

*The crystal structure of gersdorffite (III), a distorted
and disordered pyrite structure*

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Summary. The crystal structure of gersdorffite (III) has been examined with three-dimensional Weissenberg X-ray diffraction data. The unit cell is isometric with $a\ 5.6849 \pm 0.0003\ \text{\AA}$, space group $P1$, and four formula units per cell. This structure has the sulphur and arsenic atoms equally distributed over the non-metal atom sites of pyrite. All atoms show significant random displacements from the ideal pyrite positions to produce triclinic symmetry, which serves to distinguish this mineral from a disordered cubic gersdorffite (II) and a partially ordered cubic gersdorffite (I). Factors responsible for the atomic distortions are discussed.

A POWDER X-ray diffraction pattern showed a strong 001 reflection in gersdorffite (III) from Leichtenberg, Fichtelbirge, Germany (U.S.N.M. R862). Optical observations show faint though distinct anisotropism in dull orange-pink to dull blue-grey. It is unlike gersdorffite (II), which is described by Bayliss (1968) as having arsenic and sulphur atoms equally distributed over the eight equivalent positions given for pyrite by Elliott (1960) and space group $Pa3$. It is also unlike gersdorffite (I), which is described by Bayliss and Stephenson (1967) as having partial ordering of its arsenic and sulphur atoms into the two sets of four equivalent positions given for ullmannite by Takeuchi (1957) and space group $P2_13$. A structure analysis of this gersdorffite (III) was undertaken to ascertain its relationship to the ordered cobaltite of Giese and Kerr (1965) with space group $Pca2_1$.

Experimental. The impurities of gersdorffite (III) were determined by spectrographic analysis; 4% iron belongs to extraneous pyrite detected by X-ray diffraction. The substitution of 2% cobalt for some nickel and 1% antimony for some arsenic appears to have a zero net effect on the unit-cell size. Its unit-cell size of $5.6849 \pm 0.0003\ \text{\AA}$ was determined from a Debye-Scherrer photograph using the function of

Nelson and Riley (1945). This unit cell size indicates from the curve of Yund (1962) a composition of $\text{NiAs}_{0.8}\text{S}_{1.2}$.

Three-dimensional diffraction data were recorded about the a axis with equi-inclination Weissenberg geometry and $\text{Cu-K}\alpha$ radiation. Multiple films were used and intensities were estimated visually by comparison with a calibrated reflection strip. Correlation data were collected from zero-level precession photographs with $\text{Mo-K}\alpha$ radiation. Lorentz and polarization corrections were applied to the Weissenberg data by using the data-processing programmes of Rollett (1961). Similar corrections to the precession data were applied using the transparent overlay developed by Waser (1951). No corrections were made for absorption or extinction. These 219 independent hkl observed reflection amplitudes (F_o) are recorded in table I.

The reciprocal lattice of gersdorffite (III) does not have intensity relationships of the type $hkl = klh = lkh$, and it also has no fourfold axes. Therefore, it does *not* have cubic or tetragonal symmetry. There appear to be intensity relationships of the type $hkl = \bar{h}\bar{k}l = h\bar{k}\bar{l} = h\bar{k}l$, which would make the crystal class orthorhombic. In addition there are no systematic absences in spectra. A three-dimensional Patterson function, calculated with data from one-eighth of the weighted reciprocal lattice, indicated that the structure of gersdorffite (III) is essentially a pyrite-type structure. However, with no systematic absences in spectra there is no appropriate space group in the orthorhombic or monoclinic systems compatible with a pyrite-type structure. Therefore, the unit cell must be triclinic and the space group $P1$.

Structure refinement. The four nickel atoms were placed in ideal positions, which are positions 4(a) of the pyrite space group $Pa3$. The sulphur and arsenic atoms were assumed to be equally distributed over the eightfold position 8(c) with $x = 0.385$ taken from Peacock and Henry (1948). The atomic scattering curves of Thomas-Fermi for nickel, arsenic, and sulphur were taken from the 'International Tables for X-ray Crystallography' (1962), and corrections for the real components of the anomalous dispersion were made with the $\Delta f'$ values given by Dauben and Templeton (1955). Full matrix least-squares procedures with the programme of Busing *et al.* (1962) were then carried out using data from one-half of the weighted reciprocal lattice and allowing each atom to vary its parameters independently according to triclinic symmetry. The data were given unit weights in the initial refinement stages and were weighted according to $(|F_o| - |F_c|)^2$ in the latter stages of refinement. Scale factors for each Weissenberg level

alongside the observed data in table I. The interatomic distances and angles were computed with the programme of Busing *et al.* (1964).

The octahedral angles (As+S)-Ni-(As+S) range from 84° to 98°. The tetrahedral angles for Ni-(As+S)-(As+S) range from 99° to 102°, and for (As+S)-(As+S)-(As+S) from 115° to 117°. The interatomic distances for Ni-(As+S) range from 2.31 to 2.45 Å, and for (As+S)-(As+S) from 2.32 to 2.34 Å.

TABLE II. Atomic parameters (x, y, z) and thermal parameters (B), with standard deviations, for gersdorffite

Atom	Point position	x	y	z	B (Å ²)
Ni	1a	0.995 ± 0.002	0.988 ± 0.001	0.986 ± 0.001	1.5 ± 0.1
Ni	1a	0.494 ± 0.002	0.007 ± 0.001	0.499 ± 0.001	1.4 ± 0.1
Ni	1a	0.013 ± 0.002	0.503 ± 0.001	0.487 ± 0.001	1.4 ± 0.1
Ni	1a	0.512 ± 0.002	0.487 ± 0.001	0.004 ± 0.001	1.4 ± 0.1
As+S	1a	0.387 ± 0.001	0.378 ± 0.001	0.380 ± 0.001	1.1 ± 0.1
As+S	1a	0.880 ± 0.001	0.616 ± 0.001	0.114 ± 0.001	1.2 ± 0.1
As+S	1a	0.618 ± 0.001	0.113 ± 0.001	0.874 ± 0.001	1.0 ± 0.1
As+S	1a	0.121 ± 0.001	0.872 ± 0.001	0.619 ± 0.001	1.0 ± 0.1
As+S	1a	0.622 ± 0.001	0.617 ± 0.001	0.617 ± 0.001	0.9 ± 0.1
As+S	1a	0.114 ± 0.001	0.379 ± 0.001	0.878 ± 0.001	0.9 ± 0.1
As+S	1a	0.387 ± 0.001	0.875 ± 0.001	0.114 ± 0.001	1.0 ± 0.1
As+S	1a	0.887 ± 0.001	0.112 ± 0.001	0.381 ± 0.001	1.0 ± 0.1

Discussion. In pyrite-type structures where each metal atom (M) is surrounded by an octahedron of the same type or of 'average' atoms (A), the metal atom lies on a threefold axis and at a centre of symmetry as shown in fig. 1*a*. Examples of such structures are pyrite (FeS₂) by Elliott (1960) with $M = \text{Fe}$ and $A = \text{S}$, disordered cobaltite (CoAsS) by Giese and Kerr (1965) with $M = \text{Co}$ and $A = (\text{As} + \text{S})/2$, and disordered gersdorffite (NiAsS) by Bayliss (1968) with $M = \text{Ni}$ and $A = (\text{As} + \text{S})/2$; these crystal structures are isomorphous and have space group $Pa\bar{3}$.

When non-metal atom ordering occurs, so that the non-metal atoms surrounding the metal atoms are no longer equivalent, the symmetry of the structure is lowered. In the case of gersdorffite (I) by Bayliss and Stephenson (1967), shown in fig. 1*b*, the partial ordering of arsenic and sulphur atoms causes the nickel atoms to move ($-0.0065, -0.0065, -0.0065$, fractional coordinates) from their centres of symmetry and towards the sulphur atoms, since the Ni-S bond distance is shorter than the Ni-As bond distance. Since the atoms in the plane above the nickel atom in fig. 1*b* are each sulphur atoms and the atoms in the plane below the nickel atom are also internally equivalent (equal to

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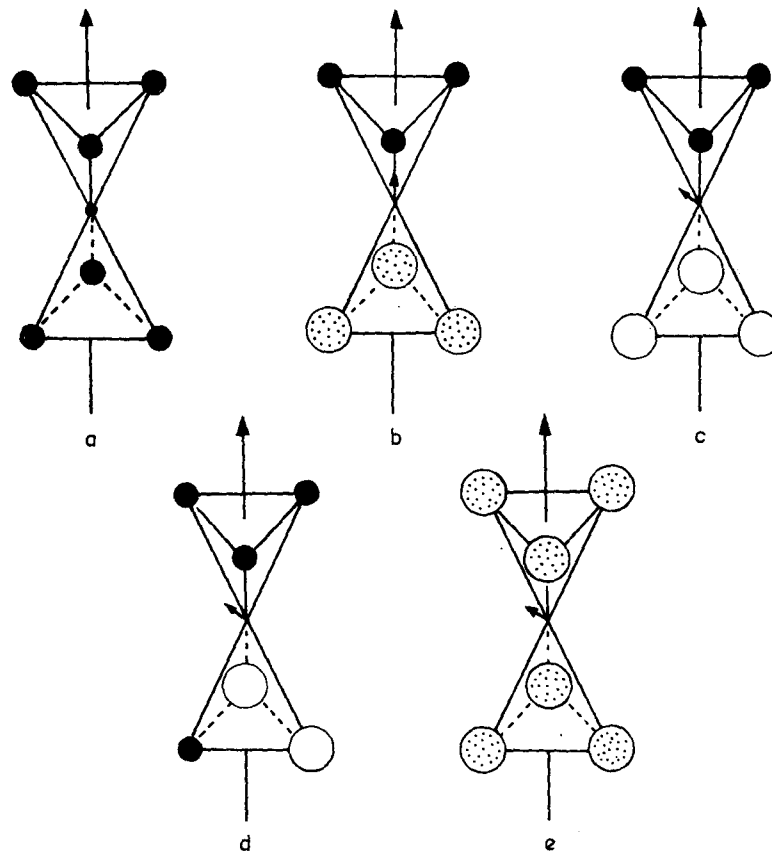


FIG. 1. Positional displacements of metal atoms arising from changes in octahedral environment. Full circles are sulphur atoms, open circles are arsenic, and hatched circles are 'average' atoms (S+As). 1*a*, pyrite (also disordered cobaltite and gersdorffite (II)); 1*b*, gersdorffite (I); 1*c*, ordered cobaltite; 1*d*, postulated arrangement for ordered gersdorffite (III); 1*e*, disordered gersdorffite (III).

0.18S+0.82 As due to disordering) the nickel atom remains on a threefold axis. The unit cell of gersdorffite (I) remains cubic but the space group degenerates to $P2_13$.

In the case of ordered cobaltite shown in fig. 1*c* by Giese and Kerr (1965), the non-metal atoms are ordered into a set of four arsenic atoms and a set of four sulphur atoms. In addition the cobalt has moved significantly ($-0.010, 0.006, 0.011$, fractional coordinates) from the metal atom position in disordered cobaltite, whereas the arsenic and

sulphur atoms have not moved from the non-metal positions in disordered cobaltite. Although the unit cell is isometric, this cobalt movement is reflected in the lower symmetry of space group $Pca2_1$.

The octahedral and tetrahedral angles for pyrite (FeS_2), cattierite (CoS_2), and vaesite (NiS_2), which were determined from the unit-cell sizes and atomic coordinates of Elliott (1960), are listed in table III.

TABLE III. Tetrahedral and octahedral angles for pyrite, cattierite, and vaesite derived from data of Elliott (1960). Numbers in parenthesis denote numbers of angles

	<i>Tetrahedral angles</i>	<i>Octahedral angles</i>
Pyrite	{ Fe-S-Fe (6) 115.7° S-S-Fe (6) 102.1	S-Fe-S (6) 94.9° S-Fe-S (6) 85.6
Cattierite	{ Co-S-Co (6) 114.9 S-S-Co (6) 103.3	S-Co-S (6) 94.0 S-Co-S (6) 86.0
Vaesite	{ Ni-S-Ni (6) 113.8 S-S-Ni (6) 104.7	S-Ni-S (6) 93.5 S-Ni-S (6) 86.5

This table shows that the octahedral angle distortion increases from 3.5° for vaesite to 4° for cattierite and to 5° for pyrite. This shows that the substitution of transition metal atoms by transition metal atoms with fewer electrons increases the angular distortion. These values confirm the 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. The angles listed earlier show gersdorffite (III) to be near this upper distortion limit.

The chemical compositions of all three gersdorffites presented are similar so that any crystal structure differences are unrelated to composition. The structure of gersdorffite (III) is of the pyrite type. The nickel atoms therefore have an octahedral environment, while the arsenic and sulphur atoms are each tetrahedrally coordinated.

A disturbing feature of the refined structure is the persistently high value for the discrepancy index R of 0.19. There are, however, satisfactory features of the gersdorffite (III) refinement, such as temperature factors for the nickel atom of 1.4 \AA^2 and the sulphur-arsenic atom of 1.0 \AA^2 , which are similar to values obtained for like structures. Standard deviations were calculated with data from one-half of the weighted reciprocal lattice and assuming the space group $P1$. These standard deviations are low and the small shifts undergone by the individual metal and non-metal atoms from the ideal positions on threefold axes are therefore significant. However, the average positions of all similar atoms lie on threefold axes as indicated by values in table II. The

movement of nickel atoms from the ideal metal atom positions found in pyrite is $x = -0.009$ (fractional shift), while the sulphur-arsenic atoms occupy the two sets of fourfold positions with average fractional coordinates of $x = 0.381$ and 0.618 . These values are in fact similar to corresponding atomic coordinates in gersdorffite (I).

Further ordering may occur in gersdorffite. If each atom is an integer in $4\text{Ni}(\text{As}, \text{S})_2$ such as $\text{Ni}_4\text{As}_3\text{S}_5$, the triclinic symmetry would arise when four sulphur atoms were ordered in a set of fourfold positions and the remaining one sulphur and three arsenic were distributed over the other fourfold position but with the atoms ordered (fig. 1*d*). However, if there are fractional atoms such as $\text{NiAs}_{3.2}\text{S}_{4.8}$ for gersdorffite, then disordering occurs on one position to give an average atom. The extent of the disordering depends on the deviation of each atom from integers in $4\text{Ni}(\text{As}, \text{S})_2$. The unit cell remains isometric, although the space group degenerates through individual position-ordering into $P1$.

In a completely ordered gersdorffite, fractional atoms are avoided by using a larger unit cell. The size of this larger unit cell may be determined from the superlattice reflections, while the space group remains $P1$.

An average arsenic plus sulphur scattering curve was used during least-squares refinement, and the occupancy factors for non-metal atoms did not deviate significantly from unity. This result would seem to indicate that no ordering of atoms occurs in gersdorffite (III), although the displacement of atoms from ideal pyrite positions and the triclinic symmetry of gersdorffite (III) would suggest that ordering of non-metal atoms does occur.

A possible explanation is twinning, which is not revealed by reflection splitting in the diffraction data from the isometric unit cell. An optical examination of polished material from the same specimen used for the crystal structure analysis revealed a complex twin pattern with a strong suggestion of some lamella twinning diagonal to the cubic cleavage faces. The only twin type found to give a similar unit cell is twinning through an inversion centre. This will produce averaged disordered non-metal atom positions from individual twin lamella with ordered non-metal atoms, but also will centre the metal atom positions around the ideal pyrite position. Therefore, twinning is not an acceptable explanation.

Another possible explanation is that gersdorffite (III) is similar to ordered cobaltite. To obtain a reciprocal lattice with no systematic absences, composite twins about the $[010]$ and $[001]$ axes are required.

With this type of twinning, the atoms in the unit cell do not fall in approximately equivalent positions. Therefore, this is not an acceptable explanation.

Gersdorffite (III) is summarized to have a pyrite-type structure in which sulphur and arsenic atoms are disordered about the nickel atoms. The average atomic displacements of each set of four atoms indicate movement along the threefold axes, with a resultant environment that closely resembles that found in partially ordered gersdorffite (I). In addition there are small random displacements of atoms from their ideal positions on the threefold axes as shown in fig. 1e. Since this sulphur-rich gersdorffite deviates significantly from stoichiometry, most nickel atoms occupy sulphur-rich octahedra and slight anisotropy in temperature factors is observed. These random atom displacements result in the degeneration of the crystal class to triclinic $P1$.

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