

THE STRUCTURAL LATTICE OF HESSITE¹

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ABSTRACT

Artificial crystals of hessite, formed from aqueous alkaline sulphide solutions at moderate temperatures, are of three types:

Type I. Orthorhombic, with probable space group *Immm*. The unit cell, with $a=16.27$, $b=26.68$, $c=7.55\text{Å}$; $a:b:c=0.610:1:0.283$ contains 48 $[\text{Ag}_2\text{Te}]$. Specific gravity 8.35 calculated, 8.41 measured on natural hessite (Thompson 1949). The crystals are small (0.2 to 0.3 mm.) and show the forms: $b(010)$ $a(100)$ $m(110)$ $n(120)$ $l(130)$ $k(150)$ $d(011)$ $s(132)$ $o(121)$ $r(141)$ (161) $p(211)$ $q(231)$ with axial ratio from two circle measurements: $a:b:c=0.599:1:0.284$.

Type II. Orthorhombic crystals showing the forms $c(001)$ $a(100)$ $l(120)$ $m(110)$ $n(320)$ $d(011)$ $p(111)$ with axial ratio from two circle measurements: $a:b:c=0.776:1:0.650$.

Type III. Rough cubic crystals modified by the forms $o(111)$ and $d(011)$.

Type II and the cubic crystals do not give single crystal x -ray photographs but give the same x -ray powder photograph as Type I crystals and natural hessite. At 155°C . Ag_2Te is isometric with $a=6.64\text{Å}$ and cell content $4[\text{Ag}_2\text{Te}]$.

Hessite occurs in hydrothermal veins with other tellurides and gold. In Canada it has been recognized in polished sections and by x -ray powder photographs, usually as small anhedral grains or compact masses, from numerous localities (Thompson 1949). Hessite has been described in highly modified, distorted cubic or pseudocubic crystals from Botés, Roumania and Boulder County, Colorado. In polished section hessite shows twinning lamellae which disappear at 149.5°C ., the mineral also becomes isotropic above this temperature (Dana, 1944). On the basis of the morphology the crystals have been described as triclinic, orthorhombic, rhombohedral or monoclinic by different authors. Ramsdell (1925) showed that the x -ray pattern of hessite is not isometric. Rahlfs (1936) obtained an isometric powder pattern for artificial Ag_2Te at elevated temperature.

Tokody (1932, 1934) obtained monoclinic crystal lattice dimensions from powder photographs and one rotation photograph about the cube edge of a relic isometric form. Thompson (1949) reports that the x -ray powder pattern will not index with the elements given by Tokody. Koern

¹ Extracted from an unpublished M.Sc. thesis by J. F. Rowland: An x -ray study of gold and silver tellurides—*Queen's University* 1950. This work was carried out with the aid of a bursary from the National Research Council (Canada) 1948-49, and is published with the permission of the Council, and with permission of the Director-General of Scientific Services, Department of Mines and Technical Services, Ottawa, Canada.

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(1939) reports in abstract that Ag_2Te can be formed in two modifications and gives orthorhombic crystal lattice dimensions for the lower temperature form which show some similarity to the monoclinic elements of Tokody.

SYNTHESIS OF HESSITE

Direct fusion of silver and tellurium, in vacuo, in the proportions 2:1 results in homogeneous material (Thompson, 1946, 1948), which gives the same x -ray powder pattern as natural hessite.

During a study of the synthesis of gold and silver tellurides from aqueous solutions (Rowland, 1950), crystals of hessite were obtained. The x -ray powder photograph of these crystals is identical with the pattern of natural material. The crystals were synthesized from aqueous alkaline sodium sulphide solutions in a graphite lined steel bomb as devised by Smith (1947) and used by Robinson (1948). Hessite was identified in the products of five bomb runs. The composition of the charges and the conditions are shown in table 1.

TABLE 1. HESSITE: BOMB CHARGES AND PRODUCTS

No.	Charges				Conditions		Products
	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	Ag	Te	H_2O	Time	Max. Temp.	
1	10 g.	0.5 g.	0.6 g.	20 cc.	3 days	400° C.	Hessite
2	40 g.	0.5 g.	0.6 g.	20 cc.	7 days	370° C.	Orthorhombic hessite
3	40 g.	0.5 g.	0.6 g.	20 cc.	7 days	360° C.	Hessite
4	50 g.	0.5 g.	0.6 g.	20 cc.	4 days	490° C.	Hessite
5	20 g.	0.75 g.	0.9 g.	10 cc.	7 days	350° C.	Isometric hessite

The bomb product identified as hessite from runs 3 and 4 was massive material with no crystal faces. These aggregates were generally fine, but some were rather large and blocky; all were covered with a yellow to purple tarnish.

The hessite present in the product of run 1 consisted of blocky, yellow or grey, metallic crystals, showing some good faces. Certain of these were long, prismatic, silvery, with prismatic striations. As good faces were not observed on these crystals, they were used only to obtain a powder diffraction pattern.

Well-formed blocky prismatic single crystals, parallel growths and aggregates, and flattened platy crystals which occurred in the product of run 2 were identified as hessite. The crystal aggregates generally displayed prismatic striations, and the crystal faces present were poorly

formed but the single crystals were bounded by well defined prismatic and pyramidal forms. Most of the measured crystals of hessite came from this run.

Small cubic crystals giving the powder diffraction pattern of hessite were observed in the product of run 5. These isometric crystals are rounded with poorly defined crystal faces, and a dark purple tarnish. The principal forms are the cube, octahedron and dodecahedron.

GEOMETRICAL CRYSTALLOGRAPHY

Twenty-eight crystals of hessite from the product of run 2 were mounted for measurement on the two-circle optical goniometer. The measurements were plotted in gnomonic projection. The crystals were of two types, both orthorhombic but with different crystal forms and axial ratio. Nine crystals were distinctly type I and the measurements led to the axial ratio.

$$\text{Type I } a:b:c=0.599:1:0.284$$

The observed forms together with measured and calculated ϕ and ρ angles are given in Table 2. The form (132), which is present on three crystals, shows only $(\bar{1}32)$ and $(1\bar{3}2)$ and thus suggests sphenoidal symmetry on two of these crystals, on the third all four faces were present; all other (hkl) forms show holohedral symmetry. Figure 1 is an idealized drawing of a typical crystal of type I.

Ten of the measured crystals were distinctly type II and the measurements led to the axial ratio.

$$\text{Type II } a:b:c=0.776:1:0.650$$

The observed forms together with the measured and calculated ϕ and ρ angles are given in Table 3. The symmetry appears to be orthorhombic holohedral. Figure 2 is an idealized drawing of typical crystal of type II.

STRUCTURAL CRYSTALLOGRAPHY

Hessite crystals of types I and II were mounted on the Weissenberg goniometer with the prismatic axis, c , as the axis of rotation. Five crystals of type II gave rotation films with all diffractions drawn out on powder rings indicating that the prism axis is not a rational axis in the lattice or that the crystals are no longer single crystals. Sharp rotation zero and first layer Weissenberg films were obtained from a crystal of type I. Film measurements led to the following dimensions for the unit cell

$$a=16.28, \quad b=26.68, \quad c=7.55 \text{ \AA}^1$$

with the axial ratio

$$a:b:c=0.610:1:0.283$$

¹ Using $\text{CuK}\alpha$ 1.5418, mass factor 1.6602.

TABLE 2. HESSITE TYPE I: CRYSTAL MEASUREMENTS

Orthorhombic, *Immm* (artificial crystals) $a:b:c=0.599:1:0.284$; $p_0:q_0:r_0=0.474:0.284:1$

Form	Measured		Calculated		Obs.
	ϕ	ρ	ϕ	ρ	
<i>b</i> (010)	0°00'	90°00'	0°00'	90°00'	12
<i>a</i> (100)	90 00	90 00	90 00	90 00	13
<i>m</i> (110)	59 15	90 00	59 04½	90 00	12
<i>n</i> (120)	39 30	90 00	39 51	90 00	7
<i>l</i> (130)	28 35	90 00	29 06	90 00	7
<i>k</i> (150)	18 50	90 00	18 28	90 00	2
<i>d</i> (011)	0 00	15 45	0 00	15 51½	6
<i>s</i> (132)	28 35	26 00	29 06	25 59½	3
<i>o</i> (121)	39 50	36 00	39 51	36 30	7
<i>r</i> (141)	22 15	51 25	22 39	50 54½	2
(161)	18 30	61 10	15 33	60 13	1
<i>p</i> (211)	73 10	44 15	73 19½	44 42½	3
<i>q</i> (231)	48 05	51 15	48 03½	51 53	6

TABLE 3. HESSITE TYPE II: CRYSTAL MEASUREMENTS

Orthorhombic (artificial crystals)

 $a:b:c=0.776:1:0.650$; $p_0:q_0:r_0=0.838:0.650:1$

Form	Measured		Calculated		Obs.
	ϕ	ρ	ϕ	ρ	
<i>c</i> (001)	—	0°00'	—	0°00'	8
<i>a</i> (100)	90°00'	90 00	90°00'	90 00	10
<i>l</i> (120)	30 00	90 00	32 48	90 00	9
<i>m</i> (110)	52 30	90 00	52 11	90 00	4
<i>n</i> (320)	62 10	90 00	62 39	90 00	4
<i>d</i> (011)	0 00	32 50	0 00	33 01	9
<i>p</i> (111)	52 30	46 25	52 11	46 40	8

in good agreement with the geometrical axial ratio. The observed diffractions conform to the condition: (hkl) present only with $h+k+l=2n$ indicating the space group $Im\bar{3}m$ if the crystals are holohedral. These lattice dimensions show very little similarity to those given by Tokody (1932, 1934) and Koern (1939) for hessite and artificial α - Ag_2Te

$$a = 6.57 \quad b = 6.14 \quad c = 6.10 \text{ \AA} \quad \beta = 61^\circ 15' \text{ (Tokody, 1934)}$$

$$a = 13.0 \quad b = 12.7 \quad c = 12.2 \text{ \AA} \quad \text{(Koern, 1939)}$$

The a lengths given by Tokody and Koern are approximately $\frac{1}{4}$ and $\frac{1}{2}$, respectively, of the b length found for our artificial crystals of type I.

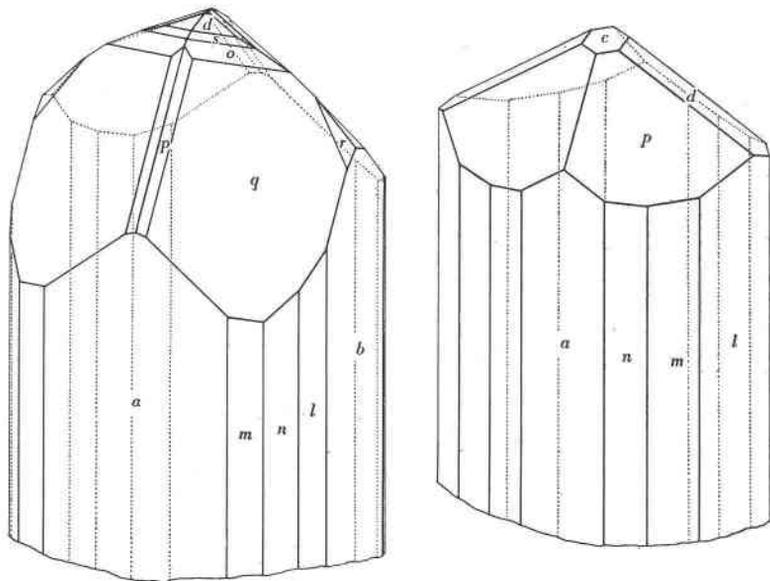


FIG. 1.—Artificial hessite crystals, type I, stable at room temperatures. Idealized crystal drawing showing the forms; $b(010)$, $a(100)$, $m(110)$, $n(120)$, $l(130)$, $d(011)$, $s(132)$, $o(121)$, $r(141)$, $p(211)$, $q(231)$.

FIG. 2.—Artificial hessite crystal, type II, not stable at room temperatures. Idealized crystal drawing showing the forms; $c(001)$, $a(100)$, $l(120)$, $m(110)$, $n(320)$, $d(011)$, $p(111)$.

The cubic hessite crystals from run 5 were mounted in several positions on the Weissenberg goniometer but failed to give rational rotation patterns. All three types of artificial hessite crystals give the same x -ray powder pattern as natural hessite. Presumably type II orthorhombic crystals and the cubic crystals represent forms stable at higher temperature which have inverted on cooling to the structure represented by type I crystals.

In Table 4 the x -ray powder pattern of hessite as given by Thompson

TABLE 4. HESSITE—Ag₂Te: X-RAY POWDER PATTERN
 Orthorhombic, *Immm*; *a* = 16.27, *b* = 26.68, *c* = 7.55Å; *Z* = 48

Mineral ¹			Artificial crystals			Calculated	
<i>I</i>	θ (Cu)	<i>d</i> (meas.)	<i>I</i>	θ (Cu)	<i>d</i> (meas.)	<i>hkl</i>	<i>d</i> (calc.)
$\frac{1}{2}$	6.2	7.14A	—	—	—	011	7.265A
1	9.8	4.53	—	—	—	{ 330 060	{ 4.630 4.470
$\frac{1}{2}$	11.9	3.74	—	—	—	002	3.775
$\frac{1}{2}$	13.1	3.40	—	—	—	{ 202 071 132	{ 3.424 3.402 3.398
2	14.0	3.19	1	14.15	3.15	{ 510 271	{ 3.230 3.139
6	14.85	3.01	5	14.95	2.99	{ 152 501	{ 3.028 2.988
8	15.6	2.87	9	15.65	2.86	062	2.878
$\frac{1}{2}$	16.0	2.80	—	—	—	{ 550 402	{ 2.778 2.767
$\frac{1}{2}$	16.65	2.69	$\frac{1}{2}$	16.75	2.67	{ 262 600 422 352 0.10.0 381	{ 2.713 2.712 2.709 2.679 2.668 2.659
1	18.35	2.45	1	17.75	2.53	{ 2.10.0 570 512 123	{ 2.535 2.475 2.454 2.445
10	19.5	2.31	10	19.65	2.29	{ 233 710 660 192	{ 2.321 2.315 2.315 2.308
7	20.05	2.25	10	20.25	2.23	{ 323 730 552 4.10.0	{ 2.250 2.249 2.238 2.231

Table 4 (Continued)

Mineral ¹			Artificial crystals			Calculated	
<i>I</i>	$\theta(\text{Cu})$	<i>d</i> (meas.)	<i>I</i>	$\theta(\text{Cu})$	<i>d</i> (meas.)	<i>hkl</i>	<i>d</i> (calc.)
2	20.5	2.20	8b	20.95	2.16	581 0.12.0 2.11.1 602 253 721 590	2.226 2.223 2.216 2.202 2.192 2.191 2.191
6	21.1	2.14	7b	21.45	2.11	392 413 750 482 671	2.142 2.133 2.131 2.129 2.121
1	22.55	2.01	1	22.45	2.02	1.11.2	2.025

Mineral ¹		Artificial crystals		Mineral		Artificial crystals	
<i>I</i>	<i>d</i> (meas.)	<i>I</i>	<i>d</i> (meas.)	<i>I</i>	<i>d</i> (meas.)	<i>I</i>	<i>d</i> (meas.)
$\frac{1}{2}$	1.957A	—	—	2	1.447A	2	1.441A
$\frac{1}{2}$	1.926	$\frac{1}{2}$	1.933A	4	1.389	6	1.391
$\frac{1}{2}$	1.845	$\frac{1}{2}$	1.859	$\frac{1}{2}$	1.341	2b	1.342
$\frac{1}{2}$	1.824	—	—	2	1.305	4	1.301
1	1.771	$\frac{1}{2}$	1.762	1	1.278	1	1.276
$\frac{1}{2}$	1.734	—	—	1	1.247	2	1.248
1	1.695	$\frac{1}{2}$	1.678	$\frac{1}{2}$	1.192	$\frac{1}{2}$	1.192
$\frac{1}{2}$	1.600	—	—	—	—	$\frac{1}{2}$	1.000
$\frac{1}{2}$	1.585	$\frac{1}{2}$	1.578	—	—	$\frac{1}{2}$	0.941
$\frac{1}{2}$	1.544	—	—				

¹ *I* and θ from Thompson (1949).

b—broad line.

(1949) is given together with the pattern given by our artificial crystals also the indices and interplanar spacings calculated from the lattice dimensions found for hessite type I crystals. Our pattern agrees line for line with a pattern of natural hessite (Q.U. polished section TE-8, unknown locality) but the tabulated data show minor differences with Thompson's data. Some of these differences are undoubtedly due to dif-

ferences in sample preparation, camera design and exposure. One or more calculated interplanar spacings agree fairly well with each measured spacing down to $d = 2.0$; below this value there are many possibilities in a lattice of large unit dimensions.

X-ray powder patterns of natural hessite and artificial crystals were obtained at room temperature and at several higher temperatures in the x-ray powder camera designed by Buerger, Buerger & Chesley (1943) at

TABLE 5. HESSITE— Ag_2Te : X-RAY POWDER PATTERN (at 155°C .)
Isometric P : $a = 6.64\text{\AA}$; $Z = 4$

I	$\theta(\text{Cu})$	$d(\text{meas.})$	hkl	a
5	9.5	4.657	100	6.59
2	11.5	3.860	111	6.68
10	19.1	2.349	220	6.64
8	20.3	2.213	300, 221	6.64
3	22.5	2.009	311	6.66
3	27.5	1.665	400	6.66
2	34.8	1.347	422	6.64
			Average	6.64

about 125°C . the powder pattern is similar to the pattern at room temperature but with some changes in intensities. At 155°C . the pattern is much simpler in appearance and can be indexed with reference to a simple cubic lattice. The intensities measured spacings, indices and the cube edge values are given in Table 5. The indexed powder pattern leads to an average value for the cube edge.

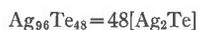
$$a = 6.64 \text{ \AA}$$

in fair agreement with the value given by Rahlfs (1936)

$$a = 6.572 \text{ \AA}$$

COMPOSITION AND CELL CONTENT

Analyses of hessite from various localities clearly indicate a composition Ag_2Te . The measured specific gravity is 8.24 to 8.45 (Dana, 1944) 8.41 (Thompson, 1949). The unit cell volume combined with the latter value gives $M = 16610$. This value divided by the gram molecular weight for Ag_2Te gives $Z = 48.37$. Therefore the unit cell probably contains



This structural formula gives a calculated specific gravity of 8.35 in good

agreement with the measured values. The cubic unit cell of hessite at high temperature contains $4[\text{Ag}_2\text{Te}]$

CONCLUSIONS

Orthorhombic crystals, type I, appear to be structurally identical with natural hessite. The unit cell dimensions, which differ markedly from those reported by Tokody (1932, 1934) and Koern (1939) serve to index the identical x -ray powder pattern obtained from the artificial crystals, artificial Ag_2Te and natural hessite. The unit cell contains $48[\text{Ag}_2\text{Te}]$ with calculated gravity in close agreement with measured values.

Orthorhombic crystals, type II, and cubic crystals are, at room temperature, also structurally identical with natural hessite but are clearly paramorphs of structures not stable at room temperature and pressure. Hessite, both natural and artificial, gives an isometric x -ray powder pattern at 155°C . which presumably corresponds to the isometric polymorph. No powder pattern was found which could be correlated with type II orthorhombic crystals.

REFERENCES

- BUERGER, M. J., BUERGER, N. W. & CHESLEY, F. G. (1943): Apparatus for making x -ray powder photographs at controlled, elevated temperatures, *Am. Mineral.*, **28**, 285-302.
- DANA, J. D. & E. S. (1944): *System of Mineralogy* 1, by C. Palache, H. Berman & C. Frondel, New York.
- KOERN, V. (1939): Das binäre Legierungssystem Ag-Te, *Naturwiss.*, **27**, 432.
- RAHLFS, P. (1936): Über die kubischen Hochtemperaturmodifikationen der Sulfide, Selenide und Telluride des Silbers und des einwertigen Kupfers, *Zeits. phys. Chem.*, (B), **31**, 157-194.
- RAMSDELL, L. S. (1925): The crystal structure of some metallic sulfides, *Am. Mineral.*, **10**, 281-304.
- ROWLAND, J. F. (1950): An x -ray study of gold and silver tellurides, M.Sc. thesis, *Queen's University, Kingston*.
- ROBINSON, S. C. (1948): Synthesis of lead sulphantimonites, *Econ. Geol.*, **43**, 293-312.
- SMITH, F. G. (1947): Transport and deposition of the non-sulphide vein minerals, *Econ. Geol.*, **42**, 251-264.
- THOMPSON, R. M. (1946): Descriptive mineralogy of the tellurides, Ph.D. thesis, *University of Toronto*.
- (1948): Pyrosyntheses of telluride minerals, *Am. Mineral.*, **33**, 209 (abstract).
- (1949): The telluride minerals and their occurrence in Canada, *Am. Mineral.*, **34**, 342-382.
- TOKODY, L. (1932): Über Hessit, *Zeits. Krist.*, **82**, 154-157.
- (1934): Berichtigung zu meiner Mitteilung, "Über Hessit," *Zeits. Krist.*, **89**, 416.