

The crystal structure of gersdorffite

By P. BAYLISS and N. C. STEPHENSON

School of Applied Geology, University of New South Wales, Australia,
and School of Chemistry, University of New South Wales, Australia

[Taken as read 12 January 1967]

Summary. Gersdorffite belongs to space group $P2_13$ in the cubic system with cell dimension $a\ 5.6885 \pm 0.0003\ \text{\AA}$ and four formula units per cell. The $hk0$ data were measured from precession photographs obtained with Mo- $K\alpha$ radiation. The structure was solved by Patterson methods and refined by least-squares techniques. This structure has complete ordering of arsenic and sulphur similar to ullmannite.

THE mineral gersdorffite is considered by Palache *et al.* (1944) to be a comparatively rare mineral, occurring as octahedra, cubooctahedra, pyritohedra, lamellae, and massive granules in vein deposits with other nickel and sulphide minerals. It is a nickel sulpharsenide (NiAsS) in which Klemm (1965) indicates from natural and synthetic material that iron and cobalt may substitute for nickel, Yund (1962) indicates from natural and synthetic material that sulphur and arsenic may substitute for each other, and Palache *et al.* (1944) indicate from natural material that antimony may substitute for arsenic to give variety corynite.

The pyrite space group $Pa3$ is given by Peacock and Henry (1948) with nickel at the fourfold position $4(a)$ and an equal distribution of sulphur and arsenic over the eightfold position $8(c)$ with $x = 0.385$. However the space group of $P2_13$ is given by Ramsdell (1925), Olshausen (1925), Bokii and Tsinokev (1954), Yund (1962), and Giese and Kerr (1965), which indicates an ullmannite-type structure.

Experimental and structure determination. Gersdorffite from Wolfsberg, Harz, Germany, was used in this initial single crystal study. Its impurities were determined by spectrographic analysis; 1% iron and 2% silica belong to the extraneous minerals detected by X-ray diffraction, pyrrhotine and quartz. Since substitution of nickel by 2% cobalt decreases its unit cell but the substitution of arsenic by 1% antimony has the opposite effect, their net effect is assumed to be zero. Its unit cell of $5.6885 \pm 0.0003\ \text{\AA}$ was determined from a Debye-Scherrer photograph using the function of Nelson and Riley (1945). This unit cell

value indicates from the curve of Yund (1962) a composition of $\text{NiAs}_{0.82}\text{S}_{1.18}$. A $50\ \mu$ fragment of this gersdorffite with cube and octahedron faces was examined by precession and equi-inclination Weissenberg photographs. The reciprocal lattice exhibits the Laue symmetry 23 and systematic absences occur for $h00$ with $h \neq 2n$, $0k0$ with $k \neq 2n$, and $00l$ with $l \neq 2n$, which confirm the space group $P2_13$. Forty-nine $hk0$ data were recorded on a Buerger precession camera ($\mu = 30^\circ$,

TABLE I. Observed $hk0$ reflection amplitude (F_o) and calculated structure factors (F_c)

hk	F_o	F_c	hk	F_o	F_c	hk	F_o	F_c
02	86	107	27	41	43	51	16	19
04	35	34	31	16	18	52	17	18
06	19	18	32	20	17	53	<8	2
11	34	24	33	24	23	54	<8	2
12	64	45	34	<8	4	55	<8	1
13	16	19	35	17	20	56	17	15
14	17	16	36	17	16	60	19	18
15	26	17	37	<8	1	61	40	40
16	<8	4	40	35	34	62	38	33
17	<8	2	41	13	13	63	42	42
20	86	107	42	36	45	64	45	41
21	76	93	43	11	12	65	12	19
22	82	79	44	122	106	71	17	18
23	97	84	45	<8	7	72	<8	7
24	39	45	46	37	41	73	<8	1
25	37	37	47	13	8	74	<8	4
26	29	33						

$\text{Mo-K}\alpha$) with a timed exposure series that gave a 10:1 interfilm density ratio. The intensities were measured with a densitometer. Then the asymmetric Lorentz and polarization corrections were made from the transparent overlay chart of Waser (1951), but no correction was made for absorption or extinction. These observed reflection amplitudes (F_o) are recorded in table I.

A Patterson vector map indicates its similarity to the pyrite structure rather than the ullmannite structure, so a trial structure was based upon the space group $P2_13$ and the coordinates of Peacock and Henry (1948). 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 dispersion correction. The structure was refined with the Oak Ridge Fortran least squares program of Busing *et al.* (1962) using an IBM 7040 computer. The function $\sum w(|F_o| - |F_c|)^2$ was minimized,

initially with unit weights and then with weights inversely proportional to $|F_o - F_c|^2$.

In the refinement with an average anion scattering curve and assumed thermal parameters for each atom, the occupancy factors for all atomic positions were varied. The nickel occupancy factor indicated the overall scale factor, whilst the other occupancy factors indicated that 4.0 sulphur

TABLE II. Atomic parameters (x), thermal parameters (B), interatomic distances, tetrahedral and octahedral angles, with standard deviations and atomic radii for gersdorffite. As atom is $As_{0.82}S_{0.18}$. Numbers in parenthesis denote number of angles or distances

Atom	Point position	x	B (\AA^2)	Atomic radii (\AA)	
Ni	4a	-0.0065 ± 0.0005	1.4 ± 0.1	1.22	
S	4a	0.3825 ± 0.0010	1.0 ± 0.2	1.12	
As	4a	0.6164 ± 0.0005	1.6 ± 0.1	1.19	
Interatomic distances (\AA)		Tetrahedral angles		Octahedral angles	
Ni-S(3)	2.338 ± 0.006	Ni-As-S(3)	$102.4 \pm 0.1^\circ$	As-Ni-S(3)	$85.3 \pm 0.2^\circ$
Ni-As(3)	2.409 ± 0.003	Ni-As-Ni(3)	115.5 ± 0.1	S-Ni-As(3)	85.6 ± 0.1
S-As(1)	2.306 ± 0.010	Ni-S-As(3)	101.4 ± 0.2	As-Ni-As(3)	92.7 ± 0.1
		Ni-S-Ni(3)	116.2 ± 0.1	S-Ni-S(3)	96.3 ± 0.2

atoms are located in position 4(a) with $x = 0.385$ and the remaining 0.7 sulphur and 3.3 arsenic atoms are equally distributed over position 4(a) with $x = 0.615$. Further least squares cycles with the above atomic distribution were undertaken to refine the overall scale factor, positional parameters, and individual isotropic thermal parameters (B). The resultant final parameters with their standard deviations are listed in table II, whilst the calculated structure amplitudes (F_c) are listed alongside the observed data (F_o) in table I. This structure gave an overall reliability index R with both observed and unobserved data of 0.144.

The interatomic distances and angles, which were computed on an IBM 7040 machine with the programme of Busing *et al.* (1964), are also recorded with their standard deviations in table II.

Structure description and discussion. This structure is distorted from a pyrite type structure similarly to ullmannite. The 4.0 nickel atoms are moved from the special position in pyrite along a threefold axis to position 4(a) with $x = -0.0065$. The arsenic and sulphur are *not* equally distributed over the eightfold position of pyrite, but there are 4.0 sulphur atoms in four-fold position 4(a) with $x = 0.3825$, whilst the remaining 0.7 sulphur and 3.3 arsenic atoms are equally distributed over position 4(a) with $x = 0.6164$ to form an 'arsenic-rich atom'. Not only is this eightfold pyrite position destroyed by ordering but also by position shift, although each atom still has threefold symmetry.

Each nickel is octahedrally coordinated to three sulphur and three 'arsenic-rich' atoms with significant deviations from the theoretical angle of 90° ; each sulphur (or arsenic-rich) atom is tetrahedrally coordinated to three nickel and one arsenic-rich (or sulphur) atoms with significant deviations from the regular tetrahedral angle of 109.5° . These deviations lie near the average distortion limits of 4° to 5° given by Hulliger and Mooser (1965) for the change from a pyrite-type structure to a marcasite-type structure.

The nickel to sulphur bond distance of $2.338 \pm 0.006 \text{ \AA}$ does not differ significantly from that reported for ullmannite ($2.34 \pm 0.03 \text{ \AA}$) by Takeuchi (1957), indicating normal covalent bonding, while the nickel to 'arsenic-rich' bond distance of $2.409 \pm 0.003 \text{ \AA}$ represents a value between the nickel to sulphur and nickel to arsenic bond distances. Each atom may be anisotropic by elongation along the threefold axis and would then require two independent thermal parameters to define its asphericity. In addition the 'arsenic-rich' atom, due to its dual nature, occupies a position between the real atomic centres of sulphur and arsenic, and its shape is a resultant of these 0.18 sulphur atoms in a given position with two independent thermal parameters and 0.82 arsenic atoms in a nearby position also with two independent thermal parameters. Despite this intractable situation the calculated atomic radii (table II) are similar to 1.18 \AA for arsenic and 1.12 \AA for sulphur in cobaltite given by Giese and Kerr (1965) and 1.08 \AA for sulphur and 1.26 \AA for nickel in ullmannite by Takeuchi (1957).

Further publication is intended on gersdorffite studies in progress.

Acknowledgements. The authors wish to thank Professor C. Frondel of Harvard Mineralogical Museum for the gersdorffite sample and Mr. L. Rannit of the School of Chemistry, University of New South Wales, for the semi-quantitative spectrographic analysis.

References

- [Бокпий (Г. Б.) и Цинокев (Л. И.)] Бокпий (G. B.) and Цинокев (L. I.), 1954. [Труды Инст. крист. Акад. наук СССР, vol. 9, p. 239]; abstr. in Chem. Abstr., vol. 48, p. 13553H.
- BUSING (W. R.), MARTIN (K. O.), and LEVY (H. A.), 1962. Oak Ridge National Laboratory, TM 305, 75pp.
- 1964. Ibid., TM306, 83pp.
- GIESE (R. F. Jr.) and KERR (P. F.), 1965. Amer. Min., vol. 50, p. 1002.
- HULLIGER (F.) and MOOSER (E.), 1965. Journ. Phys. Chem. Solids, vol. 26, p. 429.
- International Tables for X-ray Crystallography, 1962, vol. 3, Kynoch Press, Birmingham.
- KLEMM (D. D.), 1965. Neues Jahrb. Min., Abh., vol. 103, p. 205.
- NELSON (J. B.) and RILEY (D. P.), 1945. Proc. Phys. Soc., vol. 57, p. 160.
- OLSHAUSEN (S. K. V.), 1925. Zeitsch. Krist., vol. 61, p. 463.

- PALACHE (C.), BERMAN (H.), and FRONDEL (C.), 1944. *The System of Mineralogy*, 7th edn, vol. 1.
- PEACOCK (M. A.) and HENRY (W. G.), 1948. *Univ. Toronto Studies Geol.* ser. no. 52, p. 71.
- RAMSDELL (L. S.), 1925. *Amer. Min.*, vol. 10, p. 281.
- TAKEUCHI (Y.), 1957. *Min. Journ. (Japan)*, vol. 2, p. 90 [M.A. 14-102].
- WASER (J.), 1951. *Rev. Sci. Instrum.*, vol. 22, p. 567.
- YUND (R. A.), 1962. *Amer. Journ. Sci.*, vol. 260, p. 761.

[*Manuscript received 6 September 1966*]
