THE CRYSTAL STRUCTURE OF PARARAMMELSBERGITE
(NiAs₂)

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Abstract

Pararammelsbergite (NiAs₂) is orthorhombic with $a = 5.753(6)$ Å, $b = 5.799(6)$ Å, $c = 11.407(9)$ Å, space group *Pbca*, $Z = 8$. Comparison of the unit cell constants with those of rammelsbergite (NiAs₂) suggests that pararammelsbergite should have a pyrite-like structure. The crystal structure has been determined by application of a direct method of phase determination to three-dimensional intensity data collected from a crystal from Cobalt, Ontario and refined to a conventional R of 0.048. The As and Ni coordinations are the same as and the associated interatomic distances are comparable to those in rammelsbergite. The structure is transitional between the marcasite and pyrite structures, in that the metal-ligand octahedra are arranged so that one octahedral edge is shared with an adjacent octahedron, compared to two in the marcasite structure and none in the pyrite structure. The distance between the Ni atoms across the shared octahedral edge is increased over the ideal distance, suggestive of metal t_{2g} orbital interaction between them. However, the resulting destabilization must be less than in rammelsbergite and may explain why pararammelsbergite is the low-temperature polymorph of NiAs₂.

Introduction

Pararammelsbergite is a low temperature polymorph of NiAs₂ (Yund, 1961). It has a similar paragenesis to rammelsbergite, a more familiar polymorph of NiAs₂, occurring in certain arsenide and sulfarsenide assemblages, notably in the Cobalt area, Ontario. It was first described as rammelsbergite (Peacock and Michener, 1939) from the Ontario localities of Elk Lake, Cobalt, and South Lorrain, but later recognised as a separate mineral (Peacock and Dadson, 1940). Peacock and Michener found it to be orthorhombic (or pseudo-orthorhombic) with $a = 5.74$ Å, $b = 5.81$ Å and $c = 11.405$ Å, apparent space group *Pbma* or *Pb2a*, $Z = 8$. These authors remarked that Weissenberg X-ray films showed the cell to be dimensionally orthorhombic but there were some serious departures in the intensities of some reflections from that required for orthorhombic symmetry. The available chemical

analyses indicate that Co, and to a lesser extent Fe and Cu, may substitute for Ni and that S, and to a lesser extent Sb, may substitute for As (Table 1).

<div align="center">EXPERIMENTAL</div>

Of the type-specimens described by Peacock and Dadson, the one from Elk Lake, Ontario, appeared the most suitable for the present purposes, because it had the least chemical substitution and had yielded a single crystal in the original study. Unfortunately it could not be located. The type-material from the Hudson Bay Mine, Cobalt, was obtained from the Royal Ontario Museum and examination showed that it would be too difficult to obtain single crystal fragments of the requisite quality. The material used in this study came from an unusual specimen collected at Cobalt, Ontario, and obtained from Ward's Natural Science Establishment, Rochester, New York. The arsenide assemblage has a dendritic, almost fernlike, habit and is developed in a cherty matrix. The pararammelsbergite occurs dominantly as rather large, elongated crystals oriented parallel to the long axes of the dendrites. A small part of the hand specimen was crushed in a percussion mortar and the arsenide minerals were concentrated by heavy liquids. Crystal fragments were hand picked from the concentrate for the X-ray study.

Optical examination of a polished section of the concentrate mounted in epoxy suggested that the pararammelsbergite exists in three generations of grains: as large rectangular crystals 1 to 2 mm in largest dimension, which appear to be fragments of the large axial crystals; as smaller, more rounded grains; and as small grains within the groundmass of other arsenides. Preliminary data from an electron microprobe study by K. C. Misra indicated that there were slight but consistent differences in the chemical compositions of these three types. The composition reported in Table 1 is the average for the large rectangular crystals, since one of this type was used for the crystal structure analysis; it

<div align="center">TABLE 1.   CHEMICAL ANALYSES OF PARARAMMELSBERGITE</div>

	1	2
Ni	27.08	27.68
Co	1.94	1.74
Cu	0.16	n.d.
Fe	0.56	0.22
As	65.78	67.72
Sb	0.91	0.45
S	3.05	2.19

1.   Hudson Bay Mine, Cobalt, Ontario.   Walker and Parsons (1921).

2.   Present study.

compares quite favorably with the analysis of the type material from Cobalt. The lattice parameters are $a = 5.753(6)$ Å, $b = 5.799(6)$ Å, $c = 11.407(9)$ Å; these data were obtained by least-squares refinement of twelve centered reflections on a four-circle diffractometer.

Precession films of single crystal fragments of pararammelsbergite confirmed the unit cell of Peacock and Michener. However, the space group is *Pbca* and not *Pbma* or *Pb2a*, as reported in the earlier study. Peacock and Michener reported that there were no extinctions for reflections of the type *h0l*; this observation could be attributed to a twinned crystal. In this connection, since the unit cell edges approximate to integer multiples of the ideal cube edge, the twinning would be difficult to detect. Also, the present study indicated no departures from orthorhombic symmetry in equivalent sets of reflections, such as those noted by Peacock and Michener.

The crystal fragment selected for the structure analysis was approximately tabular in shape, with the tabular development parallel to (010) and not (001), the cleavage plane noted by Peacock and Michener. The crystal was bounded by plane surfaces and had a volume of $0.54 \times 10^{-6} cm^3$. The X-ray intensity data were collected on a Picker facs 1 four-circle diffractometer system at the University of Western Ontario. All reflections with $2\theta \leq 65°$ were measured with Zr-filtered MoKα ($\lambda = 0.7107$Å) radiation using the 2θ scan technique: 40 second stationary background counts and peakbase widths of $2.5°$ 2θ (uncorrected for dispersion). The resulting data were processed by a data correction routine which removed space group extinctions and corrected for background, Lorentz and polarization effects and absorption, and assigned standard deviations to the corrected data based on the summed variances of the counting rates of the peaks and associated backgrounds. Transmission factors for the absorption correction were calculated by a direct analytical procedure using a modified version of program ABSCOR (Tompa and Alcock); the value of the linear absorption coefficient being 433.1 cm^{-1}. Each reflection whose intensity was less than the associated background plus one standard deviation was given zero intensity.

CRYSTAL STRUCTURE INVESTIGATION

In an earlier study on the structural transformation of marcasite to pyrite (Fleet, 1970) the correlation between the b parameter and $d(101)$ of marcasite and the unit cell edge of pyrite was emphasized and attributed to the fact that each is related to a direction of an Fe–S chain, formed from an arrangement of alternating Fe atoms and S_2 groups lying at an angle to the direction of the chain. Rammelsbergite has the marcasite structure (Kaiman, 1947), with $a = 4.70$ Å, $b = 5.79$ Å, $c = 3.54$ Å (Peacock and Dadson). The b parameter of rammelsbergite correlates very well with a, b, and $c/2$ of pararammelsbergite so that, dimensionally, the unit cell of the latter is made of two pyrite-like cubes stacked parallel to c. Further, by analogy with the relationship between marcasite and pyrite, the a, b, and c directions of pararammelsbergite must be directions of Ni-As chains and it is to be expected that its structure will have similarities with that of pyrite.

The structure factor data were processed for Wilson statistics by
program FAME (R. B. K. Dewar, Illinois Institute of Technology,
Chicago). Statistical analysis of the normalised structure factors (E's)
gave a centric distribution, confirming the centrosymmetric character
of the structure. An attempt was made to phase those structure factors
with $E \geq 1.5$ by a reiterative application of Sayre's equation using
program REL1 (adapted from R. E. Long, Ph.D. Thesis, Univ. Calif.
Los Angeles, 1965). In the solution with the largest consistency index
(0.140), the procedure was unable to phase 96 of the 136 structure
factors processed. An E map was prepared using the 40 phased struc-
ture factors. The E map indicated that the phasing procedure had
produced a multiple solution of the crystal structure; each site was
quadruply defined in the b-direction. The selection of the correct y
parameters and the placement of the Ni and As in the appropriate
sites were determined by comparing the coordinations and interatomic
distances of trial structures with those in rammelsbergite. The value
of the conventional residual index at this stage was 0.33.

The structure was refined further by full-matrix least-squares re-
finement using program RFINE (L. Finger, Geophysical Laboratory,
Washington), assuming a composition of $(Ni_{0.94}Co_{0.06})$ $(As_{0.93}S_{0.07})_2$
which was a practical compromise between the ideal and actual com-
positions. The scattering factor data for Ni^{2+}, Co^{2+}, and As were from
Cromer and Mann (1968), that for S^{2-} was from The International
Tables for X-ray Crystallography, Vol. III, and the anomalous dis-
persion coefficients for Ni, Co, As, and S were from Cromer (1965).
Isotropic and anisotropic thermal parameters were added successively
to the refinement, giving values of the weighted and conventional
residual indices of 0.059 and 0.060 for isotropic and 0.050 and 0.048 for
anisotropic. The improvement in the refinement when anisotropic
parameters are included is significant at the 0.005 level. The positional
and anisotropic thermal parameters, and associated standard devia-
tions, are given in Table 2 and the observed (F_o) and calculated (F_c)
structure factors are given in Table 3.[1]

DISCUSSION

In the pararammelsbergite structure (Fig. 1) the As atoms are
associated in pairs and, as predicted, we can recognise chains of Ni
atoms and As_2 groups oriented parallel to the a and b directions and a

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TABLE 2. POSITIONAL AND THERMAL PARAMETERS (STANDARD DEVIATIONS IN PARENTHESES, $B_{11} = 8\pi^2 \overline{U}_{11}^2$ etc.)

	Ni	As(1)	As(2)
$\underline{x}$	0.9970(2)	0.1196(2)	0.3664(2)
$\underline{y}$	0.1755(2)	0.0547(2)	0.3084(2)
$\underline{z}$	0.3717(1)	0.1809(1)	0.4308(1)
$\underline{B}_{11}$	0.39(4)	0.46(3)	0.56(3)
$\underline{B}_{22}$	0.08(4)	0.06(4)	0.10(4)
$\underline{B}_{33}$	0.12(4)	0.18(3)	0.21(3)

twisted chain parallel to the c direction. Each As atom is coordinated to three Ni and one As and each Ni atom is coordinated octahedrally with As. The As and Ni coordinations are the same as and the associated interatomic distances (Tables 4 and 5) are comparable to those in rammelsbergite.

The pararammelsbergite structure is transitional between the marcasite-type and the pyrite-type structures. The essential difference between all three structures is in the manner in which the metal-ligand octahedra are linked together. In the pyrite structure none of the twelve octahedral edges is shared with an adjacent octahedron. Each edge is linked to that of a neighboring octahedron via a common ligand atom and ligand group (S_2, As_2, AsS, etc.), the atoms being arranged in five-membered rings formed of three ligand atoms and two metal atoms. In contrast, only eight of the octahedral edges in the marcasite structure are linked in this way. The octahedra are arranged so that the two edges parallel to (001) are shared with adjacent octahedra; the other two edges, normal to (001), are linked to adjacent octahedra via common ligand groups, forming six-membered rings of two ligand groups and two metal atoms. In pararammelsbergite, ten octahedral edges are linked as in the pyrite structure, one edge is shared and the other is linked via common ligand groups. The shared edge passes through a centre of symmetry.

Nickel (1968) synthesised the work of previous investigators, principally Goodenough (1960), Hulliger and Mooser (1965), and Pearson (1965), into a general hypothesis for the structural stability of minerals with the pyrite and marcasite-like structures. The structural
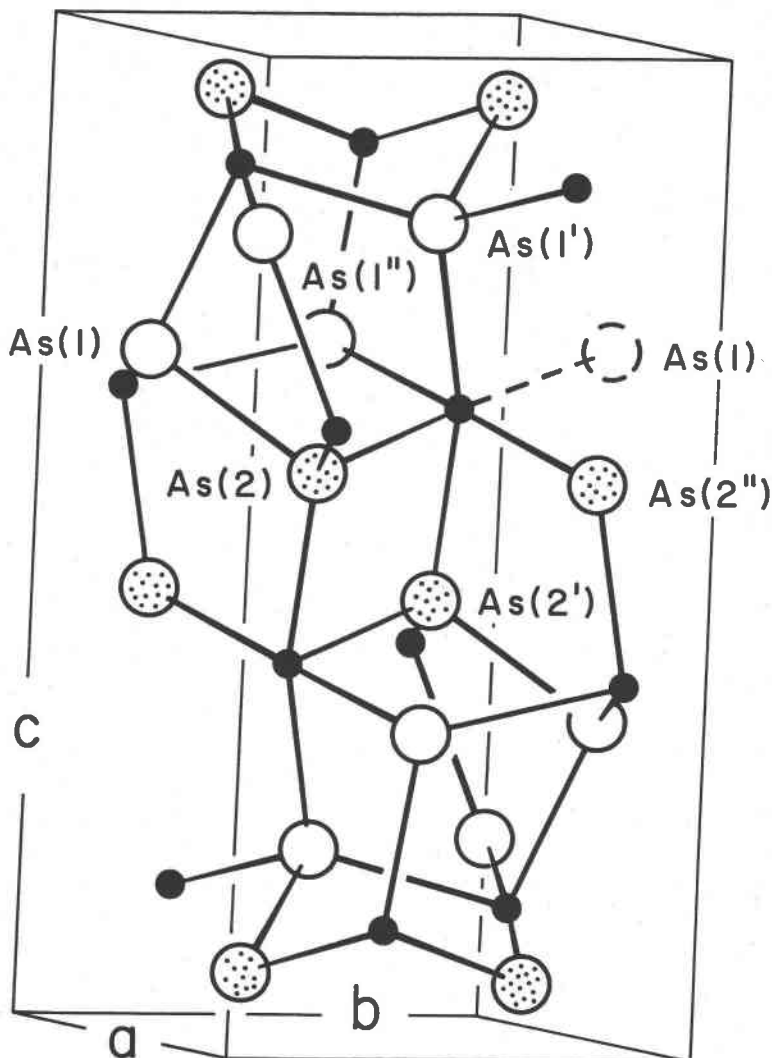
FIG. 1. The unit cell of pararammelsbergite: As(1)—large circles; As(2)—large, stippled circles; Ni—small, full circles.

feature of greatest significance is the shared octahedral edges in the marcasite-like structures since this allows for a closer approach of the metal atoms than would otherwise be possible and results in varying amounts of metal-metal orbital interaction within the various minerals.

The outer electron configuration of Ni is $3d^8 4s^2$ and that of As is $4s^2 4p^3$. In terms of molecular orbital bonding theory, each $NiAs_2$ mole-

cule must contribute fourteen electrons (five from each As and four from Ni) to form the seven σ bonds. The d-electron configuration of the Ni is, then, $3d^6$, so that $NiAs_2$ is isolectronic with FeS_2. Pyrite and marcasite have very low paramagnetic susceptibilities leading to the conclusion that the six $3d$ electrons have the low spin configuration and occupy the three non-bonding t_{2g} orbitals. The three t_{2g} orbitals are available to form π bonds with the ligands, and, in doing so, increase the stability of these compounds. In marcasite, one t_{2g} orbital

TABLE 4.   INTERATOMIC DISTANCES AND BOND ANGLES

(STANDARD DEVIATIONS IN PARENTHESES)

Ni −As(1) = 2.376(3)Å	As(1) −Ni−As(1') = 97.13(7)°
−As(1') = 2.392(2)Å	−As(1") = 87.16(7)°
−As(1") = 2.359(3)Å	−As(2') = 96.54(6)°
−As(2) = 2.367(3)Å	−As(2") = 91.40(8)°
−As(2') = 2.376(2)Å	As(1')−Ni−As(1") = 87.29(6)°
−As(2") = 2.359(2)Å	−As(2) = 84.14(7)°
As(1) −As(2) = 2.432(2)Å	−As(2") = 95.17(7)°
−As(1') = 3.575(3)Å	As(1")−Ni−As(2) = 96.38(8)°
−As(1") = 3.264(3)Å	−As(2') = 87.82(7)°
−As(2') = 3.547(3)Å	As(2) −Ni−As(2') = 82.56(6)°
−As(2") = 3.389(3)Å	−As(2") = 85.03(7)°
As(1')−As(1") = 3.279(3)Å	As(2')−Ni−As(2") = 90.07(6)°
−As(2) = 3.189(3)Å	
−As(2") = 3.508(3)Å	
As(1")−As(2) = 3.523(3)Å	
−As(2') = 3.284(3)Å	
As(2) −As(2') = 3.129(3)Å	
−As(2") = 3.194(3)Å	
As(2')−As(2") = 3.350(3)Å	

TABLE 5. INTERATOMIC DISTANCES IN RAMMELSBERGITE (DATA AND LABELS
FROM KAIMAN, 1947)

Ni-As Distances	As-As Distances
OA = 2.38Å	AB = 2.55Å
OF = 2.36Å	AC = 3.29Å
	AF = 3.41Å
	AA' = 3.54Å
	AB' = 3.12Å

interacts with neighboring orbitals across the shared octahedral edges, increasing the metal-metal distance over the ideal distance (the enclosed S–Fe–S bond angle is 82°) and causing some destabilisation in the structure; an analogous situation exists in rammelsbergite.

Pararammelsbergite is diamagnetic so that the d-electron configuration is the low spin one. As in the structures of marcasite (FeS_2) and rammelsbergite there is evidence of t_{2g} orbital interaction across a shared octahedral edge; the Ni-Ni distance (3.56 Å) and enclosed bond angle (82.6°) are very comparable to the data for rammelsbergite (3.54 Å and 83° respectively). However, since only one quarter of a t_{2g} orbital reacts with a neighbor, the destabilisation caused by the interaction must be less than that in rammelsbergite. This observation is in accord with the thermochemical evidence which indicates that pararammelsbergite is the low temperature polymorph.

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