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The Atomic Arrangement and Bonds of the Gold–Silver Ditellurides*

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The structures of sylvanite, calaverite and krennerite, the three gold–silver ditellurides occurring naturally, are basically similar, although they have three different space-group symmetries. In all three minerals the gold and silver atoms are surrounded by six tellurium atoms, which are not all at the same distance, however. In sylvanite and calaverite, each tellurium atom is surrounded by three gold or silver atoms and three tellurium atoms. In krennerite, part of the tellurium atoms are surrounded by three gold or silver atoms and three tellurium atoms, part by one gold or silver atom and five tellurium atoms, part by five gold or silver atoms and one tellurium atom. An analysis is given of the interatomic distances in terms of the resonating-valence-bond theory.

Descriptions of the atomic arrangements in sylvanite, calaverite and krennerite

The gold–silver ditellurides form a group of three crystallographically related minerals, sylvanite ($AuAgTe_4$), calaverite ($(Au, Ag)Te_2$) and krennerite ($(Au, Ag)Te_2$). All three have metallic luster and are electrical conductors. The conductivities of the three minerals were found by Harvey (1928) to be smaller than the conductivities of native silver, copper and gold and larger than the conductivity of native tellurium. All three minerals are brittle. Sylvanite and krennerite have each one perfect cleavage; calaverite has no cleavage.

Crystallographic data for the three minerals are summarized in Table 1.

Sylvanite has the following atomic arrangement:

Au in (a) $0, 0, 0;\ 0, 0, \frac{1}{2};$
Ag in (e) $0, y, \frac{1}{4};\ 0, \bar{y}, \frac{3}{4}$, with $y = 0{\cdot}433$;
two sets of Te in (g) $x, y, z;\ \bar{x}, \bar{y}, \bar{z};\ \bar{x}, y, \frac{1}{2}-z;\ x, \bar{y}, \frac{1}{2}+z$, with $x_1=0{\cdot}298$, $y_1=0{\cdot}031$, $z_1=0{\cdot}999$, and $x_2 = 0{\cdot}277$, $y_2 = 0{\cdot}425$, $z_2 = 0{\cdot}235$.

The gold atoms are on symmetry centers and the silver atoms are on twofold rotation axes (Tunell, 1941).

Analyzed crystals of sylvanite from Cripple Creek, Colorado, and from Baia-de-Aries (Offenbánya), Transilvania, have a gold:silver atomic ratio slightly in excess of 1:1.† Thus random substitution of gold atoms for a small percentage of the silver atoms in these crystals is indicated.

The atomic arrangement in calaverite is as follows:

Au in (a) $0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, 0;$
Te in (i) $x, 0, z;\ \bar{x}, 0, \bar{z};\ x+\frac{1}{2}, \frac{1}{2}, z;\ \frac{1}{2}-x, \frac{1}{2}, \bar{z}$, with $x = 0{\cdot}689$, $z = 0{\cdot}289$.

The gold atoms are on symmetry centers and the tellurium atoms are in mirror planes (Tunell & Ksanda, 1935, 1936*b*; Tunell, unpublished work).

Naturally occurring crystals of calaverite contain some silver. In the analyses of crystallographically studied material the silver ranges from 0·40 to 3·23 weight % and consequently the atomic ratio of gold to silver ranges from 54·2:1 to 6·6:1. The silver atoms substitute for part of the gold atoms, as the agreement of measured and calculated densities shows,

Table 1. *Crystallographic data for sylvanite, calaverite and krennerite*

	Space group	a_0 (Å)	b_0 (Å)	c_0 (Å)	β	Cell content
Sylvanite	C_{2h}^4–$P2/c$	8·96†	4·49†	14·62†	145° 26′§	$2AuAgTe_4$*
Calaverite	C_{2h}^3–$C2/m$	7·19††	4·40††	5·07††	90° 13′§§	$2(Au,Ag)Te_2$**
Krennerite	C_{2v}^4–Pma	16·54†††	8·82†††	4·46†††		$8(Au,Ag)Te_2$***

† ±0·02 Å. § ±20′. * Tunell (1941). (The values of the cell dimensions were given in this paper in kX. units.)
†† ±0·01 Å. §§ ±10′. ** Tunell (unpublished work).
††† ±0·03 Å. *** Tunell & Murata (1950).

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† Some old analyses of material from other localities leading to slightly higher atomic ratios of gold to silver were made on samples not identified crystallographically and hence cannot be relied upon.

but whether or not the substitution is entirely random has not been proved. Weissenberg photographs of calaverite, unlike those of sylvanite and krennerite, have some extra spots that indicate the presence of a superstructure, but the superstructure has not yet been elucidated.

In krennerite the arrangement of the atoms is as follows:

Au in (*a*) $0, 0, z$; $\frac{1}{2}, 0, z$, with $z = 0$ (arbitrary), in (*c*) $\frac{1}{4}, y, z$; $\frac{3}{4}, \bar{y}, z$, with $y = 0{\cdot}319$, $z = 0{\cdot}014$, and in (*d*) x, y, z; $\bar{x}, \bar{y}, z$; $\frac{1}{2}-x, y, z$; $\frac{1}{2}+x, \bar{y}, z$, with $x_2 = 0{\cdot}124$, $y_2 = 0{\cdot}666$, $z_2 = 0{\cdot}500$;

two sets of Te in (*c*) with $y_3 = 0{\cdot}018$, $z_3 = 0{\cdot}042$, and $y_4 = 0{\cdot}617$, $z_4 = 0{\cdot}042$;

three sets of Te in (*d*) with $x_5 = 0{\cdot}003$, $y_5 = 0{\cdot}699$, $z_5 = 0{\cdot}042$, $x_6 = 0{\cdot}132$, $y_6 = 0{\cdot}364$, $z_6 = 0{\cdot}500$, $x_7 = 0{\cdot}119$, $y_7 = 0{\cdot}964$, $z_7 = 0{\cdot}500$.

The gold atoms in (*a*) are on twofold rotation axes, the gold and tellurium atoms in (*c*) are in mirror planes (Tunell & Ksanda, 1936*a*; Tunell & Murata, 1950).

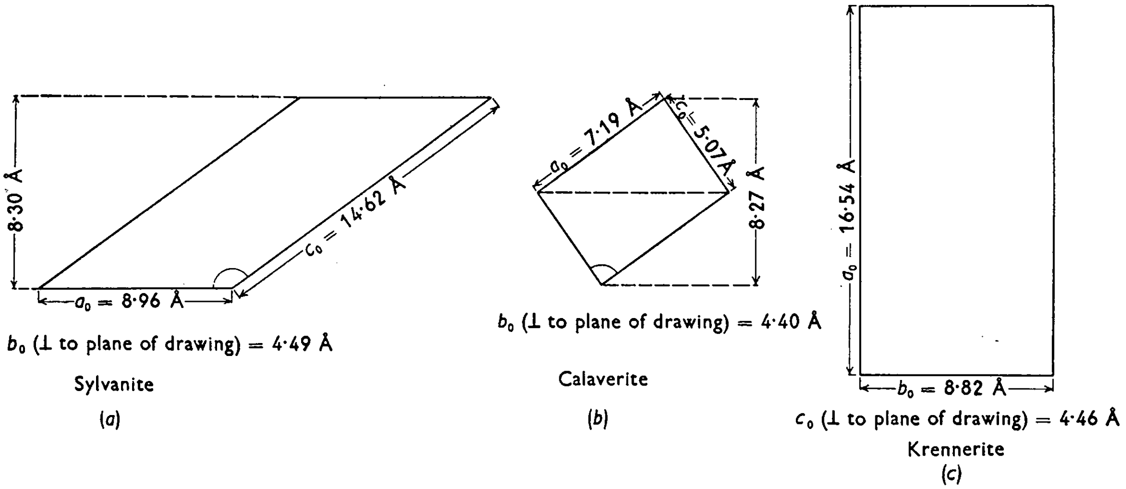
Naturally occurring crystals of krennerite also contain some silver. In two analyses by K. J. Murata of good crystals from Cripple Creek, Colorado, carefully freed from impurities by the senior author, the weight percentage of silver in the mineral was determined to be 4·87 (Moose Mine) and 5·4 (Vindicator Mine); the corresponding atomic ratios of gold to silver are 4·07:1 and 3·56:1. In krennerite the substitution of silver atoms for gold atoms appears to be random.

Geometric interrelations of the atomic arrangements of sylvanite, calaverite and krennerite

Although the three minerals have three different space-group symmetries, their structures are closely related. Fig. 1 shows the relationship of the unit cells. Projections of the structures of the three minerals on analogous planes are shown in Fig. 2.

The relationship of the structure of sylvanite to that of calaverite can be described in the following way. If a silver atom is substituted for the gold atom at $\frac{1}{2}, \frac{1}{2}, 0$ in the structure of calaverite, and if slight changes are made in the parameters of the silver and tellurium atoms, we can obtain the structure of sylvanite (Fig. 2). Substitution of the silver atom for one gold atom in the structure of calaverite results in a structure with a unit cell of approximately twice the volume of the unit cell of calaverite. This substitution also causes a change in the space-group from $C2/m$ to $P2/c$.

From the projections of the structures of the minerals on analogous planes (Fig. 2) it is evident that the arrangement of the atoms in the unit cell of krennerite between the planes $x = \frac{1}{4}$ and $x = \frac{3}{4}$ is the same as that in a corresponding block of calaverite, except for very slight changes in the parameters. The



Sylvanite (*a*)

Calaverite (*b*)

Krennerite (*c*)

Fig. 1. Projections of the unit cells of sylvanite, calaverite and krennerite on the analogous planes 010 of sylvanite, 010 of calaverite, and 001 of krennerite. The unit cells of sylvanite and calaverite have been rotated on their 010 planes into positions in which the directions in this plane are analogous to the parallel directions in the 001 plane of krennerite. The resulting orientations are as follows: sylvanite—the origin is the lower right-hand corner of the projection of the unit cell; the positive direction of the *a* axis is horizontal and parallel to the plane of the drawing from right to left, the positive direction of the *b* axis is perpendicular to the plane of the drawing toward the reader, the positive direction of the *c* axis is parallel to the plane of the drawing diagonally upward to the right; the angle between the positive *a* axis and the positive *c* axis is 145° 26′; calaverite—the origin is the uppermost corner of the projection of the unit cell, the positive direction of the *a* axis is parallel to the plane of the drawing downward to the left, the positive direction of the *b* axis is perpendicular to the plane of the drawing away from the observer, the positive direction of the *c* axis is parallel to the plane of the drawing downward to the right; the angle between the positive *a* axis and the positive *c* axis is 90° 13′; krennerite—the origin is the lower left corner of the projection of the unit cell, the positive direction of the *a* axis is parallel to the plane of the drawing vertically upward, the positive direction of the *b* axis is parallel to the plane of the drawing horizontal to the right, the positive direction of the *c* axis is perpendicular to the plane of the drawing away from the observer. The unit cells of the three minerals have the same orientations in Figs. 1 and 2.

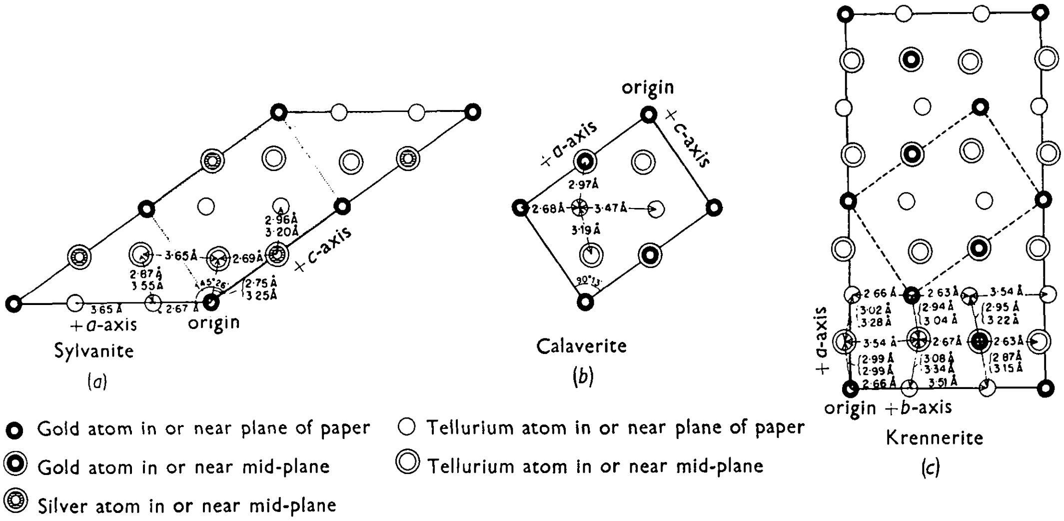


Fig. 2. Projections of the structures of sylvanite, calaverite and krennerite on the analogous planes 010 of sylvanite, 010 of calaverite, and 001 of krennerite. The dotted lines are the boundaries of a block in the sylvanite structure analogous to the unit cell of calaverite; the dashed lines are the boundaries of a block in the krennerite structure analogous to the unit cell of calaverite.

plane $x = \frac{1}{4}$ is a mirror plane in the unit cell of krennerite, and the structure in the part of the cell between $x = 0$ and $x = \frac{1}{4}$ can be obtained by reflecting the structure in the central part across the plane $x = \frac{1}{4}$; the plane $x = \frac{3}{4}$ is likewise a mirror plane, and the structure in the part of the cell between $x = \frac{3}{4}$ and $x = 1$ can be obtained by reflecting the structure in the central part across the plane $x = \frac{3}{4}$. These two mirror planes are not present in calaverite; thus the portion of the structure of krennerite analogous to the structure of the unit cell of calaverite (outlined by dashed lines in Fig. 2(*c*)) lies within the block of the krennerite cell between the two mirror planes $x = \frac{1}{4}$ and $x = \frac{3}{4}$.

In all three minerals the gold and silver atoms are surrounded by six tellurium atoms, which are not all at equal distances, however.* The six tellurium neighbors of each gold or silver atom lie at the vertices of considerably distorted octahedra. In sylvanite each gold atom has two tellurium neighbors at 2·67 Å, two at 2·75 Å, and two at 3·25 Å;† the four neighbors at 2·67 Å and 2·75 Å lie in a plane at the corners of a parallelogram which is nearly a square. Each silver atom in sylvanite has two tellurium neighbors at 2·69 Å, two at 2·96 Å, and two at 3·20 Å; the two neighbors at 2·69 Å make an angle of nearly 180° with the silver atom. In calaverite each gold (or silver) atom has two tellurium neighbors at 2·68 Å and four at 2·97 Å.** In krennerite the gold (or silver) atoms are of three kinds. The first has two tellurium neighbors at 2·66 Å and four at 2·99 Å; the second has one tellurium neighbor at 2·63 Å, one at 2·67 Å, one at 2·87 Å, one at 2·95 Å, one at 3·15 Å, and one at 3·22 Å; the third has one tellurium neighbor at 2·63 Å, one at 2·66 Å, two at 2·94 Å, and two at 3·04 Å.††

In sylvanite and calaverite each tellurium atom is surrounded by three gold or silver atoms and three tellurium atoms. In sylvanite each tellurium atom is much closer to one of its three tellurium neighbors than to the other two; all the tellurium atoms are thus members of well defined Te_2 groups. In calaverite each tellurium atom is equally close to two of its three tellurium neighbors, the third lying at a greater distance; the structure contains endless chains of tellurium atoms. In krennerite part of the tellurium atoms are surrounded by three gold or silver atoms and three tellurium atoms, part by one gold or silver atom and five tellurium atoms, part by five gold or silver atoms and one tellurium atom. The interatomic distances indicate that Te_2 and Te_3 groups are present as well as tellurium atoms bonded only to gold or silver atoms. There are no endless chains of tellurium atoms in krennerite similar to those in calaverite. In the Te_2 groups in sylvanite the interatomic distance is 2·87 Å; in the Te_2 groups in krennerite it is 3·08 Å;

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* The interatomic distances in the three minerals are shown in Fig. 2.

† The interatomic distances in sylvanite given here differ slightly from those of Tunell (1941), which were in kX. units and were obtained by graphical methods; the largest difference, when both sets of distances are expressed in the same units, is 0·02 Å, which is less than the tolerance ±0·10 Å attached to all the interatomic distances in sylvanite.

** The interatomic distances in calaverite are based on a Patterson projection and a Fourier projection as well as on comparisons of calculated and observed intensities by Tunell (unpublished work); they are all subject to a tolerance of ±0·05 Å.

†† The interatomic distances in krennerite are based on a Fourier projection as well as on comparisons of calculated and observed intensities (Tunell & Murata, 1950) and are all subject to a tolerance of ±0·15 Å.

in the Te_3 groups in krennerite it is 3·02 Å; in the endless chains of tellurium atoms in calaverite it is 3·19 Å. These distances may be compared with the interatomic distance in the endless chains of tellurium atoms in native tellurium, which is 2·86 Å. The maximum distance from one tellurium atom to any one of its other tellurium neighbors with which it forms weaker bonds is 3·65 Å in sylvanite, 3·47 Å in calaverite, and 3·54 Å in krennerite. These distances are less than the shortest distance between non-bonded atoms in native tellurium, which is 3·74 Å.

It is noteworthy that there is a progressive increase in volume of corresponding blocks in the series calaverite, krennerite, sylvanite correlated with the progressive increase in the silver:gold ratio. This is shown in Table 2. The volume of the unit cell of crystals of pure silver is slightly greater than that of crystals of pure gold, but the increase in volume with silver:gold ratio in the ditellurides is considerably greater. In the isostructural pair cesium argentous auric chloride and cesium aurous auric chloride, on the other hand, Elliott & Pauling (1938) have shown that the volume of the unit cell of the argentous compound is smaller than that of the aurous compound. In the gold–silver ditellurides the silver appears to have a slightly smaller oxidation number than the gold. With this probable slight difference in oxidation numbers the increase in volume in the series of gold–silver ditellurides with increasing silver:gold ratio may be correlated, and the apparently limited solid solution of silver in calaverite and krennerite and the limited solid solution of gold in sylvanite may be connected.

Table 2. *Correlation of the volumes of corresponding blocks in calaverite, krennerite and sylvanite with the silver: gold ratios*

	Volume of block (Å^3)	Atomic ratio silver : gold
Calaverite	160·4	1 : 16·3*
Krennerite	162·6 (= $\frac{1}{4}\times$ 650·6)	1 : 3·81*
Sylvanite	166·9 (= $\frac{1}{2}\times$ 333·7)	1 : 1·15*

* Average value.

Electronic structures of sylvanite, calaverite and krennerite

The structures of these three minerals can be interpreted in an illuminating way in terms of the modern theory of electronic structure and valence. The three crystals are intermediate in nature between metals and intermetallic compounds, on the one hand, and normal salt-like compounds, on the other.

The possible valence states of neutral silver and gold atoms showing integral values of the valence are represented in Table 3. There are nine stable outer orbitals, formed by hybridization of the five *d* orbitals, one *s* orbital, and three *p* orbitals of the outer shells of the atoms. If all nine orbitals are occupied by one or two of the eleven outermost electrons, the valence of the atom is 7, as shown in the first line of the table. Such an atom does not have the extra orbital required for the stability of a metallic system (Pauling, 1948*a*, *b*). In elementary silver and gold the valence is about $5\frac{1}{2}$, representing resonance between the first valence state in the table, with no metallic orbital, and the second valence state, with a metallic orbital, in the ratio 1:3. The normal compounds of silver and gold correspond to the valences 3 and 1, represented in the third and fourth rows of the table, with gold tending toward oxidation number +3 and silver toward oxidation number +1.

Table 3. *Valence states of silver and gold atoms*

Valence	Electron distribution among the nine outer orbitals								
7	↑↓	↑↓	·	·	·	·	·	·	·
5	↑↓	↑↓	↑↓	·	·	·	·	·	0
3	↑↓	↑↓	↑↓	↑↓	·	·	·	0	0
1	↑↓	↑↓	↑↓	↑↓	↑↓	·	0	0	0

In compounds with more electronegative elements there is a strong tendency for the atom to form covalent bonds in number one greater than the oxidation number. Unipositive silver tends to form two covalent bonds, which are oppositely directed, leading to a linear complex. Examples of such linear complexes are $[H_3NAgNH_3]^+$ and $[NCAgCN]^-$. Terpositive gold tends to form square covalent complexes, corresponding to the use of bond orbitals formed by dsp^2 hybridization. Complexes of these two kinds are present in the crystal $Cs_2AgAuCl_6$, investigated by Elliott & Pauling (1938). In this crystal, both silver and gold show rough octahedral co-ordination. Of the six chlorine ligates of each silver atom, two are at a small distance, 2·36 Å, and the other four at a considerably larger distance, 2·92 Å. The two at the small distance may be considered to be combined with the silver atoms to form the linear complex $[ClAgCl]^-$. The small distance corresponds essentially to a single covalent bond, and the large distance to a bond number less than 0·1, representing a bond of essentially negligible strength. The gold atom is surrounded by six chlorine atoms, of which four are at the small distance 2·30 Å, corresponding to a single bond, and two at the larger distance 3·13 Å, corresponding to a negligibly small bond number. The increase of covalence by one unit above the numbers indicated in Table 3 can be accounted for with use of the principle of electroneutrality (Pauling, 1948*c*, *d*). The differences in electronegativity of silver and chlorine and of gold and chlorine correspond to a significant amount of ionic character of the covalent bonds, and permit the increase in covalency by one unit above the oxidation number without producing a large resultant charge on the metal atom.

It is evident that sylvanite, calaverite and krennerite are more closely similar to the normal compounds of silver and gold than to intermetallic compounds. Silver, gold and tellurium are closely similar in size, the single-bond covalent radius of each of the three atoms being about 1·35 Å. Accordingly, if these elements were to form a normal intermetallic compound, the ligancy of each atom would be expected to be about 12; instead, the observed ligancy of each atom in these three minerals is 6, as in the crystal $Cs_2AgAuCl_6$. Moreover, the six ligates of a silver or gold atom in these minerals are not equally removed from the central atom; instead, either two or four are drawn in to smaller distances than the others, as in the crystal $Cs_2AgAuCl_6$. The analogy with the normal valence compounds of gold is not complete, however, because in calaverite and krennerite each gold atom has only two closely-bound ligates, whereas in the normal valence compounds of terpositive gold there are four of these ligates.

We may first ask why the formula of the stable gold telluride is $AuTe_2$, rather than Au_2Te_3, as would be required by the normal oxidation numbers of gold and tellurium, +3 and −2, respectively. Investigation in the laboratory of the binary system gold–tellurium has shown that the only compound formed is $AuTe_2$; its stability is small: its melting point is only 464° C., as compared with 452·5° C. for tellurium and 1063° C. for gold. It could be predicted that the heat of formation of any compound of gold and tellurium would be small, since the two elements differ only slightly in electronegativity (electronegativity 2·3 for gold, 2·1 for tellurium). It seems probable that the relative instability of the compound Au_2Te_3* can be attributed to the geometrical difficulty in formulating an unstrained structure for this composition. Whereas there are several ways of achieving the composition AB_2 with ligancy 6 for A (the cadmium iodide structure, cadmium chloride structure, rutile structure, anatase structure, brookite structure, etc.), all of the known structures A_2B_3 suffer from one or another disadvantage: for example, the corundum structure requires the sharing of faces between octahedra, and the C-modification of the rare earth sesquioxides involves a great distortion of the octahedra. If the tellurium atoms would form tellurium–tellurium covalent bonds to the average extent of one-half a bond per atom, the formula $AuTe_2$ would be made compatible with the normal oxidation numbers of gold and tellurium, and the compound would be able to select a geometrically satisfactory arrangement. The following analysis of the structures of the three minerals under discussion supports this explanation of the observed stability of the compound $AuTe_2$.

The structures of the three minerals can be described as derived by small distortions from a simple cubic arrangement, with an atom of gold, silver or tellurium at each lattice point. The ligancy of each atom for such an arrangement is 6. Each drawing in Fig. 2 corresponds to such a simple cubic lattice with the cube edge [100] horizontal in the plane of the paper and the face diagonal [011] vertical. For the undistorted simple cubic lattice the krennerite axes $\frac{1}{4}a_0:\frac{1}{3}b_0:c_0$ should be in a ratio $\sqrt{2}:1:\sqrt{2}$; actually their ratios are 1·41 : 1 : 1·52.

In sylvanite and calaverite each gold (silver) atom has six tellurium atoms as its ligates, and each tellurium atom has three gold (silver) atoms and three tellurium atoms as ligates. The structures are closely similar to the cadmium iodide structure, $C6$, which has hexagonal symmetry. The hexagonal axis for the ideal $C6$ structure is parallel to the c axis of calaverite. For the ideal $C6$ structure the axes a_0 and b_0 of calaverite should be in the ratio $\sqrt{3}:1$; their ratio is in fact 1·63 : 1.

The interpretation of the observed interatomic distances in the three minerals in terms of bond numbers (Pauling, 1938a, 1947) is given in Table 4. The bond numbers have been calculated with use of the equation

$$D(n) = D(1) - 0{\cdot}600 \log n \qquad (1)$$

(Pauling, 1947), in which $D(n)$ is the observed interatomic distance, $D(1)$ is the sum of the single-bond covalent radii for the two bonded atoms, and n is the bond number. Since the electronegativities of gold, silver and tellurium are nearly the same, we may expect from the electroneutrality principle that tellurium will have its normal covalence 2, and that gold and silver will have one or another of the covalences indicated in Table 3. A rough calculation of bond numbers indicates that the valences of gold and silver in all of the compounds are approximately 3. The valence 3 for silver and gold in an essentially non-metallic structure (in which the amount of d character of metallic orbitals can be neglected) corresponds to 33% d character for the bond orbitals, and to the single-bond radius 1·351 Å for gold* and 1·353 Å for silver.† The single-bond radius for tellurium has essentially the same value, 1·348 Å.**

In Table 4 there are given bond numbers corresponding to all of the bond distances in the three minerals, as calculated by means of equation (1), and with $D(1)$ taken equal to 2·70 Å for each bond. The smallest observed distances lie in the range 2·63–2·69 Å. The value 1·00 has been assigned as bond number for each for these bonds, although the application of equation (1) leads to slightly larger values. It seems not unlikely that differences in hybridization of bond orbitals involved in the formation of the stronger bonds and the weaker bonds lead to a small decrease in interatomic distance for single covalent bonds below the value calculated on the assumption of equal hybridization.

The calculated valence numbers of seven of the eight

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* Recently a new mineral with the formula Au_2Te_3 was discovered; it has a complicated structure with triclinic symmetry (Peacock & Thompson, 1946).

* Calculated by means of equation (12 c) (Pauling, 1948 b).

† Calculated by means of equation (11 c) (Pauling, 1948 b).

** Calculated by means of equation (11 d) (Pauling, 1948 b).

Table 4. *Interatomic distances, bond numbers, and valences in sylvanite, calaverite and krennerite*

		Bond numbers	Valence
Sylvanite			
Ag:	6 Te at 2·69(2), 2·96(2), 3·20(2)	1·00, 0·37, 0·15	3·04
Au:	6 Te at 2·67(2), 2·75(2), 3·25(2)	1·00, 0·83, 0·12	3·90
Te I:	1 Ag at 2·69	1·00	1·00
	2 Au at 2·75, 3·25	0·83, 0·12	0·95
	3 Te at 2·87, 3·55, 3·65	0·52, 0·04, 0·03	0·59
			2·54
Te II:	2 Ag at 2·96, 3·20	0·37, 0·15	0·52
	1 Au at 2·67	1·00	1·00
	3 Te at 2·87, 3·55, 3·65	0·52, 0·04, 0·03	0·59
			2·11
Calaverite			
Au:	6 Te at 2·68(2), 2·97(4)	1·00, 0·35	3·40
Te:	3 Au at 2·68, 2·97(2)	1·00, 0·35	1·70
	3 Te at 3·19(2), 3·47	0·15, 0·05	0·35
			2·05
Krennerite			
Au I:	6 Te at 2·66(2), 2·99(4)	1·00, 0·33	3·32
Au II:	6 Te at 2·63, 2·67, 2·87, 2·95, 3·15, 3·22	1·00, 1·00, 0·52, 0·38, 0·18, 0·14	3·22
Au III:	6 Te at 2·63, 2·66, 2·94(2), 3·04(2)	1·00, 1·00, 0·40, 0·27	3·34
Te I:	3 Au at 2·66, 2·87, 3·15	1·00, 0·52, 0·18	1·70
	3 Te at 3·08, 3·34, 3·51	0·23, 0·09, 0·04	0·36
			2·06
Te II:	3 Au at 2·67, 2·94, 3·04	1·00, 0·40, 0·27	1·67
	3 Te at 3·08, 3·34, 3·54	0·23, 0·09, 0·04	0·36
			2·03
Te III:	3 Au at 2·63, 2·99(2)	1·00, 0·33	1·66
	3 Te at 3·02, 3·28, 3·54	0·29, 0·11, 0·04	0·44
			2·10
Te IV:	5 Au at 2·63, 2·95(2), 3·22(2)	1·00, 0·38, 0·14	2·04
	1 Te at 3·54	0·04	0·04
			2·08
Te V:	1 Au at 2·66	1·00	1·00
	5 Te at 3·02(2), 3·28(2), 3·54	0·29, 0·11, 0·04	0·84
			1·84

kinds of tellurium atoms lie within the range 1·84–2·11, and may accordingly be taken as equal to the expected value 2. The valence number for the anomalous kind of tellurium, Te I of sylvanite, is given in Table 4 as 2·54. This high value may be due to the transfer of half an electron from each of the Te I atoms to gold; or the deviation of the value from the normal value 2 may not be real. It is possible that the gold–tellurium interatomic distance 2·75 Å is low by a few hundredths of an Ångström unit, and also that the single-bond distance 2·70 Å used in the calculation of the bond number 0·83 for this bond is high, because of hybridization, as discussed above.

Each of the eight kinds of tellurium atoms except Te IV of krennerite forms bonds of significant strength with other tellurium atoms. The average number of tellurium–tellurium bonds formed by tellurium atoms is 0·45 per atom. This result provides support for the suggestion made above that the formula $AuTe_2$ is made compatible with the expected oxidation numbers of the atoms through the formation of tellurium–tellurium bonds, to the extent of one-half bond per tellurium atom.

The calculated valence for gold is 3·40 in calaverite, and 3·32, 3·22 and 3·34 in krennerite. A somewhat higher value, 3·90, is found for gold in sylvanite. The deviation of about 10% from the expected value 3 in the case of calaverite and krennerite may result from the unreliability of the calculation. It seems not unlikely, however, that the high value 3·90 for gold in sylvanite results from some electron transfer from Te I atoms. The valence found for silver in sylvanite, 3·04, is in good agreement with the expected value 3.

The study of the three minerals under discussion has provided information about the nature of the bonds formed by an atom of a transition element with covalence 3 and with one *d* orbital available. When one *d* orbital is available and two bonds are formed, the bonds are linearly directed, as was shown by quantum mechanical calculation of the two best *spd* hybrid bond orbitals that can be constructed with only one *d* orbital available (Pauling, 1931). When four bonds are formed with use of one *d* orbital, they are directed toward the corners of a square. The configurations observed for gold and silver in the three minerals under discussion indicate that maximum stability is achieved for a tercovalent element with one *d* orbital available for bond formation through the formation of two oppositely directed single bonds, the remaining valences being used for the formation of bonds in the plane at right angles to the line formed by the first two (Pauling, 1931). These considerations suggest a refinement in the method of calculating bond numbers. On the assumption that the bond-forming power of an orbital is proportional to its concentration in the bond direction, the two equivalent orbitals corresponding to the two best bonds that can be formed with the use of a single *d* orbital are of the form

$$\frac{1}{2\sqrt{3}}s \pm \frac{1}{\sqrt{2}}p_z + \frac{\sqrt{5}}{2\sqrt{3}}d_z \qquad \text{(Pauling, 1931).}$$

They have $\frac{5}{12}d$ character (the square of the coefficient of d_z in the above equation), which corresponds to the single-bond radius for gold 1·309 Å.* We accordingly predict, with use of the single-bond radius for tellurium, 1·348 Å, that the gold–tellurium distance for two oppositely directed single bonds would be 2·66 Å, which agrees exactly with the average of the values for the corresponding bonds in Table 4, which range from 2·63 to 2·68 Å. With this refinement, the bond numbers of the longer gold–tellurium bonds would be calculated with use of the radius 1·43 Å† for gold, and their values would be correspondingly a little larger.

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* Calculated by means of equation (12 *c*) (Pauling, 1948 *b*) with $\delta = \frac{5}{12}$.

† Calculated by means of equation (12 *c*) (Pauling, 1948 *b*) with $\delta = \frac{2}{12}$.

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The Height of the Vector Rods in the Three-Dimensional Patterson of Haemoglobin

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A method is described for calculating the average height of the vector rods in the three-dimensional Patterson of haemoglobin. The calculations have been carried out for the α-helix. They show that the simple models previously considered for haemoglobin give peaks which are too high, and that to obtain even rough agreement either less than about half the protein must be put into chains parallel to the *X* axis or considerable irregularity must be introduced. The evidence suggests that the folded polypeptide chain does not run in one direction for more than 20 Å at a stretch.

Introduction

The three-dimensional Patterson synthesis of horse methaemoglobin has, as one of its features, rod-shaped regions of high vector density, parallel to the *X* axis, which Perutz (1949) interpreted in terms of straight rods of high electron density in the molecule; he suggested that these rods were due to folded polypeptide chains arranged in hexagonal close packing