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THE CRYSTALLOGRAPHY OF PETZITE, Ag_3AuTe_2

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ABSTRACT

From small single crystals of petzite found intimately intergrown with hessite (Ag_2Te) from Bótes, Transylvania, the space group was determined to be cubic, $I\ 4_132$ with a cell edge of 10.38 Å. There are 8(Ag_3AuTe_2) per cell and the atoms are located on the following special positions: 24 silver atoms on x, 0, $\frac{1}{4}$, etc. with $x=.365$; 8 gold atoms on $\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$, etc.; 16 tellurium atoms on x, x, x, etc. with $x=.266$.

The powder diffraction record of a high temperature form of petzite was obtained, and the material was observed to return to the low form upon rapid cooling. Heating experiments indicate some hessite-petzite solid solubility above 250° C.

INTRODUCTION

While investigating the crystallography of hessite, Ag_2Te, it was discovered that the small single crystals of that mineral from Bótes, Transylvania, obtained from the Harvard University Museum (#99348) and from the U. S. National Museum (U.S.N.M. #R9556) all contained small amounts of an additional phase. The x-ray powder diffraction pattern of this phase proved to be identical with the pattern of petzite, Ag_3AuTe_2, synthesized from the elements and described by Thompson (1948, 1949). This pattern could be successfully indexed on the basis of a body-centered cubic cell of $a=10.38$ Å. Table I compares the d spacings reported by Thompson with the calculated values and with those measured from the Bótes samples.

The petzite appeared as irregular-shaped blebs within the small single crystals of hessite (Fig. 4). By fracturing the hessite at liquid nitrogen temperature, a minute, irregular-shaped fragment of petzite was obtained from which single crystal data could be gathered.

Crystal Structure

From Buerger precession data, using Mo Kα radiation, the space group was unequivocally determined as $I\ 4_132$ and the edge of the body-centered cubic cell was found to be 10.38 Å as previously determined

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TABLE I. *X*-RAY POWDER DATA FOR PETZITE

hkl	Thompson (1949)		Calculated; $a = 10.38$ Å	Bótes, Transylvania	
	I	*d*	*d*	I	*d*
110	2	7.5	7.34	5	7.31
220	2	3.67	3.67	3	3.66
310	½	3.27	3.28	1	3.27
222	1	2.99	3.00	3	2.99
321	10	2.77	2.77	10	2.77
400	½	2.59	2.59	2	2.59
411, 330	3	2.44	2.45	6	2.44
420	3	2.31	2.32	6	2.32
332	—	—	2.21	1	2.21
422	5	2.11	2.12	8	2.12
510, 431	4	2.02	2.04	7	2.03
521	3	1.897	1.895	5	1.893
440	2	1.826	1.835	3	1.835
611, 532	—	—	1.684	1	1.683
622	1	1.558	1.565	2	1.565
631	1	1.525	1.531	2	1.532
444	1	1.492	1.498	2	1.499
710, 550, 543	1	1.458	1.468	2	1.469
640	1	1.434	1.439	2	1.440
721, 633, 552	1	1.405	1.413	3	1.403
642	2	1.380	1.387	—	—
732, 651	3	1.312	1.318	5	1.316
800	1	1.292	1.298	3	1.296
811, 741, 554	1	1.271	1.278	3	1.276
831, 750, 743	1	1.200	1.207	3	1.205
752	1	1.170	1.175	3	
910, 833	½	1.142	1.146	1	1.146
842	½	1.126	1.133	2	1.132
921, 761, 655	½	1.114	1.119	2	1.119
664	½	1.101	1.106	2	1.106
930, 851, 754	½	1.089	1.094	2	1.093
844	1	1.069	1.059	3	1.070
941, 853, 770	½	1.043	1.049	2	1.048
950, 943, 1,031	½	1.004	1.008	1	1.008
952, 765	1	.988	.990	4	.990

from the powder record. From the density of 8.7–9.4 the number of formula weights per cell was determined as $Z=8$. This yields a theoretical x-ray density of 8.74.

Intensity data for the a axis zero through fifth level were gathered by an equi-inclination Geiger-counter spectrometer using Cu Kα radiation. The data were corrected for Lorentz and polarization factors by the accepted method (Buerger and Klein, 1945).

The constancy of the chemical composition listed in Doelter (1926) and in the Dana system (Palache, Berman and Frondel, 1941), as well as the

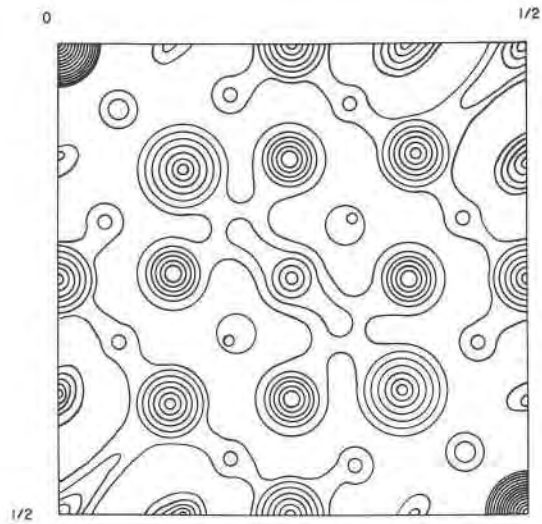


FIG. 1. Patterson projection of petzite on (001).

work of Thompson (1948, 1949) indicate that petzite is a compound with a definite silver-to-gold ratio which would suggest distinct ordered positions for the gold and silver atoms. The symmetry of the space group requires that the 8 gold atoms be located on one of the two special positions 8a or 8b (notation used is that of the International Tables for X-ray Crystallography, 1952). As the two positions are centrosymmetrically related, the position 8a, with a gold atom at $\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$, etc., was arbitrarily chosen. The 16 tellurium atoms then must be located on the 16e special positions at x, x, x, etc. This means that the interatomic distance vector between gold and tellurium as seen in projection on the Patterson projection (001), must lie along the body-diagonal in vector space. Such a peak is easily discernible on this Patterson projection (Fig. 1), and an approximate parameter ($x=.275$) for tellurium was obtained.

With a knowledge of the gold and tellurium locations, the Patterson could be easily interpreted to yield a reasonable silver parameter utilizing special position 24*f* or x, 0, $\frac{1}{4}$; etc.; with $x=.375$.

An electron density projection on (001) from the observed data and from signs calculated from these assumed positions confirmed the validity of the assumptions (Fig. 2). The tellurium and silver parameters were further refined by the electron density map and by means of a ($Fo-Fc$) synthesis. The final parameters are as follows: 8 gold atoms at $\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$, etc.;

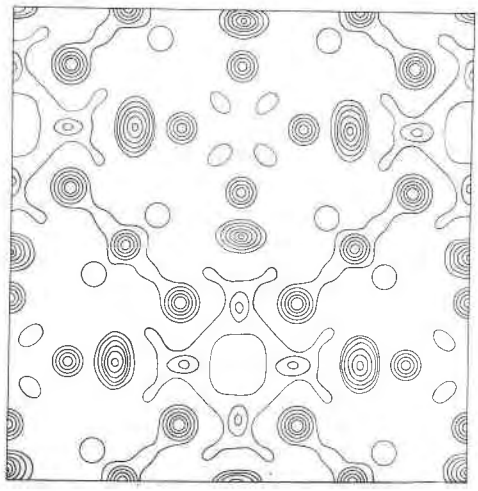


FIG. 2. Electron density projection of petzite on (001).

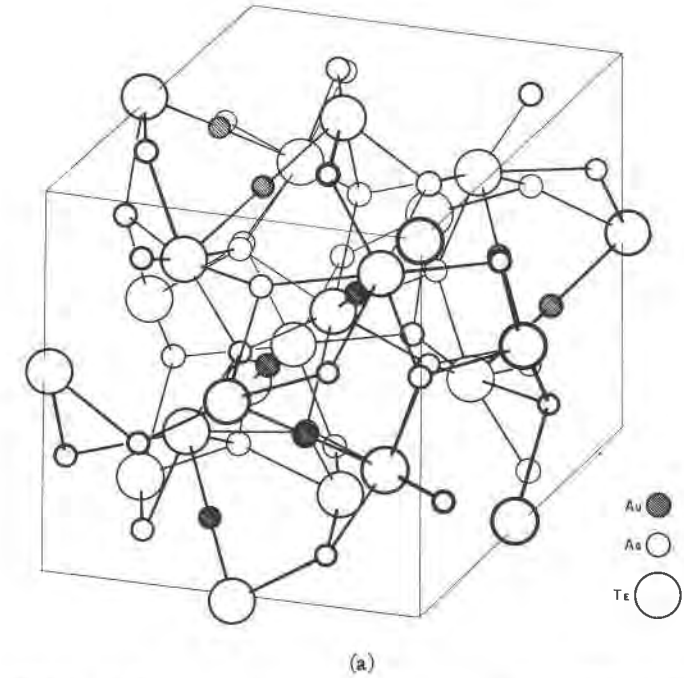
24 silver atoms at x, 0, $\frac{1}{4}$, etc., with $x=0.365$; 16 tellurium atoms at x, x, x, etc., with $x=0.266$.

These values yield a standard discrepancy factor $R=.14$ for the zero level reflections and an $R=.25$ for all observed reflections. The intensities for all reflections as calculated from these parameters are compared with those observed (Table II).

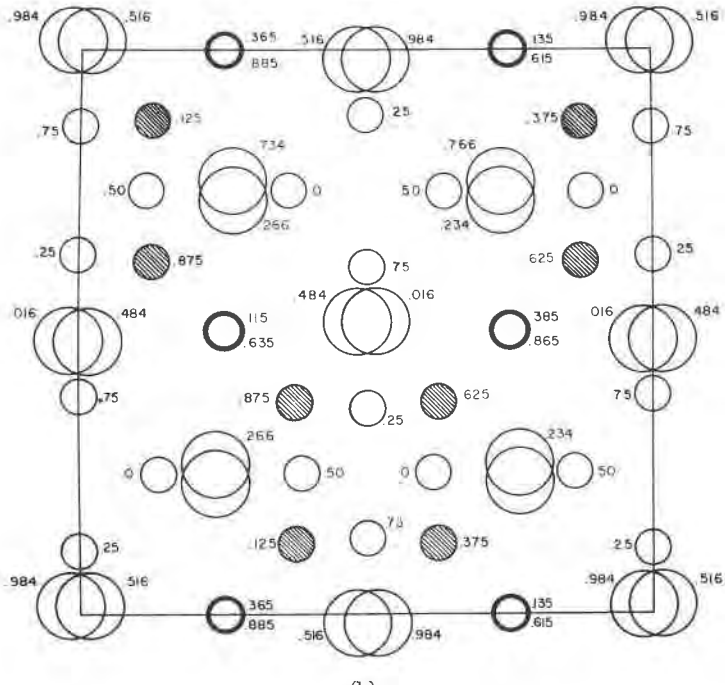
The structure is illustrated in Figs. 3*a* and *b*. Each gold atom has two close tellurium neighbors at a distance of 2.53 Å. The silver atoms are tetrahedrally surrounded by Te atoms, with two of the Te atoms at 2.90 Å and two at 2.95 Å. The Te-Ag-Te bond angles are 108° and 140° respectively. The tellurium atoms are each surrounded by six silver atoms, one gold atom, and one close tellurium atom in the following manner. If one considers an axis with a tellurium atom at the center and a gold atom 2.53 Å away at one pole of the axis, then at the other pole 3.91 Å away from the central tellurium another tellurium atom is located.

TABLE II. OBSERVED AND CALCULATED |F| VALUES

Index	|F| obs.	|F| cal.	α in degrees	Index	|F| obs.	|F| cal.	α in degrees
110	223	255	90	891	181	104	346
130	86	110	270	222	343	560	270
150	472	467	270	242	570	823	0
170	297	305	90	262	413	454	90
190	—	81	90	282	142	146	0
1, 11, 0	196	94	90	2, 10, 2	261	338	270
220	343	373	0	332	96	179	0
240	522	569	0	352	129	252	90
260	206	195	0	372	584	263	180
280	—	27	0	392	449	434	325
2, 10, 0	—	37	0	3, 11, 2	182	179	256
2, 12, 0	239	298	0	442	74	17	270
330	523	580	270	462	589	604	0
350	153	114	270	482	366	376	356
370	—	31	90	4, 10, 2	306	388	0
390	211	239	90	552	105	27	180
3, 11, 0	458	470	270	572	537	472	209.6
400	407	397	0	592	422	374	31.4
440	708	725	0	662	348	447	270
460	490	458	180	682	—	75	0
480	—	104	0	6, 10, 2	393	365	90
4, 10, 0	378	373	180	772	135	56	180
550	235	112	270	792	397	217	271
570	274	257	270	882	171	42	90
590	400	358	270				
5, 11, 0	303	321	90	343	—	33	90
660	155	111	0	363	170	154	180
680	98	0	0	383	363	360	270
770	340	280	270	3, 10, 3	134	33	0
800	973	1,396	0	453	348	294	284
880	1,199	1,025	0	473	431	346	276
				493	159	394	102
121	—	30	0	4, 11, 3	185	242	288
141	363	293	270	563	153	220	97
161	73	38	180	583	229	254	229
181	154	186	90	673	309	304	329
1, 10, 1	103	15	0	693	508	450	333
1, 12, 1	103	161	270	783	159	100	54
231	434	593	350	444	643	706	180
251	361	253	31	464	—	42	90
271	288	267	280	484	280	415	0
291	251	229	263	4, 10, 4	99	52	90
2, 11, 1	359	398	343	554	554	494	270
341	304	351	98	574	156	147	124
361	320	415	351	664	434	478	0
381	150	141	281	684	301	67	270
3, 10, 1	281	364	184	6, 10, 4	160	322	0
451	—	55	41	774	111	92	90
471	158	144	119	794	160	201	112
491	276	275	283	884	92	16	180
4, 11, 1	372	238	253				
561	491	509	196	565	166	110	180
581	316	317	258	585	85	32	90
5, 10, 1	89	215	0	5, 10, 5	208	159	180
671	314	220	247	675	273	371	209
691	288	213	241	695	396	467	201
781	257	109	0	785	277	266	300



(a)



(b)

FIG. 3. (a) Oblique drawing of petzite. (b) Projection of petzite on (001).

The six silver atoms are fairly evenly distributed, three a little above and three a little below the plane which is perpendicular to this axis and passes through the central tellurium. This axis is always parallel to one of the body-diagonals of the unit cell.

The Au-Te distance of 2.53 Å is somewhat closer than that of the closest Au-Te distance (2.63 Å) found in the gold-silver ditellurides (Tunell & Pauling, 1952). At the same time the Te-Te distance of 3.91 Å is a little greater than the greatest distance (3.65 Å) found in the gold-silver ditellurides. If one adjusted the parameter (x, x, x) of tellurium to $x=.273$, one would increase the Au-Te distance to 2.66 Å while decreasing the Te-Te distance to 3.65 Å. However, where intensities are computed after any change in x is made, the R factor from the zero level is observed to increase. The minimum R value of .14 is obtained when the parameters are as originally stated above. Until better data are obtained from a crystal for which absorption and temperature corrections can be made, these parameters and interatomic distances must be accepted.

An explanation of the closer Au-Te distance may rest in the fact that in the ditellurides the gold atoms are bonded to six fairly close tellurium atoms, while in petzite the gold has only two close neighbors. A similar explanation can be offered for the larger Te-Te distance. In the ditellurides the tellurium is bonded to three gold or silver atoms and three other tellurium atoms, while in petzite the tellurium atoms are bonded to six silver, one gold, and one tellurium atom.

High Temperature Behavior

As noted above, the petzite was found intimately intergrown with hessite. Attempts were made to see if these intergrowths would form a single phase at higher temperatures. Several specimens, similar to and including that illustrated in Fig. 4*a*, of irregular-shaped pieces of petzite surrounded by hessite were heated in sealed evacuated pyrex tubes to 150° C. and held for 72 hours. This temperature is slightly above that at which hessite inverts to a high temperature phase (Rahlfs, 1936). No change was apparent in the shape or character of the inclusions after this treatment.

The same samples were then raised to 250° C. and held for 72 hours. After this treatment the surface of both the hessite and the petzite had a similar tarnished appearance and further polishing was necessary to distinguish the petzite (Fig. 4*b*). The petzite appeared to become smaller in extent and its outlines less sharp. Some of the change may be due to the fact that a slightly different cross section is viewed every time this rather soft material is given an additional polish. However, as the several

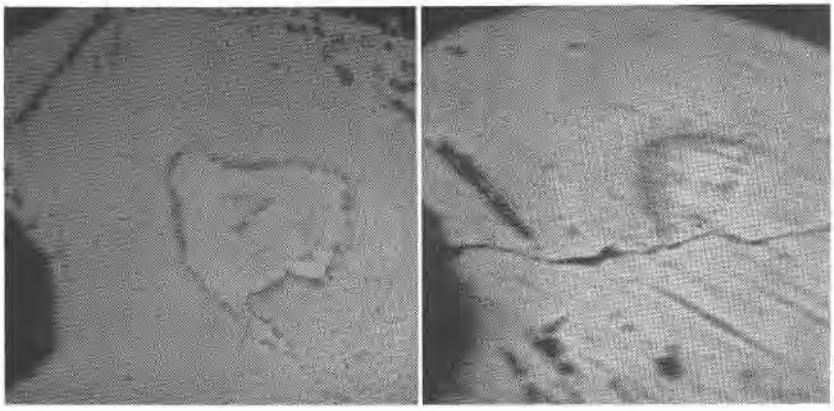


FIG. 4. (a) Polished section of petzite surrounded by hessite.
(b) Same section after heat treatment. 70×

specimens observed appeared to undergo a similar change, a slight increase in the solubility of gold in hessite with increasing temperature can be assumed. No transformation twinning such as that described by Stillwell (1931) was observed on any of the heat-treated samples.

Petzite itself undergoes a rapid and reversible transformation between

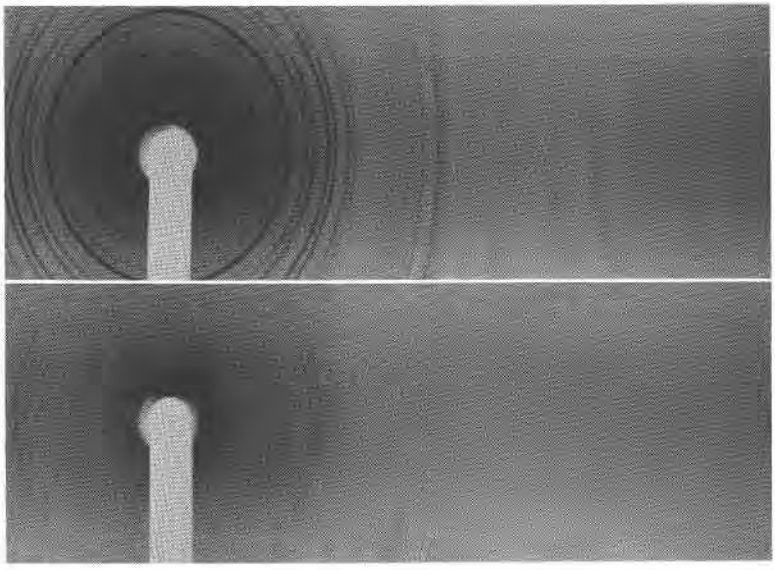


FIG. 5. (a) Powder photograph of petzite at room temperature.
(b) Powder photograph of petzite at 250° C.

TABLE III. *X*-RAY POWDER DATA FOR HIGH TEMPERATURE FORM

I	*d*	I	*d*	I	*d*
2	3.802	2	2.156	2	.943
6	3.121	5	2.071	1	.921
3	2.797	1	1.955	2	.839
9	2.392	4	1.495	5	.791
10	2.254	5	1.247		

150°–250° C.* The powder diffraction record of the high form taken with Cu Kα is illustrated in Fig. 5*b* in conjunction with the room temperature form (Fig. 5*a*). Table III lists the *d* spacings and estimated intensities of the high form. No attempt has been made to index the pattern.

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* F. C. Kracek and C. J. Ksanda, by thermal analysis found a transition in petzite at 210±10° C. (private communication).