STRUCTURAL ASPECTS OF THE MARCASITE-PYRITE TRANSFORMATION

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ABSTRACT

Oriented single crystals of marcasite have been inverted to pyrite by heating under vacuum in the temperature range 425 to 475°C. *X*-ray diffraction studies reveal two preferred orientations of pyrite, with a_2 of pyrite parallel to b of marcasite and a_1 and a_3 sub-parallel to [101] of marcasite, agreeing with the orientation of some natural intergrowths of the two minerals. It is suggested that the inversion occurs by rotation of the Fe–S chains in alternate layers of the {101} planes of marcasite. The shape of the *x*-ray reflections recorded in the plane normal to the common b axis suggests that the crystallites have been rotated about this axis: the nature and extent of the movement and the displacement between the two pyrite orientations within this plane tend to agree with the proposed transformation model.

INTRODUCTION

Pyrite and marcasite are regarded commonly as polymorphic forms of FeS_2: pyrite is cubic, $a = 5.417$ Å (Swanson, Gilfrich & Ugrinic 1955), $Z = 4$; marcasite is orthorhombic, $a = 4.436$ Å, $b = 5.414$ Å, $c = 3.381$ Å (Buerger 1937*a*), $Z = 2$. Their stability relationship has been the subject of much discussion over the years. Pure natural marcasite readily inverts to pyrite at temperatures greater than 400°C. However, the reaction is irreversible and it is not known if marcasite has a field of stability at stoichiometric FeS_2 at temperatures less than this. It has been suggested that the two are not polymorphic, since marcasite appears to be S deficient* (Buerger 1934). However, marcasite readily precipitates from acid aqueous solutions (Allen, Crenshaw, & Merwin 1914) but has not been synthesized under dry conditions and this prompted Kullerud (1967) to speculate that H–S bonds might be significant in stabilizing it. The present study is devoted to the structural aspects of the transformation; the stability relation is not treated although the results might throw some light on this problem.

The structure of pyrite (Bragg 1914; Parker & Whitehouse 1932) and of marcasite (Buerger 1931; 1937*b*) are well known, and only certain aspects pertinent to the present discussion will be presented. The FeS_2 molecule contains a disulphide group. The basic structural unit in each modification is a chain of alternating Fe atoms and disulphide groups, in which the

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*The deviation from the theoretical composition is probably within the limits of analytical errors (Dana, *System of Mineralogy*, 1944) disulphide groups lie at an angle to the directions of the chain, giving it a zig-zag appearance. In the marcasite structure the chains extend in the *b* direction, arranged in layers parallel to the basal plane, and in directions normal to the *b* axis within the {101} planes (Fig. 1). Each S atom is in four-fold co-ordination, three Fe atoms in a triangular group on the opposite side to the other S in the disulphide group, and each Fe atom is in a slightly distorted octahedral co-ordination (Table 1). In the pyrite structure the Fe–S chains extend in three mutually perpendicular directions (*a*-axes), so that the disulphide groups are centred on the mid-points of the cube edges and cube body-centre, and lie on four non-intersecting triad axes (Fig. 2). The co-ordinations of the Fe and S atoms are similar to those in marcasite.

A comparison of some of the interatomic distances in the two structures is given in Table 1. In marcasite, the disulphide groups of adjacent chains within the same basal layer are relatively close to each other (2.97 Å). In contrast, the S-S distance between equivalent basal layers is relatively large (3.38 Å); in fact, there is a slight gap in the structure between the disulphide groups of these layers. There is a good correlation between

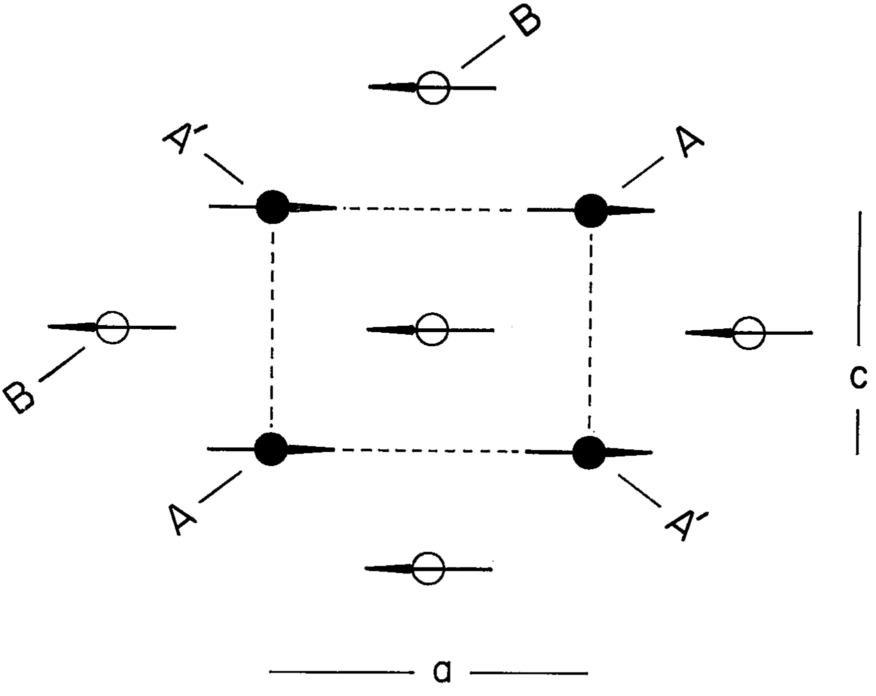

FIG. 1. Representation of the crystal structure of marcasite. Full circles, Fe at 0: open circles, Fe at 1/2: arrows indicate the direction of inclination of disulphide groups.

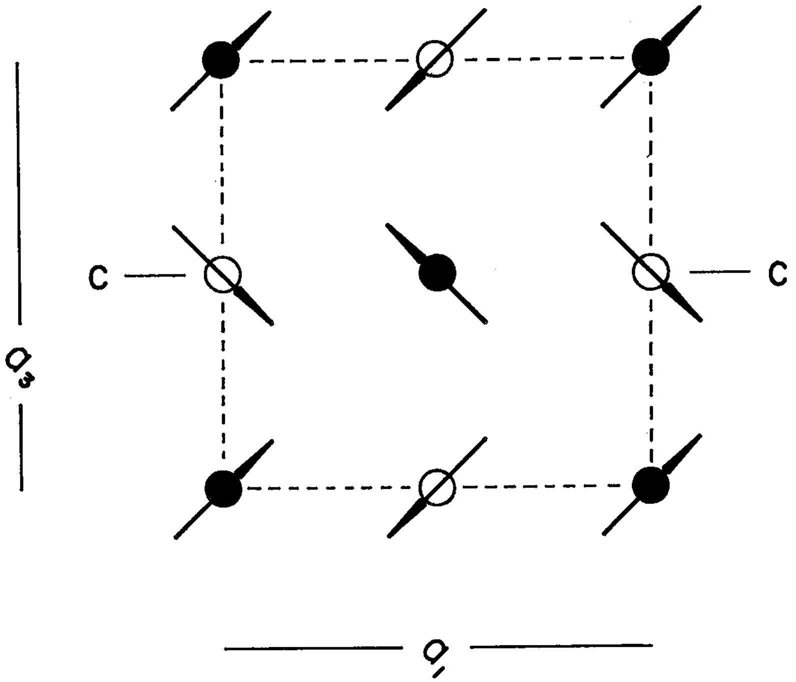

FIG. 2. The crystal structure of pyrite.

TABLE 1

Bond	Bond Length (Å)		
	Pyrite	Marcasite	
Fe–S	2.26	2.23	Within same basal layer
		2.25	Between adjacent basal layers
S–S (S_2 group)	2.14	2.21	
S–S	3.20	3.38	Between equivalent basal layers
		3.11	Between adjacent basal layer
		2.97	Within same basal layer

the *b* parameter and *d*(101) of marcasite and the cell edge of pyrite. The fact that all are related to directions of Fe–S chains emphasizes the importance of these chains in these two structures. A related phenomenon is that natural intergrowths with {101} of marcasite parallel to {001} of pyrite are quite common when the two minerals occur together.

EXPERIMENTAL INVESTIGATION

Natural marcasite, from Bird Dog Mine, Cardin, Oklahoma, was used in the investigation. A prismatic piece from the edge of a 'cockscomb' crystal aggregate, bounded in part by a pair of {101} faces and elongated in the *b* direction, was placed in a 0.3 mm. diameter quartz glass capillary. The marcasite fragment was held in place at the end of the capillary by a flush-fitting, glass fibre and the capillary was evacuated and sealed to a length of $\frac{1}{4}$ to $\frac{3}{8}$ inches.

The inversion experiments were carried out in an *x*-ray heating camera, which, essentially, consisted of a water-cooled, cylindrically wound, heating element, suspended coaxially inside the cassette of a Unican rotation camera. The heating process was controlled manually with a variable transformer, and a chromel-alumel thermocouple, placed near the specimen was used to record the temperature at that point. The temperature of the sample was inferred by calibrating the furnace temperature against the known thermal expansion of gold (Merryman 1964). The calibration was done by recording powder diffraction patterns, at various temperatures, of a small piece of gold supported in a capillary tube. The recorded sample temperatures are believed accurate to within ±10°C, although the precision is much better.

The sealed capillary tube, supported at the end of a small ceramic tube, was mounted on a goniometer head so that, during a run with the furnace in place, all of the vapour space surrounding the specimen was within the furnace and heated by it, albeit with a thermal gradient along the length. Although the marcasite had previously been oriented and precession and rotation exposures taken, it was not possible to record an *x*-ray pattern at high temperature since, when oriented, the capillary tube was invariably inclined at a greater angle than was allowed by the internal diameter of the furnace. The normal procedure, then, was to heat the specimen, remove the furnace and reset the goniometer arcs to the values obtained previously and obtain a rotation pattern to estimate the extent, if any, of the inversion of the marcasite to pyrite. Experience with several samples indicated that the inversion was partially complete after heating for 12 hours at 425°C and essentially complete at 475°C with less than 4 hours heating.

Precession photographs were taken at the conclusion of each experiment with the specimen mounted in the capillary tube (*i.e.* with the original marcasite *b* direction parallel to the dial axis) and with the specimen (or a fragment of it) removed and remounted to allow for precession about this direction.

DISCUSSION

Rotation and precession photographs showed that pyrite had developed from the marcasite with a preferred orientation, with one cube axis (arbitrarily designated a_2) parallel to the marcasite *b* axis. The other cube axes (a_1 and a_3) are subparallel to the [101] directions of marcasite. On precession photographs taken with *b* parallel to the dial axis the reflections of the pyrite are relatively sharp. It is evident from the apparent four-fold symmetry that two pyrite orientations had developed. On precession photographs precessed about the marcasite *b* axis the diffraction spots are spread about this axis (Fig. 3): the two pyrite orientations are made more evident because of the extinction rule for *h*0*l* reflections, $l \neq 2n$. Each orientation is related to a [101] marcasite direction and has been rotated (or spread) toward the original marcasite *c* direction.

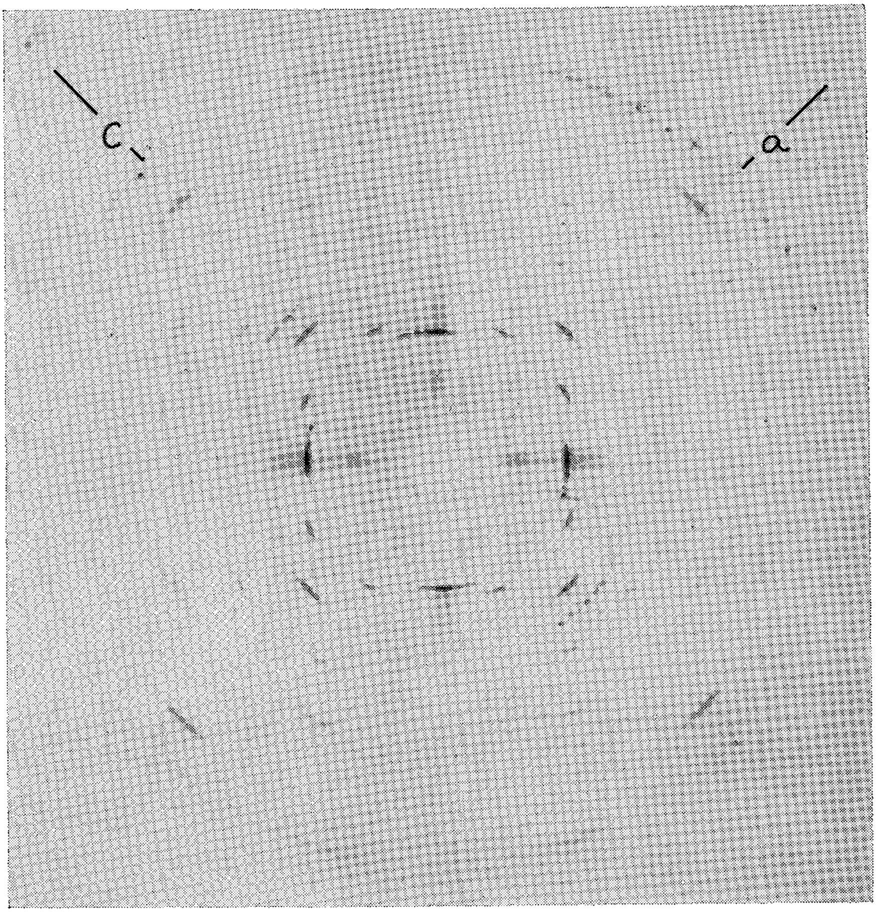

FIG. 3. Zero level, precession photograph of partially inverted marcasite crystal, precessed about the marcasite *b* axis. The diffraction streaks of the remnant marcasite are identified by the spots within them. The original *a* and *c* axes of marcasite are indicated. Mo $K\alpha$ radiation, 35 kv, 20 ma, 16 hour exposure.

The preferred orientation of the pyrite and the rapidity of the reaction suggest that the structural reorganization involved in the transformation is minimal. A model for the transformation, based on the structural elements common to both minerals, is outlined below. The diagonal layer of Fe–S chains in the marcasite structure (A-A in Fig. 1) is similar to the layer C–C in pyrite (Fig. 2). A distorted pyrite structure can be produced from the marcasite structure, simply by rotating those Fe–S chains in the adjacent layers (of type B–B in Fig. 1) approximately 90 degrees clockwise about the chain axes (Fig. 4), and translating the whole structure 1/2 along *b*. The disulphide groups within these layers, then, are directed toward the adjacent 'basal' layers, fitting into the gap, noted above, in the marcasite structure. In the transformation, only one in six of the Fe–S bonds are broken: these are the chain-to-chain bonds within the B–B layers. Because of the new positions taken by the disulphide

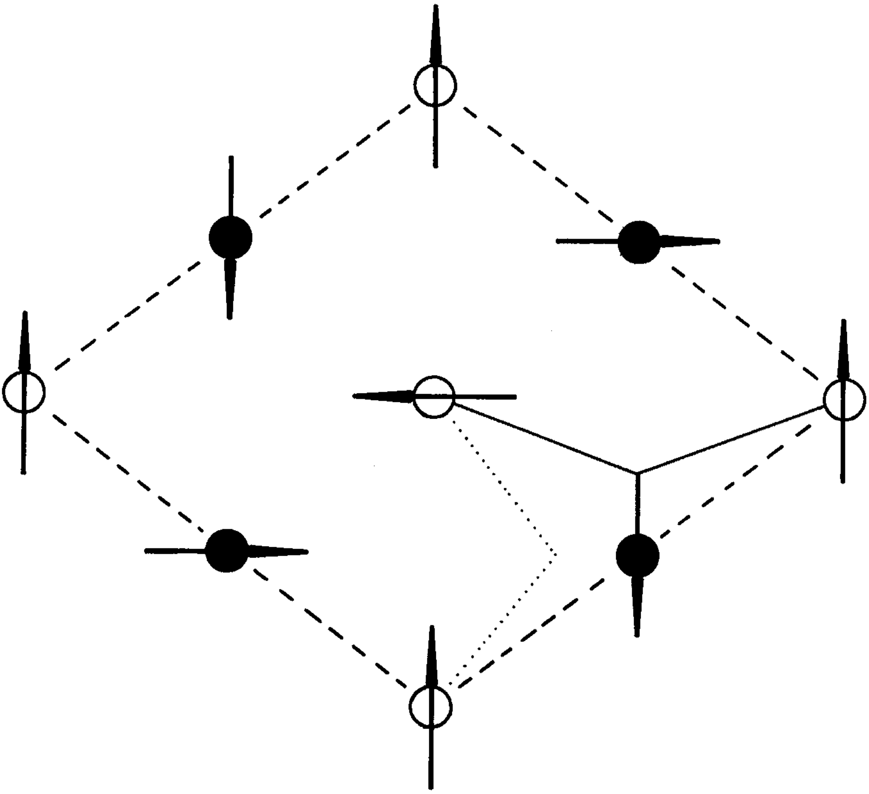

FIG. 4. Development of the pyrite structure from that of marcasite, illustrating the redistribution of the Fe–S bonds.

groups in these diagonal layers, the structure is contracted in the marcasite *a* direction and expanded in the marcasite *c* direction. The original marcasite crystal will be stressed in these directions, and those crystallites in it which invert to pyrite in the manner outlined (*i.e.* based on layers parallel to (101)) will tend to be rotated counter-clockwise. It is possible to produce a second pyrite orientation by counter-clockwise rotation of the Fe–S chains in the layers of the type A′-A′ (Fig. 1), *i.e.* based on layers parallel to $(10\bar{1})$. Crystallites formed with this orientation will tend to be rotated clockwise.

The {101} planes in marcasite intersect at 74°36′. Ideally, the two pyrite orientations should each be rotated 7°42′ so that they are superimposed (a_1 of the one parallel to a_3 of the other *etc.*). However, each crystallite is subject to interference from neighbouring crystallites in the host crystal and there is an overall reduction in volume of 2.1 per cent. The angular separation of the two orientations in several separate crystals varied from 2 to 7 degrees. In the specimen illustrated (Fig. 3) the separation is 3 degrees, and the spread of the (002) and (400) reflections of the remnant marcasite crystallites is in the range 15 to 20 degrees, suggesting that they have been displaced up to 10 degrees from their mean position in the original marcasite crystal. These observations agree quite well with the proposed mode of the transformation.

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