

LATTICE CONSTANTS IN THE PYRITE GROUP

PAUL F. KERR, RALPH J. HOLMES AND MARGARET S. KNOX,
Columbia University, New York, N. Y.

ABSTRACT

Lattice constants for minerals corresponding to NiS_2 and CoS_2 in the pyrite group are compared with that of pyrite. A cobalt sulphide from the Shinkolobwe mine in the Belgian Congo gives $a_0 = 5.52346 \pm .00048 \text{ \AA}$. A high nickel specimen from the Kasompi mine in the Belgian Congo gives $a_0 = 5.66787 \pm .00008 \text{ \AA}$. Pyrite from Leadville, Colorado, is found to yield the value $a_0 = 5.40667 \pm .00007 \text{ \AA}$.

Through the courtesy of M. Schuiling and M. Vaes of the Union Minière du Haut Katanga, Belgian Congo, two specimens close to the cobalt and nickel end-members of the pyrite group have been made available for study. One specimen was obtained in a core in the process of diamond drilling at the Kasompi mine in Katanga and on chemical analysis has been shown to be close to NiS_2 . The other specimen was found in the Shinkolobwe mine near Jadotville in Katanga and has a composition close to CoS_2 . Both are described independently, the name *cattierite* being applied to the cobalt mineral and *vaesite* to the nickel mineral. It is the purpose of this paper to record the lattice constants of these natural compounds in comparison with pyrite.

In a study of pyrite and nickelian pyrite Peacock and Smith (1941) determined the lattice constant of nickel-free pyrite from Leadville, Colorado, as $5.4079 \pm .0005 \text{ \AA}$. At the same time pyrite from Rio Marina, Elba, was found to have a lattice constant of $5.4063 \pm .0005 \text{ \AA}$. These lattice constants were based on measurements made on patterns obtained in a Debye camera using iron radiation. Only high angle lines (115), (025), and (125) were used. The Straumanis (1936) method of eliminating errors was employed in obtaining precision lattice constants. At the same time nickelian pyrite from the Denison mine, Sudbury district, Ontario, containing Ni=6.50 per cent was shown to have a larger lattice constant of $5.419 \pm .002 \text{ \AA}$.

de Jong and Willems (1927) have prepared both NiS_2 and CoS_2 synthetically and have given lattice constants to two decimal places. The figures recorded are: $\text{CoS}_2 = 5.64 \text{ \AA}$ and $\text{NiS}_2 = 5.74 \text{ \AA}$. Previous descriptions of naturally occurring nickelian and cobaltian end-members of the pyrite group do not appear to have been made.

Members of the pyrite group containing the largest amount of nickel which have been previously described are bravoite from Chitina, Alaska, as recorded by Buddington (1924) and bravoite from Mechernich, Prussia, as recorded by Kalb and Meyer (1926). The specimens from

both of these localities contain slightly more nickel than iron. In each case, however, the specimen in question falls far short of yielding the percentages necessary to constitute a nickelian end-member. The original bravoite of Hillebrand (1907) was even lower in nickel content and actually contained more iron than nickel.

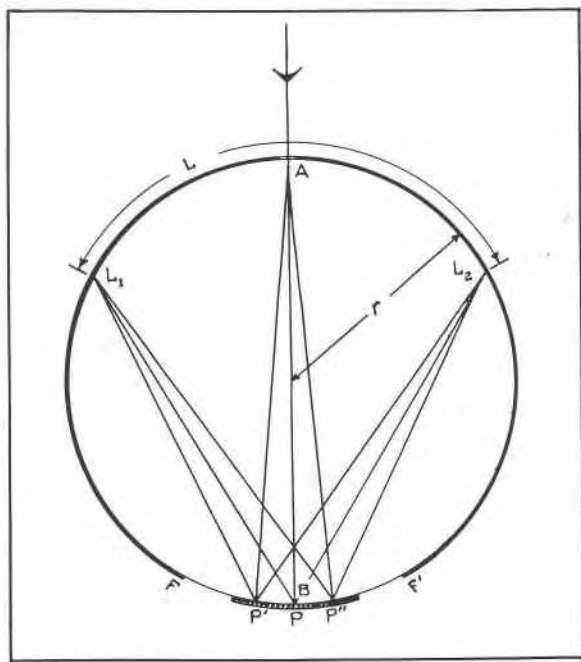


FIG. 1. Schematic diagram of a symmetrical back reflection focussing powder camera (precision camera).

The incident x -ray beam enters the camera defined by a single narrow slit on the circumference of the camera at "A." The divergent beam crosses the camera and strikes a considerable area of the sample "B" which is placed on the circumference of the camera diametrically opposite the slit. All particles P, P, P'' in the sample oriented to reflect from a given set of atomic planes (hkl) will do so at the same angle and the reflected beams from different portions of the sample will be "focussed" at points " L_1 " and " L_2 " symmetrically disposed on either side of the center of the film $F-F'$, which is located at the slit "A."

Bannister (1940) has studied bravoite from the Mill Close mine in Derbyshire. In the Mill Close specimens more iron was present than nickel although the specimens were substantially nickelian in composition. The work of Bannister suggested the existence of a smooth curve correlating the variation in lattice constant between FeS_2 and NiS_2 with chemical composition.

Lattice constants of three natural specimens essentially end-members of the pyrite group, FeS_2 , NiS_2 , and CoS_2 , have been obtained from x -ray diffraction patterns taken with a back reflection precision focussing camera. The precision determinations have followed the technique of

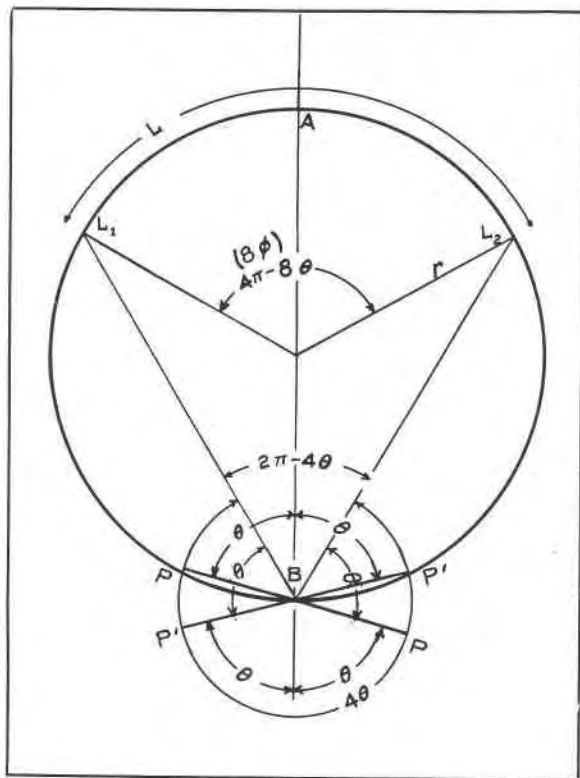


FIG. 2. The geometry of the symmetrical back reflection focussing (precision camera). In terms of the Bragg angle θ and the radius of the camera it is found that the distance " L " separating two corresponding lines on the film is a function of ϕ , the complement of θ rather than θ itself. The distance between corresponding lines " L " in millimeters and the angle ϕ are related by the equation $\phi = L/8R$. The lines $(P-P)$ and $(P'-P')$ represent two orientations of the same set of atomic planes providing the two reflections at points L_1 and L_2 on the film. For simplicity the sample " B " is assumed to be located at a point diametrically opposite the slit " A ."

Jette and Foote (1935), and we are indebted to Professor Eric Jette for the camera used in this study. The analytical methods of Cohen (1935) and Jette and Foote (1935) have been employed in order to eliminate systematic errors and provide precision lattice constants for each of the

minerals. The method, as used, eliminates systematic errors and, at the same time, handles the random errors due to measurement by a least squares solution which provides the best average representation of the experimental data. The schematic diagram, Fig. 1, will make clear the principle of the symmetrical focussing camera. The geometry of the camera is shown diagrammatically in Fig. 2. The influence of systematic errors due to absorption, film shrinkage, deviation of sample or film from true geometrical position in the camera and other sources of error in lattice constants have been amply treated in the papers of Cohen, and also Jette and Foote.

X-ray patterns were first obtained in a Debye camera using iron radiation in order to index the lines. The lines in a symmetrical focussing precision camera are not indexed directly, since only a few high-angle lines are recorded. The indexing is accomplished by comparing the lines on the precision film with those on a Debye film previously indexed. The distances between corresponding lines "L" on the precision films were measured to hundredths of a millimeter with a microscope and measuring screw calibrated to 0.001 mm. The values were obtained from these measurements (average of four) by means of the equation $\phi = L/8r$ multiplied by the shrinkage correction. The value ϕ instead of θ is used since the separation of corresponding lines in a back reflection camera is a function of ϕ rather than θ in which $\phi = (\pi/2) - \theta$. Using the observed ϕ values, the corresponding $\sin^2 \theta$ and $(\phi \sin 2\phi)$ values were obtained from Foote's unpublished tables.* This data and the indices of the lines were then used in setting up the simultaneous equations required by Cohen's method (see references). The solution of these equations for two unknowns (in the case of the isometric system) provides two values A and D . A is the $\sin^2 \theta_{100}$ free of systematic errors from which a precise lattice constant a_0 may be obtained by the use of the quadratic form of the Bragg equation, in the case of the isometric system,

$$a_0 = \sqrt{\frac{(\lambda^2/4)(h^2 + k^2 + l^2)}{A}}$$

The corrected $\sin^2 \theta$ for any line on the film is then found from the equation $\sin^2 \theta = A \cdot (h^2 + k^2 + l^2)$. The value D called the "drift constant" or constant of proportionality indicates the magnitude of the systematic errors in the observed data.

In order to determine the magnitude of the random errors in the observed $\sin^2 \theta$ for each line, a set of theoretical $\sin^2 \theta$ values is prepared using

* Tables were made available through the courtesy of Dr. Frank Foote of the Metallurgical Laboratories of the School of Mines, Columbia University.

the equation $\sin^2\theta = A \cdot (h^2 + k^2 + l^2) + D(\phi \sin 2\phi)$. Cohen's study showed that the systematic errors in $\sin^2\theta$ were proportional to $(\phi \sin 2\phi)$. The difference (Δ) between the observed and theoretical $\sin^2\theta$ is determined and used in a series of computations (see Jette and Foote, 1935) which permit an evaluation of the magnitude of the error (standard error) in the precision lattice constant obtained. Precision lattice constants with a standard error as low as $\pm .00002$ (Jette and Foote, 1935, p. 615) have been obtained under favorable conditions using symmetrical focussing cameras and Cohen's method. The precise lattice constant obtained by the use of Cohen's method is based on an analytical extrapolation to $\sin^2\theta = 100$. It represents within the standard error the best possible lattice constant for the data employed. The "standard error" should be less than $\pm .0001$ for a film with a fair number of sharp lines, as exemplified in the following lattice constants. Pyrite and NiS_2 as shown in Fig. 3 ex-

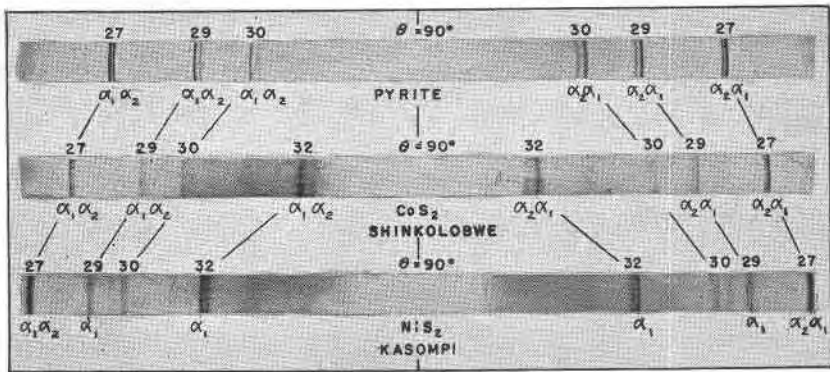


FIG. 3. Precision photographs of natural FeS_2 (pyrite), CoS_2 (cattierite) and NiS_2 (vaesite) as recorded in Table 1. Only the lines recorded are listed as α_1 , or α_2 . The figures shown above each line are the $(h^2 + k^2 + l^2)$ values. The relative distances in millimeters between lines $27\alpha_1$, in the three diffraction photographs are 154.27, 175.62 and 196.80.

hibit good resolution, whereas the lines of CoS_2 were somewhat diffused, limiting the accuracy of measurement.

Pyrite, Leadville	$5.40667 \pm .00007 \text{ \AA}$
NiS_2 , Kasompi	$6.66787 \pm .00008 \text{ \AA}$
CoS_2 , Shinkolobwe	$5.52346 \pm .00048 \text{ \AA}$

Lattice constants were calculated from the individual lines in each film using the observed $\sin^2\theta$ values and are compared with the precision value obtained by the use of Cohen's method. These a_0 values computed from individual lines show in a striking manner in the pyrite and Kasompi ma-

terial that the accuracy of the lattice constants determined from individual lines increases with increasing $\sin^2\theta$ value. The same trend is indicated in the less satisfactory Shinkolobwe material.

TABLE 1

The " a_0 " values calculated from individual lines observed in the patterns of pyrite, the cobalt mineral, and the nickel mineral compared with the " a_0 " calculated by the use of Cohen's method.

<i>Pyrite</i>									
Precision Lattice Constant " a_0 " = 5.40667 ± .00007									
Shrinkage correction = $\frac{130.008}{129.745}$					$1/8R = .00244933$				
$(h^2+k^2+l^2)$	(hkl)	"L" mm.	Sin ² θ Obs.	Sin ² θ Cor.*	Δ Sin ² θ	" a_0 " obs.	" a_0 " adj.*	"d"	
27 α_1	333, 511	154.97	.862199	.862163	-.000036	5.40595	5.40605	1.04051	
27 α_2	333, 511	152.90	.862152	.862150	-.000004	5.40610	5.40608	1.04051	
29 α_1	520, 432	112.33	.925905	.925925	+.000020	5.40642	5.40635	1.00399	
29 α_2	520, 432	109.37	.925892	.925920	+.000028	5.40646	5.40637	1.00399	
30 α_1	521	84.27	.957836	.957806	-.000030	5.40641	5.40648	.98712	
30 α_2	521	80.24	.957812	.957800	-.000012	5.40648	5.40650	.98712	

<i>Cobalt Mineral</i>									
Precision Lattice Constant " a_0 " = 5.52346 ± .00048									
Shrinkage correction = $\frac{215.01}{214.74}$					$1/8R = .00244933$				
$(h^2+k^2+l^2)$	(hkl)	"L" mm.	Sin ² θ Obs.	Sin ² θ Cor.*	Δ Sin ² θ	" a_0 " obs.	" a_0 " adj.*	"d"	
27 α_1	333, 511	175.62	.825693	.825838	+.000245	5.52417	5.52368	1.06299	
27 α_2	333, 511	173.58	.826105	.825839	-.000266	5.52279	5.52368	1.06299	
29 α_1	520, 432	139.92	.886804	.887038	+.000234	5.52433	5.52360	1.02568	
29 α_2	520, 432	137.39	.887087	.887040	-.000047	5.52344	5.52359	1.02568	
32 α_1	440	59.38	.978943	.978842	-.000101	5.52319	5.52348	.97642	
32 α_2	440	53.63	.978807	.978843	+.000036	5.52358	5.52348	.97642	

<i>Nickel Mineral</i>									
Precision Lattice Constant " a_0 " = 5.66787 ± .00008									
Shrinkage correction = $\frac{130.008}{129.775}$					$1/8R = .00244933$				
$(h^2+k^2+l^2)$	(hkl)	"L" mm.	Sin ² θ Obs.	Sin ² θ Cor.*	Δ Sin ² θ	" a_0 " obs.	" a_0 " adj.*	"d"	
27 α_1	333, 511	196.80	.784379	.784377	-.000002	5.66778	5.66779	1.09078	
27 α_2	333, 511	195.21	.784391	.784376	-.000015	5.66774	5.66779	1.09078	
29 α_1	520, 432	166.33	.842472	.842471	-.000001	5.66784	5.66782	1.05250	
32 α_1	440	109.78	.929561	.929612	+.000051	5.66800	5.66785	1.00159	

* Calculated from a_0 and includes systematic error $D(\phi \sin 2\phi)$.

Δ = random errors.

ACKNOWLEDGMENTS

The courtesy of M. Schuiling and M. Vaes of the Union Minière du Haut Katanga in the Belgian Congo in supplying the nickel and cobalt minerals used for lattice determinations is gratefully acknowledged. We also appreciate the kindness of Professor Eric Jette in supplying a symmetrical focussing camera.

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