THE CRYSTAL STRUCTURE OF SILVER–PALLADIUM AND SILVER–GOLD ALLOYS.

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Synopsis.

Crystal Structure of Silver, Gold and Palladium and of Ag-Au and Ag-Pd Alloys. —Thin ribbons of the pure metals and of seven binary alloys of each series were prepared by fusing into small ingots and then swaging, drawing and rolling to thicknesses of from 1/400 to 1/200 cm. The x-ray diffraction patterns were photographed by allowing the K-radiation of Mo to fall for 8 to 20 hours on each ribbon. It was found that all these metals and alloys have their atoms arranged in face-centered cubic lattices. The parameter a of each lattice, the edge of the cube, has the values 4.08×10^{-8}, 4.075×10^{-8} and 3.90×10^{-8} cm. for pure Ag, Au and Pd respectively. For the Ag-Pd series, the parameter is nearly a linear function of the atomic per cent. of either component and this is also true for the Ag-Au series except that for the alloys with 30, 40 and 60 per cent. Ag the values of a came out one per cent. too high. These results are for the most homogeneous and isotropic condition and are believed to be correct to within about 1/3 per cent. *The effect of annealing* at from 830 to 940° C. for an hour or more in vacuo was to increase the size of individual crystals, to render them more homogeneous and to make their orientations more isotropic. *The effect of moderate cold working,* rolling, pressing or hammering is to reduce the size of the individual crystals and to make them less isotropic.

Densities of crystals of silver, gold and palladium, computed from the above results of X-ray crystal analysis and the atomic weights, come out 10.49, 19.24 and 11.87 respectively. The Ag and Au were pure and the Pd contained only 0.5 per cent. impurity.

Introduction.

A STUDY of the arrangement of atoms in alloys which are solid solutions of the components may throw some light on the cause of the abnormally high resistivity of such alloys. This report covers somewhat completely the crystal structure in two series of alloys, those of silver with gold and palladium, which are particularly interesting in this connection because silver and gold both possess high conductivity, whereas the conductivity of palladium is much lower than that of silver. The conductivity of the alloys is not, however, treated in this report.

Preparation of Alloys.

The component metals were all purchased from Baker and Company, and were of high purity, the silver and gold containing less than 0.01 per cent. of impurities, the palladium containing about 2 per cent. of impurities, chiefly copper and noble metals. The chemical and metallurgical processes outlined below were conducted by Mr. J. E. Harris

and Mr. H. T. Reeve, both of this laboratory, who have had extensive experience in the preparation of alloys of known composition and exceptional homogeneity. All three metals were repurified chemically and obtained in finely divided form, the principal effect of these processes upon their purity being that the palladium finally contained less than 0.5 per cent. of impurities, copper, in particular, being completely removed. The metal powders were weighed, mixed, and pressed into small cylindrical rods of the desired compositions. The Ag-Au alloys were fused in an electrically heated furnace open to the air; the Ag-Pd alloys were fused on alundum or magnesia by the oxyhydrogen flame. The ingots, which weighed about 10 grams each, were swaged and drawn into wires about one millimeter in diameter. Short pieces of these wires were rolled to a thickness of from 0.0025 to 0.0050 cm., the rolling being carried farthest for alloys containing large proportions of gold, and hence having the highest absorption coefficients for x-rays. The condition resulting from these operations is indicated below by the letter R.

The annealing process consisted in maintaining the temperature of the sample at from 830° C. to 940° C. for an hour or more, in vacuo, in a quartz tube furnace, electrically heated. When several alloys were annealed at one time the samples were placed in individual quartz tubes, open at one end, to prevent mutual contamination. Temperatures were read by a calibrated platinum-platinum-rhodium thermocouple. The Ag-Au alloys required much longer annealing at these temperatures than did the Ag-Pd alloys, before the results indicated even fair homogeneity and isotropy. The longest time of annealing actually used was about 13 hours. The annealed condition is indicated by the letters RA.

In order to determine whether certain high values of a for condition R were due to distortion of the space-lattice by cold-working or to some other cause, the Ag-Pd alloys in condition A, were rerolled after the x-ray examination so as to reduce the thickness by from 30 to 50 per cent. The increase in stiffness caused by this second rolling was very noticeable. The condition is indicated by the letters RAR. Finally, after examination in condition RAR, these same strips were reannealed and again examined. This final condition is indicated by the letters $RARA$.

METHOD OF X-RAY ANALYSIS.

The apparatus used has been fully described by Davey,[1] and only a brief statement to define the experimental conditions will here be given. The K-radiation of molybdenum, sufficiently isolated for photographic purposes by ZrO_2 filters, is allowed to fall, for from 8 to 20 hours on the

[1] W. P. Davey, Opt. Soc. of Am. Jl., 5, 479–493 (Nov., 1921).

face of a thin ribbon of the metal to be analyzed. The shadow cast by
the edge of the ribbon, and the diffracted beams due to its suitably
oriented crystals are caught by a strip of photographic film wrapped on a
cylinder, the axis of which coincides with the edge of the ribbon. The
current through the x-ray tube is about 30 milliamperes, the potential
across it about 30,000 volts. The radius of the film (sensitive side)
is $r = 20.36$ cm. for the particular film-holders here used.

The diffracted beams due to the individual crystals form full-sized
images of the source,[1] which are separately distinguishable if the crystals
are large enough, and which, when distinguishable, are more clearly
defined the more homogeneous is the arrangement of atoms in the indi-
vidual crystals. By keeping the sample at rest we thus gain information
as to the dimensions of the crystals and their homogeneity. It should
be mentioned that if the crystals are very large the images of the source
are characteristically blurred at certain points, but this aperture effect
is easily distinguishable from the general blurring of the spots due to
imperfections in a smaller crystal. If the spots are numerous and intense,
as in the present series of photographs, the more remote edges of the
bands which they form on the photographic film are easily located within
a couple of tenths of a millimeter, whether the individual spots are dis-
tinguishable or not.[2] The relative intensities of the bands will differ
from the normal if the crystals are not oriented isotropically.[3] The
distance from the edge of the shadow of the ribbon to the corresponding
(more remote) edge of any band is $s = 2r\,\theta$, where θ is the grazing
angle of incidence at which "reflection" takes place. The data, then,
are the values of s, which range in these photographs from 6 to 30 cm.
From these data the corresponding values of the perpendicular distance,
d, between consecutive planes can be directly computed by the formula

$$d = \frac{\lambda}{2} \csc\left(\frac{s}{2r}\right),$$

where λ is the wave-length of the x-rays. In order to reduce the labor of
computation by this formula a table was constructed giving $\log_{10} d$ to
four decimals for the argument s at every 0.01 cm. from 2.50 cm. to 30.00
cm. The value of λ_2 for the longer wave-length component of the $K\alpha$
doublet, 0.71212×10^8 cm., used in the construction of this table, was
that given by Duane and Patterson.[4] The same table was used for the

[1] L. W. McKeehan, Frank. Inst. Jl., *194* (1922).

[2] L. W. McKeehan, Frank. Inst. Jl., *193*, 231–242 (Feb., 1922).

[3] M. Polanyi, Zs. f. Phys., *7*, 149–180 (Nov., 1921).

[4] W. Duane, Nat. Res. Counc. Bull., *1*, 383–408 (Nov., 1920): W. Duane and R. A.
Patterson, Nat. Acad. Sci. Proc., *8*, 95–90 (May 15, 1922).

shorter wave-length component of the doublet, $\lambda_1 = 0.70783 \times 10^{-8}$ cm., when the doublet was resolved in the photographs, by subtracting a constant correction (0.0026) from the tabulated values of $\log_{10} d$.

The values of $\log_{10} d$ were computed in this way for every measured value of s. The indices of the corresponding planes (hkl) of the space-lattice were determined by inspection, the order and spacing of the bands being characteristic of the face-centered cubic space-lattice always found for the alloys here studied. The order of reflection is conveniently included in the indices h, k, l; e.g., the second order from the planes (210) is indicated by the symbol (420). An auxiliary table was computed which gives $\log_{10} a/d$ for the first 54 bands of a simple cubic space-lattice, 22 of which, having h, k, l all even or all odd, are also found in the pattern for a face-centered cubic space-lattice. With this notation the usual formula[1] becomes

$$\frac{a}{d} = \sqrt{h^2 + k^2 + l^2}.$$

Adding the corresponding tabular numbers gives $\log_{10} a$ which should be the same for all the bands. Table I. shows how nearly this condition is satisfied. The mean value of $\log_{10} a$ was taken without weighting the separate values, since the more remote bands, on account of their relative faintness, have larger absolute errors in s and yield only slightly better values of a than do the more intense bands nearer the shadow of the specimen. The first band of the pattern, which is very intense, was sometimes rejected, however, if the values of s were inaccurate on account of a poorly defined shadow. A poorly defined shadow may be due either to use of too thin a sample or to over-exposure and partial reversal of the unshaded area.

<div align="center">ACCURACY.</div>

An example of the data and calculations from a single film is given in Table I., which is self-explanatory. From calculations of this kind it is apparent that the probable error in the value of a from a single experiment is low; it is estimated at about 1 part in 500. Examination of different samples presumably alike showed however that these may differ in the value of a by as much as one per cent., although generally agreeing much closer. The widest variations occurred in condition R. Such variation is not surprising, since the value of a is really determined for a sample of metal which originally occupied only about one cubic millimeter in the ingot. In conditions RA and $RARA$ it is thought that the agreement of results for different samples justifies the statement

[1] A. W. Hull, Phys. Rev., (2), *10*, 661–696 (Dec., 1917).

that a is known to 1 part in 300. The compositions of the alloys, as given in Table I., are subject to errors which it is difficult to estimate.

TABLE I.

Material: Ag₂ Pd₃			Condition : RA		Film No. 298
Relative Intensity.	Arc Length, s, in cm.	Due to $K\alpha_1$ or $K\alpha_2$.	$\log (d \times 10^8)$.	Miller Indices.	$\log (a \times 10^8)$.
10........	6.35	2	0.3603	111	0.5989
4........	7.34	2	0.2979	200	0.5989
6........	10.42	2	0.1482	220	0.5997
4........	12.28	2	0.0787	311	0.5994
4........	12.82	2	0.0606	222	0.6002
1........	14.86	1	9.9963	400	0.5984
4........	16.28	1	9.9586	331	0.5980
1........	16.34	2	9.9597	331	0.5991
3........	16.72	1	9.9477	420	0.5982
1........	16.79	2	9.9486	420	0.5991
3........	18.42	1	9.9083	422	0.5984
1........	18.53	2	9.9085	422	0.5986
3........	19.64	1	9.8825	$\binom{333}{511}$	0.5982
1........	19.75	2	9.8828	$\binom{333}{511}$	0.5985
1........	21.52	1	9.8462	440	0.5988
3........	22.65	1	9.8262	531	0.5982
1........	22.78	2	9.8266	531	0.5986
2........	22.99	1	9.8205	$\binom{442}{600}$	0.5987
1........	23.13	2	9.8207	$\binom{442}{600}$	0.5989
1........	24.41	1	9.7974	620	0.5984
1........	24.56	2	9.7977	620	0.5987
1........	25.45	1	9.7816	533	0.5983
1........	25.78	1	9.7768	622	0.5985

Mean value $\log (a \times 10^8) = 0.59873$,
$a = 3.969 \times 10^{-8}$ cm.

Even in the silver-palladium series an error as great as two or three per cent., which is improbably high, would not affect the conclusions drawn from the results. Evidence is given below for the belief that the composition was not appreciably altered by annealing.

NUMERICAL RESULTS.

Table II. contains the values of a determined from the photographs, together with the densities computed for the most homogeneous condition examined. The values of a as a function of the atomic per cent. of silver

TABLE II.

Formula.	Atomic % Ag.	Values of $a \times 10^8$.				Computed Density.	
		R.	RA.	RAR.	RARA.	RA.	RARA.
Ag......	100	4.080[1]	4.080[1]			10.49	
Ag$_4$Au...	80	4.104	4.081[2]			11.93	
Ag$_3$Au$_2$ ..	60	4.112	4.126[2]			13.50	
AgAu ...	50	4.082	4.088[2]			14.74	
Ag$_2$Au$_3$ ..	40	4.091	4.114			15.31	
Ag$_3$Au$_7$ ..	30	4.072	4.122[2]			16.06	
AgAu$_4$...	20	4.082	4.079[2]			17.44	
AgAu$_9$...	10	4.096	4.084[2]			18.24	
Au......	0	4.075	4.075[1]			19.24	
Ag......	100	4.080[1]	4.080[1]			10.49	
Ag$_9$Pd...	90	4.090	4.056	4.053	4.055		10.67
Ag$_3$Pd...	75	4.075	4.037	4.014	4.020		10.93
Ag$_3$Pd$_2$ ..	60	4.023	4.001	3.992	4.004		11.08
AgPd ...	50	4.006	3.982	3.974	3.975		11.28
Ag$_2$Pd$_3$ ..	40	4.004	3.969	3.949	3.956		11.43
AgPd$_3$...	25	3.949	3.945	3.952	3.934		11.60
AgPd$_9$...	10	3.924	3.921	3.930	3.909		11.81
Pd......	0	3.900[1]	3.900[1]			11.87	

are also presented graphically in Fig. 1, for the conditions used in the computation of densities. In determining the mass to be ascribed to each unit of structure the value $N = 6.0594 \times 10^{23}$, as given by Birge,[3] and the 1921 atomic weights: Ag, 107.88; Au, 197.2; Pd, 106.7, were chosen. The densities for the pure metals: Ag, 10.49; Au, 19.24; Pd, 11.87, are within the range of values usually obtained, those for gold and silver being very close to the accepted values. The density of palladium has been a matter of some doubt, values from 11.40 to 12.16 having been reported. It is thought that the value given here is the most accurate yet obtained.

The previously published values for the space-lattice parameters of these three metals are due to Vegard [4, 5] and Hull.[6] Vegard's data has been recomputed using $\lambda = 0.614 \times 10^{-8}$ cm. for the mean wave-length of the $K\alpha$ radiation of rhodium[7] and gives for silver, $a = 4.11 \times 10^{-8}$ cm., and for gold, $a = 4.09 \times 10^{-8}$ cm. both slightly higher than the values here found. Hull's value for palladium, $a = 3.95 \times 10^{-8}$ cm. is also

[1] Mean of several concordant values, including both conditions, R and RA.
[2] Mean of two concordant values.
[3] R. T. Birge, PHYS. REV. (2), *14*, 361–368 (1919).
[4] L. Vegard, Phil. Mag., (6), *31*, 83–88 (1916). Ag.
[5] L. Vegard, Phil. Mag., (6), *32*, 65–95 (1916). Au.
[6] A. W. Hull, PHYS. REV., (2), *17*, 571–588 (1921).
[7] W. Duane, loc. cit.

higher than those here determined by the same method, but he states that the lines on the photograph which he obtained were rather faint and diffuse, which in the light of the present study suggests inhomo-
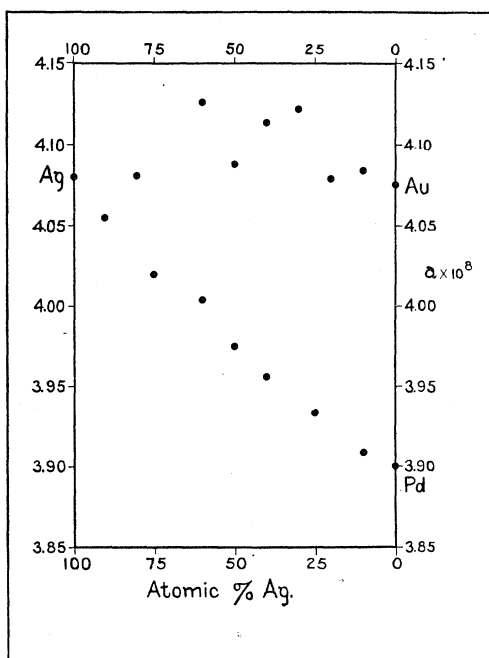

Fig. 1.

geneity. The presence of occluded hydrogen is a possible source of high values of a for this metal.[1]

QUALITATIVE RESULTS.

The variation in the parameter of the space-lattice is, to a first approximation, a linear function of the atomic per cent. of either component. There is, however, a tendency for the chemically unlike components, Ag and Pd, to be packed more closely than this, and a tendency for the components of widely differing mass, Ag and Au, to be packed less closely when mixed in certain proportions. Whether the correlation between the observed facts and the properties to which attention is invited by this choice of words is accidental or not cannot be determined from such meagre data.

The abnormally high values of a obtained for Ag_3Au_2, Ag_2Au_3, Ag_3Au_7 suggest that Tammann[2] is right in concluding that in the face-centered cubic arrangement of atoms solid solutions of the compositions A_3B,

[1] L. W. McKeehan, Amer. Phys. Soc. Washington Meeting, April, 1922.

[2] G. Tammann, Zs. f. anorg. u. allgem. Chem., *107*, 1–239 (1919).

AB, AB_3 are particularly symmetrical and homogeneous. The compositions of the abnormal members of the Ag-Au series fall between these points, and the alloy Ag-Au appears to be normal in its value of a. The high value for the alloy Ag_3Pd_2 may be due to the same effect, but the distance of this point from the smooth curve hardly exceeds the probable error in its position.

It should be mentioned that the method of measurement favors low values of a at the expense of high values, so that what is actually determined is the smallest a (and the largest density) possessed by a considerable fraction of the crystals. The sag in the Ag-Pd curve might accordingly be attributed to a greater variability in a for the intermediate members. The reason for preferring the hypothesis of increased interatomic attraction is that the bands are no broader and no more diffuse for those members of the series which give low values of a than for those which give high values, and no wider than the width of the sample requires.[1] In fact it is for the highest points on the Ag-Au curve that the difficulty of determining a is most increased by diffuseness in the bands. It is perhaps not irrelevant that the excess of the melting point over the annealing temperature is least in the Ag-Au series, so that diffusion may be more effective here than in the Ag-Pd series in preventing regular arrangements, even if once established, from persisting.

Recent work by Bain[2] indicates that the gradual variation in crystal structure here found occurs in other solid solution alloys. He also obtained evidence, in the case of Cu-Ni and Cu-Au alloys, of the special regularity of distribution at the critical compositions, A_3B and AB_3, predicted by Tammann.[3] No such evidence was obtained in this study, perhaps because Ag and Pd have atomic numbers too nearly equal to give a "reflection" due to their difference and because these particular compositions were missing from the Ag-Au series.

The high values of a frequently found in condition R cannot be the immediate result of the cold-working which the material has suffered, for they do not recur in condition RAR. They are accordingly ascribed to inhomogeneity, existing in the original ingot, in the arrangement of atoms within each crystal, which does not permit the interatomic forces between unlike atoms to have their maximum effect. It will not suffice to suppose that different crystals have different compositions, for, as stated above, those with the more compact arrangements would be the ones for which a would actually be measured. After annealing, which renders the individual crystals more homogeneous, as proven by the

[1] L. W. McKeehan, Frank. Inst. Jl., *193*, 231–242 (Feb., 1922).

[2] E. C. Bain, Min. and Met., Preprint 1139–N (Feb., 1922).

[3] G. Tammann, loc. cit.

better definition of the diffracted images of the source, the effect of cold-working is only to break up the existing homogeneous space-lattice into smaller units, and to shear and displace these fragments into less isotropic arrangements. The increase in intercrystalline area, and in the number of atoms thereon which do not fit into both the adjacent space-lattices, would account for the normal decrease in average density associated with cold-working where there is much shear. If working is so severe, however, that the space-lattice is destroyed throughout considerable volumes it is possible that some segregation of the components can occur at the same time. Subsequent crystallization may then leave the components less well mixed than before this severe working, and thus give rise to crystals with abnormal values of a. Some of the Ag-Au alloys were rolled until brittle, and in this condition gave hardly any evidence of crystalline structure, which would represent the end of the first stage in the supposed process. As noted above, recrystallization is particularly slow in the case of Ag-Au alloys, so that no attempt was made to reëstablish the crystal structure in these samples, especially since, if the supposed segregation exists, heating in this condition would change the composition by evaporation of silver.

The relative volatility of silver, mentioned in the last paragraph, is a possible source of error in the composition of the alloys, and this, particularly in the Ag-Pd series, might vitiate the conclusions as to the dependence of a upon the composition by changing the latter to an unknown extent. In order to estimate the possible effect of this volatility a sample of the alloy AgPd was repeatedly annealed at 870° C. for periods of 2 hours. No change in the value of a indicating a progressive change in composition could, however, be detected, so that any error due to this cause is negligible.

In conclusion I desire to express my indebtedness to my colleague Dr. E. F. Kingsbury, who placed at my disposal his first-hand knowledge of certain physical and chemical characteristics of the alloys here studied which suggested or confirmed the conclusions here presented.