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## The Dependence of Bond Lengths in Intermetallic Compounds on the Hybrid Character of the Bond Orbitals

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The observed bond lengths in some intermetallic compounds can be made compatible with those in the constituent metals by consideration of the possibility of distributing the *d* character unequally among the bond orbitals of an atom.

I met Paul Ewald forty-one years ago, not long after I had arrived in Munich to work in Arnold Sommerfeld's Institute of Theoretical Physics (April 1926). When I visited Ewald in his laboratory in Stuttgart he was hard at work, with C. Hermann, on the preparation of the first volume of the *Strukturbericht*. He asked me what I thought about the structure of calcium carbide. A reported structure determination placed the carbon atoms in groups of four, at the corners of a regular tetrahedron with edge 1.62 Å. Ewald asked if I thought that there was any chance that this structure determination could be correct. I answered that in my opinion the structure was unlikely, but could not be ruled out as impossible, because the strain energy of the six bent bonds in the tetrahedron might be no greater than the instability of two carbon-carbon triple bonds, relative to six unstrained single bonds (110 kcal.mole<sup>-1</sup>). This question, and others that he asked, impressed me strongly as to the amount of care and thought that Ewald was devoting to the task of writing this important volume.

Another matter that we discussed was the extent to which knowledge of the sizes of atoms could be used as the basis of a decision about the correctness or incorrectness of a reported structure determination. Although Bragg (1920), Huggins (1926), and Goldschmidt (1926) had published tables of atomic radii, there were still great doubts as to their general applicability and reliability. As late as 1928 it was possible for a well-trained investigator (in Sommerfeld's Institute) to consider his structure determination to be acceptable and worth publication even though it placed atoms of two elements, zirconium and silicon, only 0.59 Å apart, only twenty per cent as far from one another as the average of the smallest interatomic distances in the crystals of the two elementary substances (Seyfarth, 1928). By 1936, when the second volume of the *Strukturbericht* was published, there had been developed enough confidence in the reliability of atomic radii to permit this reported structure to be described as very unlikely.

In 1922, when I began my graduate work in the California Institute of Technology, I started to collect the information about interatomic distances from the literature, and to make an effort to formulate a system of bond lengths. I had become interested in metals and alloys in 1920, and I was especially interested in making a structure determination of an intermetallic compound. This interest resulted in the assignment of the fluorite structure to Mg<sub>2</sub>Sn, and to the observation that the distance between magnesium atoms and tin atoms in magnesium stannide (in the compound) is 2.94 Å, somewhat smaller than the average of the observed magnesium-magnesium distance and tin-tin distance in the elements, with either allotrope of tin (Pauling, 1923).

Goldschmidt (1926) grouped metals and covalent crystals together, and Bernal (1929) pointed out that many properties of metals indicate that metallic bonds are closely similar to covalent bonds. I developed this idea further (Pauling, 1938), and formulated a set of metallic radii in 1947, with use of the empirical equation

$$D(n) = D(1) - 0.600 \text{ \AA} \log n \quad (1)$$

for the dependence of interatomic distance on the bond number *n*.

The set of metallic radii and the equation permit the reasonably satisfactory discussion of observed interatomic distances in many intermetallic compounds. In some crystals, however, the simple application of the radii and the equation leads to disagreement with observation.

Also, for some elementary metals, such as with the A2 structure (cubic body-centered), there has been uncertainty about how to divide the total valence of the atom between the non-equivalent bonds, and consequent uncertainty in the value of the single-bond radius of the metal.

A way to overcome some of these difficulties can be developed on the assumption that in metals and intermetallic compounds the nonequivalent bond orbitals in an atom may have different hybrid character, such as to correspond to suitable values of *R*<sub>1</sub>, the single-bond radius of the atom. A set of empirical equations giving the single-bond radius as a function

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of the hybrid character of the orbital and the atomic number of the element, formulated nearly twenty years ago (Pauling, 1949), includes the following three, which show, for metals of the three long periods, the single-bond radius as a function of  $z$ , the number of electrons beyond the corresponding noble-gas structure, and  $\delta$ , the amount of  $d$  character of the bond orbital:

First long period (iron-transition metals):

$$R_1(\delta, z) = 1.825 - 0.043z - (1.600 - 0.100z)\delta \quad (2a)$$

Second long period (palladium-transition metals):

$$R_1(\delta, z) = 2.001 - 0.043z - (1.627 - 0.100z)\delta \quad (2b)$$

Third long period (platinum-transition metals):

$$R_1(\delta, z) = 1.850 - 0.030z - (1.276 - 0.070z)\delta \quad (2c)$$

As a first example of the application of these equations we may evaluate the single-bond radius for tungsten from the observed bond lengths in  $\beta$ -tungsten\* and  $\alpha$ -tungsten. In  $\beta$ -tungsten the two tungsten atoms of the first kind form twelve bonds with neighboring  $W_{II}$  atoms, with the length 2.822 Å. The valence of 6 requires that the bonds be half bonds, if we assume that no electron transfer occurs between the two kinds of tungsten atoms. Each  $W_{II}$  atom forms four of these bonds with the neighboring  $W_I$  atoms, two bonds to  $W_{II}$  at 2.543 Å, and eight bonds to  $W_{II}$  at 3.092 Å. Of the valence 6 of  $W_{II}$ , two valence units are used in forming the bonds to  $W_I$ . The two short bonds, at 2.543 Å, may be assumed to have  $n=1$ . The other eight bonds formed by  $W_{II}$  accordingly have  $n=\frac{1}{2}$ . With use of equation (1), the value of  $R_1$  found for the  $W_I$ - $W_{II}$  bonds is 1.321 Å, and the corresponding value of the amount of  $d$  character, given by equation (2c), is 40.8%. The corresponding values of  $R_1$  and  $\delta$  for the bonds of the other two kinds are 1.273 Å, 46.6%, and 1.365 Å, 35.6%. The weighted average of the amount of  $d$  character is 41.0%, which corresponds to the average value  $R_1 = 1.319$  Å.

In  $\alpha$ -tungsten each atom is surrounded by eight atoms at 2.741 Å and six atoms at 3.165 Å. We may answer the question as to how the total valence 6 is to be divided among the fourteen bonds by assuming that the amount of  $d$  character varies with bond length in the same way as for  $\beta$ -tungsten. This assumption leads to the bond numbers 0.60 for the eight stronger bonds and 0.20 for the six weaker bonds. Application of equations (1) and (2c) then gives 1.304 Å, 42.8% and 1.373 Å, 34.7%, average amount of  $d$  character 41.1%. This amount of  $d$  character corresponds to the average  $R_1 = 1.318$  Å, in excellent agreement with the value 1.319 Å from the  $\beta$  form. I think that this value should replace the older values 1.299 Å (Pauling, 1947) and 1.304 Å (Pauling, 1949, 1960), which were ob-

tained by more arbitrary methods of interpreting the observed bond lengths.

A similar method may be used to interpret the observed bond lengths for other  $A2$  metals. For vanadium, niobium, and tantalum we may assume that the total valence is divided among the stronger and weaker bonds in the same ratio as for tungsten; the stronger bonds then have  $n=0.50$  and the weaker bonds have  $n=0.167$ . In vanadium the eight strong bonds at 2.622 Å correspond to  $R_1 = 1.221$ ,  $\delta = 35.4\%$ , and the six weak bonds at 3.028 Å to  $R_1 = 1.281$ ,  $\delta = 30.0\%$ , average  $\delta = 34.3\%$ , leading to  $R_1 = 1.233$  Å (older value 1.224 Å). The corresponding values for niobium are 2.858 Å,  $R_1 = 1.339$  Å,  $\delta = 39.7\%$ , 3.300 Å,  $R_1 = 1.417$ ,  $\delta = 32.8\%$ , average  $\delta = 38.3\%$ , giving the single-bond radius 1.354 Å (older value 1.342 Å); and for tantalum 2.860 Å, 1.340, 38.9%, 3.302 Å, 1.418, 30.5%, average  $\delta = 37.2\%$ , single-bond radius 1.356 Å (older value 1.343 Å).

From among the many intermetallic compounds that might be used to illustrate the procedure, I select  $Nb_3Sn$ , which is of a special interest because of its high superconducting transition temperature (18.05°K). This compound has the  $\beta$ -tungsten structure, with tin atoms in the  $W_I$  positions and niobium atoms in the  $W_{II}$  positions. Each tin atom has twelve niobium neighbors, at 2.957 Å. Each niobium atom has four tin neighbors, two niobium neighbors at 2.645 Å, and eight niobium neighbors at 3.239 Å. The small interatomic distance strongly indicates that the tin atom is quadrivalent, with pivoting resonance of its four bonds among the twelve positions, leading to bond number  $\frac{1}{3}$  for the tin-niobium bonds. I assume that the shorter Nb-Nb bonds are single bonds, with  $n=1$ . To achieve the valence 5 for niobium the longer Nb-Nb bonds must have  $n=0.208$ . With use of the single-bond radius 1.405 Å for quadrivalent tin and of equations (1) and (2b),  $R_1$  for niobium in the niobium-tin bonds is found to have the value 1.266, corresponding to  $\delta = 42.6\%$ . For the stronger and weaker niobium-niobium bonds the corresponding values are 1.322, 41.2%, and 1.415, 32.9%. The average value of  $\delta$  is 39.8%, somewhat larger than the value for elementary niobium, 38.3%. Similarly, the single-bond radius of niobium in the compound, 1.338 Å, is somewhat smaller than that for the element, 1.354 Å.

The tetragonal crystal  $WSi_2$  (Zachariasen, 1927) may serve as another example. Each silicon atom forms five bonds with surrounding silicon atoms at 2.633 Å and five bonds with tungsten atoms at the same distance. Each tungsten atom forms ten bonds with silicon atoms at 2.633 Å and four bonds with tungsten atoms at 3.214 Å. Application of equation (1) with single-bond radii of silicon and tungsten taken as 1.173 and 1.315 Å, respectively, leads to bond numbers corresponding to valences 4.67 for silicon and 6.16 for tungsten. These values of the valence are too large; the valence of silicon may be taken as 4 (with pivoting resonance of the bonds among the ten positions), and that of tung-

\* It is possible that a small amount of oxygen is necessary to stabilize the  $\beta$ -tungsten structure (see, e.g. Moss & Woodward, 1959). A consideration of the effect of this oxygen might lead to a small revision in the values of the single-bond radii and amounts of  $d$  character.

sten as 6, which with equation (1) would lead to bond lengths an average of 0.027 Å larger than those observed. If the assumption is made that the two kinds of bond orbital of the tungsten atom have different amounts of *d* character, we may assign the values  $n=0.333$  to the silicon-silicon bonds (as given by equation (1) and the single-bond radius of silicon),  $n=0.467$  to the silicon-tungsten bonds, and  $n=0.333$  to the tungsten-tungsten bonds. The values of  $R_1$  and  $\delta$  for the bond orbitals of tungsten involved in the bonds to silicon atoms are 1.262 Å and 47.7%, and for the bonds to tungsten atoms 1.464 Å and 24.1%, respectively. The average value of  $\delta$ , 42.5%, corresponds to  $R_1=1.306$  Å for the tungsten atom, which is 0.012 Å less than for the element.

A similar discussion of transition-metal bond lengths has been reported for FeSi and other silicides with the B31 structure (Pauling & Soldate, 1948), and Co<sub>2</sub>Al<sub>9</sub> (Pauling, 1951).

In the above discussion the effect of difference in electronegativity of unlike atoms on bond length (usually a decrease) has been ignored. There is the possibility also of a small change in bond length between unlike atoms, such as of a metal and a metalloid, that reflects the difference in the nature of the overlapping orbitals, in addition to the effects of partial ionic character and of electron transfer. I believe that a thorough

analysis of this problem, with consideration of the present great amount of experimental information about bond lengths in metals and intermetallic compounds, would now permit the formulation of a table of metallic radii reliable to 0.001 Å and a set of structural principles that would allow bond lengths and lattice constants to be predicted to within about 0.1%.

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## Laves Structures, MgCu<sub>2</sub>, MgZn<sub>2</sub>, MgNi<sub>2</sub>

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It is in some measure demonstrated that the formation of A-B and B-B contacts provides the energy for the compression of the A atoms and permits AB<sub>2</sub> phases with radius ratios so much larger (up to 1.67) than the ideal (1.225) to adopt the MgCu<sub>2</sub> type structure. At radius ratios somewhat lower than the ideal, the B atoms are insufficiently compressed for A-B and A-A contacts to form. This is probably a consequence of there being twice as many B atoms as A atoms, and it results in fewer known Laves phases with radius ratios below the ideal value than above it.

There have been many reviews and discussions of the crystal chemistry of the Laves phases (among the more recent see Berry & Raynor, 1953; Laves, 1956; Elliott & Rostoker, 1958; Bardos, Gupta & Beck, 1961; Dwight, 1961; Nevitt, 1963) but none of these explicitly discuss what we find to be their most remarkable features:

(i) Phases adopt structures which result mainly from the geometrical facility of packing together two components in the proportion AB<sub>2</sub> if the ratio of their radii,  $r_A/r_B$ , is 1.225, when the actual size ratios of the components may differ greatly (values from 1.05 to 1.67) from the ideal value.

(ii) Structural compression in the Laves phases may amount to more than 35% in unit-cell volume compared with the sums of the elemental volumes. Such large compressions might be expected in structures of phases with strong A-B interactions, but scarcely in those of the ideal Laves structures which, on the hard sphere atomic model, have only A-A and B-B contacts.

Space filling models based on the concept of incompressible atoms (Laves, 1956; Parthé, 1961) are of no assistance in understanding these features, but the problem can be discussed in terms of a model which allows compression of the A (or B) atoms to establish