal fragments had to be used, and the Berman density balance was found to be well suited for this purpose. The absolute density values were determined by comparison with a diamond crystal as described by Peacock and Smith (1941).

The density of fragments weighing 20 mg. was determined for several of the analyzed crystals of pyrite, using toluene as the immersion liquid. In most cases the average of at least three similar values was taken, more weight being placed on the density of those fragments with clean conchoidal bounding surfaces and less on those with rough surfaces. The results are shown as  $G_{\text{meas.}}$  in Table 3, opposite the corresponding theoretical density  $G_{\text{calc.}}$ , interpolated from the results of Peacock and Smith (1941). The measured density tended to approach the theoretical density, but was considerably lower in some cases, notably for No. 22.

Let it be assumed that lattice discontinuities do occur in pyrite, and that they are filled by air ( $G=0.001$ ). Then the relation between  $G_{\text{calc.}}$ ,  $G_{\text{meas.}}$ , and the percentage volume of the crystal occupied by air in lattice discontinuities,  $S$ , is as follows:

$$S = \frac{G_{\text{calc.}} - G_{\text{meas.}}}{G_{\text{calc.}} - 0.001} \times 100\%.$$

<sup>2</sup> In the case of No. 27 the analysis of the part of the crystal whose electrical properties were studied gave  $\text{FeS}_{1.95}$  while analysis of two other parts gave  $\text{FeS}_{1.99}$  and  $\text{FeS}_{1.97}$

Using this relation,  $S$  was calculated and is shown in Table 3. It is also shown plotted against  $\log_{10} \rho_{20^\circ}$  in Fig. 3. When the composition of each specimen is indicated as shown, a series of curves can be drawn, one for each composition interval, and this figure then becomes similar to Fig. 2. The resemblance probably means that secondary crystal imperfection and thermal coefficient of resistance are closely related, as postu-

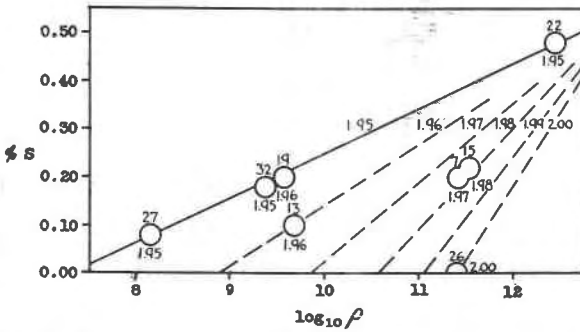


FIG. 3. Relation between percentage of open space and logarithm of the specific resistance of specimens of pyrite of known composition and specific gravity.

lated. For instance, prism 22 has the highest resistance, the most negative thermal coefficient of resistance and also the lowest density, all of which may be referred to a high degree of crystal imperfection. Direct evidence of the character of the crystal imperfection of this crystal will be described later.

#### OPTICAL BEHAVIOUR AND CRYSTAL STRUCTURE

The crystal structure of pyrite is well known. It is cubic face-centered, and the relation of the iron and sulphur positions are such that if the iron atoms are at the lattice points, the sulphur atoms are in pairs whose axes are in the directions of the four non-intersecting body-diagonals. If one sulphur atom in a like position in every unit cell is replaced by iron, then the symmetry of the structure is changed from cubic to ditrigonal polar, and the formula becomes  $\text{FeS}_{1.4}$ . It has been shown by Peacock and Smith (1941) that iron may replace sulphur in pyrite. It is also generally known that pyrite is sometimes slightly anisotropic in polarized light. Smith (1940) has shown that the electrical resistance symmetry of one crystal of pyrite studied was rhombohedral (ditrigonal) and that heating to  $135^\circ \text{C}$ . rendered an optically anisotropic specimen isotropic.

An experiment was carried out to see if the symmetry of the optical anisotropism is the same as that of the electrical anisotropism. A cube

truncated by artificial octahedron planes was cut from a fragment of a cubic crystal from Leadville. All the faces were then polished by hand on a lap. On examination in polarized light, with the nicols very nearly crossed, all the cube faces were distinctly anisotropic. The position of the cube faces giving maximum blue and maximum red colors was such that the vibration directions of the nicols were parallel to face diagonals. Octahedron faces normal to the remaining body diagonal were isotropic. Thus the crystal is uniaxial and possibly ditrigonal.

Optical anisotropism of pyrite has been suggested by Schneiderhöhn (1930) to be due to the presence of arsenic. This cannot be the only explanation, since specimens Nos. 26 and 27, with no detectable arsenic, were moderately anisotropic. It is here postulated that when iron replaces some sulphur in pyrite, the replacement may take place in a random or regular manner. When random, the crystal remains isotropic, but when regular, it develops ditrigonal symmetry, with one of the cube body diagonals as the unique axis.

An attempt was made to determine the exact temperature at which anisotropic pyrite may become isotropic. A small plane parallel to a cube face on a large cubic crystal from Leadville was polished by hand on a lap. The section was distinctly anisotropic in reflected light. The polished face was protected by a coating of cellulose nitrate and the fragment was suspended in water and oil baths for 30 to 60 minutes at various temperatures between 100° and 214° C. The section was lightly polished after each heating and examined as before. No noticeable change in the degree of anisotropism was noticed during the series of heat treatments.

The effect of large crystal size on damping the transition was considered. A number of fragments of various sizes from an unheated part of the same crystal as the above were enclosed in a glass tube and heated in the oil bath to  $214^{\circ} \pm 0.5^{\circ}$  C. for 15 minutes. They were then mixed with a hard wax and polished. One of the larger pieces, one about  $3 \times 2$  mm. in section, was slightly anisotropic and all the rest were isotropic. It was evident that the smaller the size of the crystal fragment, the more readily the transition takes place.

Since only the moderate heating during mounting in bakelite is sufficient to destroy the anisotropism of some crystals of pyrite, a number of chips from most of the crystals of pyrite were mounted for polishing in a hard wax. The maximum temperature reached by the chips was about 70°C., and cooling to room temperature took about 10 seconds. A number of pieces were embedded in holes in a bakelite mould and were then polished by a Harvard-type machine.

On examination in plane-polarized light, about one-half of the fragments of pyrite were found to be anisotropic. The interference colors

with the nicols crossed, or nearly crossed, were shades of blue or blue-green and red or orange. With very weak anisotropism the colors were steel-grey to buff-grey. Four color changes were seen in every case during one complete rotation of the stage.

Only one set of randomly-oriented chips was examined; therefore the relative degree of anisotropism seen between different specimens could not be taken as the relative degree of anisotropism of the crystals from which they were taken. However, two degrees of anisotropism were recognized, relatively strong (*s*) and weak (*w*), as well as the isotropic (*o*) variety, and these are recorded in Table 3.

A few generalizations can be made from the above observations. Those crystals, thought to have been formed at high temperatures, such as cubes in schist and from pneumatolytic deposits (Nos. 4, 5, 18) were isotropic, and one known to have been formed at a low temperature, the Joplin pyrite (No. 23), was anisotropic. Many of the isotropic crystals were assumed to be sulphur-deficient, both from their place on the series of curves of Fig. 2 and from their density. Since they are isotropic, the iron replacing sulphur must be in purely random positions. It is reasoned that if an anisotropic crystal becomes isotropic on heating and does not return to its original condition on cooling, the originally somewhat ordered condition of the lattice irregularity (iron in sulphur positions) becomes irreversibly disordered or random. As both isotropic and anisotropic sulphur-deficient pyrite exists in nature, the former is postulated to have formed above and the latter below, some critical temperature, which is believed to be between room temperature and 135° C.

#### SECONDARY CRYSTAL STRUCTURE

Various theories of secondary crystal structure have been postulated to explain the departure from the theoretical strengths and other properties of crystalline solids. The proof of regular secondary structure is not conclusive and Buerger (1934*b*) has vigorously contested the theory from which such structures were deduced. However, a secondary structure which is not regular but is a morphological phenomenon of crystals, has been described and has been given the name *lineage structure* by Buerger (1934*a*).

Buerger (1934*a*) considers the growth from a crystal nucleus to be branched, very much like a filled-in dendritic structure, the central part being called the trunk, the main subdivisions, branches, and the filling between them, boughs. The entire crystal is viewed as an agglomeration of units which when traced back from the crystal faces towards the nucleus, join with neighboring units. Imperfection of this sort may be non-existent, giving an ideally perfect crystal, or great, giving an ideally

imperfect crystal. It may be so well developed that the crystal aggregate becomes an arborescent group of radiating crystals rather than one crystal.

Among the pyrite crystals studied, a few were nearly perfect in the foregoing sense, showing plane, mirror-like faces; but most of them had faces that gave a wavy reflection. No. 22 was so imperfect that the cube faces were rounded and partly covered by neighboring cube and octahedron secondary terminations mutually inclined up to  $20^\circ$ . This suggested that lineage structure might correspond to the lattice discontinuities inferred to explain the electrical effects.

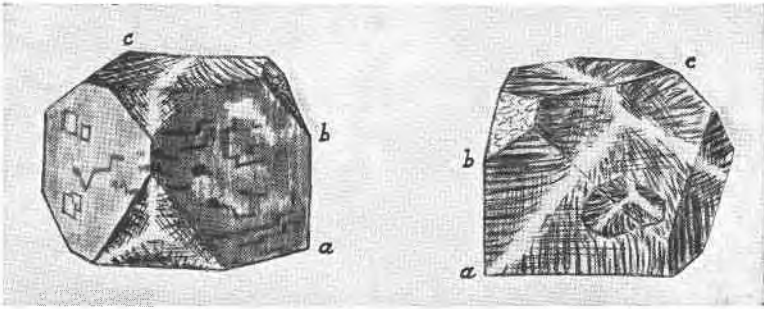


FIG. 4. Sketch of the lineage structure developed on pyrite crystal No. 22 after etching with concentrated nitric acid.

A cubical crystal, from a part of which prism No. 22 was obtained, was prepared for etching by grinding and smoothing the natural cube faces, and also grinding octahedron planes on the corners. The cube was then immersed in warm fuming nitric acid for about two minutes, washed and dried.

A very striking pattern had been etched into the surface. A sketch of the crystal, only slightly idealized, is shown in Fig. 4. One body diagonal of the crystal is a unique polar axis of three-fold symmetry. There are also three planes of symmetry intersecting in this axis. The symmetry may be considered to be ditrigonal polar. Following Buerger's terminology, one body diagonal is the trunk of the lineages. There are three main branches which divide the whole crystal into three zones, the boughs in each zone all growing parallel to each other and perpendicular to the three cube faces around one extremity of the trunk. In addition to the lineage structure, fine lines were seen running perpendicular to the boughs, parallel to the three cube faces mentioned above. The lines represent planes parallel to these cube faces, and possibly they are growth lines. While being prepared for density measurements, a fragment from

the same crystal showed a grain such that it broke much like a columnar basalt into shining rather irregular polygonal prisms approximately 1 mm. across. These were probably the main boughs in the filled-in part between the branches.

Several other crystals were etched on ground surfaces with nitric acid. The Joplin pyrite, No. 23, showed a well developed lineage structure, but in others only traces of this structure were evident. On those crystals inferred to be more nearly perfect from electrical measurements, either smooth surfaces were formed or small, regular, lenticular pitting.

From the interpretation of the electrical measurements, Nos. 22 and 23 were the two specimens with the greatest amount of lattice discontinuity. They also were the only two which had a lineage structure gross enough to be brought out by etching. This was thought to be sufficient evidence to state that the crystal imperfection in pyrite, detected by a negative temperature coefficient of resistance, is due to the development of lineage structure.

Earlier it was remarked that the positive thermo-electric potential increases outward from the centre of the crystals. This corresponds to an increase in crystal imperfection, here considered to be due to lineage structure.

#### CRYSTAL HABIT, COLOR AND LUSTRE

In the older literature two kinds of pyrite were recognized, positive and negative. Positive pyrite was said to be characterized by striations on the pyritohedron parallel to the trace of the cube edge. That is, oscillatory combination between  $\{021\}$  and  $\{001\}$ . This variety was said to be a poor conductor of electricity and to have a positive thermo-electric potential against metals. The negative variety has striations on the pyritohedron perpendicular to the trace of the cube edge, formed by oscillatory combination of  $\{012\}$  and  $\{124\}$  or  $\{112\}$ . It is a good conductor and has a negative thermo-electric potential (Tutton, 1911, p. 168).

From the results of the previous work (1940) on 36 specimens of pyrite, it is apparent that there is no sharp division into good and poor conductors. Also from the tabulation of the thermo-electric potential on the same specimens, there is no basis for a sharp division. In fact some crystals are zoned gradationally from negative in the center to positive on the crystal faces. However, there must be some relation between these properties and the crystal habit, because the above relation has not been definitely disproved. Accordingly, the major crystal forms on most of the specimens were noted and are listed in Table 3, to see if any relations could be established with the other properties.

While not very definite, some generalizations can be made. The faces of any crystal showing the diploid had a negative thermo-electric poten-

tial to copper. Such crystals were good conductors, and from their position in Fig. 2, were also decidedly sulphur-deficient. However, No. 37, which showed the pyritohedron and diploid, so that the striations from their combination were perpendicular to the cube edges, was negative on the crystal faces, but positive in the interior of the crystal and had an average resistance. In addition, many crystals showing the pyritohedron and cube, which should from the older ideas be positive and poor conductors, were negative and good conductors.

The color and lustre of the pyrite crystals studied varied a little. The two crystals with the highest amount of sulphur, No. 15 ( $\text{FeS}_{1.98}$  and No. 26 ( $\text{FeS}_{2.00}$ ), were noticeably yellower and nearer a true brass color than those deficient in sulphur, which tended toward a rather pale brass color. The lustre of the former two was metallic, but also somewhat adamantine, and both were splendid. The sulphur-deficient varieties had a metallic lustre, from bright to somewhat dull.

The conclusion was reached that the composition plays some part in controlling the crystal habit, but the forms seen are indicative of only the outer part of the crystal. The interior may have different properties. The older concept of two distinct types of pyrite has not been confirmed. The only agreement is that a crystal with striations on the pyritohedron perpendicular to the trace of the cube edge is likely to be sulphur-deficient, a good conductor and thermo-electrically negative against copper, on the crystal faces and often in the interior as well. Pyritohedrons striated the other way, if the color is brassy and the lustre bright to splendid, are, at least on the surface, usually nearer the ideal composition, poor conductors and often thermo-electrically positive against copper.

#### DISCUSSION AND CONCLUSIONS

It is postulated that the variation of the properties of pyrite is a function of two independent variables. One is the composition and the other is the secondary crystal structure. The former is measured by departure from the ideal formula  $\text{FeS}_2$ , and this seems to be always in the one direction, toward a deficiency of sulphur. Iron takes the place of some sulphur in such crystals, and this is known to affect the lattice dimensions and probably also its symmetry. The secondary crystal structure observed is a growth phenomenon known as lineage structure.

Variation in composition seems to affect the conductivity of pyrite. Other things being equal, the lower the sulphur content of the pyrite, the lower the resistance. This is to be expected if iron replaces some sulphur in sulphur-deficient specimens. The unit of structure may be pictured as a pair of sulphur atoms each of which is in contact with three iron atoms. If an iron atom replaces one of the sulphur atoms, it is likely the bond type between the three iron atoms around the replacing iron



atom would be much more metallic than the iron-sulphur linkage.

The habit, color and lustre of pyrite also seem to be affected by variation in composition. A splendid metallic lustre and a brass color is characteristic of pyrite with nearly the ideal formula, while sulphur-deficient varieties have a bright to rather dull metallic lustre and a pale brass color. The crystals low in sulphur seem to favor the diploid more than those richer in sulphur.

It was inferred that iron replacing sulphur in sulphur-deficient pyrite may be in regular positions, giving optically anisotropic pyrite, or it may be in irregular positions, giving the isotropic variety. The regular replacement may be made random by heating above 135°C. and this change is irreversible over the short period of laboratory experiments. It is probably irreversible in nature, since isotropic pyrite with a deficiency of sulphur does occur. The hypothesis is presented that pyrite formed in nature above approximately 135°C. was isotropic and remained so when cooled to room temperature, but when formed below this temperature it was anisotropic. This provides another geological thermometer which should be of use in economic deposits. However, since the bakelite moulding temperature is above the order-disorder temperature, some other mounting medium should be used when the optical anisotropism of pyrite is being studied.

Secondary crystal structure has a very much greater effect than composition on the electrical properties. Crystals with a well developed lineage structure have a high resistance and a large negative temperature coefficient of resistance. There is some evidence that the reverse holds true: that nearly perfect crystals have a low resistance and a positive coefficient. The thermo-electric potential against metals is related very closely to the coefficient and so to the secondary structure. With the sign conventions as described above, those crystals with a positive, zero, or small negative coefficient have a negative thermo-electric potential against copper and those with a large negative coefficient have a positive potential.

The density of pyrite fragments is low when the crystal shows evidence of lineage structure. The difference between the density as measured and calculated is not great, however, which must mean that the interlineal spaces are very small.

The lineage symmetry on one crystal was found to be ditrigonal polar, a symmetry possible from a regular replacement of iron in sulphur positions. There is a tendency for those crystals with a relatively strong optical anisotropism (regular lattice replacement) to show a well-developed lineage structure, so that it is probable that a regular replacement with ditrigonal polar symmetry controlled the development of a lineage structure having the same symmetry.

TABLE 3. SUMMARY OF OBSERVATIONS ON PYRITE

No.	[uvw]	$\rho_{20^\circ}$	$10 + \log_{10} \rho_{20^\circ}$	$\alpha \times 10^4$	$E$		$n$	$G_{calc}$	$G_{meas.}$	$S$	Opt.	Habit
					Centre	Face						
1	—	1.1	10.041	0.0	±	—	..	..	..	..	..	..
2	{110}	0.069	8.839	- 8.8	—	—	..	..	..	..	0	<i>a c</i>
3	{111}	0.15	..	..	—	—	..	..	..	..	0	<i>a e</i>
4	{100}	0.17	..	..	—	—	..	..	..	..	0	<i>a e</i>
	{—}	0.23	9.362	- 36.6	—	—	..	..	..	..	0	<i>e</i>
5	{—}	0.40	9.602	- 47.7	—	—	..	..	..	..	0	<i>e</i>
	{—}	0.039	8.591	- 24.6	—	—	..	..	..	..	0	<i>e</i>
6	{—}	0.052	8.716	- 13.1	—	±	..	..	5.020	..	..	<i>e</i>
	{—}	0.086	8.934	- 27.2	—	—	..	..	..	..	..	..
	{—}	0.59	9.770	+ 26.5	—	—	..	..	..	..	..	..
7	{—}	7.4	10.869	- 46.1	++	+	1.97*	5.015	5.005	0.20	0	<i>a e</i>
	{—}	4.1	10.613	- 37.6	—	—	..	..	..	..	..	..
8	{100}	2.83	10.452	- 12.0	—	—	..	..	..	..	..	..
9	{100}	0.98	9.991	- 2.1	—	—	..	..	..	..	..	<i>e a</i>
10	{—}	7.03	..	..	+	—	..	..	..	..	..	..
	{—}	0.125	9.097	+ 14.3	—	—	..	..	..	..	..	..
11	{—}	0.404	9.606	+ 0.9	—	—	..	..	..	..	..	..
	{—}	0.064	8.806	+ 22.1	—	—	..	..	..	..	..	..
12	{—}	1.7	..	..	±	—	..	..	..	..	..	..
13	{—}	0.470	9.681	0.0	±	—	1.96*	5.020	5.015	0.10	0	..
14	{100}	0.19	9.279	+ 13.1	—	—	..	..	..	..	..	<i>a e</i>
	{110}	132	12.121	- 168	—	—	..	..	..	..	..	..
15	{110}	8.6	10.934	- 40.3	⊕	⊕	1.98*	5.011	5.000	0.22	w	<i>a e</i>
	{001}	31.6	11.500	- 102	—	—	..	..	..	..	..	..
	{100}	3.16	10.500	- 58.5	—	—	..	..	..	..	..	..
16	{010}	2.94	10.468	- 48.1	± to +	⊕	..	..	..	..	0	<i>a e</i>
	{001}	11.4	11.057	- 102	—	—	..	..	..	..	..	..
	{100}	0.860	9.934	- 78.1	—	—	..	..	..	..	..	..
17	{010}	0.886	9.947	- 81.3	++	+	..	..	5.025	..	s	<i>a e</i>
	{001}	1.35	10.130	- 86.9	—	—	..	..	..	..	..	..
18	{100}	0.085	8.929	- 14.1	—	—	..	..	..	..	0	<i>a o</i>
	{010}	0.030	8.477	0.0	—	—	..	..	..	..	..	..
	{100}	0.456	9.659	+ 13.4	—	—	..	..	..	..	..	..
19	{010}	0.613	9.787	+ 10.4	--	++	1.96*	5.020	5.010	0.20	0	<i>a e</i>
	{001}	0.20	9.301	0.0	—	—	..	..	..	..	..	..
	{100}	7.05	10.848	- 100	++	⊕	..	..	..	..	s	<i>a o</i>
21	{—}	8.26	10.917	- 109	+	+	..	..	..	..	s	<i>o</i>
22	{100}	256	12.408	- 214	0	0	1.95	5.024	5.000	0.48	s	<i>a o</i>
23	{—}	60.8	11.784	- 168	⊕	⊕	..	..	..	..	..	<i>o a</i>
24	{100}	1.39	10.143	- 26.7	++	++	1.94	..	..	..	0	<i>a e</i>
25	{—}	0.043	8.633	+ 11.1	±	++	..	..	..	..	0	<i>e a</i>
	{001}	17.7	11.248	- 33.6	—	—	..	..	..	..	..	..
26	{110}	14.1	11.149	- 28.4	⊕	⊕	{2.01*}	5.003	5.005	0.00	w	<i>a e n o</i>
	{110}	72.4	11.860	- 124	—	—	{2.00}	..	..	..	..	..
27	{—}	0.014	8.146	+ 16.6	—	—	1.95	5.024	5.020	0.08	w	<i>e t o a</i>
	{111}	70.7	11.849	- 126	—	—	..	..	..	..	..	..
28	{110}	16.2	11.209	- 49.3	⊕	⊕	..	..	5.005	..	w	<i>a e n o</i>
	{112}	4.46	10.649	0.0	—	—	..	..	..	..	..	..
29	{—}	0.20	9.301	+ 16.8	±	—	..	..	5.010	..	0	<i>t o</i>
	{—}	5.88	10.769	- 71.4	- to ++	+	..	..	..	..	s	<i>e a</i>
30	{—}	2.43	10.386	- 17.0	—	—	..	..	..	..	..	..
31	{—}	1.35	10.130	- 17.5	- to ++	+	..	..	..	..	..	<i>a e o</i>
32	{100}	0.231	9.367	- 18.0	—	—	1.95*	5.024	5.015	0.18	0	<i>a</i>
	{—}	4.58	10.661	- 6.2	—	—	..	..	..	..	..	..
33	{—}	0.19	9.279	+ 21.2	±	±	..	..	..	..	w	..
	{—}	0.48	9.681	- 14.3	—	—	..	..	..	..	..	..
34	{100}	0.87	9.940	- 7.1	—	—	..	..	..	..	..	<i>a e</i>
35	{100}	0.064	8.806	0.0	—	++	..	..	..	..	..	..
36	{100}	5.0	..	..	- to ++	+	..	..	..	..	s	<i>e a</i>
	{100}	2.34	10.369	- 74.9	—	—	..	..	..	..	..	..
37	{010}	1.92	10.283	- 72.8	++	—	..	..	..	..	..	<i>e t a</i>
	{001}	2.08	10.318	- 70.5	—	—	..	..	..	..	..	..

Explanation of Table 3. No., specimen number. [uvw], crystallographic direction in which resistance was measured.  $\rho_{20^\circ}$ , specific resistance in ohms/cm. cube.  $\alpha$ , temperature coefficient of resistance,  $\Delta \log \rho / \Delta t$ .  $E$ , thermo-electric potential against copper as indicated by voltmeter deflections: --, strong negative; -, weak negative; ±, weak, positive or negative; ++, strong positive; +, weak positive; ⊕, positive near zero; 0, zero.  $n$ , sulphur-iron ratio in  $FeS_n$ .  $G_{calc}$ , density calculated from cell dimensions and composition.  $G_{meas.}$ , measured density.  $S$ , calculated percentage open space. Opt., optical anisotropism: *s*, strong; *w*, weak; 0, none. Habit, observed forms in order of importance: *a*(100), *e*(210), *o*(111), *t*(421), *n*(211).

## REFERENCES

- BECKMAN, B., *Verh. Amsterdam Acad.*, **21**, 1281 (1912).  
BUERGER, M. J., *Zeits. Krist.*, **89**, 195 (1934 a).  
———, *Zeits. Krist.*, **89**, 242 (1934 b).  
DEAN, R. S., AND KOSTER, J., *U. S. Bur. Mines*, Rept. Invest., No. **3268** (1935).  
DOELTER, C., *Handb. Mineralchem.*, **4** (1) (1926).  
FRIEDEL, C., *Compt. Rend.*, **78**, 508 (1874).  
GIAUQUE, W. F., *Ind. Eng. Chem.*, **28**, 743 (1936).  
HARVEY, R. D., *Econ. Geol.*, **23**, 778 (1928).  
HEAD, R. E., *U. S. Bur. Mines*, Rept. Invest., No. **3226**, 27 (1934).  
JUZA, R., AND BILTZ, W., *Zeits. anorg. Chem.*, **205**, 273 (1932).  
KOENIGSBERGER, J., AND REICHENHEIM, O., *Phys. Zeits.*, **7**, 572 (1906).  
MELLOR, J. W., *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, **14** (1935).  
PEACOCK, M. A., AND SMITH, F. G., *Univ. Toronto Studies, Geol. Ser.*, in press (1941).  
ROSE, G., *Sitzber. Akad. Berlin*, **333** (1870).  
SCHNEIDERHÖHN, H., *Chemie der Erde*, **5**, 385 (1930).  
SMITH, F. G., *Univ. Toronto Studies, Geol. Ser.*, **44**, 83 (1940).  
TUTTON, A. E. H., *Crystallography* (1911).