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On the Valence and Atomic Size of Silicon, Germanium, Arsenic, Antimony, and Bismuth in Alloys*

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The metalloids silicon and germanium usually show the valence 4 in alloys, and arsenic, antimony, and bismuth the valence 3, the single-bond radii being equal to the normal covalent radii of the atoms. Analysis of the lattice constants of solid solutions of these elements in lead, copper, and other metals with the *A*1 structure shows that in these solid solutions, on the other hand, the metalloids usually function as metals, with a metallic valence of about 2·5 for silicon and germanium and 1·5 for arsenic, antimony, and bismuth. These lower valences correspond to about 0·75 metallic orbital per atom, the normal amount for metals.

The recently reported expansion of the lead lattice by solid solution of bismuth (Tyzack & Raynor, 1954) raises the question of the nature of the bismuth atoms in the solid solution. The single-bond radius of bismuth, 1·510 Å, is slightly less than that of lead, 1·538 Å, and the radius of bismuth for ligancy 12, 1·70 Å, is also less than that of lead, 1·746 Å (Pauling, 1947, 1949); it would accordingly be predicted that a small contraction of the lead lattice would result from solid solution of bismuth. However, the value 1·70 Å for the single-bond radius of bismuth for ligancy 12 is calculated for the valence 3, which is the normal covalence of bismuth. Although the point has not previously been discussed, it might be expected that bismuth atoms would function in some alloys in the way characteristic of a metal, with utilization of about 0·75 atomic orbital as a metallic orbital (Pauling, 1949).

Bismuth has four outer orbitals, $6s6p^3$, and five electrons to fill them, which is normally done by two electrons pairing and filling one orbital ($6s$), leaving in the three remaining orbitals three unpaired electrons capable of forming covalent bonds and giving bismuth the valence 3. In order for bismuth to be in a metallic state, approximately one orbital to which no electron is assigned is required for each atom; this means that the five outer electrons must be contained in three orbitals, which can only be done by having two pairs of electrons in two orbitals and one electron in the third, permitting one covalent bond to be formed and giving bismuth the valence 1. It has been found that usually 0·75 unoccupied orbital is enough to give metallic character to an atom, corresponding to the valence 1·5 for bismuth.

It would hence be predicted that bismuth would have metallic valence between 1 and 1·5. The corresponding values 1·834 Å and 1·781 Å are calculated for the effective radius of the metallic bismuth atom with ligancy 12, by use of the equation

$$R = R_1 - 0{\cdot}300 \log_{10} n\,. \qquad (1)$$

In this equation n is the bond number of each bond, equal in this case to the valence, 1 or 1·5, divided by the ligancy, 12. R_1 is the single-bond radius of bismuth, with the value 1·510 Å.

The second of these predicted values of the metallic radius of bismuth for ligancy 12 agrees closely with the effective radius of bismuth in solid solution in lead, 1·792 Å, as found by extrapolation of their measurements of the lattice constant of the solid solutions by Tyzack & Raynor. It is accordingly to be concluded that bismuth atoms in solid solution in lead show a metallic behavior, involving the normal amount of metallic orbital, 0·75 per atom, and the normal metallic radius, 1·781 Å. The fact that the metallic valence is less than the normal covalence causes the effective radius to be larger than that of lead, rather than smaller, and thus accounts for the expansion of the lead lattice on solid solution of bismuth.

The reported effective radius of bismuth in solid solution in lead can be used together with the single-bond radius of bismuth and the equation connecting effective radius and bond number (equation (1)) to evaluate the valence of bismuth: the value obtained is 1·38. This represents a reasonable extrapolation of the sequence gold, mercury, thallium and lead, with metallic valencies approximately $5\frac{1}{2}$, $4\frac{1}{2}$, $3\frac{1}{2}$, and $2\frac{1}{2}$, respectively.

The value 1·18 for the valence of bismuth in thallium is calculated from the effective radius (Table 1) of bismuth in solid solution in the phase with the *A*1 structure, which extends from 4 to 33 atomic % bismuth (Ölander, 1934). We conclude that bismuth in solid solution in thallium is also in the metallic state.

The extrapolated effective radii of antimony and arsenic in metals with the *A*1 structure, including lead,

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copper, silver, and gold, also correspond to the valence approximately 1·5, rather than 3, showing that arsenic and antimony in these solid solutions behave as metals, with about 0·75 metallic orbital per atom. Values of the effective radius of the solute atom obtained by linear extrapolation of the observed lattice constants, as a function of the atomic fraction of the solute, are given in Table 1, together with the single-bond radii of the atoms and the calculated value of the valence. In the cases where the results of different investigators do not agree, a mean value of the reported effective radius has been used in calculating the valence. It is seen that these metalloids in solid solution in hyperelectronic metals (Pauling, 1950) behave as metallic atoms.

Table 1. *Effective radius and valence of solute atoms in solid solutions*

System	$R_{\text{eff.}}$ (Å)	Mean $R_{\text{eff.}}$ (Å)	R_1 (Å)	Valence
As in Cu	1·437 OR	—	1·210	2·10
As in Ag*	1·482 BE	—	—	1·48
Sb in Pb	1·734 TR 1·685 Ax	1·715	1·391	1·00
Sb in Tl	1·71 S	—	—	1·03
Sb in Cu	1·676 O 1·747 ÔS	1·712	—	1·02
Sb in Ag	1·682 H-R 1·655 O	1·669	—	1·42
Sb in Au	1·618 OO	—	—	2·10
Bi in Pb	1·792 TR	—	1·510	1·38
Bi in Tl	1·814 Ö	—	—	1·18
Si in Al	1·368 Ax	—	1·173	2·68
Si in Cu	1·298 Ax	—	—	4·60
Ge in Al	1·483 Ax	—	1·252	2·03
Ge in Cu	1·396 OR 1·393 Ax	1·395	1·230	3·38
Ge in Ag	1·453 Ax	—	1·245	2·42
Ge in Au	1·468 Ax 1·471 OO	1·470	1·249	2·20
Sn in Pb	1·703 TR	—	1·434	1·51
Sn in Tl	1·688 S	—	1·434	1·72
Sn in Cu	1·621 OI 1·637 O	1·629	1·425	2·57
Sn in Ag	1·586 H-R 1·591 OR 1·593 Ax	1·590	1·413	3·08
Sn in Au	1·582 OO 1·573 Ax	1·578	1·409	3·28
Ga in Al	1·433 OL	—	1·260	3·17
Ga in Cu	1·377 OR	—	1·231	4·16
Ga in Au	1·421 OO	—	1·254	3·33
In in Pb	1·685 TR	—	1·461	2·15
In in Cu	1·612 O	—	1·437	3·12
In in Ag	1·546 OR 1·537 H-R	1·541	1·404	4·18
In in Au	1·539 OO	—	1·401	4·16
Tl in Pb	1·724 TR	—	1·493	2·04
Zn in Al	1·460 Ax	—	1·272	2·83
Zn in Cu	1·346 OR 1·358 JW 1·358 OP	1·354	1·220	4·29
Zn in Ag	1·384 NA	—	1·235	3·82
Zn in Au	1·379 OO	—	1·233	3·91
Cd in Pb	1·671 TR	—	1·461	2·40
Cd in Ag	1·506 H-R	—	1·384	4·70
Hg in Pb	1·627 TR	—	1·442	2·87
Hg in Au	1·527 OO	—	1·394	4·26

Table 1 (*cont.*)

AK:	Ageew & Krotov, 1936.
Ax:	Axon & Hume-Rothery, 1948.
BE:	Broderick & Ehret, 1931.
H-R:	Hume-Rothery, Lewin & Reynolds, 1936.
JW:	Johansson & Westgren, 1933.
NA:	Nial, Almin & Westgren, 1931.
O:	Owen, 1947.
Ö:	Ölander, 1934.
OI:	Owen & Iball, 1935.
OL:	Owen, Liu & Morris, 1948.
OO:	Owen & O'Donnell Roberts, 1945.
OP:	Owen & Pickup, 1935.
OR:	Owen & Roberts, 1939.
ÔS:	Ôsawa & Shibata, 1939.
S	Sekito, 1930.
SH:	Sully, Hardy & Heal, 1949.
TR:	Tyzack & Raynor, 1954.

We have not been able to find any system in which phosphorus appears to function as a metal. The observed equality of atomic size of phosphorus and iron in the iron-rich solid solutions (Hägg, 1929) corresponds to the effective radius 1·26 Å for ligancy 12, agreeing with the value 1·28 Å calculated for the normal covalence 3 rather than the value 1·37 Å calculated for the metallic valence 1·5. Phosphorus does not dissolve significantly in many metals, and no other values for its effective size in metallic solid solutions have been reported.

The metalloids of the fourth group of the periodic table can also function as metals in alloys. Tin and lead have been assigned the metallic valence 2·5, but this valence has not previously been reported for silicon or for germanium. The effective radius of silicon atoms in solid solution in aluminum is 1·368 Å (Table 1), which, with use of the single-bond radius 1·173 Å, corresponds to the valence 2·68. The effective sizes of germanium in aluminum, gold, and silver correspond to the valence 2·03, 2·20, and 2·42, respectively. Hence silicon and germanium are functioning as metals in these alloys.

It seems likely that silicon and germanium have valence 4 in most intermetallic compounds and other alloys. The observed interatomic distances show that they have approximately this valence in Mg_2Si, Mg_2Ge, FeSi, and many other compounds, as well as in the solid solutions in copper.

In general care must be taken in the interpretation of effective radii because of the possibility of significant effects resulting from electron transfer or from partial ionic character of bonds (Pauling, 1950). In particular, alloys of hyperelectronic and hypoelectronic

Table 2. *Metallic radii of metalloids and some metals*

All values in Ångström units

							Si				
						(4)	1·173	1·316			
						(2½)	1·173	1·377			
						(2)	1·173	1·407			
	Zn			Ga			Ge			As	
(6)	1·176	1·266	(5)	1·206	1·320	(4)	1·223	1·366	(3)	1·210	1·391
(4½)	1·214	1·342	(3½)	1·248	1·408	(2½)	1·244	1·448	(1½)	1·210	1·481
(4)	1·229	1·372	(3)	1·266	1·447	(2)	1·253	1·487	(1)	1·210	1·534
	Cd			In			Sn			Sb	
(6)	1·343	1·433	(5)	1·377	1·491	(4)	1·399	1·542	(3)	1·391	1·572
(4½)	1·384	1·512	(3½)	1·423	1·583	(2½)	1·423	1·627	(1½)	1·391	1·662
(4)	1·400	1·543	(3)	1·442	1·623	(2)	1·434	1·668	(1)	1·391	1·715
	Hg			Tl			Pb			Bi	
(6)	1·345	1·435	(5)	1·387	1·501	(4)	1·430	1·573	(3)	1·510	1·691
(4½)	1·388	1·516	(3½)	1·439	1·599	(2½)	1·506	1·710	(1½)	1·510	1·781
(4)	1·403	1·546	(3)	1·460	1·641	(2)	1·540	1·774	(1)	1·510	1·834

elements usually involve interatomic distances that can be correlated with the normal metallic radii of the elements and the normal metallic valences only with use of large correcting terms. In the case of silicon and aluminum no correction for electron transfer is needed, because the elements do not differ greatly in electronegativity, and because a metallic orbital cannot be gained by a transfer of an electron from silicon to aluminum, inasmuch as each of the two atoms has the same orbitals ($3s3p^3$) in the outer shell.

Single-bond radii and effective radii for ligancy 12 for different valences for the elements silicon, germanium, arsenic, antimony, bismuth and some of the metals are given in Table 2. The calculations are made for the normal covalences and for the normal metallic valences, 2·5 for silicon and germanium and 1·5 for the elements of the fifth group, as well as for the valences 2 for silicon and germanium and 1 for the elements of the fifth group, which correspond to a complete metallic orbital for each atom. The single-bond radii for the elements of the fifth group are the p-bond radii, as given by the equations previously communicated (Pauling, 1949); the radii for silicon are the pure p-bond radius for valency 2, the sp^3 radius for valency 4, and the interpolated value for the normal metallic radius. The dependence of the effective radius for ligancy 12 on atomic number is shown in Fig. 1; the dashed lines indicate the discontinuities introduced by the shift from metallic valence to normal covalence.

It is reasonable to expect that, in order to minimize the lattice strain due to a solute atom of different size from the solvent atoms, the valence of the solute might show some variation, such as to cause the effective radius of the solute atom to approach that of the solvent atom. The valences are expected usually to vary between the limit represented by no metallic orbital (normal covalence) and that represented by one atomic orbital, but in some cases may become still smaller (for example, tin in lead and in thallium).

The limiting valences 4 and 2 for germanium, corresponding to zero and one metallic orbital per atom, lead to the values 1·366 Å and 1·487 Å, respectively, for the effective radius for ligancy 12. In the series of solvents gold, silver, and copper, which have effective radii 1·439 Å, 1·442 Å, and 1·276 Å, respectively, the valence of germanium is 2·20, 2·42, and 3·38, respectively; the trend reflects the increasing difference in size of atoms of metallic germanium and the solvent metals. The effective valence of germanium is 2·03 in solid solution in aluminum, which has effective radius 1·429 Å.

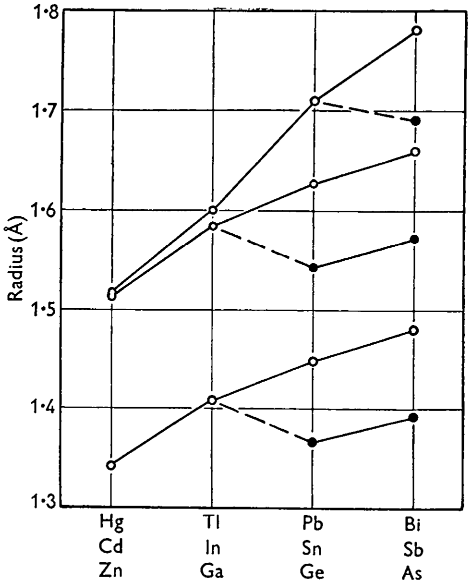

Fig. 1. Effective metallic radii (open circles) and covalent radii (filled circles) for ligancy 12, for some transition metals and metalloids. The dashed lines indicate the discontinuity accompanying the transition from the values corresponding to the metallic valences of the elements to those corresponding to the normal covalences.

The same explanation applies to the difference in metallic valence of cadmium in the solvents silver and lead, in which it has effective valence 4·70 and 2·40, respectively. A number of other examples can be seen in Table 1. An exception is the low valence 2·34 of tin dissolved in copper, as compared with 3·11 in silver and 3·29 in gold. We have no explanation for the abnormality in behavior in this series of systems.

It is likely that the valences of solute atoms calculated from the lattice expansion or contraction in solid solutions are more reliable than those calculated from observed values of interatomic distances in intermetallic compounds. Let us consider a solid solution containing a few atoms of bismuth, for example, in lead. The bismuth atom has an effective radius larger than the lead atom, and each bismuth atom is accordingly squeezed into a hole surrounded by twelve lead atoms. The introduction of this larger atom causes strain in the crystal, such that the distance from the bismuth atom to each of the twelve surrounding lead atoms is slightly smaller than the value calculated with equation (1), with use of the valence 1·38 for bismuth: these bonds are under compression. Also, some of the distances between lead atoms in the surrounding region are somewhat larger than the normal values corresponding to their bond numbers: these bonds are under tension. The effects of the compressions and tensions are, however, cancelled out in the average lattice constant, in such a way that the effective radius of bismuth obtained by extrapolation of the lattice constant does not require correction. If, on the other hand, a direct experimental determination were made of the distance between the bismuth atom and the surrounding lead atoms and the valence of bismuth were calculated from this distance, without correction for the compressional effect of the strain, an erroneously large value of the valence would be obtained. In applying equation (1) care must be taken that the interatomic distances refer to unstrained bonds.

Note added 24 *August* 1955.—It seems likely that under high pressure bismuth undergoes transition to crystalline forms with metallic valence $1\frac{1}{2}$. With $v=1\frac{1}{2}$ and $R(12) = 1{\cdot}781$ Å, the predicted value of the atomic volume for a closest-packed structure is 31·8 Å^3/atom. The value for ordinary bismuth is 35·2 Å^3/atom; accordingly there is predicted a 9·7% decrease in volume. A close-packed structure with valence 3 and $R(12)$ 1·691 Å would correspond to a predicted decrease in volume of 21·5%. Bridgman (1941, 1942) has reported five high-pressure modifications of bismuth. The transition from the normal modification, I, to modification III at 25,000 kg.cm.$^{-2}$ (the intermediate modification II has a very narrow range of stability) is accompanied by a decrease in volume $-\Delta V/V_0$ of 8·6% (5·3% from I to II, 3·3% from II to III (Bridgman, 1935)). The successive transformations to IV, V and VI have $-\Delta V/V_0$ equal to 0·6%, 0·5% and 1·2%, respectively, the total volume decrease for all transitions (from I to VI) being 10·9%. It accordingly seems not unlikely that some or all of the forms III to VI have approximately close-packed structures with the metallic valence $1\frac{1}{2}$ for the bismuth atoms. The electric conductivity of II is about six times that of I, and of III about three times that of I (Bridgman, 1938).

Antimony has a single transition, at 85,000 kg.cm.$^{-2}$, with volume decrease 3·7% (Bridgman, 1941, 1942). This presumably does not correspond to transition to a close-packed structure. Arsenic, germanium and silicon show no transitions in the pressure region investigated, which reaches to 100,000 kg.cm.$^{-2}$ (Bridgman, 1948).

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