ON RAMMELSBERGITE AND PARARAMMELSBERGITE: DISTINCT FORMS OF NICKEL DIARSENIDE

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Abstract

Rammelsbergite from Eisleben and Schneeberg (type locality) is orthorhombic; space group D_{2h}^{12}—*Pmnn*; $a_0 = 3.53$, $b_0 = 4.78$, c_0 (fibre axis) = 5.78Å; twin plane (110); cleavage {110}; unit cell contains 2[NiAs$_2$]; G = 6.97 (meas.), 7.05 (calc.); the structural data are similar to those of marcasite. A new analysis is given.

Pararammelsbergite from three mines in Ontario is orthorhombic (or pseudo-orthorhombic); apparent holohedral space group D_{2h}^{11}—*Pbma*; $a_0 = 5.74$, $b_0 = 5.81$, $c_0 = 11.405$Å; twinning not seen; cleavage {001}; unit cell contains 8[NiAs$_2$]; G = 7.12 (meas.), 7.24 (calc.).

In polished sections both minerals are hard, white and strongly anisotropic, with perceptible differences in habit, twinning, polarization colours, and resistance to moist air. They are easily distinguished by their unlike x-ray powder patterns.

INTRODUCTION

The existence of an orthorhombic form of nickel diarsenide, as distinct from the cubic mineral of similar composition, was suspected by Breithaupt (1835) and later confirmed by the same author (1845). For the orthorhombic mineral Breithaupt retained the early name *Weissnickelkies*, proposing *Chloanthit* for the cubic modification. Haidinger (1845) introduced the name *Rammelsbergit* for *Weissnickelkies*, without recognizing the orthorhombic symmetry. This caused some confusion of nomenclature which was rectified by Dana (1845), whose use of rammelsbergite for the orthorhombic mineral, and chloanthite for the cubic species, was generally accepted.

The characterization of rammelsbergite still rests mainly on Breithaupt's description (1845) of the indistinctly crystallized mineral from Schneeberg, Saxony, and Riechelsdorf, Hesse. Later reported occurrences, particularly in the Cobalt and South Lorrain districts of Ontario (Walker and Parsons, 1921; Walker, 1925; Thomson, 1930) have confirmed the individuality of a presumably orthorhombic mineral with the essential composition NiAs$_2$ and have yielded the valuable mineralographic characters summarized in Schneiderhöhn and Ramdohr (1931) and Short (1934).

The specific description of rammelsbergite remains incomplete, however, for lack of accurate crystallographic or structural data. The scanty goniometric observations of Breithaupt (1845), Palache and Wood (1904), and Dürrfeld (1911), all made on small, poor crystals, show no agreement; nor does the isolated suggestion by De Jong (1926), that rammelsbergite is structurally the same as loellingite, carry conviction.

An effort was therefore made to obtain single crystal x-ray measurements on rammelsbergite in order to determine the symmetry, cell dimensions and cell content of the species and to find its systematic position. The single European specimen at first available, from Schneeberg, offered no hope of obtaining a measurable crystal. Canadian specimens were therefore studied, and eventually the desired information was obtained on material from Gowganda and Cobalt, Ontario, with the chemical and physical properties of rammelsbergite (Peacock and Michener, 1939).

But again the new crystallographic data showed no agreement with any of the previous observations; and therefore the description of the Canadian mineral was concluded with the statement:

At present we can say that if rammelsbergite is defined as the orthorhombic or pseudo-orthorhombic diarsenide of nickel, then our material is rammelsbergite of unusual purity; if it can be shown, however, that the original or typical rammelsbergite (if such can be obtained) is a homogeneous mineral essentially different from ours, then the Ontario mineral is a distinct substance.

Further work on this problem confirmed the second of the foregoing alternatives. Specimens from Eisleben, Thuringia, gave complete data which certainly refer to rammelsbergite, as shown by the chemical composition, physical properties, and above all the x-ray powder photograph, all of which are the same as those of rammelsbergite from Schneeberg. The structural data of the Canadian mineral bear no simple relation to those of rammelsbergite or of smaltite-chloanthite. The Canadian mineral previously named rammelsbergite is therefore a distinct species for which the name *pararammelsbergite* was recently proposed (Peacock, 1939); this name alludes to the fact that the composition of the new mineral is the same as that of rammelsbergite.

The principal object of the present paper is to give the new observations on rammelsbergite from Eisleben and Schneeberg. To establish the individuality of pararammelsbergite the essential properties of the Canadian mineral will be restated, together with some further observations. The name pararammelsbergite may thus be considered to apply retroactively to the mineral already described in detail by Peacock and Michener (1939).

MATERIALS AND ACKNOWLEDGMENTS

The following specimens served as the basis of the present study:

1. Rammelsbergite, Royal Ontario Museum of Mineralogy, M/4036, Schneeberg, Saxony, Germany (type locality).

2. Rammelsbergite, ROMOM, M/19708, Eisleben, Mansfeld district, Thuringia, Germany.

3. Rammelsbergite, United States National Museum, C-693, Eisleben, Mansfeld district, Thuringia, Germany.

4. Pararammelsbergite, ROMOM, M/12411, Moose Horn Mine, Elk Lake, Gowganda, Ontario (specimen 1 in Peacock and Michener, 1939).

5. Pararammelsbergite, ROMOM, M/11772, Hudson Bay Mine, Cobalt, Ontario (three specimens); 5*a* (specimen 2 in Peacock and Michener, 1939) is almost pure pararammelsbergite, 5*b* and 5*c* contain visible amounts of other white metallic ores.

6. Pararammelsbergite, ROMOM, M/14242, Keeley Mine, South Lorrain, Ontario.

The specimens from the Royal Ontario Museum were kindly made available for study by Professor A. L. Parsons. The specimen from the United States National Museum is a fragment representing material analyzed by the International Nickel Company; the sample came to us through Dr. G. A. Harcourt who was also good enough to exchange notes on some of the critical points in this paper and to confirm the distinction between the two minerals hitherto named rammelsbergite.

In the present account the second author has supplied the observations on polished sections, the first being responsible for the remainder of the work.

RAMMELSBERGITE

HAND SPECIMENS

On freshly broken surfaces rammelsbergite appears tin-white with minute cleavage surfaces revealing a compact, fine-grained, fibrous to bladed texture. On the Schneeberg specimen the rammelsbergite assumes definitely spherulitic forms with interstitial, sharply crystallized quartz; the specimens from Eisleben show some tendency to internal spherulitic arrangement, with veinlets and interstitial areas of calcite. None of the specimens shows isolated crystals or measurable crystal faces.

POLISHED SECTIONS

Rammelsbergite takes a fine polish, appearing smoother and whiter than the other white arsenides of nickel, cobalt and iron when in contact with these minerals. The mineral appears typically in straight-sided blades in random to radiated arrangement. Anisotropism strong; twinning, simple or lamellar, shown by nearly every grain; hardness E, estimated with the steel needle. Etch reactions: HNO_3, effervesces and etches rapidly to dark brown or black, obscuring the texture; $FeCl_3$, etches

quickly to dark brown, bringing out the texture; $HgCl_2$, slowly gives a dark brown to iridescent stain which does not rub off; HCl, negative; KCN, negative; KOH, negative. In air saturated with water vapour rammelsbergite is almost completely etched after twelve hours; after one week there is usually some development of white or green bloom.

Eisleben. A section from the specimen used for the analysis (material 3) consists almost wholly of relatively coarsely crystallized rammelsbergite with some interstitial and intergrown calcite (Figs. 1, 2). Impurities, amounting to less than one per cent, are niccolite and a few small inclu-
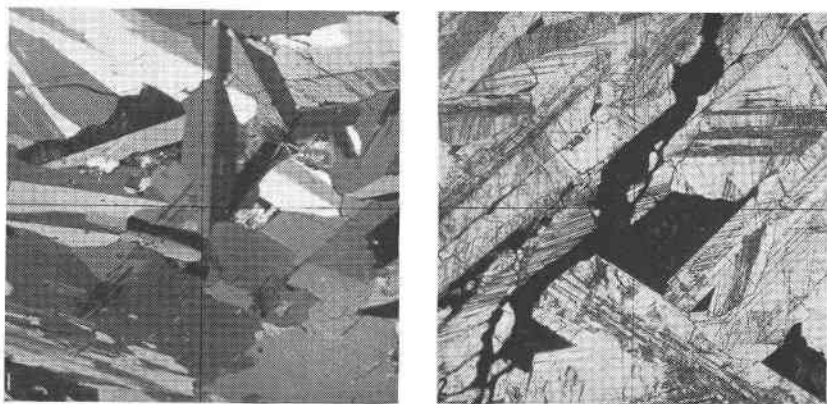

FIG. 1. Rammelsbergite, Eisleben (material 3); interlocking blades showing prominent twinning. Crossed nicols (×67).

FIG. 2. Rammelsbergite, Eisleben (material 3); interlocking blades and interstitial calcite, etched with $FeCl_3$. Plain polarized light (×67).

sions which appear to be bismuth, argentite and silver. The crystals of rammelsbergite range from straight-sided blades, exceeding 1.0×0.1 mm. in size, to grains as small as 0.02 mm. The well-formed blades make an interlocking to rudely radiated texture. With crossed nicols nearly all the crystals show simple or multiple twinning with straight sharp twin junctions parallel to the elongation. The polarization colours are salmon-pink, russet brown, yellowish brown, yellow, sky-blue, ink-blue, gray, varying somewhat with the orientation of the crystal section. In the elongated (prismatic) sections the ink-blue colour is prominent while the sky-blue colour is commonly shown by the granular (basal) sections.

A section from the specimen which yielded the crystal fragments used for x-ray measurements (material 2) is similar to the foregoing section. The minerals are rammelsbergite with sparse grains of niccolite, small

inclusions of cobaltite, and calcite filling fractures in the ore. The texture is likewise granular to bladed without noticeable radiated arrangement. After one week in wet air the rammelsbergite was completely and deeply etched and partly coated with white bloom.

Schneeberg. The polished section (Figs. 3, 4) shows sheaves of fine-textured, bladed to granular rammelsbergite, with included grains of bismuth (about 1 per cent), bounded by incomplete circular rims (0.4 mm. wide) consisting of loellingite together with a smaller proportion of rammelsbergite and smaltite.[1] The resulting reniform structure shows well
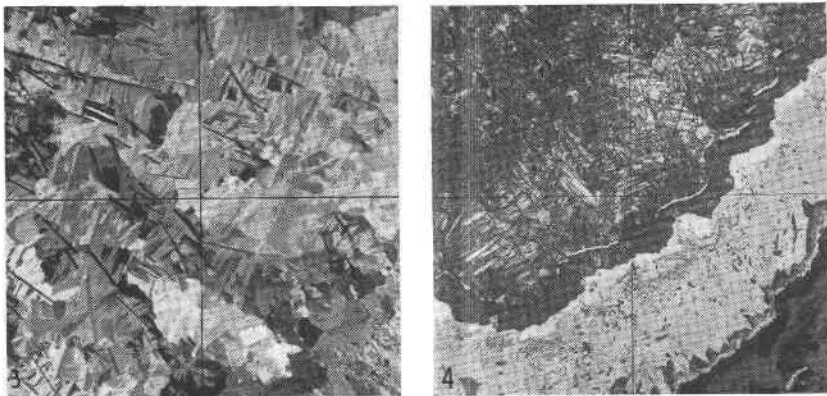

Fig. 3. Rammelsbergite, Schneeberg (material 1); part of a sheaf of bladed rammelsbergite showing complex twinning. Crossed nicols (×67).

Fig. 4. Rammelsbergite, Schneeberg (material 1); a similar area showing rammelsbergite (dark), with smaltite (white) and loellingite (gray) in the banded rim, etched with FeCl₃. Plain polarized light (×67).

under crossed nicols (Fig. 3) and even better after etching with FeCl₃ (Fig. 4), which attacks rammelsbergite without affecting smaltite; loellingite shows only faint differential etching. The polarization colours of the rammelsbergite are dark russet brown, yellowish brown, sky-blue, dark gray. Most of the rammelsbergite shows complex twinning which appears to be a combination of simple twinning on (110) together with lamellar twinning according to an undetermined law. The rim minerals reveal rhythmic precipitation, the complete succession being: smaltite—rammelsbergite—smaltite—loellingite—rammelsbergite—smaltite.   Of these, loellingite is the most abundant, forming radially arranged crystals

[1] Smaltite is used in these descriptions to denote zoned cubic arsenides of the skutterudite-smaltite-chloanthite series.

terminating sharply in the outer zone of rammelsbergite. In wet air the rammelsbergite was mostly etched in twelve hours; in a week a green bloom had begun to form in some places.

The Schneeberg rammelsbergite thus shows slight differences as compared with the mineral from Eisleben, namely, lack of the ink-blue polarization colour, more complex twinning, and alteration to a green bloom. In view of the structural identity of the two materials, as shown by x-ray powder photographs, these differences must lie within the range of the properties of rammelsbergite.

SPECIFIC GRAVITY

Table 1 gives some existing measurements of the specific gravity of European rammelsbergite, together with two new measurements obtained with the Berman balance, and the value calculated from the structural cell constants. As compared with the specific gravity calculated from the structural cell, the mostly higher values for Schneeberg are probably due to included bismuth ($G = 9.8$) which has been reported in all the analyses and was noted in the polished section; the slightly lower value for Eisleben is due to included calcite.

TABLE 1. RAMMELSBERGITE: SPECIFIC GRAVITY

Locality	Specific Gravity	Observer
Schneeberg	7.129 7.188 7.19 6.9 7.23	Breithaupt (1845) Breithaupt (1845) Hilger, in Dana (1892) McCay, in Dana (1892) Peacock (meas.)
Riechelsdorf	7.099 7.14	Breithaupt (1845) Linck, in Dürrfeld (1911)
Eisleben	6.97 7.05	Peacock (meas.) Peacock (calc.)

CRYSTALLOGRAPHY

Cell dimensions and space group. Crystals fairly suitable for x-ray measurements were obtained from one of the specimens from Eisleben (material 2), by coarsely crushing a fragment with the compact, bladed texture and searching the debris for particles with a distinct long edge made by intersecting cleavage planes. This edge, the direction of elongation of the needles, was taken as the vertical axis, the cleavage being

{110}. Even the smallest crystals secured in this way proved to be twins on (110), with perceptible fibre texture causing some lateral extension of the Weissenberg spots.

On two crystals the following x-ray photographs were made with copper radiation: rotation about [001]; Weissenberg photographs of the zero, first and second layers about [001]; Weissenberg photograph about the normal to (110). The films and projections showed orthorhombic symmetry, the observed diffractions conforming to the conditions:

hkl present in all orders
$0kl$ present in all orders
$h0l$ present only with $h+l$ even
$hk0$ present only with $h+k$ even

giving the space group $D_{2h}^{12} - Pmnn$, assuming holohedral symmetry.

The cell dimensions of rammelsbergite, with a probable error of 0.01 Å, are given below in comparison with those of marcasite—FeS_2 (Buerger, 1931; 1937 B) and loellingite—$FeAs_2$ (Buerger, 1932).

TABLE 2. RAMMELSBERGITE, MARCASITE, LOELLINGITE:
SPACE GROUPS AND CELL DIMENSIONS

	Rammelsbergite	Marcasite 1931	Marcasite 1937B	Loellingite
Space group	*Pmnn*	*Pmnn*	*Pmnn*	*Pmnn*
a_0	3.53 Å	3.37 Å	3.381 Å	2.85 Å
b_0	4.78	4.44	4.436	5.25
c_0	5.78	5.39	5.414	5.92

These data bring out a close similarity in the cell constants of rammelsbergite and marcasite, a similarity supported by the cleavage {110} and twinning on (110) which is common to both species. Loellingite, on the other hand, differs substantially from marcasite and rammelsbergite in cell dimensions, cleavage and twinning.[2] Thus we regard rammelsbergite as closely related to marcasite, rather than to loellingite as suggested by Buerger (1937 A, p. 55).

Crystal form, cleavage and twinning. The dimensions of the structural cell of rammelsbergite give the geometrical elements:

$$a_0:b_0:c_0 = 0.738:1:1.209$$
$$p_0:q_0:r_0 = 1.637:1.209:1$$

[2] The lack of agreement between the crystallographic constants of loellingite from Norway (Brögger, 1890, p. 8) and those for loellingite from Franklin, N. J. (Bauer and Berman, 1927; Buerger, 1932) has not yet been explained.

The more widely spaced lattice planes, with indices conforming to the space group conditions, are as follows:

hkl	(011)	(101)	(002)	(110)	(111)	(012)	(020) . . .
d	3.68	3.01	2.89	2.84	2.55	2.47	2.39Å

From these spacings we would expect the crystals to show {011} as the dominant form and likely cleavage, accompanied by the forms {101}, {002}, . . . The elongation along [001] with cleavage {110} is thus anomalous. On the other hand some crystals of marcasite (Dana, 1892, p. 95, Fig. 2) conform almost perfectly to the above theoretical order of decreasing form importance.

The prism angle of 56°–57°, noted on rammelsbergite by Breithaupt (1845), does not correspond to any simple prism angle in the structural lattice. The elements and forms of Palache and Wood (1904) were derived from crystals doubtfully identified as rammelsbergite. These crystals prove, however, to be maucherite, as shown in a recent description of that mineral (1940). The only other morphological data on rammelsbergite are due to Dürrfeld (1911), whose description of poor crystals from Riechelsdorf is roughly compatible with our crystal lattice. Dürrfeld's elements:

$$a:b:c=0.6798:1:1.1622$$

were obtained from short prismatic crystals formed by {110} (curved faces), with {001}, {011}, {101}.

|	Dürrfeld (measured)	Peacock (calculated)
$(110):(1\bar{1}0)$	67°—69°36′	72°53$\frac{1}{2}$′
$(001):(011)$	49 17$\frac{1}{2}$	50 24$\frac{1}{2}$
$(001):(101)$	60 25	58 35
	(Schimmermessung)	

The measured and calculated angles show sufficient resemblance to indicate that the Riechelsdorf crystals are rammelsbergite of vertical prismatic habit.

The cleavage {110}, already known on rammelsbergite, was confirmed by measurement on the fragments used for the x-ray measurements. The twinning on (110) was revealed by all the Weissenberg photographs about [001]. In Friedel's notation this twin law is a case of twinning by reticular pseudo-merohedry with index 3 and obliquity 2°20$\frac{1}{2}$′.

Powder Photographs

Rammelsbergite and pararammelsbergite are most conveniently and definitely distinguished by means of x-ray powder photographs, which show totally dissimilar patterns for the two minerals (Figs. 5–10). The pattern for Schneeberg (Fig. 5) shows a few lines which are absent in the

identical patterns for Eisleben (Figs. 6, 7); these lines correspond to the strongest lines of bismuth, an observed impurity.
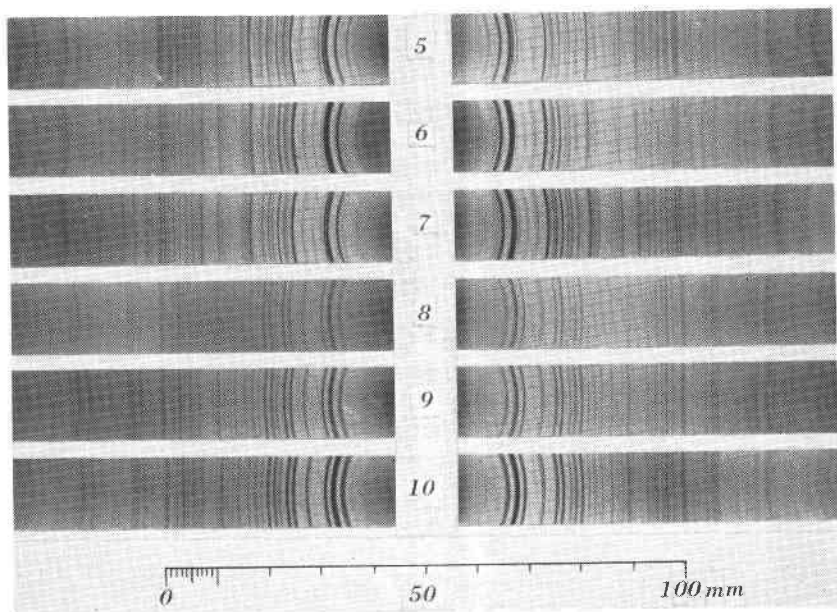
FIGS. 5–10. Rammelsbergite and pararammelsbergite; x-ray powder photographs with unfiltered copper radiation. Camera radius, $360/4\pi$ mm. Exposures, 0.7–1.0 KWH.

FIG. 5. Rammelsbergite, Schneeberg (material 1); the extra lines, as compared with FIGS. 6, 7, are the strong lines of native bismuth.

FIG. 6. Rammelsbergite, Eisleben (material 2); represents the material which gave the single crystal x-ray measurements.

FIG. 7. Rammelsbergite, Eisleben (material 3); represents the material used for analysis.

FIG. 8. Pararammelsbergite, Elk Lake (material 4); represents material used for single crystal x-ray measurements and analysis.

FIG. 9. Pararammelsbergite, Cobalt (material 5 a).

FIG. 10. Pararammelsbergite, South Lorrain (material 6).

A full discussion of the powder spectrum of parammelsbergite has been given by Peacock and Michener (1939); a similar presentation of the powder spectrum of rammelsbergite will be given here to assist in the future recognition of the mineral.[3]

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[3] The statement by De Jong (1926) that the cell sides of safflorite and rammelsbergite are the same as those of loellingite is misleading; one of us has likewise obtained the pattern of loellingite from materials labelled "safflorite" and "rammelsbergite"; these appear to be cobalt and nickel bearing varieties of loellingite.

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The powder photographs were taken with unfiltered copper radiation, the nickel in the mineral serving almost completely to suppress the β-diffractions. Camera radius $360/4\pi$ mm.

TABLE 3. RAMMELSBERGITE: X-RAY POWDER SPECTRUM

s	I_P	d (meas.)	hkl	d (calc.)	I_W
12.1 mm.	m	3.68 Å	011	3.68 Å	m
14.2	vw (β)	2.84	110	2.84	m (β)
14.8	vw	3.02	101	3.01	w
15.7	s	2.85	110	2.84	vs
17.5	s	2.56	111	2.55	s
18.2	s	2.47	012	2.47	vs
18.7	vw	2.40	020	2.39	s
20.45	w	2.21	021	2.21	s
21.8	vw (β)	1.875	121	1.872	m (β)
22.4	w	2.02	112	2.03	m
24.3	s	1.871	121	1.872	s
25.4	w	1.796	013	1.787	—
25.9	m	1.763	200	1.765	s
27.1	m	1.690	103	1.691	—
28.1	m	1.635	122	1.633	s
28.9	m	1.593	113	1.594	—
			211	1.592	s
30.2	m	1.530	031	1.536	vs
32.35	s	1.439	212	1.437	vs
34.1	vw	1.373	221	1.379	m
38.5	m	1.236	024	1.237	—
41.7	m	1.157	133	1.160	—
			231	1.159	s
43.35	w	1.121	311	1.121	m
44.6	w	1.096	232	1.095	s
45.9	w	1.071	115	1.071	—
			034	1.070	—
47.0	w	1.052	142	1.054	s
47.9	w	1.037	321	1.038	s
48.7	m	1.024	134	1.024	—
49.5	m	1.011	224	1.013	—
			233	1.008	—
51.1	vw	0.988	240	0.990	m
52.2	w	0.973	241	0.975	m
54.4	w	0.946	330	0.946	m
56.6	w	0.921	150	0.923	s
			044	0.921	—
61.0	w	0.879	400	0.883	m
			243	0.880	—
			152	0.879	w

TABLE 3 (*Continued*)

s	I_P	d (meas.)	hkl	d (calc.)	I_W
62.5	vw	0.867	126	0.866	—
67.5	w	0.832	216	0.833	—
			153	0.832	—
			251	0.832	m
			412	0.831	vs
			045	0.831	—
71.4	vw	0.811	017	0.814	—
			315	0.813	—
73.2	w	0.803	342	0.805	vs
			107	0.804	—
			136	0.803	—
76.5	w	0.791	117	0.793	—
			334	0.792	—
			413	0.791	—

Table 3 represents the Eisleben pattern, giving for each powder ring the half diameter as measured on the film (s mm.); the relative intensity of the powder ring by inspection (I_P); the planar spacing (d meas.) as given by $\theta = s - 0.05$ mm.; the indices of the set or sets of planes contributing to the ring (hkl); the planar spacings calculated from the lattice elements obtained from single crystal measurements (d calc.); the relative intensity of the Weissenberg spot (I_W), if in the range of the Weissenberg photographs taken.

COMPOSITION AND CELL CONTENT

One of the specimens from Eisleben (material 3) provided a sample which was analyzed by the International Nickel Company, giving the values under 1A in Table 4. Since the polished section showed very little impurity, apart from the carbonate gangue, the elements other than nickel and arsenic evidently enter into the structure of the rammelsbergite. From the cell volume (97.53 Å^3) and the measured specific gravity (6.97) the cell content closely approaches $Ni_2As_4 = 2[NiAs_2]$, with a small amount of cobalt in place of nickel as the only considerable extra constituent. An increase of about 1 per cent in the specific gravity, which is almost certainly on the low side due to intergrown calcite, would give exact agreement with the calculated specific gravity (7.05) of a crystal with the ideal composition Ni_2As_4 (3, Table 4).

The composition of rammelsbergite from Schneeberg is represented by three early analyses, all reporting substantial amounts of bismuth (2.19–5.11 per cent). The best of these analyses (2A, Table 4) also gives

TABLE 4. RAMMELSBERGITE: ANALYSES AND CELL CONTENTS

| | 1 | | 2 | | 3 | |
	A	B	A	B	A	B
Ni	24.58	1.74 ⎤	26.65	2.15	28.14	2
Co	2.86	0.20 ⎪	trace	—	—	—
Fe	0.03	0.00 ⎬ 1.98	2.06	—	—	—
Cu	0.56	0.04 ⎦	—	—	—	—
As	70.13	3.90 ⎤	68.30	3.97	71.86	4
Sb	0.48	0.02 ⎪	—	—	—	—
Bi	trace	— ⎬ 3.97	2.66	—	—	—
S	0.35	0.05 ⎦	trace	—	—	—
Gangue	1.45	—	—	—	—	—
	100.44		99.67		100.00	
G	6.97 (meas.)		7.23 (meas.) 7.16 (corrected for Bi)		7.05 (calc.)	

1. Eisleben, Thuringia; A—Anal. International Nickel Company; B—Atomic content of the structural cell, after deducting gangue.

2. Schneeberg, Saxony; A—Anal. Hilger (Dana, 1892, p. 101); B—Atomic content of the structural cell, after deducting all Fe as loellingite (7.59 per cent) and all Bi as native bismuth.

3. Ideal composition; A—Percentage composition; B—Atomic content of the structural cell.

2.06 per cent of iron. Since loellingite and native bismuth were noted in the polished section, a fair estimation of the cell content is obtained by withdrawing Fe as $FeAs_2$ and Bi as such, and using the specific gravity (7.16) obtained by appropriate correction of the measured value (7.23). The resulting cell content approaches Ni_2As_4 as nearly as we might expect, considering the uncertainties of the case. The excess of Ni over two atoms suggests, but hardly proves, that Ni may partly replace As in rammelsbergite as does Fe in substantial amount in loellingite.[4]

PARARAMMELSBERGITE

SUMMARY OF ESSENTIAL PROPERTIES

The properties of pararammelsbergite are as follows. Orthorhombic (or pseudo-orthorhombic); $a_0:b_0:c_0 = 0.988:1:1.963$ (from single crystal x-ray measurements). Habit, tabular {001}. Forms: c{001}, d{104}, e{304}, p{113}, q{112}. Apparent space group, $D_{2h}^{11} - Pbma$ or $C_{2v}^5 - Pb2a$. Cell edges, $a_0 = 5.74 \pm 0.01$, $b_0 = 5.81 \pm 0.01$, $c_0 = 11.405 \pm 0.03$ Å.

[4] Buerger (1932, p. 167).

Cell content $Ni_8As_{16} = 8[NiAs_2]$. Cleavage $\{001\}$, perfect and easy. Hardness E. Specific gravity 7.12 (meas.), 7.24 (calc.). Hand specimen tin-white, massive, in part minutely crystallized. Polished sections pure white, strongly anisotropic.

The composition is given by the three analyses in Table 5. Analysis 1 represents the material on which the specific data were obtained; analyses 2 and 3 are earlier analyses representing, as nearly as could be ascertained, the materials used for the powder photographs, figures 9, 10, and the polished sections described below. The high cobalt content in analysis 3 suggests that the analyzed sample contained even more smaltite than the specimens described here.

TABLE 5. PARARAMMELSBERGITE: ANALYSES

	1	2	3	4
Ni	28.1	27.08	17.46	28.1
Co	0.4	1.94	11.24	—
Cu	none	0.16	—	—
Fe	none	0.56	0.73	—
As	68.5	65.78	66.61	71.9
Sb	—	0.91	—	—
S	2.6	3.05	3.30	—
SiO_2	—	—	0.84	—
	99.6	99.48	100.18	100.0
G	7.12	7.02	6.73	7.24 (calc.)

1. Moose Horn Mine, Elk Lake, Gowganda, Ontario; anal. Rogers, in Peacock and Michener (1939).

2. Hudson Bay Mine, Cobalt, Ontario; anal. Todd, in Walker and Parsons (1921).

3. Keeley Mine, South Lorrain, Ontario; anal. Rickaby, in Walker (1925).

4. $NiAs_2$.

FURTHER OBSERVATIONS ON POLISHED SECTIONS

A further examination of polished sections of pararammelsbergite was made with a view to finding whether this mineral could be distinguished from rammelsbergite without the help of x-ray photographs. The observations given below confirm and supplement the brief descriptions already given in Peacock and Michener (1939).

Pararammelsbergite, like rammelsbergite, takes a fine polish and appears smoother and whiter than the associated white arsenides. The typical crystal shape is rectangular, representing transverse sections of

basal tablets. Anisotropism strong, but not as strong as in rammelsberg-
ite; twinning not observed in typical grains; hardness E, estimated,
with the steel needle. Etch reactions: HNO_3, effervesces and etches
rapidly brown to black; $FeCl_3$, etches quickly light to dark brown, bring-
ing out the texture; $HgCl_2$, slowly gives a brown to iridescent stain which
does not rub off; HCl, negative; KCN, negative; KOH, negative. In air
saturated with water vapour etching is already perceptible after four
hours; in twelve hours the surface is deeply etched; after a week white
and green bloom are formed. Pararammelsbergite appears to decompose
more rapidly than rammelsbergite in moist air.

Moose Horn Mine, Gowganda. The section consists almost wholly of
pararammelsbergite in a mosaic of interlocking grains (0.05 to 0.08 mm.).
Crossed nicols reveal no twinning. The polarization colours are russet
brown, light brown, yellow, gray; no blue colour was observed. The as-
sociated minerals are interstitial niccolite (about 2 per cent) and smaltite
(less than 1 per cent) in isolated grains and seams. The pararammels-
bergite shows no crystal outlines except in the larger niccolite areas
where rectangular outlines appear. These outlines lack the extreme
sharpness of the typical blades of rammelsbergite.

Hudson Bay Mine, Cobalt. Sections were made from three different
specimens. One of these consists almost entirely of pararammelsbergite
with granular texture, passing in places to a rudely radial arrangement of
sub-rectangular crystals. The associated minerals are smaltite, cobalt-
ite and gersdorffite (?) which tend to form rims outlining the reni-
form margin of the main mass of pararammelsbergite. Twinning is not
shown. The polarization colours are russet brown, brown, yellow, gray.

A section from another specimen (Fig. 11) shows a marked increase in
the amount of cubic minerals (smaltite and cobaltite) which surround
roughly elliptical areas (1–8 mm.) consisting largely of typical pararam-
melsbergite in untwinned, sub-parallel to radial tabular crystals ($0.5 \times$
0.05 mm.) with the normal polarization colours. Associated with the
pararammelsbergite there are some interstitial grains showing the sky-
blue polarization and lamellar twinning characteristic of the Schneeberg
rammelsbergite. The amount of this mineral is small and its identity with
rammelsbergite could not be proved.

In a section from the third specimen, the cubic minerals, together with
loellingite, constitute about one-half of the surface. Typical pararam-
melsbergite with the normal polarization colours occupies the centres of
spheroidal areas which are separated by the cubic minerals and loelling-
ite. The outer parts of the spheroidal areas are made up of a mineral
with sky-blue polarization and occasional lamellar twinning, which ap-
pears to have crystallized after the pararammelsbergite. This mineral

has the appearance of rammelsbergite, but again its identity could not be confirmed.

Keeley Mine, South Lorrain. The section (Fig. 12) shows a reniform structure, the central part consisting of pararammelsbergite while the rim is made up of smaltite and gersdorffite (?). Pararammelsbergite
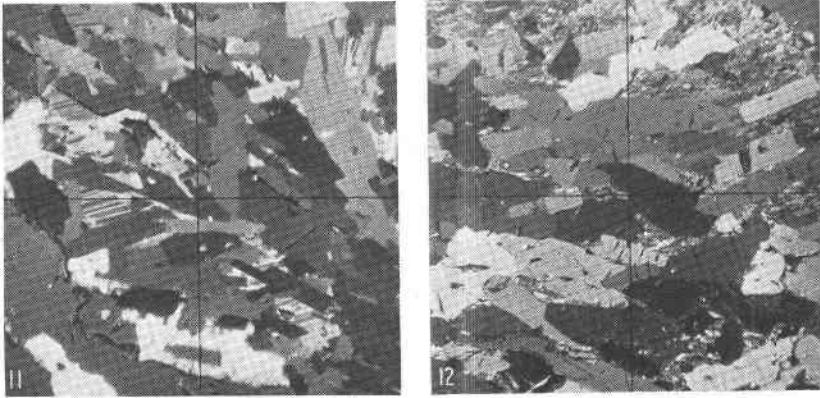

Fig. 11. Pararammelsbergite, Cobalt (material 5 *b*); untwinned tabular crystals with a few interstitial crystals of rammelsbergite (?) showing lamellar twinning. In the lower left is seen a part of the isotropic rim, enclosing gangue. Crossed nicols (×67).

Fig. 12. Pararammelsbergite, South Lorrain (material 6); sub-parallel untwinned tabular crystals with an interstitial mosaic of rammelsbergite (?) in the upper right. Crossed nicols (×67).

forms a granular mosaic passing outward into well formed, diverging, tabular crystals with the normal appearance. As the rim is approached an interstitial mineral appears in increasing amount in a fine grained (0.01–0.02 mm.) mosaic separating the well formed crystals of pararammelsbergite and clearly of later crystallization. This mineral shows slate-blue polarization reminiscent of the Eisleben rammelsbergite. In wet air an abundant green bloom formed on the pararammelsbergite; the mineral resembling Eisleben rammelsbergite etched deeply and turned black but showed no bloom.

Distinguishing characters. From the foregoing it is clear that rammelsbergite and pararammelsbergite have many characters in common; at the same time certain differences have emerged which may serve to distinguish these minerals in polished sections if positive identification by *x*-ray photographs cannot be made. The distinguishing characters are the following. Rammelsbergite typically forms bladed crystals which are almost invariable twinned; it gives blue polarization colours and is relatively slow to form bloom in a moist atmosphere. Pararammelsbergite

tends to form tabular crystals which are free from twinning; blue polarization colours are not characteristic, and the mineral is relatively prone to the formation of bloom in wet air.

The relation of the mineral resembling rammelsbergite to pararammelsbergite in several of the Canadian specimens indicates that rammelsbergite has the lower temperature of formation and is therefore the more stable modification. But since the identity of the later mineral could not be proved this indication is inconclusive.

THE NATURAL MODIFICATIONS OF $NiAs_2$

The recognition of pararammelsbergite, as distinct from rammelsbergite and chloanthite, would seem to bring the number of natural modifications of $NiAs_2$ up to three. However, the existence of a cubic mineral properly represented by the formula $NiAs_2$ is very doubtful. Chloanthite is commonly intergrown with smaltite, for which the formula $CoAs_2$ is generally given, in zoned cubic crystals physically very similar to skutterudite, whose composition approaches $CoAs_3$. Oftedal (1928) obtained practically identical x-ray measurements from skutterudite and smaltite-chloanthite[5] and found a structure in terms of $CoAs_3$; the composition $CoAs_2$ gave an irrational cell content. Although the bulk composition of smaltite-chloanthite commonly lies in the range (Co, Ni)-$As_{1.5-2.5}$, it would seem that this mineral is structurally the same as skutterudite with extensive and variable replacement of As by (Co, Ni). Furthermore the cell edge of the cubic mineral, $a_0 = 8.19 - 8.27$, shows no relation to the cell edges of the orthorhombic modifications. Rammelsbergite and pararammelsbergite thus appear to be the only well established natural modifications of nickel diarsenide.

[5] Recent work in this laboratory has confirmed these measurements.

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