

MINERALOGICAL NOTES

THE CRYSTAL STRUCTURE OF DISORDERED GERSDORFFITE

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This publication presents a disordered nonmetal cubic structure in contrast to the ordered nonmetal cubic structure already presented by Bayliss and Stephenson (1967). The earlier paper also briefly reviewed the occurrence, composition and crystallography of gersdorffite (NiAsS).

Gersdorffite from east of Ferro, Dobsina, Slovakia, Czechoslovakia of hydrothermal origin was used in this second crystal study. Its impurities were determined by spectrographic analysis as 6 percent iron, 2 percent cobalt, 1 percent antimony and 0.2 percent silicon. The 6 percent iron belongs to the extraneous mineral siderite detected by X-ray diffraction. Since substitution of nickel by 2 percent cobalt decreases the unit-cell size but the substitution of arsenic by 1 percent antimony has the opposite effect, their net effect is assumed to be zero. The unit-cell size of $5.7053 \pm 0.0003 \text{ \AA}$ was determined from a Debye-Scherrer photograph using the function given by Nelson and Riley (1948). The unit-cell size indicates from the curve of Yund (1962) a composition of $\text{NiAs}_{1.23}\text{S}_{0.77}$. A 40μ cleavage fragment of this gersdorffite with cube faces was examined. The reciprocal lattice was examined from two precession photographs taken with Moka radiation 90° apart. It exhibits the Laue symmetry $m\bar{3}$ and systematic absences occur for $h0l$ and $h00$ with $h \neq 2n$, $hk0$ and $0k0$ with $k \neq 2n$, and $0kl$ and $00l$ with $l \neq 2n$, which indicate space group $Pa\bar{3}$. Sixty-seven independent hkl data were recorded on equi-inclination Weissenberg photographs with four films packed into the casket to give an exposure series with a 3:1 interfilm density ratio. Data from five levels were collected and scaled from the relationship $hkl = klh = lkh$ given by Henry *et al.*, (1961). These intensities were measured by comparison with a spot series collected under known conditions. Then the asymmetric Lorentz and polarization corrections were computed on a Deuce machine, but no correction was made for absorption or extinction. The observed reflection amplitudes (F_o) are recorded in Table 1.

A Patterson vector map indicates its similarity to the pyrite structure with four formula units per cell, so a trial structure was based upon the space group $Pa\bar{3}$ and the coordinates of pyrite from Elliott (1960). The scattering curves of Thomas-Fermi for nickel, arsenic and sulphur were taken from the International Tables for X-ray Crystallography (1962), with both the real and imaginary components of the anomalous disper-

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TABLE 1. OBSERVED (hkl) REFLECTION AMPLITUDES (F_o) AND CALCULATED STRUCTURE FACTORS (F_c) OF GERSDORFFITE WITH SPACE GROUP $Pa\bar{3}$

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
020	99	84	151	91	74	136	29	30
040	60	65	161	36	38	146	8	1
060	10	18	122	<8	4	222	71	55
012	98	110	132	57	54	232	<8	4
022	61	64	142	<8	0	242	50	39
032	90	92	152	58	47	252	<8	2
042	35	38	162	<8	2	262	31	25
052	63	55	123	69	65	233	56	50
062	27	26	133	12	11	243	78	67
014	<8	7	143	<8	5	253	28	31
024	42	38	153	<8	0	263	<8	7
034	<8	7	163	32	36	234	<8	0
044	116	116	124	76	70	244	42	33
054	<8	4	134	<8	4	254	<8	0
064	23	30	144	<8	5	235	56	45
016	48	53	154	<8	4	245	46	42
026	28	26	164	25	41	236	<8	2
036	52	51	125	40	39	333	79	62
046	22	30	135	<8	0	343	<8	4
111	14	15	145	<8	3	353	46	49
121	80	76	155	<8	6	344	<8	5
131	79	101	126	<8	7	444	49	41
141	<8	5						

sion correction. The structure was refined with the Oak Ridge Fortran least-squares program of Busing *et al.* (1962), using an IBM7040 computer. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, initially with unit weights and then with weights inversely proportional to $|F_o - F_c|^2$.

In the refinement with an average nonmetal scattering curve and assumed thermal parameters for each atom, least-squares cycles were undertaken to refine the over-all scale factor, position parameters (x) and individual isotropic thermal parameters (B). The resultant final parameters with their standard deviations are listed in Table 2, whereas the calculated structure amplitudes (F_c) are listed alongside the observed data (F_o). This structure gave an overall reliability index R with both observed and unobserved data of 0.111.

The interatomic distances and angles, which are computed on a IBM-7040 machine with the program of Busing *et al.*, (1964) with their standard deviations are also recorded in Table 2.

This structure is similar to pyrite. The 4.0 nickel atoms lie in special position 4(a) with $x=0.0000$. The 4.92 arsenic and 3.08 sulphur atoms

TABLE 2. ATOMIC PARAMETERS (x), THERMAL PARAMETERS (B); INTERATOMIC DISTANCES, TETRAHEDRAL AND OCTAHEDRAL ANGLES WITH STANDARD DEVIATIONS AND ATOMIC RADII FOR GERSDORFFITE WITH SPACE GROUP $Pa\bar{3}$. NUMBERS IN PARENTHESES DENOTE NUMBER OF ANGLES OR DISTANCES

Atom	Point Position	x	$B(\text{\AA}^2)$	Atomic Radii (\AA)
Ni	4a	0.0000	1.2 ± 0.1	1.17
S+As	8c	0.3785 ± 0.0005	0.9 ± 0.1	1.20
Interatomic distances (\AA)		Tetrahedral angles ($^\circ$)		Octahedral angles ($^\circ$)
Ni-S+As(3) 2.372 ± 0.002		Ni-S+As-S+As(3) 100.8 ± 0.1		S+As-Ni-S+As(3) 85.1 ± 0.1
S+As-S+As(1) 2.400 ± 0.002		Ni-S+As-Ni(3) 116.5 ± 0.1		S+As-Ni-S+As(3) 94.9 ± 0.1

are equally distributed over the eight-fold position 8(c) with $x=0.3785$. Each nickel atom is octahedrally coordinated to six arsenic-sulphur atoms with significant deviations from the theoretical angle of 90° . Each arsenic-sulphur atom is tetrahedrally coordinated to one arsenic-sulphur and three nickel atoms with significant deviations from the regular tetrahedral angle of 109.5° . These deviations lie near the average distortion limit of 4 to 5° given by Hulliger and Mooser (1965) for the change from a pyrite-type structure to a marcasite-type structure.

Normal covalent bonding is indicated by the bond distances. The nickel to arsenic-sulphur bond distance of $2.372 \pm 0.002 \text{ \AA}$ represents a value between the nickel to sulphur and nickel to arsenic bond distances. It lies between these values of 2.34 \AA and 2.41 \AA reported for gersdorffite by Bayliss and Stephenson (1967). The arsenic-sulphur to arsenic-sulphur bond distance of $2.400 \pm 0.002 \text{ \AA}$ is larger than the 2.30 \AA and 2.31 \AA given for cobaltite by Giese and Kerr (1965) and the 2.31 \AA given for gersdorffite by Bayliss and Stephenson (1967).

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THE COBALTIFEROUS PYRITE SERIES

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INTRODUCTION

Klemm (1964) established that phases over the whole range of the series FeS_2 - CoS_2 could be prepared synthetically, though a complete series was not attained until 700°C. A regular variation in cell size was also observed.

The author (1965) reported the natural existence of an intermediate member of the series FeS_2 (pyrite)- CoS_2 (cattierite), and the following results are a completion of that investigation.

Sixteen mineral samples, members of the natural binary system FeS_2 (pyrite)- CoS_2 (cattierite) were examined, both by X-ray diffraction and wet chemical analysis. The object was to establish the presence of naturally occurring phases of this composition, and to observe the effect of iron-cobalt substitution on cell dimension.

Eight of the samples were selected for examination by electron probe micro-analyser, to establish any sub-microscopic chemical variations occurring across the pyrites.

EXPERIMENTAL

All the samples examined were from the Copperbelt of Central Africa. The experimental methods used, except for the electron probe techniques, are essentially those reported in the author's previous mineralogical