Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

Acta Cryst. (1957). **10**, 374

A set of effective metallic radii for use in compounds with the β-wolfram structure.* By

Linus Pauling, *Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.*

(*Received* 2 *January* 1957)

Geller (1956) has recently discussed the lattice constants of the 32 intermetallic compounds A_3B known to have the β-wolfram structure. He formulated a set of effective radii for the 20 elements represented in these compounds, such that, on the assumption that the distance A–B in these compounds is correctly given by adding the radii for elements A and B, the lattice constant is then obtained by multiplying by the geometric factor $4/\sqrt{5}$, which is 1·7888. Geller states in his abstract, in the body of his article, and in the summary that 'the Pauling resonating-valence-bond theory of intermetallic compounds does not apply to the β-wolfram structure'.

In fact, however, the resonating-valence-bond theory does apply to the β-wolfram structure as well as it does to structures for other intermetallic compounds. Indeed, by use of this theory it is possible to formulate an empirical set of effective metallic radii for the β-wolfram structure that is much better than the set formulated by Geller.

In the β-wolfram structure the shortest interatomic distances are those between A atoms; each A is ligated to two A atoms at the distance $\frac{1}{2}a_0$. In addition, each A atom has four B ligands at a distance 12% greater, and six A ligands at a distance 34% greater. Each B atom has twelve A ligands about it. There is no doubt that in general the shorter interatomic distances in an intermetallic compound correspond to stronger bonds than the longer distances, and hence it is not reasonable to assume, as did Geller, that the distance A–B, which might be expected to be given by the sum of radii of atoms A and B, would alone determine the value of the lattice constant a_0.

Instead, the metallic radii of atoms A and B would be expected to contribute to the determination of the lattice constant of the compound A_3B in proportion to the number and strength of the bonds formed by the three atoms A and the one atom B. As a first approximation the metallic valences of atoms A and B can be taken as a measure of the strength of the bonds that they form. Accordingly the contributions of the radii of atoms A and B to the determination of the lattice constants would be expected to be in the ratio of three times the valence of atom A to the valence of atom B. If atoms A and B have the same valence, as in the compound Cr_3Ir, the relative weights of the radii of Cr and Ir in determining the lattice constant would be 3:1; for a compound V_3Ir the relative weights would be 5:2, for V_3Si 15:4, and so on. It is, of course, not unlikely that these ratios should be changed somewhat to take into account the different strengths of electron-pair bonds formed by atoms of different kinds.

It is found by trial that the refinement of considering the difference in valence of atom A and atom B is not

Table 1. *Effective radii for metals in β-wolfram structures*

Metal	β-W radius	R(L12)	Metal	β-W radius	R(L12)
V	1·332 Å	1·338 Å	Ru	1·360 Å	1·336 Å
Nb	1·459	1·456	Rh	1·336	1·342
Ta	1·453	1·457	Co	1·234	1·252
Cr	1·292	1·267	Ni	1·272	1·244
Mo	1·401	1·386	Au	1·456	1·439
Ti	1·414	1·467	Hg	1·560	1·570
Zr	1·551	1·597	Si	1·260	1·316
Os	1·352	1·350	Ge	1·314	1·366
Ir	1·354	1·355	Sn	1·536	1·542
Pt	1·388	1·385	As	1·314	1·391

Table 2. *Lattice constants of compounds with the β-wolfram structure*

Compound	a_0 calculated	a_0 observed	Δ (in 0·001 Å)
V_3Ir	4·785 Å	4·785 Å	0
V_3Pt	4·815	4·815	0
V_3Rh	4·768	4·767	1
V_3Co	4·676	4·676	0
V_3Ni	4·710	4·710	0
V_3Au	4·876	4·88	(−4)
V_3Si	4·699	4·722	−23
V_3Ge	4·748	4·769	−21
V_3Sn	4·948	4·94	(8)
V_3As	4·750	4·75	0
Nb_3Os	5·123	5·121	2
Nb_3Ir	5·124	5·131	−7
Nb_3Pt	5·155	5·153	2
Nb_3Rh	5·109	5·115	−6
Nb_3Au	5·216	5·21	(6)
Nb_3Sn	5·289	5·289	0
Ta_3Sn	5·276	5·276	0
Cr_3Ir	4·678	4·678	0
Cr_3Pt	4·708	4·711	−3
Cr_3Ru	4·683	4·683	0
Cr_3Rh	4·662	4·656	6
Cr_3Si	4·594	4·564	30
Cr_3Ge	4·642	4·623	19
Mo_3Os	4·967	4·973	−6
Mo_3Ir	4·969	4·965	4
Mo_3Si	4·885	4·890	−5
Mo_3Ge	4·934	4·933	1
Ti_3Ir	5·005	5·007	−2
Ti_3Pt	5·035	5·033	2
Ti_3Au	5·096	5·096	0
Ti_3Hg	5·189	5·189	0
Zr_3Hg	5·558	5·558	0

---

* Contribution No. 2158 from the Gates and Crellin Laboratories.

necessary. A simple calculation based on the assumption that each atom has the same effect in determining the lattice constant as any other atom leads to a satisfactory system. On this assumption the lattice constant is given by the following equation:

$$a_0 = 1{\cdot}7888\left(\tfrac{3}{2}R_A+\tfrac{1}{2}R_B\right) . \qquad (1)$$

The factors $\frac{3}{2}$ and $\frac{1}{2}$ reflect the composition A_3B of the crystal.

The set of radii formulated for use with this equation is given in Table 1, and the values of a_0 calculated from them are compared with the observed values for the 32 compounds in Table 2. It is seen that for 21 of the compounds the deviation between the calculated and observed values is 0·004 Å or less. Only for 11 of the compounds is the deviation greater than 0·004 Å. The radii and equation used by Geller, in which the radii R_A and R_B are given equal weights instead of the weights 3:1, led to deviations with experiment of 0·01 Å or greater for 23 of the compounds. The mean deviation in lattice constant for the 32 compounds given in Table 1 is 0·004 Å, whereas Geller reported a mean deviation of 0·01 Å, over twice as great.

The effective radii for the β-wolfram structure used in preparing Table 2 are compared in Table 1 with the effective metallic radii for ligancy 12 reported a number of years ago (Pauling, 1947). It is seen that for most of the elements the two radii are in good agreement with one another, the mean deviation being 0·02 Å. The mean deviation between the effective radii suggested by Geller and the metallic radii for ligancy 12 is 0·04 Å.

It may be possible to find explanations for some of the differences between the effective radii for the β-wolfram structure and the standard metallic radii for ligancy 12. For example, the effective radii for Ti and Zr are about 0·05 Å smaller than the standard radii. The only compounds of Ti and Zr are those with Ir, Pt, Au, and Hg, all of which may be expected to transfer electrons to the hypoelectronic atoms Ti or Zr (Pauling, 1950), and in this way to lead to an increase in the number of bonding electrons for the crystal, and a decrease in the lattice constant. The decrease in the radii may be taken as evidence that this expected electron transfer has occurred.

There is no need to discuss Geller's arguments against the resonating-valence-bond theory in detail; one argument may serve as an example. Geller states 'The case of V_3Au is even more vivid. Pauling's radii would give 5·05 Å and Wells' 4·99 Å, 0·16 and 0·10 Å, respectively, too large'. In fact, the standard metallic radii for ligancy 12 (Pauling, 1947) lead to perfect agreement with experiment for V_3Au. These radii (Table 1) are 1·338 Å and 1·439 Å, respectively. When these values are substituted in equation (1) the value $a_0 = 4{\cdot}878$ Å is obtained, agreeing exactly with the reported experimental value 4·88 Å. The fallacy in Geller's argument is, of course, that of giving the radii of the small atom V and the large atom Au the same weight.

References

Geller, S. (1956). *Acta Cryst.* **9**, 885.
Pauling, L. (1947). *J. Amer. Chem. Soc.* **69**, 542.
Pauling, L. (1950). *Proc. Nat. Acad. Sci., Wash.* **36**, 533.

Acta Cryst. (1957). **10**, 375

The unit cell and space group of HCN tetramer.

By Ronald L. Sass and Jerry Donohue, *Department of Chemistry, University of Southern California, Los Angeles 7, California, U.S.A.*

(*Received* 15 *February* 1957)

In a recent physical study of HCN tetramer by Webb, Frank & Schneider (1955), evidence was presented which supported the diaminomaleonitrile structure for that substance. The data presented in the present paper were obtained from a sample of HCN tetramer kindly provided by Dr Webb.

The material was recrystallized from isopropyl alcohol, and small single crystals were chosen for goniometric and X-ray examination. The crystals were six-sided needles with ill-formed terminations. Rotation and Weissenberg photographs showed that the substance was monoclinic, with

$$\mathbf{a} = 6{\cdot}47,\ \ \mathbf{b} = 18{\cdot}20,\ \ \mathbf{c} = 5{\cdot}23\ \text{Å},\ \ \beta = 123^\circ .$$

The forms of the needle are {010} and {021}. The density, as measured pycnometrically with carbon tetrachloride, is 1·409 g.cm.$^{-3}$; the density calculated for four molecules per unit cell is 1·388 g.cm.$^{-3}$. The absences on the Weissenberg photographs, namely, $(0k0)$ with k odd and $(h0l)$ with l odd, indicate that the space group is C_{2h}^5–$P2_1/c$. Since there are four molecules in the unit cell, no molecular symmetry is required.

On the Weissenberg photographs the reflection (041) is unusually intense, and on the **a**-axis rotation photograph this reflection is accompanied by streaks (not wheaks) in the direction of its normal. These observations suggest that the structure consists of planar, or nearly planar, molecules lying in planes roughly parallel to {041}, but since the outline of this plane in the unit cell is almost square, packing and hydrogen-bonding considerations alone were unable to lead to a trial structure. Obviously, the above discussion contains no evidence whatever for or against the diaminomaleonitrile structure for $(HCN)_4$—such evidence will be obtained in a complete crystal structure determination.

This study was supported by the National Science Foundation. We wish to thank Dr Richard Webb for the sample of $(HCN)_4$, and Dr Richard Marsh for interesting discussion.

Reference

Webb, R. L., Frank, S. & Schneider, W. C. (1955). *J. Amer. Chem. Soc.* **77**, 3491.