

On maucherite (nickel-speiss, placodine, temiskamite).

(With Plate XXIV.)

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NICKEL-SPEISS (Nickelspeise), an impure arsenide of nickel obtained as a by-product in the manufacture of smalt, has long been known as a source of distinct crystals representing a definite chemical compound. Such crystals were already analysed by Döbereiner (1823), who concluded that the material was an artificial form of niccolite, NiAs. Later analyses showed that the composition of the crystallized furnace product approaches Ni_3As_2 , a compound unknown in nature at that time.

A substance corresponding to the crystallized nickel-speiss, but thought to be of natural origin, was first described by Breithaupt (1841), who named the material *Plakodin* (πλακώδης, broad) in allusion to the tabular habit of the crystals. These were said to have occurred in the Jungfer mine at Müsen in Westphalia, associated with chalybite and gersdorffite and to have been salvaged by a smalt-works official from a shipment of ores. Breithaupt stated that he possessed no attached crystals and was therefore obliged to rely wholly on the foregoing information regarding the origin of the material. Since nothing resembling placodine was subsequently found at the Jungfer mine, and the properties of the material agreed with those of the known smalt-works product, Breithaupt's species became discredited and identified with crystallized nickel-speiss.

Eventually this nickel arsenide was found as an undoubted mineral, associated with niccolite, chloanthite, bismuth, manganite, calcite, baryte, anhydrite, and gypsum, at Eisleben in Thuringia, and named maucherit by Grünling (1913), after W. Maucher, who had detected the new material. The material was crystallized as rectangular tablets; its composition was found to be close to Ni_3As_2 .

Almost simultaneously, Walker (1914) described a new nickel arsenide which occurred in important amounts in the form of rounded masses of radiated fibrous structure in calcite at the Moose Horn mine, Elk Lake, Temiskaming district, Ontario. An analysis of this material, named temiskamite by Walker, yielded the composition Ni_4As_3 .

Since the physical properties given for temiskamite are similar to those of maucherite and the chemical formulae ascribed to the two minerals are not very different, it has been suggested that the two substances are identical. Indirect evidence bearing on the chemical identity of the two materials was given by Palmer (1914), who deduced the formula Ni_4As_3 for both minerals from experiments involving the precipitation of silver by the nickel arsenides from an aqueous solution of silver sulphate. OrceI (1928) confirmed the physical identity of the two minerals in polished sections, but recommended the chemical formula Ni_3As_2 as the more probable composition. Since the original analyses of maucherite are inadequate and further analyses have not been made, it cannot be said that maucherite and temiskamite have been definitely identified or that either of the proposed compositions has been confirmed.¹

Material and Acknowledgements.

The suggestion that further work on maucherite and temiskamite might decide the uncertainties mentioned above came independently from Prof. A. L. Parsons (University of Toronto) and Dr. H. Berman (Harvard University). For the purpose of this work the following materials were assembled:

1. Maucherite (Royal Ontario Museum of Mineralogy), Eisleben, Thuringia, Germany (type locality). Three specimens, $1\frac{1}{4}$ – $5\frac{1}{4}$ inches, of the nearly pure massive mineral with attached baryte and carbonates. On some unbroken surfaces the maucherite occurs as meshworks of minute tabular crystals. These specimens provided single crystals for X-ray measurements and nearly pure material for an analysis.

2. Maucherite, Sudbury, Ontario. A slab of nearly pure material, $1\frac{1}{4}$ inches, and some clean fragments, picked from the concentrator. Similar material was used for an analysis.

3. Maucherite (Harvard Mineralogical Museum), 2600-foot level, Frood mine, Sudbury, Ontario. Two specimens, 2–3 inches, of massive material associated with pyrrhotine, chalcopyrite, pentlandite, and gangue.

4. Maucherite (Harvard Mineralogical Museum), Orford, Quebec. Minute imperfect crystals which had been separated from an association of chrome-garnet,

¹ For further details of previous work on nickel-speiss and placodine see Hintze (1904, p. 621); on maucherite and temiskamite see Hintze (1938, p. 347).

pyroxene, calcite, and millerite. These crystals had been doubtfully referred to rammelsbergite (NiAs_2) by Palache and Wood (1904) before maucherite was known.

5. Temiskamite (Royal Ontario Museum of Mineralogy), Moose Horn mine, Elk Lake, Temiskaming district, Ontario (type material). Several fine specimens, 1-5 inches, showing the characteristic rosettes with radiated fibrous structure, associated with niccolite and calcite.

Specimens 1 and 5 were kindly placed at my disposal by Prof. A. L. Parsons; specimen 2 by Dr. Harcourt of the International Nickel Company, Copper Cliff, Ontario; and specimens 3 and 4 by Prof. C. Palache. Dr. G. A. Harcourt also took an important part in the work, particularly in contributing the descriptions of the polished sections. Mr. C. E. Michener, now with the Company, assisted in working out the powder photographs. Dr. H. Berman kindly made a series of density measurements on his specially adapted micro-balance (1939).

Physical Properties.

On freshly broken surfaces maucherite and temiskamite are platinum-grey with a faint but distinct reddish hue and a bright metallic lustre. This colour is easily distinguished from the pure tin-white of rammelsbergite and the pale copper-red of niccolite. Exposed surfaces are often bronzy-yellow to dull coppery-red and consequently the tarnished material tends to resemble niccolite. The fracture is irregular, controlled by the state of aggregation, which ranges from granular to radial-fibrous. No cleavage was obtained from single crystals.

Measurements of specific gravity are assembled in table I, which includes the value calculated from the structural cell, published measured values, and new measurements on small selected fragments. The collected values show a satisfactory consistency, confirming the older

Table I. Maucherite (placodine, temiskamite): measured and calculated density.

Locality.	Density.	Weight of sample.	Observer.
—	8.04	—	Calculated
Artificial?	8.062	—	Breithaupt (1841)
(placodine)	7.988	—	Breithaupt (1841)
Sudbury	8.00	12.66 mg.	Berman
(maucherite)	7.89	16.57 mg.	Berman
Elk Lake	7.95	28.36 mg.	Berman
(temiskamite)	7.92	28.34 mg.	Berman
	7.901	—	Walker (1914)
Eisleben	7.83	—	Prantl, in Grünling (1913)
(maucherite)	7.77*	10.53 mg.	Berman

* Contained some visible intergrown carbonate gangue.

measurements and showing that there is no significant difference in the specific gravities of the materials named placodine, maucherite, and temiskamite.

Polished sections from materials nos. 1, 2, 3, 5, were examined with a view to verifying the specific properties given in the literature and ascertaining the degree of purity of the materials to be used for chemical analyses. In all the sections the maucherite or temiskamite is pinkish-grey, similar to cobaltite, and weakly but distinctly anisotropic. The polarization colours are dark grey to light grey. Numerous grains show twinning. The Talmage hardness, estimated with a steel needle, is E. The etch reactions are as follows: HNO_3 , effervesces instantly and stains black; HCl , negative; KCN , negative; FeCl_3 , slowly stains brown, bringing out the grain boundaries; KOH , negative; HgCl_2 , slowly stains brown.

In a section from the Eisleben material (no. 1) the ore mineral consists almost wholly of maucherite with less than 1% of niccolite which encloses white, anisotropic grains (0.1 mm. in diameter) of a soft bismuth-bearing mineral amounting to about 1%. The Sudbury material (no. 2) showed up to about 5% of chalcopyrite and 2% of silicates. In the Sudbury specimens (no. 3) the maucherite is associated with about 10–15% of pyrrhotine, 3–4% of chalcopyrite, and 1% of pentlandite. In the Elk Lake temiskamite (no. 5) etching with HNO_3 brings out fine hair-like stringers of a white mineral intergrown with the fibrous temiskamite and unaffected by the acid; FeCl_3 reveals the same structure.

These observations agree substantially with recent standard descriptions (Schneiderhöhn and Ramdohr, 1931, p. 227; Short, 1934, p. 22), confirming the anisotropism which was definitely noted by Orcel (1928) but rarely observed by Schneiderhöhn and Ramdohr. As stated by Orcel, maucherite and temiskamite are alike in the specific properties observable in polished sections.

Chemical Composition.

Samples of the materials from Eisleben (no. 1) and Sudbury (no. 2) were analysed for comparison with previous analyses of maucherite and temiskamite.¹ As shown in table II the new analyses (I, III) closely

¹ These analyses presented unexpected difficulties. It was found that the constituents other than arsenic could be reliably determined only after arsenic had been completely removed by prolonged distillation.

resemble the old ones (II, IV, V) in their main constituents. Cobalt and a small amount of sulphur appear to enter the composition of the mineral; the remaining reported constituents may be referred to the observed associated minerals. A discussion of these analyses will be given in connexion with the determination of the atomic content of the structural cell.

TABLE II. Maucherite and temiskamite: chemical analyses.

	I.	II.	III.	IV.	V.
Ni	49.96	49.07	50.03	49.51	52.71
Co	0.20	1.73	0.84	0.93	2.15
Fe	0.84	—	trace	—	0.40
Cu	0.69	—	0.13	—	—
Pb	—	—	—	—	0.20
As	45.88	46.34	45.90	45.66	43.67
S	0.97	1.03	0.18	—	0.17
Bi	—	0.55	—	—	—
H ₂ O	0.36	—	—	—	—
Gangue	0.32	—	1.66	—	0.40
	<u>99.22</u>	<u>98.72</u>	<u>98.74</u>	<u>(96.10)</u>	<u>99.70</u>

- I. Maucherite, Sudbury, Ontario; analyst, International Nickel Company.
 II. Temiskamite, Moose Horn mine, Elk Lake, Ontario; analyst, Walker (1914).
 III. Maucherite, Eisleben, Thuringia, Germany; analyst, International Nickel Company.
 IV. Maucherite, Eisleben; analyst, Friedrich (in Grünling, 1913).
 V. Maucherite, Eisleben; analyst, Prantl (in Grünling, 1913).

Geometrical crystallography.

According to previous descriptions crystals of maucherite and the corresponding artificial material are tetragonal or pseudo-tetragonal, ranging in habit from tabular (001) to bipyramidal (*hhl*). The basal planes are sometimes of good quality; the pyramidal planes are always more or less striated parallel to the base.

Artificial crystals (nickel-speiss) were described by Rose (1833), who figured combinations of tetragonal bipyramids (*hhl*) with the basal pinakoid (001). Breithaupt (1841) interpreted his tabular crystals of placodine as monoclinic (pseudo-tetragonal) with a broad side pinakoid bevelled by forms (*hk0*) and (*Ok*l). Braun (1879) reverted to the tetragonal interpretation of placodine. Rosati (1914) confirmed the tetragonal character of placodine and natural maucherite from Eisleben and showed that the two materials are substantially alike in crystal form and chemical composition. Goldschmidt (1920, p. 13) gave a correlation of these descriptions, adopting the tetragonal notation of Braun and Rosati.

Since our crystals of maucherite appear to be poorer than the best

that have been measured in the past it will be useful first to consider the results obtained by Rosati, whose work supersedes the earlier observations. With reference to tetragonal elements his axial ratios are:

$$a:c = 1:1.0780 \text{ (maucherite)} \\ 1:1.1185 \text{ (placodine).}$$

Before the X-ray measurements were undertaken an attempt was made to find the crystal lattice from Rosati's form list (table III). The simplest indices, and the nearest approach to a normal harmonic-arithmetic series (Peacock, 1937), were obtained by assigning the indices (102) to the plane (111) of the old notation. The geometrical lattice thus obtained was found to correspond to the preferred structural lattice. The reversible transformation formulae are:

$$\text{Rosati to Peacock: } (\frac{1}{2}\frac{1}{2}0)/(\frac{1}{4}\frac{1}{4}0)/(001) \\ \text{Peacock to Rosati: } (220)/(220)/(001)$$

TABLE III. Maucherite and placodine: forms and angles.

Tetragonal; $a:c = 1:3.190$.

Forms.		ρ (measured) Rosati.		ρ (calc.).	
Peacock.	Rosati.	Maucherite.	Placodine.	Peacock.	
$c(001)$	$c(001)$	—	(4)	— (6)	$0^{\circ}00'$
$u(103)$	$u(223)$	$46^{\circ}47'$	(1)	$46^{\circ}24' - 46^{\circ}52'$	(4) $46\ 45\frac{1}{2}$
$p(205)$	$p(445)$	—	(—)	$51\ 45 - 51\ 54$	(2) $51\ 55$
$o(102)$	$o(111)$	—	(—)	$57\ 07 - 58\ 54$	(21) $57\ 55$
$?(508)$	$d(554)$	—	(—)	$62\ 42$	(1) $63\ 22$
$v(203)$	$v(443)$	$64\ 12 - 65^{\circ}14'$	(2)	$64\ 03 - 65\ 00$	(4) $64\ 49$
$?(506)$	$e(553)$	—	(—)	$69\ 52$	(1) $69\ 23$
$l(101)$	$l(221)$	$72\ 35$	(1)	$72\ 54$	(2) $72\ 35\frac{1}{2}$
$g(504)$	$g(552)$	$74\ 24 - 75\ 34$	(3)	$74\ 32 - 74\ 56$	(4) $75\ 55\frac{1}{2}$
$h(302)$	$h(331)$	$77\ 12 - 78\ 01$	(10)	$77\ 48$	(1) $78\ 12$
$k(201)$	$b(441)$	$81\ 00 - 81\ 30$	(2)	$80\ 46 - 81\ 18$	(3) $81\ 05\frac{1}{2}$
$q(301)$	$q(661)$	$82\ 56 - 84\ 15$	(2)	—	(—) $84\ 02$

The figures in brackets give the number of times each form was observed by Rosati on maucherite and placodine. The forms $x(11.11.12)$ and $i(887)$, noted on placodine by Braun but not confirmed by Rosati, are neglected.

Table III shows the two sets of form symbols and Rosati's range of measurements compared to the angles calculated from the structural axial ratio. Only d and e , each noted only once on placodine, with poor agreement between the calculated and measured angles, have somewhat complex symbols in the new notation. The calculated angles, $\rho = (001): (h0l)$, lie for the most part within the measured range. Rosati's transformed elements compare with the structural ratio as follows:

$$a:c = 1:3.049 \text{ (maucherite, Rosati)} \\ 1:3.164 \text{ (placodine, Rosati)} \\ 1:3.190 \text{ (maucherite, Peacock).}$$

In view of the striated condition of the crystals the structural ratio is in this case considered to be more reliable than the geometrical ratios.

The observed forms of maucherite and placodine all lie in one zone. Neglecting the forms (508) and (506), which may be considered doubtful, the projection points in the zone have the following gnomonic distances h/l from the pole (001):

	<i>c</i>	<i>t</i>	<i>p</i>	<i>o</i>	<i>v</i>	<i>l</i>	<i>g</i>	<i>h</i>	<i>k</i>	<i>q</i>
	(001)	(103)	(205)	(102)	(203)	(101)	(504)	(302)	(201)	(301)
<i>p</i> ...	0	$\frac{1}{3}$		$\frac{1}{2}$		1	—		2	3
<i>s</i> ...	0		$\frac{2}{3}$	$(\frac{3}{4})$	$\frac{3}{4}$	$(\frac{3}{2})$	—	$\frac{3}{2}$		

Except for $g(504)$ all the points in the zone lie in the primary (*p*) and secondary (*s*) harmonic-arithmetic series (Peacock, 1937) which follow rigorously from the classical law of Bravais as applied to a simple lattice.

Following Donnay and Harker (1937) and Donnay (1938), who generalized the law of Bravais by showing the relation between form importance and lattice-plane spacing as given by indices conforming to the space-group conditions, we may obtain further information from this zone: (1) lack of systematically weak or absent forms ($h0l$) indicates lack of extinctions in ($h0l$); (2) the absence of (100) as a form suggests that the indices are (200), as required by a screw-axis 2_1 ; (3) since the form (001) is not always dominant, although $a:c = 1:3.190$, the indices may be (002) or (004), resulting from screw-axes 4_2 or $4_{1,3}$. Actually the X-ray extinctions confirm (1), (2), and the second alternative of (3).

The zone ($h0l$) offers, however, an alternative choice of lattice, namely with *k* as (101) giving $a:c = 1:6.380$. The zone series then reads:

	<i>c</i>	<i>t</i>	<i>p</i>	<i>o</i>	<i>v</i>	<i>l</i>	<i>g</i>	<i>h</i>	<i>k</i>	<i>q</i>
	(001)	(106)	(105)	(104)	(103)	(102)	(508)	(304)	(101)	(302)
<i>p</i> ...	0	$\frac{1}{6}$	$\frac{1}{5}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$	—	—	1	—

Seven terms lie in the primary series, three in higher series. Again the absent form (100) indicates the indices (200), while the base is probably (004) in view of the axial ratio. This lattice corresponds to a well-marked pseudo-cell shown by the X-ray photographs; but the general extinction condition for the pseudo-cell, ($h+k+l$) even, does not show in the zone series. It is remarkable that the morphology should offer two choices of crystal lattice, both of which are revealed by the X-ray photographs.

The material available for the present study adds little to the foregoing account of the morphology of maucherite. The crystals on one specimen from Eisleben are minute basal tablets with rectangular or square outlines. The base gives a fair reflection permitting polar adjustment on the two-circle goniometer. The striated edge faces give trains

of feeble signals without reliable single reflections. These trains show, however, that the edges of the tablets are strictly rectangular.

The crystals from Orford, which had been doubtfully referred to rammelsbergite by Palache and Wood (1904, p. 358), gave an X-ray powder photograph identical with that of maucherite from Eisleben. These crystals were described as minute and deeply striated, not permitting satisfactory measurements. They yielded a provisional orthorhombic axial ratio:

$$a:b:c = 0.5722:1:1.1545$$

Approximate correspondence with the lattice of maucherite is obtained with the following correspondence of planes:

Palache and Wood.	Peacock.
(010)	(001)
(014)	(101)
(210)	(011)

The reversible transformations are:

$$\begin{aligned} \text{Palache and Wood to Peacock: } & (00\frac{1}{2})/(\frac{1}{2}00)/(010) \\ \text{Peacock to Palache and Wood: } & (020)/(001)/(400) \end{aligned}$$

Thus transformed the elements of Palache and Wood give pseudo-tetragonal values roughly similar to those of maucherite:

$$\begin{aligned} a:b:c &= 1.009:1:3.495 \text{ Palache and Wood} \\ a:a:c &= 1:1:3.190 \text{ Peacock} \end{aligned}$$

The form symbols¹ correspond as follows:

Palache and Wood	(010)	(120)	(110)	(210)	(014)	(013)	(012)	(021)	(102)	
Peacock	c(001)	-o(14)	o(012)	l(011)	l(101)	-o(304)	o(102)	-l(108)	-l(110)

Five of Palache and Wood's forms thus correspond to known forms of maucherite; the remaining four are new, but they cannot be regarded as established, since the material did not yield reliable measurements.

A few of the Orford crystals were examined in the hope of obtaining better measurements. In the new setting they have the appearance of tetragonal bipyramids combined with the base. The striations and general imperfection of the crystals do not permit good measurements. However, 17 reflections were noted on pyramidal planes, with a range, $\rho = (001):(h0l) = 70^\circ 15' - 74^\circ 40'$. Some of the best of these gave $72^\circ 27'$, $72^\circ 29'$, $72^\circ 30'$, $72^\circ 30'$, $72^\circ 30'$, $72^\circ 43'$, average $72^\circ 31\frac{1}{2}'$; calculated for $l(101)$, $\rho = 72^\circ 35\frac{1}{2}'$. The crystals are thus essentially combinations of $c(001)$ and $l(101)$, with other weak forms ($h0l$). A

¹ Correction: In Palache and Wood (1904, p. 359; 1905, p. 18), for $\infty 2$ 120 read 2∞ 210, and vice versa.

search for better material might lead to a more exact description of the Orford crystals, which represent the only known occurrence of distinctly crystallized maucherite in Canada.

The Orford material presents a feature which has evidently been noted before, namely a lack of strict equivalence in adjoining zones of pyramidal planes, [100] and [010]. The plane (011) may be large and bright while (101) is narrow and dull; the axes [100] and [010] appear to be 2-fold axes. This symmetry is in keeping with Breithaupt's monoclinic description (with $\beta = 90^\circ$) and with Palache and Wood's orthorhombic treatment. It is also indicated in Braun's drawing of a placodine crystal (1879, p. 423) which shows unlike forms in adjacent zones. On the other hand, it is not possible to interpret the X-ray effects on a crystal from Eisleben with reference to symmetry lower than tetragonal. An explanation may lie in the fact that maucherite apparently has a defect structure as shown later. In some crystals the vacant positions might be systematically arranged, leading to a reduction of symmetry.

Twinning.—On the specimen from Eisleben the crystals of maucherite are frequently intergrown in a regular manner, two individuals meeting obliquely in a common edge [010], often with complete interpenetration. Twinning was also noted in the polished section. From approximate measurements Rosati (1914) found two laws: twin-plane (203), common; also twin-plane (102) (new notation). We are unable to verify these laws. On several twins the angle [100]:[100]' varied from 54° to 58° , as measured on the microscope. The angle (001):(tw.-pl.) is therefore 27° – 29° . The calculated angle (001):(106) is $28^\circ 00'$. The quasi-normal plane, which might be considered the twin-plane, is (407), giving the calculated angle (001):(407) = $61^\circ 15' = 90^\circ - 28^\circ 45'$. This plane lies between (102) with $\rho = 57^\circ 55'$ and (203) with $\rho = 64^\circ 49'$. While these observations indicate that the twin-plane is (106) confirmation of the twin-law on better material is clearly necessary.

Structural crystallography.

Preliminary observations on the structure of maucherite and the laboratory compound Ni_3As_2 were given by Laves (1935), who obtained single-crystal diffraction effects indicating a tetragonal structure with a 3.45, c 21.7 Å, associated with a two-dimensional (diperiodic) superstructure with $a' = 2a = 6.9$ Å.¹ The smaller cell was defined by

¹ These data appear to have been overlooked by the reviewers; the writer found them on searching the literature for work on random structures, after he had found striking evidence of randomness in a series of photographs on maucherite.

normal sharply resolved spots; the presence of the superstructure was indicated by streaks of continuous diffraction with indices h and k determinate with reference to a , l indeterminate. Laves did not consider the space-group or the cell-content or the details of the structure, which required further investigation.

Using squarish tablets of maucherite from Eisleben (material no. 1) and a camera with radius 28.63 mm. the writer made the following X-ray photographs with unfiltered copper radiation: rotation about an edge of the tablet [100] or [010]; equi-inclination Weissenberg photographs of the zero, first, and second layer-lines about the same axis; rotation about the normal to the tablet [001]; equi-inclination Weissenberg photographs of the zero, first, second, third, and fourth layer-lines about the same axis. Powder photographs were also made on the materials nos. 1, 2, 4, 5.

These photographs serve to confirm and amplify the preliminary results of Laves. The projections conform to the Laue symmetry $4/m\bar{m}m$, which includes the classes $\bar{4}2m$, $4mm$, 422 , $4/m\ 2/m\ 2/m$. Nearly all the sharply resolved spots, and all the powder lines, can be indexed with reference to a tetragonal lattice:

$$a = 3.422 \pm 0.005, c = 21.83 \pm 0.05 \text{ \AA}.$$

The streaks of continuous diffraction appear as intercalated layer-lines in the rotation photograph about [100] and intercalated Weissenberg curves in the Weissenberg photographs about the same axis. The streaks may be given integral indices h , k only with $a' = 2a = 6.844 \pm 0.01 \text{ \AA}$. In the rotation photograph about [001] the continuous diffractions show as intercalated row-lines (Bernal curves) with l indeterminate; in the Weissenberg photographs about [001] the streaks intersect the slot of the layer-line screen, appearing as weak rectangular spots, visibly different from the normal sharp diffractions. Complete indexing of the photographs about [001] requires the larger value of the a -period. In view of the fact that the continuous diffractions do occasionally resolve into definite spots which demand the larger a -period, particularly in the third layer-line of the rotation photograph about [100], we prefer to define the lattice of maucherite with the values:

$$\begin{aligned} a &= 6.844 \pm 0.01; c = 21.83 \pm 0.05 \text{ \AA}; \\ a:c &= 1:3.190; V = 1023 \text{ \AA}^3. \end{aligned}$$

and to consider the cell with $a/2$ and $V/4$ as a pseudo-cell.

With reference to the elements of the pseudo-cell the sharply resolved spots conform to the conditions:

(hkl)	present only with $h+k+l = 2n$
(hhl) $2h+l = 4n$
$(hk0)$ $h = 2n$ and $k = 2n$
$(00l)$ $l = 4n$

These conditions conform to the general extinctions of the space-group $I4/amd = D_{4h}^{19}$, with $(00l)$ present only with $l = 4n$ as an extra and unexplained condition.

On the elements of the full cell all the diffraction effects conform to the conditions:

(hkl)	present in all orders
$(hk0)$
$(0kl)$
(hhl)	present only with $h = 2n$
$(h00)$ $h = 2n$
$(00l)$ $l = 4n$

These conditions conform to the general extinctions of the enantiomorphic space-groups $P4_12_1 = D_4^4$ and $P4_32_1 = D_4^8$, with (hhl) present only with $h = 2n$ as an extra and unexplained condition.

From the foregoing it would appear that the partially random structure of maucherite is not subject to the normal procedure of finding the space-group symmetry from the systematic extinctions; but further consideration of this problem will not be given here.

Powder photographs.

X-ray powder photographs proved indispensable in identifying the materials used in the present work. Identical patterns were obtained from maucherite from Eisleben (no. 1), maucherite from Sudbury (no. 2), maucherite (previously named rammelsbergite) from Orford (no. 4), and temiskamite from Elk Lake (no. 5). In view of the usefulness of such patterns, especially for opaque minerals, the maucherite pattern has been completely indexed with reference to the elements of the pseudo-cell (table IV). As expected, the continuous diffractions, which require the elements of the full cell, do not resolve as powder lines, since they are indeterminate in one index, l .

TABLE IV. Maucherite: powder diagram.

<i>I</i> p.	<i>s</i> mm.	<i>d</i> (meas.) Å.	(hkl) .	<i>I</i> w.	<i>d</i> (calc.) Å.
w	15.05β	2.72	(008)β	m	2.73
s	16.75	2.70	(008)	s	2.73
w	19.2	2.36	(112)	s	2.36
vw	20.3β	2.02	(116)β	m	2.02
s	22.6	2.02	(116)	s	2.02
vw	23.05	1.979	(019)	s	1.979

TABLE IV (continued).

<i>I</i> <i>p</i> .	<i>s</i> mm.	<i>d</i> (meas.) Å.	(<i>hkl</i>).	<i>I</i> <i>w</i> .	<i>d</i> . (calc.) Å.
m	24.15β	1.711	(020)β	m	1.711
w	25.2	1.819	(0.0.12)	s	1.819
s	26.8	1.717	(020)	s	1.711
w	28.5	1.621	(1.1.10)	m	1.621
w	30.85	1.508	(0.1.13)	s	1.508
s	32.3	1.447	(028)	s	1.460
vw	34.55	1.362	(0.0.16)	s	1.364
vw	36.55	1.297	(129)	w	1.294
vw	38.4	1.243	(0.2.12)	m	1.246
m	39.6	1.211	{(220)	m	1.210
			{(1.2.11)	m	1.212
m	43.0	1.131	(1.2.13)	m	1.131
m	44.35	1.104	(228)	—	1.106
m	45.5	1.081	(1.1.18)	s	1.084
w	46.4	1.065	(0.2.16)	s	1.067
w	47.75	1.042	(136)	s	1.037
vw	51.3	0.988	(0.3.11)	m	0.989
w	52.6	0.970	(1.3.10)	s	0.970
w	54.9	0.942	(0.3.13)	m	0.944
vw	56.25	0.927	(235)	—	0.929
vw	57.4	0.914	(0.1.23)	s	0.916
w	58.4	0.904	(2.2.16)	—	0.905
w	60.05	0.889	(1.3.14)	s	0.889
w	63.8	0.858	(040)	s	0.855
vw	65.35	0.847	(1.3.16)	s	0.848
w	68.6	0.827	(141)	w	0.829
w	70.3	0.817	(048)	s	0.816
w	72.5	0.807	(0.3.19)	s	0.809
w	73.6	0.802	(0.2.24)	s	0.799

The powder photographs were made with unfiltered copper radiation, the nickel of the mineral suppressing most of the β -lines. Camera radius, 28.63 mm. The table gives for each powder ring: the estimated relative intensity of the powder ring (*I**p*); the half-distance between the two branches as measured on the films (*s* mm.); the corresponding spacing (*d* meas.) using $s - 0.2 \text{ mm.} = \theta^\circ$; the indices of the corresponding set of lattice planes (*hkl*); the estimated relative intensity of the corresponding Weissenberg spot, if observed (*I**w*); the spacing calculated from the indices (*hkl*) and the elements $a = 3.422$, $c = 21.83$ (*d* calc.). The generally very good agreement between *d* (meas.) and *d* (calc.) shows that the powder lines are correctly identified, at least in the great majority of cases. The correspondence between *I**p* and *I**w* is not so close, even when the equivalence factor is applied to *I**p*. This is due to the fact that the Weissenberg photographs were all strongly exposed to bring out the weak continuous diffractions; consequently spots marked *s* are all black, concealing any differences of intensity. Where *I**w* is marked with a dash the indices are not in the range of the Weissenberg photographs taken.

Atomic content of the structural cell.

In view of the uncertainty attached to the empirical formula of maucherite and temiskamite it is essential that the cell-contents be

determined without reference to supposed simple rational proportions. For this purpose three analyses are available (analyses I, II, III of table 2) representing materials from Sudbury, Elk Lake, and Eisleben, whose physical properties and identical powder photographs have been described above.

TABLE V. Maucherite and temiskamite: atomic content of the pseudo-cell.

	I (Sudbury).		II (Elk Lake).		III (Eisleben).		Ideal.	
	A.	B.	A.	B.	A.	B.	A.	B.
Ni ...	51.75	10.93	49.99	10.49	51.54	10.65	51.85	11
Co ...	0.21	0.04	1.76	0.37	0.86	0.18	—	—
Fe ...	0.24	0.05	—	—	—	—	—	—
Cu ...	—	—	—	—	0.13	0.02	—	—
As ...	47.52	7.86	47.20	7.76	47.28	7.66	48.15	8
S ...	0.28	0.11	1.05	0.40	0.19	0.07	—	—
	100.00		100.00		100.00		100.00	
Sp.gr....	8.00		7.95		7.83		8.04	

Columns I A, II A, III A represent analyses I, II, III of table II reduced to the sum of 100% after withdrawing the impurities. Columns 1 B, 2 B, 3 B give the corresponding atomic contents of the pseudo-cell (quarter cell) with the volume $1023/4 \text{ \AA}^3$. In each case the highest (most probable) measured density has been used, without correction for impurities. Such a correction would be hardly significant in the case of I and II; in the case of III, Prantl's value was taken instead of Berman's, which was evidently slightly affected by light impurities.

As shown in table V the pseudo-cell contains $\text{Ni}_{11}\text{As}_8$ in which some cobalt takes the place of nickel and some sulphur replaces arsenic. The proportion 11:8 (1.375) lies between the 3:2 (1.5), the proportion proposed for maucherite by Grünling (1913) and generally accepted for the artificial crystal, and 4:3 (1.333), the proportion derived by Walker (1914) for temiskamite. In view of the tetragonal symmetry it is probable that the content of the pseudo-cell should be written $\text{Ni}_{12-1}\text{As}_8$ or $4[\text{Ni}_3\text{As}_2] - \text{Ni}$ indicating a defect structure in which one Ni-position is vacant. The content of the full unit cell would then be $\text{Ni}_{48-4}\text{As}_{32}$ or $16[\text{Ni}_3\text{As}_2] - 4\text{Ni}$.

This defective cell-content may be related to the partial randomness of arrangement indicated by the X-ray photographs. Since our photographs are almost exactly like those of Laves, who found that the evidence of randomness was present both in natural and artificial crystals, it would appear that the defective cell-content is characteristic of the mineral. Our work points to four vacant positions in the unit cell, a reasonable number in a structure with tetragonal symmetry; on the other hand, this number might vary in different crystals producing

appreciable variations in the bulk composition of the mineral. In that case the content of the structural cell would be written less specifically as $\text{Ni}_{48-n}\text{As}_{32}$ or $16[\text{Ni}_3\text{As}_2] - \text{Ni}_n$.

Summary.

A physical, chemical, and preliminary structural study of maucherite (Grünling, 1913) from Eisleben, Thuringia, and Sudbury, Ontario, and temiskamite (Walker, 1914) from Elk Lake, Ontario, shows that these materials have identical specific properties and therefore represent a single mineral species. Previous observations on the artificial crystals and on placodine (Breithaupt, 1841) leave no doubt that these substances are identical with the natural mineral. While admitting the possibility that Breithaupt described natural material, and giving credit to Walker for his independent discovery of the species, it is proper, and in keeping with the present usage, to retain the name maucherite for this mineral. The new observations lead to the following characterization of maucherite:

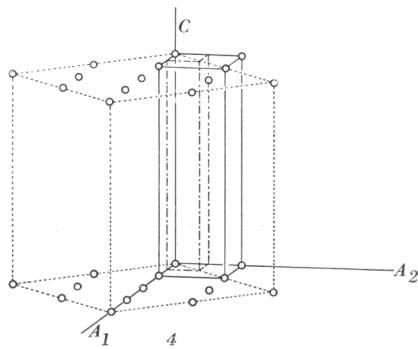
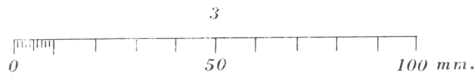
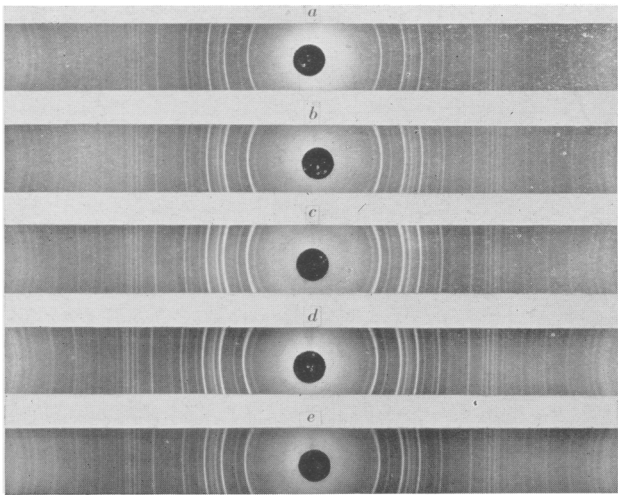
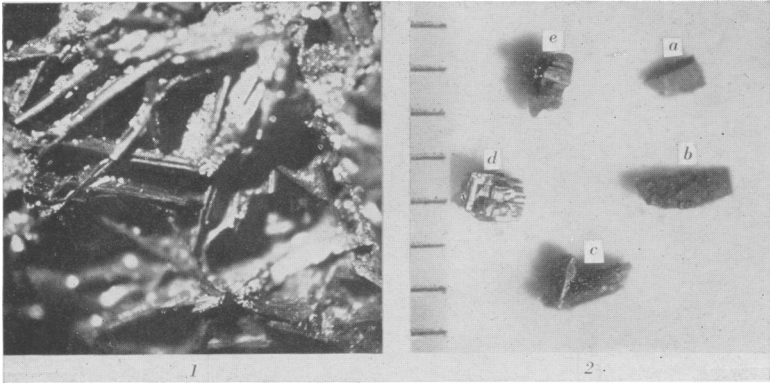
Tetragonal; $a:c = 1:3.190$ (from X-ray measurements). Forms: $c(001)$, $t(103)$, $v(203)$, $l(101)$, $g(504)$, $h(302)$, $k(201)$, $q(301)$. Habit, tabular (001) to bipyramidal (101); also radial-fibrous and granular. Twinning common, on (106)? Structure cell, $a\ 6.844 \pm 0.01$, $c\ 21.83 \pm 0.05$ Å.; contains $\text{Ni}_{44}\text{As}_{32} = 16[\text{Ni}_3\text{As}_2] - 4\text{Ni}$; a well-marked pseudo-cell has $a' = a/2$, $c' = c$, and contains $\text{Ni}_{11}\text{As}_8 = 4[\text{Ni}_3\text{As}_2] - \text{Ni}$. Cleavage not observed. Talmage hardness, E. Specific gravity, 8.00 (measured on best material), 8.04 (calculated). Fresh surfaces reddish platinum-grey, with bright metallic lustre. Polished sections pinkish-grey, weakly anisotropic. Two new chemical analyses are given.

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EXPLANATION OF PLATE XXIV.

- FIG. 1. Maucherite; Eisleben, Thuringia. Nest of elongated tabular crystals with small adhering crystals of niccolite. Scale as in figure 2.
- FIG. 2. Maucherite; (a) and (b), single crystals from Eisleben, flattened on (001) and elongated along [100]; (c), twin-crystal from Eisleben; (d) and (e), imperfect crystals from Orford, Quebec. Scale divisions, 0.5 mm.
- FIG. 3. Maucherite; X-ray powder photographs with unfiltered Cu-K radiation. Camera radius, $360/4\pi$ mm. Exposures, 0.3–0.6 KWH. (a), Eisleben; (b), Eisleben ('rammelsbergite'); (c), Sudbury, Ontario; (d), Elk Lake, Ontario ('temiskamite'); (e), Orford, Quebec ('rammelsbergite?').
- FIG. 4. Maucherite; crystal lattice. Structural cell in full lines; pseudo-cell in chain-dotted lines; previously used geometrical cell in dotted lines.
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M. A. PEACOCK: MAUCHERITE.