

The Crystal Structure of Au_2Bi .

By

T. Jurriaanse in Eindhoven (Holland).

(With 3 figures.)

In a previous communication¹⁾ a new phase was shown to exist in the system gold-bismuth, at 66.6 at. proc. gold; though the crystal structure was mentioned, its systematic deduction from the experimental results was not given.

This phase has always the same composition, whatever the ratio of the components is in the liquid from which it crystallizes, the lines of the Debye-Scherrer diagram remaining in the same place. This points to the fact, that Au_2Bi is an intermetallic compound in which none of the components dissolve.

1. Crystal System.

Crystals may be obtained by washing out the eutectic alloy with HNO_3 . The crystal planes were not smooth enough to measure the angles between them with accuracy (deviations of 5'—9') but they had the appearance of octahedra. To test this statement rotation diagrams were made around the three perpendicular axis, which gave exactly the same diagram with the same intensities. Consequently the system is cubic. The lattice constant is 7.942 Å as follows from the zône-distances and spacings.

The density, pycnometrically determined, is 15.46 from which we conclude the number of Au_2Bi -complexes is 8. The density calculated from the röntgenographical data is 15.70.

2. The Space-lattice.

The results of the powder diagram are collected in table I. In the first column the direct film measurements (in 1/10 mm) are shown, from which the corrected line-distances follow. The corrections were found by gauging the camera with metals of known structures. Gauge substances were: gold, bismuth and silver. By this method we found a mean value for $d = 7.942 \pm 0.002$ Å.

1) de Haas, W. J. and Jurriaanse, T., Comm. Leiden No. 220e. Proc. Acad. Amsterdam **35** (1932) 748.

Table I. Camera radius 44.82 mm, CuK_{α_1, α_2} radiation.

l	$l_{\text{corr.}}$	Spacings	hkl	d	I
510	496	2.814	202	7.95	3
598	584	2.404	311	7.97	10
627	613	2.292	222	7.940	5
728	714	1.983	400	7.932	1
902	887	1.620	422	7.938	3
960	945	1.529	511, 333	7.944	7
1055	1039	1.404	440	7.942	7
1198	1182	1.255	620	7.938	2
1249	1232	1.212	533	7.947	5
1267	1250	1.197	622	7.940	5
1337	1320	1.146	444	7.939	1
1470	1452	1.061	642	7.939	3.5
1522	1504	1.034	553, 731	7.942	8
1607	1588	0.994	800	7.952	3
1746	1727	0.937	822, 660	7.954	2.5
1800	1781	0.918	751, 555	7.950	8
1820	1801	0.911	662	7.942	6
1897	1878	0.888	840	7.942	1
2060	2041	0.846	664	7.937	2
2130	2112	0.833	931	7.946	10
2262	2244	0.810	844	7.936	15

As follows from the indication of the observed reflections (unmixed indices) the space-lattice is face-centered. To prove this, a rotation diagram was made round $[110]$ and compared to the z -distances of $[100]$. We found a ratio: $\frac{\sin \sigma [110]}{\sin \sigma [100]} = \sqrt{2}$ (σ is the angle of the secondary beam with the equatorial plane) the value corresponding to a face-centered space-lattice.

3. Atomic Arrangement and Space-group.

As the octahedron is not found in the crystal classes T and T_d , there remain the following face-centered space-groups:

$$T_h^3, T_h^4, O^3, O^4, O_h^5, O_h^6, O_h^7 \text{ and } O_h^8.$$

O_h^8 is excluded, this group only having point arrangements of 16-, 32- and more-fold, so that 24 atoms can never be placed.

In T_h^4 , O^4 and O_h^7 the same arrangements are possible, only with

different point-symmetry. They are the combinations of: 8f, 8g with 16b, 16c¹).

In T_h^3 , O^3 and O_h^5 the only possible arrangements are: 24c and 24a; and in O_h^6 : 24c and 24h. The latter is excluded, since we observed lines from $(hhl) = (311)$, (511) etc. which should be extinguished as h and l are odd.

The positions 24a and 24c for the space groups T_h^3 , O^3 and O_h^5 would indicate a statistical distribution of the gold- and bismuth-atoms. This is improbable, as neither of the components dissolves in the crystal. The arrangement 24c can be excluded, belonging to the forbidden group O_h^6 ; the second distribution 24a, has a parameter, the value of which is considerably limited by the atomic radii. The distances giving the limits are:

$$[[u00]] - [[0u0]] \text{ and } [[0u0]] - \left[\left[\frac{1}{2}, \frac{1}{2} - u, 0\right]\right].$$

Taking as large a variation of u as possible, by using the radius 1,44 Å of gold, we find the overlapping limits $u \leq 0.256$ respectively $u \geq 0.24$. Thus the only possibility would be $u = 0.25$; this gives the special arrangement 24h, being again a distribution in O_h^6 .

No statistical arrangement being possible, we come to the combinations of 8f, 8g with 16b, 16c.

1) Symbols of point arrangements from:

Wyckoff, Ralph W. G., The analytical expression of the results of the theory of space-groups.

8f	$0\frac{1}{2}\frac{1}{2}$ $\frac{1}{4}\frac{3}{4}\frac{3}{4}$	$\frac{1}{2}0\frac{1}{2}$ $\frac{3}{4}\frac{1}{4}\frac{3}{4}$	$\frac{1}{2}\frac{1}{2}0$ $\frac{3}{4}\frac{3}{4}\frac{1}{4}$	000 $\frac{1}{4}\frac{1}{4}\frac{1}{4}$	8g	$\frac{1}{2}00$ $\frac{3}{4}\frac{1}{4}\frac{1}{4}$	$0\frac{1}{2}0$ $\frac{1}{4}\frac{3}{4}\frac{1}{4}$	$00\frac{1}{2}$ $\frac{1}{4}\frac{1}{4}\frac{3}{4}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$ $\frac{3}{4}\frac{3}{4}\frac{3}{4}$					
16b	$\frac{111}{888}$ $\frac{177}{888}$ $\frac{717}{888}$ $\frac{771}{888}$ $\frac{888}{888}$	$\frac{551}{888}$ $\frac{537}{888}$ $\frac{357}{888}$ $\frac{331}{888}$ $\frac{888}{888}$	$\frac{515}{888}$ $\frac{573}{888}$ $\frac{313}{888}$ $\frac{375}{888}$ $\frac{888}{888}$	$\frac{155}{888}$ $\frac{133}{888}$ $\frac{753}{888}$ $\frac{735}{888}$ $\frac{888}{888}$	16c	$\frac{137}{888}$ $\frac{151}{888}$ $\frac{731}{888}$ $\frac{757}{888}$ $\frac{888}{888}$	$\frac{713}{888}$ $\frac{115}{888}$ $\frac{173}{888}$ $\frac{775}{888}$ $\frac{888}{888}$	$\frac{371}{888}$ $\frac{511}{888}$ $\frac{317}{888}$ $\frac{577}{888}$ $\frac{888}{888}$	$\frac{353}{888}$ $\frac{555}{888}$ $\frac{533}{888}$ $\frac{335}{888}$ $\frac{888}{888}$					
24a	$u00$; $\bar{u}00$; $0u0$; $0\bar{u}0$; $00u$; $00\bar{u}$;	$u + \frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2} - u, \frac{1}{2}, 0$; $\frac{1}{2}, u + \frac{1}{2}, 0$; $\frac{1}{2}, \frac{1}{2} - u, 0$;	$u + \frac{1}{2}, 0, \frac{1}{2}$; $\frac{1}{2} - u, 0, \frac{1}{2}$; $\frac{1}{2}, u, \frac{1}{2}$; $\frac{1}{2}, 0, u + \frac{1}{2}$;	$u, \frac{1}{2}, \frac{1}{2}$; $\bar{u}, \frac{1}{2}, \frac{1}{2}$; $0, u + \frac{1}{2}, \frac{1}{2}$; $0, \frac{1}{2} - u, \frac{1}{2}$; $0, \frac{1}{2}, u + \frac{1}{2}$; $0, \frac{1}{2}, \frac{1}{2} - u$.	24c	$\frac{1}{4}10$ $0\frac{1}{4}\frac{1}{4}$ $\frac{1}{4}0\frac{1}{4}$ $\frac{1}{2}\frac{3}{4}\frac{1}{4}$ $\frac{3}{4}\frac{1}{2}\frac{1}{4}$ $\frac{3}{4}\frac{1}{4}\frac{1}{2}$	$\frac{1}{4}\frac{3}{4}0$ $0\frac{1}{4}\frac{3}{4}$ $\frac{3}{4}0\frac{1}{4}$ $\frac{1}{2}\frac{3}{4}\frac{3}{4}$ $\frac{1}{4}\frac{1}{2}\frac{3}{4}$ $\frac{3}{4}\frac{3}{4}\frac{1}{2}$	$\frac{3}{4}\frac{1}{4}0$ $0\frac{3}{4}\frac{1}{4}$ $\frac{1}{4}0\frac{3}{4}$ $\frac{1}{2}\frac{1}{4}\frac{3}{4}$ $\frac{3}{4}\frac{1}{4}\frac{3}{4}$ $\frac{1}{4}\frac{1}{4}\frac{3}{2}$	$\frac{3}{4}\frac{3}{4}0$ $0\frac{3}{4}\frac{3}{4}$ $\frac{3}{4}0\frac{3}{4}$ $\frac{1}{2}\frac{1}{4}\frac{3}{4}$ $\frac{1}{4}\frac{1}{2}\frac{3}{4}$ $\frac{1}{4}\frac{1}{4}\frac{3}{2}$	24h	$\frac{1}{4}00$ $0\frac{1}{4}0$ $00\frac{1}{4}$ $\frac{3}{4}00$ $0\frac{3}{4}0$ $00\frac{3}{4}$	$\frac{1}{2}\frac{3}{4}\frac{1}{2}$ $\frac{3}{4}\frac{1}{2}\frac{1}{2}$ $\frac{1}{2}\frac{2}{4}\frac{3}{4}$ $\frac{1}{2}\frac{1}{4}\frac{1}{2}$ $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ $\frac{1}{2}\frac{1}{2}\frac{1}{4}$	$\frac{3}{4}\frac{1}{2}0$ $\frac{1}{2}\frac{3}{4}0$ $\frac{1}{4}\frac{3}{4}0$ $\frac{1}{2}\frac{1}{4}0$ $0\frac{1}{4}\frac{1}{2}$ $\frac{1}{4}0\frac{1}{2}$	$0\frac{3}{4}\frac{1}{2}$ $\frac{3}{4}0\frac{1}{2}$ $\frac{1}{2}0\frac{3}{4}$ $\frac{1}{2}0\frac{1}{4}$ $0\frac{1}{4}\frac{3}{4}$ $0\frac{1}{2}\frac{3}{4}$

The combination 8f—16c and 8g—16b are very similar the one being deduced from the other by moving all the atoms over half a space diagonal; the same applies to 8g—16c and 8f—16b. To determine which is the correct arrangement, a calculation of the intensities must be made.

The calculation was made according to the known formula:

$$I = A_{\vartheta} \frac{n(1 + \cos^2 2\vartheta)}{\sin^2 \vartheta \cos \vartheta} S^2$$

in which A_{ϑ} is the absorption factor according to Claassen¹⁾ and Rusterholz²⁾, n the relative number of reflecting planes, and S the structure factor. The values of the atomic factors were taken from James and Brindley³⁾.

Table II.

Table II shows that the intensities calculated for a few lattice planes for the combination 8g—16c and 8f—16b are not in agreement with the experiments. So the only possible atomic arrangements are: 8f—16c and 8g—16b. In that case the theoretical intensities are in perfect accordance with experimental facts as is shown in table III.

hkl	$I_{\text{Exp.}}$	$I_{\text{Calc.}}$
202	3	2.5
311	10	10
222	5	4
331	0	5
422	3	1
511, 333	7	0
440	7	4
531	0	2

Table III. 8f—16c and 8g—16b.

hkl	$I_{\text{Exp.}}$	$I_{\text{Calc.}}$	hkl	$I_{\text{Exp.}}$	$I_{\text{Calc.}}$
111	—	0	444	10	4
200	—	0	711, 551	0	2
220	30	18	640	0	0
311	100	81	642	35	28
222	50	30	731, 553	80	87
400	10	6	800	30	33
331	0	2	733	0	1
420	0	0	644, 820	0	0
422	30	32	822, 660	25	27
511, 333	70	66	751, 555	80	112
440	70	75	662	60	73
531	0	0	840	10	18
600, 442	0	0	911, 753	0	3
620	20	16	842	0	0
533	50	43	664	20	30
622	50	56	931	100	200
			844	150	390

1) Claassen, A., Philos. Mag. **9** (1930) 57.2) Rusterholz, A., Z. Physik **63** (1930) 1.3) James and Brindley, Philos. Mag. **12** (1931) 81; Z. Kristallogr. **78** (1931) 470.

The atomic arrangement is:

$$\begin{array}{l}
 Bi \left\{ \begin{array}{l} 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0, 000 \\ 1\frac{3}{4}\frac{3}{4}, \frac{3}{4}1\frac{3}{4}, \frac{3}{4}\frac{3}{4}1, 1\frac{1}{4}\frac{1}{4} \\ 4\frac{4}{4}\frac{4}{4}, \frac{4}{4}\frac{4}{4}\frac{4}{4}, \frac{4}{4}\frac{4}{4}\frac{4}{4}, \frac{4}{4}\frac{4}{4}\frac{4}{4} \end{array} \right. \\
 Au \left\{ \begin{array}{l} 1\frac{3}{8}\frac{7}{8}, \frac{7}{8}1\frac{3}{8}, \frac{3}{8}\frac{7}{8}1, \frac{3}{8}\frac{5}{8}\frac{3}{8} \\ 1\frac{5}{8}\frac{1}{8}, \frac{1}{8}\frac{5}{8}, \frac{5}{8}\frac{1}{8}\frac{1}{8}, \frac{5}{8}\frac{5}{8}\frac{5}{8} \\ 7\frac{3}{8}\frac{1}{8}, \frac{1}{8}\frac{7}{8}\frac{3}{8}, \frac{3}{8}\frac{1}{8}\frac{7}{8}, \frac{5}{8}\frac{3}{8}\frac{3}{8} \\ 7\frac{5}{8}\frac{7}{8}, \frac{7}{8}\frac{7}{8}\frac{5}{8}, \frac{5}{8}\frac{7}{8}\frac{7}{8}, \frac{3}{8}\frac{3}{8}\frac{5}{8} \end{array} \right.
 \end{array}$$

The bismuth atoms have a diamond configuration each of them having 4 *Bi*-neighbours; moreover they have 12 *Au*-neighbours. The gold atoms have 6 *Au*- and 6 *Bi*-neighbours.

It was not possible to determine the space-group with certainty, as the etching figures were not clear. The crystals are very brittle, which made it difficult to polish the planes. From what we could see, we should decide on the class O_h . This is to be expected as there is no sense in ascribing a limited symmetry to the atoms. Thus the space-group is most likely O_h^7 .

4. The Equilibrium Diagram of the System *Au—Bi*.

For the revision of the equilibrium diagram¹⁾ (see fig. 1) we need three data:

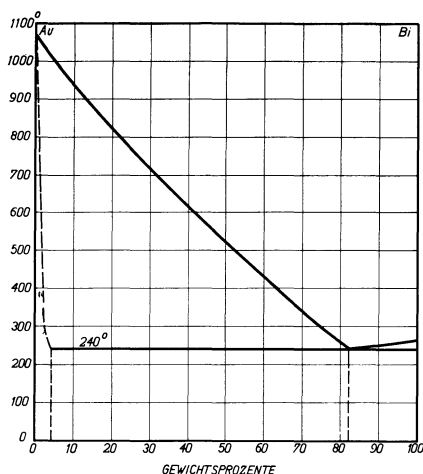


Fig. 1.

1. The homogeneity-range of the Au_2Bi -phase.
2. The melting point of Au_2Bi .
3. The homogeneity-range of the *Au*-phase.

As we mentioned before the component Au_2Bi always has the same lattice constant, whether in equilibrium with an excess of bismuth or with an excess of gold. From this we can conclude that the homogeneity-range is extremely narrow.

The second point was rather more difficult to determine. An attempt to find the melting point

by a thermal determination entirely failed, as the Au_2Bi -powder on being heated did not show the smallest trace of a thermal effect. From

1) Vogel, A., Z. anorg. allg. Chem. **50** (1906) 147.

thus we conclude that the heat of formation is small, which also explains the straight liquidus line of Vogel. Finally the melting point was found by quenching the Au_2Bi -powder from different temperatures, after which a Debye-Scherrer diagram was made. The diagram appeared to alter between 371° and 376° , so the melting point was fixed at $373^\circ \pm 2^\circ$.

The discovery of the intermetallic compound made it doubtful whether the extent of the homogeneity-range of the gold-phase, given by Vogel, was correct, as the description of the colour of the supposed solid solution with 4% Bi , entirely agreed with the appearance of Au_2Bi in the etching figures. Accordingly the homogeneity-range was suspected to be far less than 4%. This idea was confirmed by two facts. Firstly, none of the Debye-Scherrer lines from the goldphase in the various alloys experimented with (2% —, 40% —, 20% —, 40% Bi) shows the slightest displacement. Secondly, the alloys with 1% and 0.2% annealed during 48 hours, show very clear lamella of Au_2Bi (see fig. 2). So the homogeneity-range is certainly less than 0.2% and according to the röntgenographic data bismuth will not dissolve in gold at all.

The equilibrium diagram can now be constructed, assuming the correctness of the liquidus fixed by Vogel¹⁾ (see fig. 3).

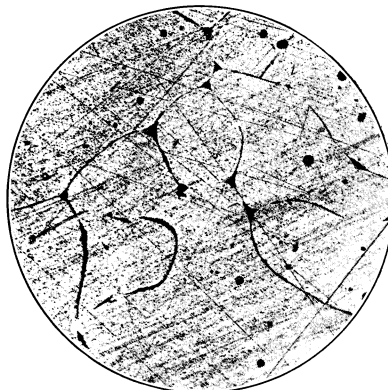


Fig. 2.

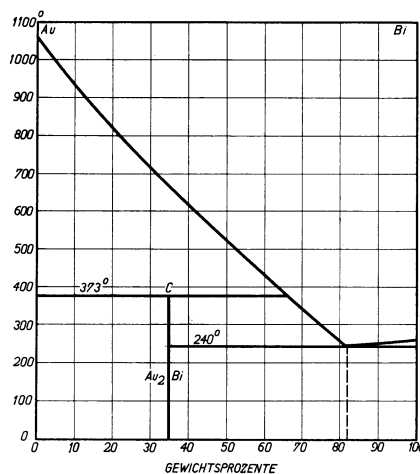


Fig. 3.

1) This determination was not repeated, as it would have been impossible to find a compound in the liquidus with the normal resources and the naturally small quantities of alloys available, the heat of formation being too small.

5. Comparison of Au_2Bi with Cu_2Mg ¹), W_2Zr ²), Bi_2K ³) and Au_2Pb ⁴).

Besides the identity of the structure type of these five intermetallic compounds, there are other points of resemblance worth mentioning. Firstly their homogeneity ranges are all very narrow. Cu_2Mg has the largest range with 1.63% Cu , and also the Au_2Pb -phase has some extent but the others have a fixed composition. Secondly the ratios of the atomic radii of the components of A_2B , r_B/r_A (for coörd. number 12 according to V. M. Goldschmidt) are narrowly limited (see table 4)⁵). Appa-

rently the building of the lattice is strongly determined by the dimensions of the constituent atoms. This is clearly expressed by the fact that the ratio of the atomic volumes $v_B/v_A \cong (r_B/r_A)^3 \cong 2$, for one can imagine that the A_2B -lattice arises from a cubic face-centered lattice (A -lattice, for instance Au - or Cu -lattice) by replacing the atoms of every other unit cell by half as many B -atoms.

To keep the lattice close-packed this B -atom must have an atomic volume twice as large as an A -atom.

A law for the electron-atom ratio as found by Hume-Rothery and Westgren and Phragmen for the β -, γ - and ε -structure types, does not apply for these five intermetallic compounds, even though we should make the most forced assumptions about the valencies of the elements.

I here wish to express my thanks to Prof. W. J. de Haas of Leiden, for placing at my disposal the instruments necessary for these experiments, and to Dr. W. G. Burgers of Eindhoven for making röntgen-diagrams to determine the melting point of Au_2Bi .

Summary.

In the system gold-bismuth there exists an intermetallic phase of the composition Au_2Bi . The crystal structure is cubic face-centred with an atomic arrangement 8f—16c and space-group O_h^7 . This intermetallic

1) Friauf, J. B., J. Amer. chem. Soc. **49** (1927) 3107; Arnfelt, H., Runquist, A. and Westgren, A., Z. anorg. allg. Chem. **175** (1928) 43.

2) Claassen, A. and Burgers, W. G., Z. Kristallogr. **86** (1933) 160.

3) Zintl, E. and Harder, Z. physik. Chem. (B) **16** (1932) 206.

4) Perlitz, H., Act. Comm. Univ. Dorpat (A) **27** (1934) 11.

5) See a remark by Zintl and Harder l. c.

compound has the same structure as Cu_2Mg , Au_2Pb , W_2Zr and Bi_2K . The ratio of the atomic radii of the constituent atoms is fairly constant for these five compounds.

The law of the electron-atom ratio is not satisfied. The homogeneity-range of the Au_2Bi -phase as well as the range of the gold-phase have no measurable extent. The melting point of Au_2Bi is 373° .

Note. During the correction I received a paper by F. Laves and K. Löhberg (Gött. Nachr. **1** (1934) 59) in which among other things the Cu_2Mg -type and the importance of the constant ratio of the atomic radii is treated in detail. The compounds $CuBe_2$ and $MgNiZn$ too seem to have the same crystal structure.

Received December 21st, 1934.