X-RAY STUDY OF THE TRANSFORMATION OF MARCASITE INTO PYRITE.

HAROLD V. ANDERSON AND KENNETH G. CHESLEY.

ABSTRACT.

Specimens of pyrite and marcasite have been examined by X-ray diffraction using the Powder Method. Upon grinding (through 200 mesh) the marcasite specimens gave rise to interplanar spacings identical with the pyrite spacings. An explanation is offered as to the reason for this similarity of these marcasite and pyrite spectrograms.

Marcasite was synthesized by the method of Allen, Crenshaw, and Johnston (6) and the recrystallization temperature and the rate of change of the transformation of marcasite to pyrite was determined by the Powder Method. At 415° C. the transformation takes place with a measurable velocity. A discussion as to the probable mechanism of the recrystallization process is presented.

INTRODUCTION.

In the course of a preceding investigation[1] an interesting problem arose which invited further investigation. This problem was encountered in the examination of the two iron sulphides, marcasite and pyrite, by the X-ray powder diffraction method. A marcasite crystal and a pyrite crystal were ground to pass 200 mesh and X-ray diffraction patterns taken of the two samples for the purpose of identification. The diffraction patterns obtained were identical. Repetition of the experiment with various specimens[2] gave the same results. Both of these minerals had been examined previously by X-ray methods. Pyrite was one of the first minerals whose crystal structure was determined by means of X-rays,[3] and recently the crystal structure of marcasite has been completely determined.[4] Earlier, de Jong had attempted to deduce the crystal structure of marcasite from powder diagrams.[5] It was obvious that our specimens of marcasite were not identical with those studied by de Jong. Although our specimens possessed the external structure of marcasite, they gave different diffrac-

[1] Anderson, H. V., and Chesley, K. G., "X-ray Analysis of Slate," this Journal, **22**, 103-12, 1931.

[2] These specimens were obtained from the mineralogical collection of the Department of Geology, Lehigh University, through the courtesy of Professor Benjamin L. Miller.

[3] Bragg, W. L., "The Analysis of Crystals by the X-ray Spectrometer," Proc. Roy. Soc. London, (A) **89**, 476-78, 1914.

[4] Buerger, M. J., "The Crystal Structure of Marcasite," Am. Mineralogist, **16**, 361-95, 1931.

[5] de Jong, W. F., "Bepaling von de Absolute Aslengten von Markasiet en darmee isomorfe Mineralen," Physica, **6**, 325-32, 1926.

tion patterns when powdered, indicating a different internal structure. The purpose of this study, then, was to investigate this internal rearrangement of marcasite.

Allen, Crenshaw, and Johnston have studied two sulphides as prepared by synthetic methods, as well as many of their properties.[6] It will be well to state their conclusions: "Marcasite changes to pyrite with the evolution of heat. The change proceeds very slowly at 450° C. and is not accelerated by pressures even of 10,000 atmospheres. Marcasite is monotropic toward pyrite. This is in accord with the greater inclination of marcasite to oxidize, its assumed greater solubility, and the fact that its formation is conditioned by the composition of the solution from which it crystallizes." They identified marcasite and pyrite in mixtures by Stokes' oxidation method. This method depends on the difference in behavior between the two minerals toward a solution of ferric sulphate. In both cases the sulphide reduces the ferric salt to ferrous sulphate, while the mineral itself is oxidized to ferrous sulphate, sulphuric acid, and free sulphur. It is in the relative quantities of the products that the difference between pyrite and marcasite shows itself. Since the reactions take place at the solid-liquid interface, their velocities would be a function of the crystal size of the minerals. Many other factors enter to influence the accuracy of this method. It seemed worth while then to establish the applicability of the X-ray diffraction method in distinguishing between the two minerals.

RESULTS.

Since the diffraction patterns obtained from our powdered crystals were identical and did not coincide with the marcasite pattern as given by de Jong, our first assumption was that they were true pyrite spectrograms. To prove that this was the case the calculations tabulated in Table I were performed. This proof depends upon the fact that for a cubic crystal

$$a_0 = d_{hkl}\sqrt{h^2 + k^2 + l^2}.$$

If we substitute for d its value from the Bragg equation ($n\lambda = 2\,d \sin\theta$) and square both sides we obtain

$$\sin^2\theta = \frac{\lambda^2}{4a^2_0}\,n^2(h^2 + k^2 + l^2)$$

[6] Allen, E. F., Crenshaw, J. R., and Johnston, J., "The Mineral Sulfides of Iron," this Journal, 33, 169-236, 1912.

We know that $n^2(h^2 + k^2 + l^2)$ will always be an integer and for a particular substance the remainder of the terms on the right side of the equation will be a constant. The problem then is to find some number which will give an integral quotient when divided into each $\sin^2\theta$ value. This divisor, then, will be the value of $n^2/4a^2_0$, from which a_0 can be easily calculated.

TABLE I.

d_{hkl}	Intensity	$\sin^2\theta$	Ratio	Integral Ratio
3.12	w	0.01295	3.00	3
2.70	s	0.01729	4.00	4
2.42	m	0.02150	4.98	5
2.20	m	0.02603	6.02	6
1.91	m	0.03454	8.00	8
1.626	ss	0.04766	11.02	11
1.556	w	0.05205	12.03	12
1.495	w	0.05638	13.05	13
1.442	w	0.06060	14.02	14
1.237	w	0.08236	18.05	18
1.207	w	0.08650	20.00	20
1.178	w	0.09081	21.03	21
1.150	ww	0.09529	22.04	22
1.102	w	0.1038	24.0	24
1.038	m	0.1170	27.0	27
1.002	w	0.1255	29.1	29
0.985	ww	0.1299	30.0	30
0.954	w	0.1385	32.0	32
0.913	ww	0.1512	34.9	35
0.899	ww	0.1559	36.1	36
0.875	ww	0.1605	37.1	37
0.854	ww	0.1728	40.0	40
0.823	ww	0.1861	43.1	43
0.749	ww	0.2246	52.0	52
0.722	ww	0.2418	55.9	56
0.703	w	0.2550	59.0	59
0.624	w	0.3237	75.0	75
0.567	ww	0.3920	90.7	91

In Table I are given the values of the interplanar spacings, d_{hkl}, obtained from the powdered crystals. The values given are an average of several patterns which check closely within themselves. The values of $\sin^2\theta$ and the integral ratios are also given. The factor which gave these ratios is 0.00432. Then

$$\frac{\lambda^2}{4a^2_0} = 0.00432,$$

from which we obtain that $a_0 = 5.40$Å. This value checks with the values obtained by other investigators[7] for the a_0 of

[7] Wyckoff, R. W. G., "The Structure of Crystals," 2d edition, 1931, The Chemical Catalog Co., Inc., page 237.

pyrite, proving that the ultimate structure of our powder was truly pyrite.

To obtain a sample of pure marcasite 10 gm. $FeSO_4.7H_2O$, 1 gm. sulphur, 0.40 gm. H_2SO_4, and 200 cc. of water saturated with H_2S at 0° C. were sealed in a flask and heated at 100° for 7 days.[8] The precipitate was purified by washing first with water, then digesting with CS_2 to remove the sulphur, washing again with water, boiling out with 20 per cent HCl and finally washing to remove acid. This precipitate was ground to pass 200 mesh and a diffraction pattern obtained. The d_{hkl} calculated from this diffraction pattern are given in Table II.

TABLE II.

d_{hkl}	Intensity
3.43	m
2.68	ss
2.40	m
2.30	w
2.22	ww
1.901	s
1.748	s
1.676	m
1.628	m
1.587	m
1.500	w
1.428	m
1.359	w
1.207	m
1.183	w
1.153	m
1.087	m
1.041	ww
1.030	ww
1.006	ww
0.984	ww
0.955	m
0.857	ww
0.636	ww

This pattern does check with that obtained by de Jong. de Jong used Fe radiation to obtain his diffraction pattern and, consequently, did not obtain lines from those planes whose spacing was less than 1.62Å. Using Mo radiation we were able to register 15 lines in addition to those given by de Jong.

By means of their characteristic diffraction patterns, pyrite and marcasite can be easily and positively identified regardless of whether they occur alone or in mixtures. It was thought desirable to redetermine the transition point of marcasite and

[8] Allen, Crenshaw and Johnston, op. cit.

identify the mineral by the X-ray spectrogram. Samples of the pure synthesized marcasite were sealed in glass tubes, in which all of the air had been displaced by H_2S. The tubes were immersed in a bath of molten KNO_3-$NaNO_3$ and heated at the desired temperature for 5 hours. Diffraction patterns were then taken of the samples to determine the temperature at which marcasite changes into pyrite. Table III is a tabu-

TABLE III.

405°		415°		425°	
3.43	w				
				3.11	ww
2.68	ss	2.69	ss	2.70	ss
2.40	m	2.40	m	2.42	m
2.30	w	2.31	ww		
2.20	w	2.20	w	2.21	m
1.900	s	1.903	s	1.91	s
1.749	s	1.747	m	1.750	ww
1.678	w				
1.625	m	1.625	ss	1.628	ss
1.588	w				
		1.558	ww	1.557	w
1.500	w	1.497	ww	1.498	w
		1.440	ww	1.441	w
1.425	w				
1.358	ww				
		1.238	ww	1.237	w
1.208	w	1.207	w	1.207	m
1.183	ww	1.177	ww	1.178	w
1.153	w	1.152	ww	1.153	ww
		1.103	ww	1.102	w
1.088	w				
1.040	w	1.039	m	1.038	m
1.030	ww				
1.005	ww	1.004	ww	1.004	w
0.985	w	0.984	ww	0.987	ww
0.954	s	0.955	m	0.954	m
				0.914	ww
				0.900	ww
				0.876	ww
				0.853	ww
				0.824	ww
				0.750	ww
				0.723	ww
		0.704	ww	0.703	w
				0.625	ww
				0.568	ww

lation of the d_{hkl} obtained from the patterns given by the samples heated at 405°, 415°, and 425° C. At 405° C. only marcasite lines are visible after 5 hours. At 415° C. both strong marcasite and pyrite lines are visible after 5 hours. Since at 425° C. every pyrite line is clearly present and only

the strong marcasite lines are faintly visible, we can conclude that at 415° C. the change is relatively rapid with at least 50% conversion occurring in 5 hours, and at 425° C. practically total conversion occurring in the same time.

On the whole the results check those of Allen, Crenshaw

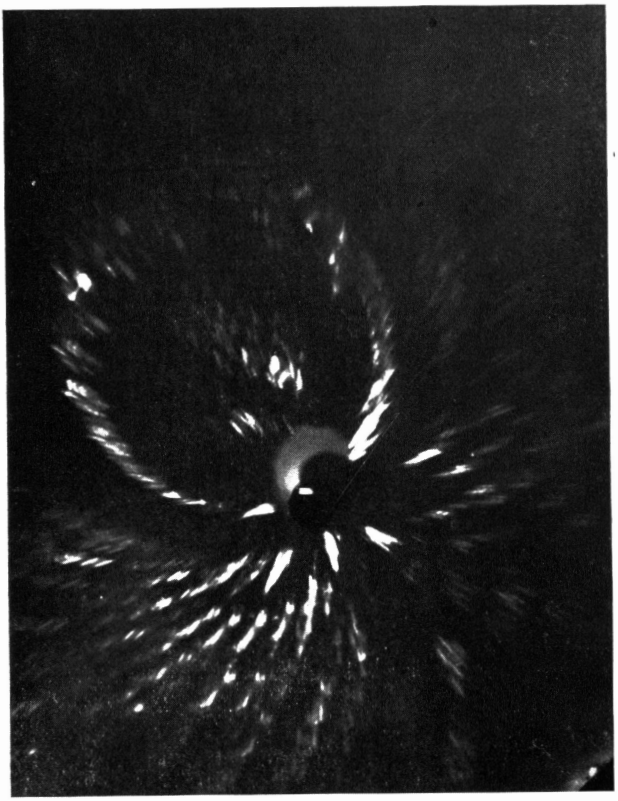

Fig. 1. Marcasite.

and Johnston very closely. The slight difference in temperature may be attributed to different methods of detection. They found that at 410° C. no measurable change occurs in 4 hours. Our results show that at 405° no change occurs in 5 hours. Above this temperature the submicroscopic change begins to take place at an appreciable rate. It should be emphasized here, however, that owing to the nature of the

change there can be no sharp transition point. Since marcasite appears to be the metastable form under all conditions there can be no temperature at which equilibrium will attain. The question is only one of rate of change.

To turn to our initial problem, we have shown that the marcasite crystals, upon grinding, changed into pyrite. We might expect from this fact that the internal structure of the original crystals did not possess a well-ordered, undistorted

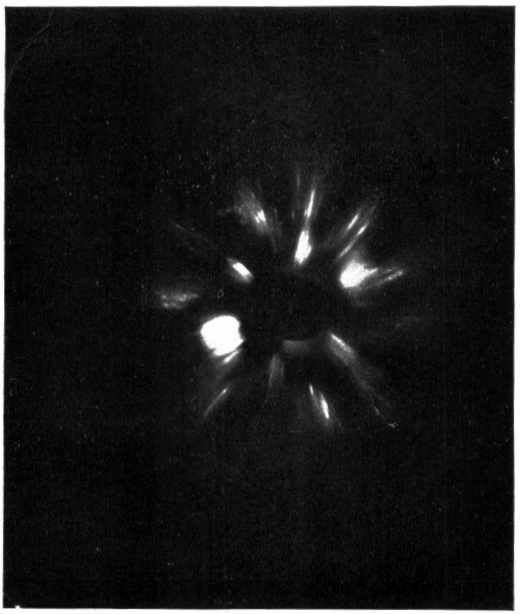

Fig. 2. Marcasite.

arrangement. To investigate this possibility we have obtained pin-hole patterns of the original marcasite crystals. Figures 1, 2, and 3 are typical of the results obtained from all of the crystals examined. That the internal structure is strained and distorted is obvious. The diagrams hardly need interpretation. Figure 1 has the nearest semblance to the Laue diagram of a perfect crystal, but even here internal strain is present to a marked degree. In Fig. 2 neither Laue spots or Debye-Scherrer rings are evident, only radial asterism; while in

Fig. 3 a recrystallization has already begun. Intense radial asterism is still present, but arcs of Debye-Scherrer rings are also registered, indicating that recrystallization has started at

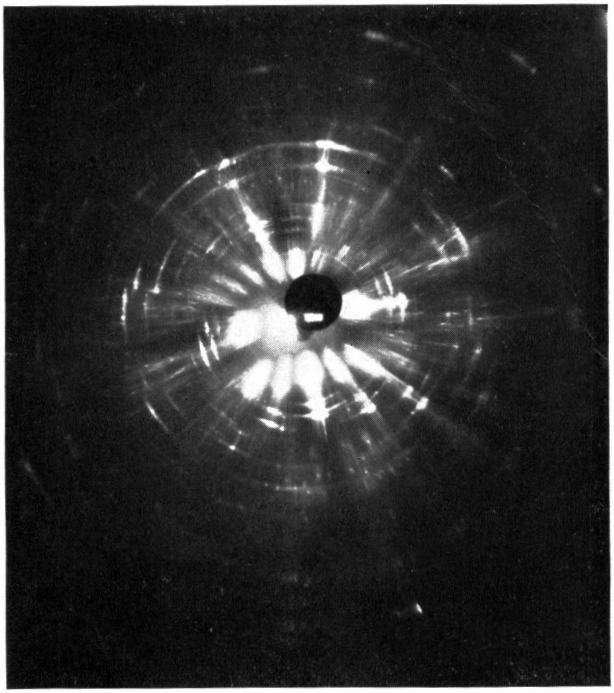

Fig. 3. Marcasite showing a beginning of recrystallization to pyrite.

numerous points in the crystal. This recrystallization must consist of the formation of minute crystallites of pyrite in the host marcasite crystal.

CONCLUSIONS.

Marcasite, being a metastable form of FeS_2, will have a tendency to undergo a recrystallization at all temperatures, i.e., it is a monotropic form. Recrystallization is considered to be merely submicroscopic grain growth, which is affected by several factors, among which should be named atomic mobility, formation of nuclei, and difference in energy content in the two states.

Atomic mobility is a function of the temperature. As the temperature is raised the volume at the disposal of each atom or ion becomes larger, and the force required to move the particles relative to each other becomes less.

All crystallization processes are greatly affected by the ease and rate of nuclei formation. In this transformation of one crystalline phase to another we should expect nuclei formation to be *controlled* largely by *grain size.* The nuclei will form first at the place where the atoms have the greatest energy content and freedom of motion. Since the particles in the surface of a solid are less affected by the attraction of their neighbors than the particles in the interior, this nuclei formation will be at the surface. It is known that the surface energy of a liquid or solid increases as the size of the drop or grain decreases. It is then to be expected that nuclei will form more readily in the solid composed of the smallest grains.

The diffraction patterns show that upon long standing marcasite crystals tend to develop strains within themselves. These strains may develop as a result of two causes. In the first place certain ions in the marcasite crystal could conceivably migrate to their new equilibrium positions in the pyrite lattice, while others would be unable to assume their new positions. This would leave the marcasite structure with certain planes distorted. This partial reorientation would tend to strain or distort the whole structure but would leave on the whole the marcasite structure intact. This condition would be equivalent to saying that pyrite nuclei could not form in the crystal. The second and, perhaps, more plausible mechanism can be pictured by carrying the above orientation process a bit further. We can conceive of pyrite nuclei forming at various loci in the crystal. At these points all of the ions would have enough energy to assume the pyrite equilibrium positions. These nuclei would tend to grow by an ion leaving the marcasite lattice and going to the adjoining pyrite lattice. This growth would not take place under the same conditions that exist in a precipitation process because of the restricted mobility of the building ions. Growth on any one nucleus would, perhaps, cease after a very short time owing to the inaccessibility of the equilibrium positions to the proper ions. The growth of these nuclei in certain directions might also be affected by the external pressure on account of the marcasite structure. This would tend to set up strains in the forming pyrite crystallites. The condition that would exist, if this is

the correct mechanism, would be different from the above. The crystal would consist of a myriad of pyrite crystallites. Each of these crystallites would be strained as a result of the forces imposed by the existing marcasite structure. The external shape of the crystal would not be changed since no one pyrite nucleus was able to grow and absorb the entire marcasite structure and thus impose its characteristic shape upon the mass.

Either, or both of these mechanisms would explain the observed facts. In both cases the marcasite crystal would possess internal strains as shown by the pin-hole diffraction patterns. In the first case the grinding could account for the formation of nuclei owing to the increased surface tension of the smaller particles. After the nuclei had formed, then, they were able to grow and completely absorb the tiny, strained host marcasite crystal. In the second case the grinding would simply relieve the imposing forces by breaking up the persisting marcasite structure and allow the pyrite crystallites to assume their normal, unstrained structure.

The difference in energy content between the two crystal phases, marcasite and pyrite, is not great enough to cause the transition to take place with measurable velocity at ordinary temperatures. However, as the temperature is raised, a certain point is reached where the atomic mobility is great enough to allow the transition to occur.

We have shown in the course of the work that the X-ray diffraction method is ideal for the identification of the two minerals, marcasite and pyrite; that certain FeS_2 crystals possessing the external form of marcasite do not possess internally the true, undistorted marcasite structure; upon grinding the strained marcasite crystal, the internal strain is relieved and the true pyrite crystals obtained; and finally, that at 415° C. the transformation of marcasite to pyrite takes place with a measurable velocity.

LEHIGH UNIVERSITY,
BETHLEHEM, PA.