

## Crystal structure refinement of a weakly anisotropic pyrite

PETER BAYLISS

Department of Geology, University of Calgary  
Alberta T2N 1N4 Canada

### Abstract

The crystal structure of a weakly anisotropic pyrite [pseudo-cubic with  $a = 5.417(1) \text{ \AA}$ ] has been refined. This pyrite is pure  $\text{FeS}_2$  within the analytical limits of the electron probe. The triclinic crystal structure postulated for this pyrite is based upon (a) similar symmetry degeneracy in the pyrite-type structure of arsenian ullmannite, (b) a significant reduction of  $R_w$  at the 0.005 level, (c) presence of forbidden reflections of  $Pa3$  of  $hk0$  with  $h$  odd,  $0kl$  with  $k$  odd, and  $h0l$  with  $l$  odd, (d) presence of forbidden reflections for  $P2_13$  of  $h00$  with  $h$  odd,  $0k0$  with  $k$  odd, and  $00l$  with  $l$  odd, (e) a greater than  $3\sigma$  movement of some atomic coordinates from a cubic crystal structure to a triclinic crystal structure, (f) weak anisotropism, and (g) low formation temperature.

### Introduction

Pyrite was one of the earliest crystal structures to be solved by X-ray diffraction (Bragg, 1913), and it illustrated that the external symmetry of a crystal is related to its atomic arrangement. Later this crystal structure was confirmed by Parker and Whitehouse (1932). In order to calculate the interatomic distances, Elliott (1960) determined the positional parameters. Later the crystal structure was refined by Brostigen and Kjekshus (1969) to an  $R$  factor of 0.075 excluding unobserved reflections, and by Finklea *et al.* (1975) to an  $R$  factor of 0.036 excluding unobserved reflections.

About a quarter of the pyrite samples examined by Klemm (1962) are weakly anisotropic. Schneiderhöhn (1930) had recognized that arsenian pyrite is often weakly anisotropic. Klemm (1962) observed weakly anisotropic zoned pyrite as well as clearly zoned isotropic pyrite, which indicates no general relationship between anisotropy and chemical variations. Pyrite subject to great deformation is isotropic. Weakly anisotropic pyrite forms at low temperatures (Smith, 1942). No theory explains all occurrences, although Gibbons (1967) suggested that the weak anisotropy results from a few disturbed surface layers.

Recently a number of minerals with the pyrite-type crystal structure (cobaltite—Giese and Kerr, 1965; gersdorffite—Bayliss and Stephenson, 1968; willyamite—Cabri *et al.*, 1970; and arsenian ullmannite—Bayliss, 1977) have been recognized as pseudo-

cubic. Therefore it appears worthwhile to investigate the symmetry of pyrite.

### Experimental

Six pyrite samples were examined under reflected light to observe anisotropism and by a precession camera with Cu radiation to check for the presence of any reflections forbidden by the space group of pyrite  $Pa3$ , which has systematic absences of  $hk0$  and  $h00$  with  $h$  odd,  $0kl$  and  $0k0$  with  $k$  odd, and  $h0l$  and  $00l$  with  $l$  odd. Some samples were isotropic with all systematic absences. A weakly anisotropic pyrite sample from the Itaya mine, Yamagata Prefecture, Japan, was found to have no systematic absences (Fig. 1), and was selected for a crystal-structure refinement. The pyrite occurs within a kaolin deposit formed by low-temperature hydrothermal alteration due to the post-volcanic activity of the Azumo volcano (Hondo, 1969).

The sample was analyzed by electron microprobe as described by Stout and Bayliss (1975). The analytical results are listed together with the theoretical values of  $\text{FeS}_2$  in Table 1 to show that the theoretical values lie within the experimental error limits of the analytical values. The limits of detection (weight percent) are Co 0.07, Ni 0.05, As 0.05, and Sb 0.03.

A 114.6 mm Debye-Scherrer photograph was taken with Cu radiation/Ni filter. All reflections are indexable on a cubic cell with the systematic absences of space group  $Pa3$ . A unit cell of  $a = 5.4166 \text{ \AA}$  was calculated by the Nelson and Riley (1945) extrapolation.

tion method to  $\theta = 90^\circ$ : This value agrees with the value of 5.417 Å published in *Selected Powder Diffraction Data for Minerals* (1974) from the National Bureau of Standards. In addition, there are no significant intensity differences between the Debye-Scherrer photograph and the National Bureau of Standards data.

A crystal with dimensions  $88 \times 107 \times 112 \mu\text{m}$  was selected because of its well-developed cube form  $\{100\}$ . This crystal was aligned along an  $a^*$  axis on a four-circle diffractometer with reflections 800,  $\bar{8}00$ , and 080. A least-squares analysis of 23 high  $2\theta$  reflections gave a cubic cell of 5.417(1) Å. Integrated intensities of all reflections from one hemisphere were collected with  $\text{MoK}\alpha$  radiation and a graphite 002 monochromator. A scanning speed of  $\frac{1}{2}2\theta$  per minute was used in the  $\omega$ - $2\theta$  scan mode within a  $6^\circ$  to  $60^\circ 2\theta$  range. Twenty-second background counts were made before and after each reflection. A standard reflection was measured after every 50 reflections.

Since the space group  $Pa\bar{3}$  requires some systematic absences, the possibility that these reflections were observed because of the Renninger effect was investigated. The reflection and then the background of four reflections ( $0k0$  with  $k$  odd from  $k = 1$  to  $k = 7$ ) were measured for 100 seconds each at every  $5^\circ$  as the crystal was rotated about the scattering vector.

Background, Lorentz polarization, and absorption corrections were made following the method of Wuensch and Prewitt (1965). The linear absorption coefficient of pyrite is  $115.5 \text{ cm}^{-1}$  and results in trans-

Table 1. Electron microprobe analysis

Weight % Sample		Weight % $\text{FeS}_2$	
Fe	46.8	Fe	46.5
Ni	0.0		
Co	0.0		
S	53.5	S	53.5
As	0.0		
Sb	0.0		
Total	100.3	Total	100.0

mission factors between 0.29 and 0.42. The extinction factor described by Zachariasen (1967) and extended by Coppens and Hamilton (1970) was calculated. From one hemisphere, 919 symmetry-independent reflections were measured and 858 were observed above the  $1\sigma$  level. All reflections were included in the refinement of the crystal structure by the least-squares program (REFINE 4) of Finger and Prince (1975). All observations were weighted according to  $w = 1/\sigma_F^2$ , where  $\sigma_F$  is the standard deviation based on counting statistics. Initial positional parameters were taken from Brostigen and Kjekshus (1969). The neutral atomic scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* (1974). The data were first refined in space group  $Pa\bar{3}$  to an  $R$  factor of 0.034. The atomic coordinates and temperature factors are listed in Table 2.

This  $R$  factor indicates that the structure is basically correct, but space group  $Pa\bar{3}$  requires systematic absences. From this group, 132 reflections were recorded, which includes 46 reflections above the  $2\sigma$  level, 34 reflections between the  $2\sigma$  and  $1\sigma$  levels, 36 reflections between  $1\sigma$  level and 0.00, and 16 reflections at 0.00. The subgroup of 12 reflections, which has  $h00$  with  $h$  odd,  $0k0$  with  $k$  odd, and  $00l$  with  $l$  odd includes 6 reflections above the  $2\sigma$  level, 2 reflections between the  $2\sigma$  and  $1\sigma$  levels, 2 reflections between the  $1\sigma$  and 0.00, and 2 reflections at 0.00. The only space group which allows all reflections to be observed with this crystal structure is  $P\bar{1}$ . This is similar to the crystal structure of gersdorffite,  $\text{NiAsS}$  (Bayliss and Stephenson, 1968) and arsenian ullmannite,  $\text{Ni}(\text{Sb,As})\text{S}$  (Bayliss, 1977). The data were then refined in this space group, initially with isotropic

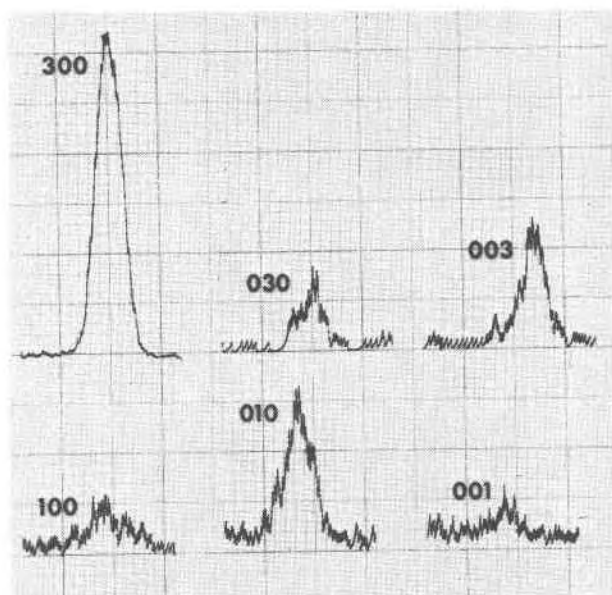


Fig. 1. Reflections from anisotropic pyrite.

Table 2. Positional parameters and isotropic temperature factors

Atom	Site Occupancy	$x$	$B(\text{Å}^2)$
Fe	1.0	0.0	0.28(1)
S	1.0	0.3851(1)	0.33(1)



Table 4. Positional parameters, anisotropic temperature factors ( $\times 10^4$ ) and extinction parameter

Atom	Site Occupancy	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Fe <sub>1</sub>	1.0	0.0010(8)	0.0020(6)	0.0030(6)	23(3)	24(3)	17(3)	0(2)	0(2)	4(2)
Fe <sub>2</sub>	1.0	0.4966(8)	0.0001(6)	0.5036(6)	26(3)	26(3)	19(3)	2(2)	-3(2)	-1(2)
Fe <sub>3</sub>	1.0	0.5001(8)	0.5020(6)	0.0011(6)	26(3)	21(3)	22(3)	7(2)	-2(2)	-3(2)
Fe <sub>4</sub>	1.0	-0.0006(8)	0.5013(6)	0.5038(6)	26(3)	26(3)	16(3)	1(2)	-2(2)	-1(2)
S <sub>1</sub>	1.0	0.3857(4)	0.3832(4)	0.3840(4)	20(6)	18(6)	4(6)	-7(4)	-3(4)	-4(4)
S <sub>2</sub>	1.0	0.1149(4)	0.6114(4)	0.8846(4)	38(7)	69(7)	50(7)	2(5)	-1(5)	-7(5)
S <sub>3</sub>	1.0	0.8854(4)	0.1157(4)	0.6143(4)	34(6)	1(6)	-2(6)	-1(4)	-4(4)	-4(4)
S <sub>4</sub>	1.0	0.6153(4)	0.8865(4)	0.1141(4)	39(7)	75(7)	39(7)	-3(5)	-8(5)	-10(5)
S <sub>5</sub>	1.0	0.6151(4)	0.6132(4)	0.6137(4)	35(6)	46(7)	49(7)	2(5)	-2(5)	0(5)
S <sub>6</sub>	1.0	0.8854(4)	0.3818(4)	0.1149(4)	26(6)	-5(6)	-2(6)	0(4)	-3(4)	2(4)
S <sub>7</sub>	1.0	0.1147(4)	0.8856(4)	0.3841(4)	35(6)	57(7)	54(7)	1(5)	-3(5)	-1(5)
S <sub>8</sub>	1.0	0.3857(4)	0.1161(4)	0.8842(4)	14(6)	-4(6)	11(6)	4(4)	1(4)	4(4)

Extinction parameter -0.0000156

temperature factors and then with anisotropic temperature factors, to an  $R$  factor of 0.032. Table 3 gives the observed and calculated structure factors, Table 4 the atomic coordinates and temperature factors, and Table 5 the interatomic distances and angles.

### Discussion

All the atoms in the cubic crystal structure of pyrite occupy special positions on one of the three-fold axes, therefore any small movement of any atom from a three-fold axis will cause the symmetry to disappear. This symmetry degeneracy has been adequately documented in arsenian ullmannite (a pyrite-type structure) by Bayliss (1977).

A list of  $R_w$  (weighted  $R$  factor), number of observed reflections, and number of parameters is given in Table 6 in order to use the significance test described by Hamilton (1965). The reduction of  $R_w$  is significant at the 0.005 level between the cubic crystal structure and the triclinic crystal structure with isotropic temperature factors; however, Parthasarthy *et al.* (1969) in another cautionary tale note the possible ambiguity of least-squares analysis.

Although the cubic space group  $Pa\bar{3}$  has forbidden reflections of  $hk0$  with  $h$  odd,  $0kl$  with  $k$  odd, and  $h0l$  with  $l$  odd, the cubic space group of  $P2_1\bar{3}$  has forbidden reflections of  $h00$  with  $h$  odd,  $0k0$  with  $k$  odd, and  $00l$  with  $l$  odd. Therefore, by minor shifts of atoms along the threefold axis, this reflection group would appear. Such an effect occurs in ullmannite (Takeuchi, 1957), where the ordering of S and Sb causes the Ni to shift along the three-fold axis. In this pyrite there is no chemical reason to cause such a shift, therefore this reason is not plausible. Alternatively this reflection group would appear by domain twinning, where the Fe atoms would remain in a single set

of positions and the S atoms would alternate between two sets of positions. Twinning has been observed in pyrite, but such twinning would increase the  $R$  factor.

The reflections  $h00$  with  $h$  odd,  $0k0$  with  $k$  odd, and  $00l$  with  $l$  odd could be observed because of the Renninger effect. As the crystal was rotated about the scattering vector, several strong Renninger reflections were observed along the  $0k0$  reflections with  $k$  odd. Therefore the reflection to background ratios were observed away from these Renninger reflections. The ratios determined were 1.8(010), 2.0(030), 2.9(050), and 1.3(070). This confirms that this series of weak reflections were not caused by the Renninger effect.

A greater than  $3\sigma$  shift of some atomic coordinates from the cubic crystal structure to the triclinic crystal structure is shown when Table 2 is compared with Table 4. The high correlation between parameters could easily lead to shifts away from the atomic coordinates of the cubic crystal structure, so that this shift is not a reliable justification of a triclinic crystal structure.

The very weak anisotropy in pyrite has been suggested by Gibbons (1967) to result from "a very thin skin having a nonisometric crystalline structure partially controlled by the orientation of the underlying lattice." The surface layers are unlikely to be disturbed, since pyrite has only strong covalent bonding and a hardness of six. In addition it is unlikely that

Table 5. Interatomic distances and angles

Atom	Distance ( $\text{\AA}$ )	Atoms	Angle ( $^\circ$ )
Fe - S	2.23 - 2.30	S - Fe - S	85 - 95
S - S	2.14 - 2.17	Fe - S - Fe	114 - 117
		Fe - S - S	101 - 103

Table 6.  $R_w$  for different crystal structure models

	$Pa\bar{3}$	$F\bar{1}$ (isotropic temperature factors)	$F\bar{1}$ (anisotropic temperature factors)
Number of Variables	5	50	110
Number of Reflections	858	858	858
$R_w$	2.9	2.6	2.5

the atoms would be disturbed to produce a coherent light effect such as anisotropism. However, the optical data agree with a non-cubic crystal structure.

Most pyrite is isotropic and hence cubic,  $Pa\bar{3}$ . The systematic absences of these isotropic pyrite samples agree with the cubic space group  $Pa\bar{3}$ . From the series of six samples, those samples formed at the higher temperatures are cubic. This observation agrees with the theory, which states the more symmetrical structures occur at higher temperatures. Magnetic susceptibility measurements show pyrite to be diamagnetic (Burns, 1970). This indicates that the  $Fe^{2+}$  has the low-spin configuration  $(t_{2g})^6(e_g)^0$ , which is a symmetrical arrangement. Such a configuration supports cubic symmetry.

The pyrite from Japan is weakly anisotropic, which by theory means it is non-cubic. This is in agreement with the crystal structure refinement, which shows triclinic symmetry. Since this pyrite was formed at lower temperatures than the others examined, a lower symmetry is acceptable. Magnetic susceptibility measurements of pyrite by Serres (1953) shows very weak paramagnetism. Therefore it is possible that this pyrite could have some non spin-paired electrons. Such degeneracy in the  $t_{2g}$  group is small (van Vleck, 1939), which agrees with the weak anisotropy and the small distortion from cubic symmetry. The complex structural chemistry of marcasite and pyrite type structures has recently been discussed by Fleet (1975).

#### Acknowledgment

Financial assistance was provided by the National Research Council of Canada.

#### References

- Bayliss, P. (1977) Crystal structure refinement of arsenian ullmanite. *Am. Mineral.*, **62**, 369–373.
- and N. C. Stephenson (1968) The crystal structure of gersdorffite (III), a distorted and disordered pyrite structure. *Mineral. Mag.*, **36**, 940–947.
- Bragg, W. L. (1913) The analysis of crystals by the X-ray spectrometer. *Proc. Roy. Soc.*, **A89**, 468–469.
- Brostigen, G. and A. Kjekshus (1969) Redetermined crystal structure of  $FeS_2$  (pyrite). *Acta Chem. Scand.* **23**, 2186–2188.
- Burns, R. G. (1970) *Mineralogical Applications of Crystal Field Theory*. Cambridge University Press.
- Cabri, L. J., D. C. Harris, J. M. Stewart and J. F. Roland (1970) Wilyamite redefined. *Proc. Aust. Inst. Mining Metallurgy*, **233**, 95–100.
- Coppens, P. and W. C. Hamilton (1970) Anisotropic extinction corrections in the Zachariasen approximation. *Acta Crystallogr.*, **A26**, 71–83.
- Elliott, N. (1960) Interatomic distances in  $FeS_2$ ,  $CoS_2$ , and  $NiS_2$ . *J. Chem. Phys.*, **33**, 903–905.
- Finger, L. W. and E. Prince (1975) A system of Fortran IV computer programs for crystal structure computations. *National Bureau of Standards Technical Note 854*.
- Finklea III, S. L., L. Cathey and E. L. Amma (1976) Investigation of the bonding mechanism in pyrite using the Mössbauer effect. *Acta Crystallogr.*, **A32**, 529–537.
- Fleet, M. E. (1975) Structural chemistry of marcasite and pyrite type phases. *Z. Kristallogr.*, **142**, 332–346.
- Gibbons, G. S. (1967) Optical anisotropy in pyrite. *Am. Mineral.*, **52**, 359–370.
- Giese, Jr. R. F. and P. F. Kerr (1965) The crystal structures of ordered and disordered cobaltite. *Am. Mineral.* **50**, 1002–1014.
- Hamilton, W. C. (1965) Significance tests in the crystallographic R factor. *Acta Crystallogr.*, **18**, 502–510.
- Hondo, S. (1969) B-1 clays of the Itaya mine, Yamagata Prefecture. *Guide to Field Trip B, C, and D Japan of International Clay Conference*, 2–6.
- Klemm, D. D. (1962) Anisotropieeffekte bei kubischen Erzmineralien. *Neues Jahrb. Mineral. Abh.*, **97**, 337–356.
- Nelson, J. B. and D. P. Riley (1945) An experimental investigation of extrapolation methods in the derivation of accurate unit-cell dimensions of crystals. *Proc. Phys. Soc.*, **57**, 160–177.
- Parker, H. M. and W. J. Whitehouse (1932) An X-ray analysis of iron pyrites by the method of Fourier series. *Phil. Mag.*, **14**, 939–961.
- Parthasarathy, R., J. G. Sime and J. C. Speakman (1969) Ambiguity in the least-squares analysis—another cautionary tale. *Acta Crystallogr.*, **B25**, 1201–1202.
- Schneiderhöhn, H. (1930) Mineralchemische und mikroskopische Beobachtung an Blei-Zink- und Kieserzen der Deutsch-Bleischarley-Grube/Oberschleisen. *Chem. Erde*, **5**, 385–395.
- Serres, A. (1953) Sur quelques composés du cobalt et du fer a paramagnetisme tres faible et constant. *J. Phys. Radium*, **14**, 689–690.
- Smith, F. G. (1942) Variation in the properties of pyrite. *Am. Mineral.*, **27**, 1–19.
- Stout, M. Z. and P. Bayliss (1975) Crystal structure of a natural titanomagnetite. *Can. Mineral.*, **13**, 86–88.
- Takeuchi, Y. (1957) The absolute structure of ullmanite (sic),  $NiSbS$ . *Mineral. J. (Japan)*, **2**, 90–102.
- van Vleck, J. H. (1939) The Jahn-Teller effect and crystalline Stark splitting for clusters of the form  $XY_6$ . *J. Chem. Phys.*, **7**, 72–84.
- Wunsch, B. J. and C. T. Prewitt (1965) Corrections for X-ray absorption by a crystal of arbitrary shape. *Z. Kristallogr.*, **122**, 24–59.
- Zachariasen, W. H. (1967) A general theory of X-ray diffraction in crystals. *Acta Crystallogr.*, **23**, 558–574.

Manuscript received, November 29, 1976; accepted for publication, June 27, 1977.