

short recoil track. The last stage in the cooling consists of  $\gamma$ -ray and probably also  $\beta$ -transitions, neither of which can be observed.

We should like to express our sincere thanks to Professor L. Leprince-Ringuet for exposing our plates in his mountain observatory at Chamonix; and to Professor A. von Muralt and Dr R. Stämpfli for providing facilities at the Jungfraujoch Scientific Station. We are also indebted to Sir George Thomson for valuable discussions and advice during the course of the work.

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## A resonating-valence-bond theory of metals and intermetallic compounds

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(Received 26 July 1948)

The resonating-valence-bond theory of metals discussed in this paper differs from the older theory in making use of all nine stable outer orbitals of the transition metals, for occupancy by unshared electrons and for use in bond formation; the number of valency electrons is consequently considered to be much larger for these metals than has been hitherto accepted. The metallic orbital, an extra orbital necessary for unsynchronized resonance of valence bonds, is considered to be the characteristic structural feature of a metal. It has been found possible to develop a system of metallic radii that permits a detailed discussion to be given of the observed interatomic distances of a metal in terms of its electronic structure. Some peculiar metallic structures can be understood by use of the postulate that the most simple fractional bond orders correspond to the most stable modes of resonance of bonds. The existence of Brillouin zones is compatible with the resonating-valence-bond theory, and the new metallic valencies for metals and alloys with filled-zone properties can be correlated with the electron numbers for important Brillouin polyhedra.

## INTRODUCTION

The difficult problem of the electronic structure of metals has in recent years been tackled mainly by molecular-orbital (one-electron-orbital) methods. This attack has led to a reasonably satisfactory understanding of some metallic properties, such as electrical conductivity, but not of others, including interatomic distances (density), hardness and other mechanical properties, and the relative stability of alternative atomic arrangements. A decade ago (1938) I pointed out that the resonating-valence-bond concept of metals permits a straightforward explanation to be given not only of the hardness, melting-point, and related properties of the transition metals but also of their ferromagnetic saturation moments, which lead to the assignment of metallic valences such as 5.78 for iron and 5.44 for copper, in place of the numbers 0.2 to 0.6 for iron and 1 for copper assumed in the usual molecular-orbital treatment. It was suggested that these valence numbers result from the hybridization of the nine stable outer orbitals (five  $nd$ , one  $(n+1)s$ , and three  $(n+1)p$ ) of a transition atom into 5.78 good bond orbitals (resembling the six  $d^2sp^3$  orbitals of the central atom in an octahedral complex), 2.44 stable atomic orbitals (largely  $d$  in character, and responsible for the magnetic moment), and 0.78 'unstable' orbital, with no obvious use.

In the course of the further investigation of resonating valence bonds in metals the nature and significance of this previously puzzling 'unstable' orbital have been discovered, and it has become possible to formulate a rational theory of metallic valence and of the structure of metals and intermetallic compounds.

**THE FUNDAMENTAL STRUCTURAL FEATURE OF A METALLIC SYSTEM: THE 'METALLIC ORBITAL'**

Let us consider lithium as an example. In the usual treatment of this metal a set of molecular orbitals is formulated, each of which is a Bloch function built from the  $2s$  orbitals of the atoms, or, in the more refined cell treatment, from  $2s$  orbitals that are slightly perturbed to satisfy the boundary conditions for the cells. These molecular orbitals correspond to electron energies that constitute a Brillouin zone, and the normal state of the metal is that in which half of the orbitals, the more stable ones, are occupied by two electrons apiece, with opposed spins.

A roughly equivalent valence-bond theory would result from allowing the  $2s$  electron of each lithium atom to be involved in the formation of a covalent bond with one of the neighbouring atoms. The wave function for the crystal would be

$$\psi = \sum_{i=1}^M a_i \psi_i, \quad (1)$$

in which†

$$\psi_i = 2^{-\frac{1}{4}N} \sum_R (-1)^R \left[ \{(2N)!\}^{-\frac{1}{2}} \sum_P (-1)^P P a(1) \beta(1) b(2) \alpha(2) \dots \right] \quad (2)$$

is the wave function representing one of the  $M$  ways of distributing the valence bonds among the interatomic positions in the metal such that each atom forms one bond.

† See Slater (1931); for the meaning of the symbols see Pauling & Wilson (1935).

If the functions  $\psi_i$  are equivalent and orthogonal  $a_i$  will equal  $M^{-\frac{1}{2}}$ , and the energy of the normal state can be written as

$$W = W_{\text{bond}} + W_{\text{resonance}}, \quad (3)$$

in which  $W_{\text{bond}} = \int \psi_i^* H \psi_i d\tau$  is the energy of any one of the valence-bond structures  $\psi_i$  and

$$W_{\text{resonance}} = \sum_{i=1}^M \sum_{j \neq i} a_i a_j K_{ij} = 2 \sum_{j=2}^M K_{1j} \quad (4)$$

is the resonance energy,  $K_{ij}$  being the resonance integral  $\int \psi_i^* H \psi_j d\tau$  between two valence-bond structures  $i$  and  $j$ .

It is this resonance energy that would be in the main responsible for the difference in energy of the crystal and the gas of diatomic molecules  $\text{Li}_2$ . But the heat of formation of  $\text{Li}_2$  molecules from atoms is only 6.6 kcal./g.-atom, whereas that of the metal is 39 kcal./g.-atom. It seems unlikely, by comparison for example with the analogous case of Kekulé-like resonance in aromatic molecules, that the great difference, 32.4 kcal./g.-atom, could result from the synchronized resonance, of type  

$$\begin{cases} \text{Li}-\text{Li} & \text{Li} & \text{Li} \\ & | & | \\ \text{Li}-\text{Li} & \text{Li} & \text{Li} \end{cases}$$
, requiring two or more bonds to shift simultaneously. A much greater amount of resonance stabilization† can be achieved by resonance of the sort  

$$\begin{cases} \text{Li}-\text{Li} & \text{Li}-\text{Li}^- \\ & | \\ \text{Li}-\text{Li} & \text{Li}^+ \text{ Li} \end{cases}$$
, in which one bond resonates independently from one position to another, through the process of electron transfer (Pauling 1948a).

However, this uninhibited resonance, involving the conversion of atoms into ions (or the transfer of ionic charges to atoms), requires that the atom receiving a bond have an orbital available for its reception. It is the possession of this extra orbital (the metallic orbital), in addition to the orbitals required on the average for occupancy by unshared

† A simple calculation may serve to illustrate this point. Let the  $2N$  atoms in a lithium crystal containing  $N$  bonds (atomic arrangement A 2) be divided into classes A and B, at 000 and  $1/2\ 1/2\ 1/2$ , respectively, in the unit cube. Let each atom be forming one bond. The total number of structures representing the eight bond positions for each atom A is  $8^N$ . But only the fraction  $(7/8)^7$  of these are, on the average, acceptable to a given atom B (the chance of its receiving a bond in any one position and not in others being  $8/8(7/8)^7$ ); and hence the number of ways of placing bonds between adjacent atoms in the A 2 structure is

$$8^N (7/8)^7 = (7^7/8^6) = 3.14^N.$$

The number 3.14 is a measure of the coefficient of the resonance integral for synchronous resonance.

If  $\text{Li}^+$  and  $\text{Li}^-$  ions (the latter bicovalent) are also present, their *a priori* probabilities in class A are 1 and 28, respectively, with geometrical mean  $2.7^{\frac{1}{2}}$  (the ions must be present in pairs), which corresponds to 8 for neutral atoms. A calculation similar to that above, on the assumption that there is no energy difference between  $\text{Li Li}$  and  $\text{Li}^+ \text{Li}^-$ , leads to  $(7^7/8^6)(1 + 7^{\frac{1}{2}}/2)^N$  for the number of ways of placing the bonds and hence to the number  $(7^7/8^6)(1 + 7^{\frac{1}{2}}/2) = 3.14 \times 2.32$  as the measure of the coefficient of the resonance integral for uninhibited resonance. This result, containing the factor 2.32, indicates the importance of uninhibited resonance.

The relative weights 8 :  $2.7^{\frac{1}{2}}$  for  $\text{Li}$  and  $\text{Li}^+ (= \text{Li}^-)$  correspond to 43 % neutral atoms and 28.5 % each of anions and cations. Calculations based on minimizing the energy of the system also indicate similar values for the ratio of atoms to anions and cations. The rule of essential electrical neutrality (Pauling 1948b) would require that only the singly-charged ions need be considered.

*electron pairs and bonding electrons, by all or many of the atoms in a condensed phase that permits the uninhibited resonance of valence bonds that gives rise to metallic properties.*

### HYBRIDIZATION OF BOND ORBITALS IN THE ALKALI METALS

In the molecule  $\text{Li}_2$  the bond involves a hybrid atomic orbital  $as + bp$  formed from the  $2s$  orbital and one of the much less stable  $2p$  orbitals. It is shown below that the amount of  $p$  character of this bond orbital (equal to  $b^2$ , with  $a^2 + b^2 = 1$ ) is small, being about 8%. On the other hand, if each of the atoms in metallic lithium requires a bond orbital and a metallic orbital and the two are equivalent they will be  $2^{-\frac{1}{2}}(s + p)$  and  $2^{-\frac{1}{2}}(s - p)$ , with 50%  $p$  character. The analysis of energy quantities supports this conclusion.

It has been suggested (Pauling 1931; Pauling & Sherman 1937) that the bond-forming power of an orbital can be taken as proportional to its concentration in the bond direction, as measured by the value of its radial factor (normalized to  $4\pi$ ). The square of this quantity, the bond strength  $S$ , is approximately proportional to the bond energy. This postulate is equivalent to assuming that the off-diagonal matrix element  $H'_{sp}$  for  $s-p$  hybridization is equal to  $S_s S_p$ , the diagonal elements being  $H_s^0 - \kappa S_s^2$  and  $H_p^0 - \kappa S_p^2$ , in which  $H_s^0$  and  $H_p^0$  are the corresponding  $s$  and  $p$  atomic energies for the two bond electrons and  $\kappa S_s^2$  and  $\kappa S_p^2$  are the bond energies.  $S_s$  and  $S_p$  have the values 1 and  $3^{\frac{1}{2}}$ , respectively, and  $\kappa$  is a proportionality factor. The bond energy for formation of the most stable hybrid bond is then given by the lowest root (with changed sign) of the secular equation

$$\begin{vmatrix} -\kappa - W & 3^{\frac{1}{2}}\kappa \\ 3^{\frac{1}{2}}\kappa & H_p^0 - 3\kappa - W \end{vmatrix} = 0, \quad (5)$$

in which  $H_s^0$  has been taken as the origin for energy. Solution of this equation gives

$$-\frac{W}{\kappa} = \frac{1}{2} \left[ \left\{ \left( \frac{H_p^0}{\kappa} \right)^2 - 4 \frac{H_p^0}{\kappa} + 16 \right\}^{\frac{1}{2}} + 4 - \frac{H_p^0}{\kappa} \right]. \quad (6)$$

The quantities  $-W$  (the bond energy  $D_e$  of the  $\text{Li}_2$  molecule) and  $H_p^0$  (twice the difference in energy of the states  $2p^2P$  and  $2s^2S$  of Li) are known from spectroscopic data, and hence their ratio  $\rho = -W/H_p^0$  is known. It is found from equation (6) that

$$\kappa = H'_s = \frac{\rho(\rho+1)}{4\rho+1} H_p^0. \quad (7)$$

The ratio  $b/a$  is the ratio of matrix elements in one row of the secular equation:

$$\frac{a}{b} = -\frac{\kappa + W}{3^{\frac{1}{2}}\kappa}. \quad (8)$$

The energy values and the derived quantities for the diatomic molecules of the alkali metals are given in table 1. It is seen that the amount of  $p$  character is calculated to lie between 5 and 14%.

TABLE 1. BOND ENERGIES AND HYBRIDIZATION OF BOND ORBITALS  
IN DIATOMIC MOLECULES OF ALKALI METALS

molecule	$D_e = -W$	$H_p^0$	$\rho$	$\kappa = H'_s$	$b/a$	amount of <i>p</i> character (%)
Li <sub>2</sub>	26.8†	85.0†	0.316	15.6†	0.41	14.0
Na <sub>2</sub>	17.9	97.0	0.185	12.2	0.27	6.8
K <sub>2</sub>	11.8	74.6	0.158	8.4	0.24	5.5
Rb <sub>2</sub>	11.2	73.0	0.153	8.0	0.23	5.0
Cs <sub>2</sub>	10.4	67.1	0.155	7.4	0.24	5.5

† The energy quantities in columns 2, 3 and 5 are in kcal./mole of diatomic molecules.

An independent estimate of the amount of *p* character of these bonds can be made with use of the assumption that a linear extrapolation of the low-lying vibrational energy levels (as indicated by the Morse potential function) will lead to the energy level of the atomic state involved in the bond. The equation

$$D_0^* = \frac{\omega_e^2}{4\omega_e x_e} - \frac{1}{2}\omega_e \quad (9)$$

for the linearly extrapolated energy of dissociation leads with use of the spectroscopic values for  $\omega_e$  and  $\omega_e x_e$  to the values of  $D_0^*$  given in column 4 of table 2. The ratio of the difference between this value and the actual energy of dissociation  $D_0$  into atoms in the normal spectroscopic state and the *p-s* separation for two atoms ( $H_p^0$ , column 3 of table 1) is then the amount of *p* character in the bond orbitals. The values found in this way lie between 7.2 and 8.6 %, and are thus in approximate agreement with those found by the first method.

TABLE 2. HYBRIDIZATION OF BOND ORBITALS AS INDICATED BY LINEAR EXTRAPOLATION OF VIBRATIONAL ENERGY LEVELS

molecule	$\omega_e$	$\omega_e x_e$	$D_0^*$	$D_0$	$D_0^* - D_0$	amount of <i>p</i> character (%)
Li <sub>2</sub>	351.4	2.59	33.6†	26.3†	7.3†	8.6
Na <sub>2</sub>	159.2	0.726	24.7	17.7	7.0	7.2
K <sub>2</sub>	92.64	0.354	17.1	11.7	5.4	7.3
Rb <sub>2</sub>	57.8	0.14	17.0	11.1	5.9	8.1
Cs <sub>2</sub>	41.99	0.08	16.0	10.4	5.6	8.3

† In kcal./mole.

It is interesting to see, by comparison of the values in column 2 of table 1 (actual bond energy) and column 5 (calculated energy of pure *s* bonds) that this small amount of *p* character increases the bond energy by as much as one-half.

The results of the application of equations (7) and (8) to the metals themselves are given in table 3. The assumption is made that the bond-resonance energy depends on the bond strength  $S$  in the same way as the bond energy itself. The bond energy  $W$  is replaced by the heat of sublimation  $W_c$ . It is found that the calculated amount of *p* character is much greater than for the diatomic molecules. The calculated values, lying between 26 and 41 %, are, however, not so large as the 50 %

expected for the simple model discussed above. It seems likely that, whereas the two bond orbitals in the bicovalent anions  $M^-$  have 50 %  $p$  character, the occupied bond orbital in the neutral atoms has less than 50 %  $p$  character and the metallic orbital more. This difference in hybridization would decrease the value of the resonance integral but increase the atomic energy, and would result in the usual compromise that minimizes the total energy of the system.

TABLE 3. RESONANCE ENERGY AND HYBRIDIZATION OF  
BOND ORBITALS IN ALKALI METALS

metal	$-W_c$	$\rho_c$	$\kappa_c$	$\kappa_c/\kappa$	$b/a$	amount of $p$ character (%)
Li	78.0†	0.918	32.0‡	2.05	0.83	41
Na	51.8	0.533	25.3	2.07	0.61	27
K	39.6	0.531	19.5	2.32	0.60	26
Rb	37.8	0.518	18.7	2.34	0.59	26
Cs	37.6	0.560	18.1	2.45	0.62	28

† Heat of sublimation in kcal./mole of bonds (2 g.-atoms of metal).

‡ Calculated energy of resonating  $s$  bonds in kcal./mole.

The ratio  $\kappa_c/\kappa$  given in column 5 of table 3 is the ratio of the energy of resonating  $s$  bonds to static  $s$  bonds. The values found, lying between 2.05 and 2.45, indicate that the energy of metallic resonance is indeed great, being as large as the bond energy (for fixed bonds). The increase by a factor of about 3 in the energy of the system accompanying the condensation of diatomic molecules to the crystalline metal can be divided into two factors; one of these, approximately 2, is due to resonance energy, and the other, approximately  $\frac{3}{2}$ , is due to change in hybridization, which is itself, to be sure, the result of the resonance energy in causing the  $p$ - $s$  separation to bear a smaller ratio to the (resonating) bond energy.

The results of a simpler calculation for the alkaline-earth metals are given in table 4. The second column ( $-W_c$ ) contains the heats of sublimation to atoms in the normal state  $s^2 1S$ . If the atoms are bicovalent, however, their hypothetical bond-forming state would be the configuration  $sp$ , with energy  $\frac{1}{4}\{3(3P) + (1P)\}$  (that is, the weighted mean of the triplet and singlet states for the configuration  $sp$ ), in case that the occupied bonding orbitals had 50 %  $p$  character (the metallic orbital being a pure  $p$  orbital), or would be a state with somewhat higher energy, in case that the metallic orbital had some  $s$  character, as in the alkali metals. If it is assumed, by analogy with the alkali metals, that the  $p$  character of the occupied bond orbitals lies midway between the values 50 and  $66\frac{2}{3}\%$ , corresponding respectively to a pure  $p$  metallic orbital and a metallic orbital equivalent to the occupied bond orbitals, the bond-forming state has energy  $7/6H_p^0$ , and the bond energy relative to this state becomes  $7/6H_p^0 - W_c$ . Values of this quantity are given in the fourth column of the table.

It is interesting that the bond energy relative to the bond-forming state of the atoms shows the same monotonic trend for the alkaline-earth metals as for the alkali metals. The irregularity in the heats of sublimation at magnesium is due to the high

energy of the bond-forming state of the atom, and not to any extraordinary property of the bonds themselves. The much larger bond energies of the alkaline-earth metals (by a factor of 2 for Be/Li and about 3 for the other pairs) is due mainly to a difference in character of the hybrid bond orbitals. If the alkaline-earth bond energies are divided by 3.88, the value of  $S^2$  for  $sp$  bond orbitals with 41.7%  $s$  character, as assumed above, there are obtained the values for the energy of resonating  $s$  bonds given in column 5 of table 4. The next column contains values of the ratio of this quantity  $\kappa'_c$  to the corresponding quantity for the alkali metals. These values are reasonable, in comparison with the ratio of single-bond radii—1.38 for Be/Li, but somewhat smaller for the other pairs.

TABLE 4. ENERGIES OF RESONATING BONDS IN ALKALINE-EARTH METALS

	$-W_c$	$H_p^0$	$-W_c + \frac{7}{8}H_p^0$	$\kappa'_c$	$\kappa'_c/\kappa_c$
Be	75†	79.4‡	168‡	43‡	1.34
Mg	36.3	83.5	133.7	34.5	1.36
Ca	47.8	58.0	116.5	30.0	1.54
Sr	47	55.2	111	28.6	1.53
Ba	49	48.1	105	27.3	1.51

† The heat of sublimation in kcal./mole.      ‡ In kcal./mole.

#### METALLIC RESONANCE AND METALLIC VALENCY

The straightforward way in which metallic valency can now be discussed may be illustrated by the example tin, which is more versatile in its behaviour than its congeners germanium and lead).

Tin has fourteen electrons outside of its krypton-like core. These may occupy the nine orbitals in the following three most stable ways (atomic electrons are indicated by spin vectors, bonding electrons by dots, the metallic orbitals by open circles):

		$4d$	$5s$	$5p$
Sn A	$v = 4$	↑↓↑↓↑↓↑↓↑↓	•	•••
Sn B	2	↑↓↑↓↑↓↑↓↑↓	↑↓	••○
Sn C	0	↑↓↑↓↑↓↑↓↑↓	↑↓	↑○○

Sn A has the maximum possible valency, 4. Because of their greater stability, it is essentially the  $d$  orbitals that are occupied by the five unshared electron pairs. The four bonding electrons occupy the four remaining orbitals, which may conveniently be considered to be hybridized to  $sp^3$  tetrahedral bond orbitals. There is no extra orbital to serve as the metallic orbital, and so this quadrivalent tin would not, alone, form a metallic phase. Instead (Pauling 1947) it forms the essentially non-metallic variety of tin, grey tin, which has the diamond arrangement, each atom being surrounded tetrahedrally by four neighbours, to which it is attached by non-resonating single bonds.

The metallic form of tin, white tin, consists largely of the bivalent atoms Sn B, which have a metallic orbital. In white tin each atom has co-ordination number 6, and the bonds resonate among the alternative positions. It is the energy of this

resonance which in the main compensates for the difference in bond energy between four bonds and two; some stabilization of bivalent tin also results from the fact that in it two electrons occupy essentially the  $5s$  orbital, which has lower energy than the  $5p$  orbitals.

White tin, to which the valency 2.44 has been assigned (Pauling 1938), does not contain bivalent Sn B alone, but also some Sn A. It seems likely that these two kinds of tin atoms occur in the ratio 3:1, leading to the average valency 2.5, a value in essential agreement with that suggested before.

Thus in general the non-integral metallic valencies shown by the transition elements are to be interpreted as averages, corresponding to resonance of each atom among two or more electronic structures with integral valencies. The relative weights of the different structures would be for a given metallic phase such as to minimize the energy of the system. A simple treatment involving consideration of the energy quantities involved, and especially of the resonance energy as affected by the ratio of metallic orbitals to atoms, permits the conclusion to be drawn that a 3:1 ratio of a lower-valent form with a metallic orbital and the higher-valent form without this orbital is reasonable; but deviations from this ratio are to be expected, and tin in its various alloys might show any valencies from 2 to 4. The zero-valent form Sn C has no virtues, and presumably does not make a contribution in any alloy of tin, but the analogous forms of certain other metals, with valency 4 less than the maximum, are important.

Similar valence structures A, B, etc., may be written for gallium, zinc, and copper and their congeners:

		3d					4s	4p		
Ga A	$v = 5$	↑↓	↑↓	↑↓	↑↓	•	•	•	•	•
Ga B	3	↑↓	↑↓	↑↓	↑↓	↑↓	•	•	•	○
Ga C	1	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	•	○	○
Zn A	$v = 6$	↑↓	↑↓	↑↓	•	•	•	•	•	•
Zn B	4	↑↓	↑↓	↑↓	↑↓	•	•	•	•	○
Zn C	2	↑↓	↑↓	↑↓	↑↓	↑↓	•	•	○	○
Zn D	0	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	○	○	○
Cu A	$v = 7$	↑↓	↑↓	•	•	•	•	•	•	•
Cu B	5	↑↓	↑↓	↑↓	•	•	•	•	•	○
Cu C	3	↑↓	↑↓	↑↓	↑↓	•	•	•	○	○
Cu D	1	↑↓	↑↓	↑↓	↑↓	↑↓	•	○	○	○

These tend to be combined to produce effective metallic valencies of 3.5 for gallium, 4.5 for zinc, and 5.5 for copper (and their congeners), but other valencies are also shown by these versatile metals.

#### *Pivoting valence-bond resonance*

In ordinary covalent molecules and crystals the co-ordination number of an atom is equal to its covalency, because the resonance energy of synchronized resonance is not great enough to overcome the additional repulsive energy between non-bonded atoms. However, in an electron-deficient substance, with extra orbitals permitting uninhibited resonance, the resonance energy often becomes great enough to stabilize

a structure with increased ligancy (co-ordination number)—the ligancy then usually increasing to a value greater than the number of orbitals.<sup>†</sup>

It is of interest to note that *in order for a given atom to increase its ligancy beyond its covalency it is not necessary that this atom have an extra orbital: it is instead sufficient for the atoms that surround it to have extra orbitals.* The valence bonds of the central atom may then resonate among their alternative positions by pivoting about the central atom.

It is this sort of pivoting resonance that permits the 25 % contribution of Sn A to white tin, in which each atom has ligancy 6. Other examples are AuSn (Pauling 1947), in which each tin atom is surrounded by a trigonal prism of gold atoms, and Mg<sub>2</sub>Sn, with the fluorite structure (Pauling 1923), in which each tin atom is surrounded by a cube of magnesium atoms. The interatomic distances show that in each case the tin is quadrivalent, and its four bonds are permitted to resonate among the six or eight positions by use of the metallic orbitals of the gold or magnesium atoms. Resonance of this sort also characterizes many carbides, such as cementite, in which each carbon atom is surrounded by six iron atoms.

#### *The stable atomic orbitals*

We now interpret the ferromagnetic saturation moments as indicating that as many as seven hybrid orbitals have such a nature (concentration in bond directions, permitting large overlapping with orbitals of adjacent atoms) as to make them useful as bond orbitals (including the metallic orbital), and that the remaining two orbitals, essentially *d* in character, are available for occupancy by unshared electrons. These orbitals are of such a nature as to lead to positive rather than negative exchange integrals (small in magnitude, however), thus causing the parallel orientation of spins of adjacent atoms that leads to ferromagnetism.

Often, however, one or more additional *d* orbitals are used as atomic orbitals. This occurs as the result of the stabilizing influence of certain configurations of the atomic electrons and of certain molecular or crystal structures requiring only a smaller valency (smaller number of bond orbitals than seven). Thus *chromium*, with six outer electrons, might have any valency from 6 to 1, the non-valence electrons occupying the atomic orbitals. By Hund's rule of maximum multiplicity for a partially filled subgroup these  $6 - v$  atomic electrons would remain unpaired, and would require one  $3d$  orbital apiece. If conditions were such as to favour a large valency the element would have its maximum valency 6. If they were to favour a small valency we might at first expect two electrons to occupy the two stable atomic orbitals, leading to  $v = 4$ . However, if three *d* orbitals combine with  $sp^3$  to produce seven most satisfactory bond orbitals, only  $2 \cdot 14d$  orbitals would be required to produce five bond orbitals (for  $v = 4$  and the metallic orbital) with the same hybrid character, or  $1 \cdot 71$  to produce four. Hence by the change to a lower valency another *d* orbital is released for use as a stable atomic orbital, and a third electron might well occupy it. Indeed, the energy stabilizing the atomic state of maximum multiplicity is three times as great for the quartet configuration  $d^3$  as for the triplet configuration

<sup>†</sup> V. Schomaker, private communication; also Conference on the Chemical Bond, Paris, 15 April 1948.

$d^2$ , and hence there is good reason to expect the lower-valent state of chromium to have three atomic electrons and valency 3. Both sexivalent and tervalent chromium exist, as forms of the elementary metal, with the structures A 2 and A 3, respectively. In addition to the evidence of the interatomic distances (Pauling 1947), the value 3 for the valency of the low-valent state is supported by the value 3 magnetons found for the magnetic moment of chromium alloyed with gold† (so far as I know, the saturation moment of A 3 chromium has not been reported).

Manganese by a similar argument would be expected to have the metallic valencies 6 and 4, as observed (Pauling 1947). The corresponding valencies 6 and 5 for iron do not occur as distinct modifications of the elementary substance, but instead both contribute, in ratio 78 : 22, to the average valency 5.78 shown for  $\alpha$ -iron by the ferromagnetic saturation moment 2.22. It may be pointed out that the quinquevalent state of iron is not expected to be so stable as the lower-valent states of chromium and manganese because the decrease in valence by 1 would liberate only 0.43 of a  $d$  orbital, and the introduction of an additional atomic electron would hence weaken the bond orbitals by decreasing their  $d$  character.‡

Cobalt in its normal metallic form involves resonance between the two following sexivalent structures, in the ratio 35 : 65, as indicated by the saturation moment 1.71 magnetons:

		$3d$	$4s$	$4p$
Co A	$v = 6$	↑↑↑··	·	···
Co B	6	↓↑···	·	···○

The contribution of Co A is presumably limited to 35 % by the destabilizing effects of absence of a metallic orbital and decreased  $d$  character of the bond orbitals, which oppose the stabilizing effect of the quartet atomic state. In the same way nickel involves resonance between the two following structures, in the ratio 30 : 70 (saturation moment 0.61):

		$3d$	$4s$	$4p$
Ni A	$v = 6$	↓↑↑··	·	···
Ni B	6	↓↓···	·	···○

The decrease in the contribution of A from 35 % (for cobalt) to 30 % is presumably due in the main to the smaller amount of resonance stabilization for the triplet state than for the quartet state.

We have thus concluded from the foregoing arguments that the high-valent states of metallic chromium, manganese, cobalt, and nickel are all sexivalent states, with only iron having the slightly lower valency 5.78, in contradiction to the assumption previously made (Pauling 1938), in ignorance of a sound theory of the nature of metals, that the valency 5.78 applies to all the transition elements. The ferromagnetic data indicate that in alloys of iron and cobalt the average valency remains about 5.78 from 0 to 25 % cobalt (the moment increasing linearly from 2.22 to 2.48), and then increases to 6 at about 50 % Co (the moment remaining roughly constant

† Personal communication from Professor P. Néel.

‡ The quinquevalent state with a pure  $p$  metallic orbital would have somewhat more  $d$  character in the bond orbitals.

at 2.48), and thereafter remains 6 (the moment decreasing rapidly). The detailed discussion of the electronic structure of these alloys in terms of Fe A, Fe B, Co A and Co B is complicated, and requires consideration also of the ions  $\text{Fe}^+ \text{A}$ ,  $\text{Fe}^- \text{A}$ , etc.

#### THE STABILITY OF STRUCTURES IN RELATION TO BOND NUMBER

The factors that determine the choice of one from among alternative crystal structures of a metal or intermetallic compound have not been well understood. In the resonating-valence-bond theory of metals a very important energy quantity contributing to the stability of the systems is the energy of resonance of bonds among interatomic positions. It is clear that some modes of resonance would make larger contributions to the energy than others, and that in particular a simple ratio of number of bonds to number of positions would be exceptional. The simplest ratios, in order, are  $\frac{1}{2}$ ,  $\frac{1}{3}$ ,  $\frac{2}{3}$ ,  $\frac{1}{4}$ ,  $\frac{3}{4}$ , etc. We are thus led to the principle that *a special stability is associated with bond numbers  $\frac{1}{2}$ ,  $\frac{1}{3}$ ,  $\frac{2}{3}$ ,  $\frac{1}{4}$ ,  $\frac{3}{4}$ , etc.*<sup>†</sup>

For example, tin, with  $v = 2.5$ , crystallizes with a unique atomic arrangement, in which each atom has six ligates, four at 3.016 Å and two at 3.175 Å. These distances have been used (1947) in assigning the bond numbers 0.48 and 0.26 to these bonds. It is clear that these bond numbers can be taken as  $\frac{1}{2}$  and  $\frac{1}{4}$ , and that the choice of the structure and the value of its axial ratio (which determines the relative lengths of the two kinds of bonds) are the result of the effort of the tin atom to use its valency 2.5 in the formation of stable bonds with simple fractional bond numbers.

Zinc and cadmium have the A 3 structure, but with abnormally large axial ratio (1.856 for zinc) instead of the value 1.633 corresponding to close packing. From the distances 2.660 Å (for six bonds) and 2.907 Å (for the other six) the bond numbers 0.54 and 0.21 have been deduced. If the axial ratio were normal each of the twelve bonds formed by a zinc atom with  $v = 4.5$  would have bond number  $\frac{3}{8}$ . The assumption of the distorted structure permits a split into two classes with the more stable bond numbers  $\frac{1}{2}$  and  $\frac{1}{4}$  (or, probably,  $\frac{1}{6}$ , with the average valency of zinc equal to 4).

A similar explanation can be given of the occurrence of other unusual structures, shown by mercury, gallium, indium,  $\beta$ -tungsten,  $\beta$ -uranium,  $\alpha$ -manganese, and  $\beta$ -manganese. There is, of course, a close relation between the principle of the stability of simple fractional bond numbers and the filling of the Brillouin polyhedra corresponding to strong perturbations of the wave functions for the resonating valence bonds, discussed below.

Because of the occasional occurrence of a difference in hybridization of the bond orbitals involved in bonds of different classes, leading to a difference in single-bond radius, the determination of the bond numbers from experimental values of the bond lengths involves some uncertainty.

#### A NEW SYSTEM OF METALLIC RADII

The interpretation of experimental values of interatomic distances for metals in terms of bond numbers, with use of the equation

$$R_n = R_1 - 0.300 \log_{10} n, \quad (9a)$$

<sup>†</sup> The importance of half bonds (with  $n = \frac{1}{2}$ ) has been emphasized by Rundle (1947).

has permitted considerable progress to be made, but has been hampered by uncertainty as to whether or not a significant change in the single-bond metallic radius of an element accompanies a change in its valence. The system described here is designed to eliminate this difficulty by permitting the prediction of the metallic radius for any element in any valence state.

This system is based on the observations (Pauling 1947) that a linear relation between single-bond radius and atomic number holds for bonds of constant hybrid character, and that for an element the single-bond radius is (at least approximately) linearly dependent on the  $d$  character of the  $dsp^3$  hybrid bond orbitals.

The values of  $R_1(sp^3)$ , the single-bond radius for  $sp^3$  bonds, for the iron-transition elements are given by the equation

$$R_1(sp^3) = 1.825 - 0.043z, \quad (10a)$$

in which  $z = Z - 18$  is the number of outer electrons in the neutral atom (outside of the argon shell). This equation represents the straight line in figure 3 of Pauling (1947).

The value  $1.165 \text{ \AA}$  for iron with valence 5.78 is an average for 78 % of sexivalent iron, with seven  $d^3sp^3$  orbitals, and 22 % of quinquevalent iron, with  $d^2sp^3$  orbitals (in each case including one metallic orbital); this value hence corresponds to 39.7 %  $d$  character, and with the assumed linear relation leads to  $1.138 \text{ \AA}$  for  $d^3sp^3$  orbitals (42.9 %  $d$  character). Similarly the value  $1.162 \text{ \AA}$  for sexivalent cobalt with 39.5 %  $d$  character (average of 65 %  $d^3sp^3$  and 35 %  $d^2sp^3$ , calculated from the magnetic moment) leads to  $1.138 \text{ \AA}$  for the  $d^3sp^3$  radius, and the value  $1.137 \text{ \AA}$  is found for nickel from the sexivalent single-bond radius  $1.154 \text{ \AA}$  for 40.0 %  $d$  character (70 %  $d^3sp^3$  and 30 %  $d^2sp^3$ ).

The essential equality of these three values suggests† that  $1.138 \text{ \AA}$  may be taken as  $R_1$  for  $d^3sp^3$  orbitals for all the elements of the first long period:

$$R_1(d^3sp^3) = 1.138. \quad (10b)$$

Equations (10a) and (10b) and the assumed linear relation between  $R_1$  and the amount of  $d$  character ( $\delta$ ) lead to the equation

$$R_1(\delta, z) = 1.825 - 0.043z - (1.600 - 0.100z)\delta. \quad (10c)$$

The radii for pure  $p$  bonds are about  $0.030 \text{ \AA}$  larger than for  $sp^3$  bonds:

$$R_1(p) = R_1(sp^3) + 0.030. \quad (10d)$$

† The treatment adopted here must be considered as an approximation, inasmuch as it involves neglect of factors that without doubt have some effect on the interatomic distances. Among these factors is the difference in the ability of single unshared electrons and electron pairs to compete with bonding electrons for the stable orbitals. It is not unlikely that the radius  $1.165$  for iron corresponds to an amount of  $d$  character larger than the assumed 39.7 %, because of the promotion of the atomic electrons to orbitals with less than 100 %  $d$  character. Moreover, it is likely, from the results of the analysis of the energy quantities for the alkali metals, that the metallic orbital has less  $d$  character than the bond orbitals, instead of the same amount as assumed. The contribution of the ionic aspects of the atoms, with one bond more or less than normal, has also not been considered explicitly. Incorporation of these effects in the treatment of interatomic distances would make the system much more complicated, without greatly changing the conclusions derived from its application.

Application of equation (10c) to the observed single-bond radii of *scandium*, *titanium* and *vanadium* (1.439, 1.324, 1.224 Å) leads to 20, 27 and 35 % of *d* character, respectively (table 5). The gradual increase presumably results from the increasing stability of the 3*d* orbitals relative to 4*s* and 4*p*.

TABLE 5. SINGLE-BOND RADII AND AMOUNT OF *d* CHARACTER FOR TRANSITION ELEMENTS

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
1.439 (3) 20	1.324 (4) 27	1.224 (5) 35	1.176 (6, 3) 39	1.171 (6, 4) 40.1	1.165 (5.78) 39.7	1.162 (6) 39.5	1.154 (6) 40.0
Y	Zr	Cb	Mo	Tc	Ru	Rh	Pd
1.616 (3) 19	1.454 (4) 31	1.342 (5) 39	1.296 (6) 43	1.271 (6) 46	1.246 (6) 50	1.252 (6) 50	1.283 (6) 46
Lu	Hf	Ta	W	Re	Os	Ir	Pt
1.557 (3) 19	1.442 (4) 29	1.343 (5) 39	1.304 (6) 43	1.283 (6) 46	1.260 (6) 49	1.265 (6) 49	1.295 (6) 44

The observed single-bond radius for both sexivalent and tervalent *chromium* is 1.177 Å, which corresponds to 39.0 % *d* character. This might result for sexivalent chromium from a large (42 %) contribution of the set of orbitals *d*<sup>2</sup>*sp*<sup>3</sup> (without a metallic orbital), or for a disproportion in the *d*<sup>3</sup>*sp*<sup>3</sup> set, with the metallic orbital having more than the average amount of *d* character. In tervalent chromium three of the orbitals (presumably largely *d*) are occupied by the three atomic electrons, and the *d*<sup>2</sup>*sp*<sup>3</sup> set remaining for the three bonds and the metallic orbital may produce the hybrid character that is most stable.

For *manganese* the quadrivalent single-bond radius 1.163 Å corresponds to 40.1 % *d* character. The sexivalent single-bond radius is the same, to within the accuracy (about 0.010 Å) of its determination from the interatomic distances in the crystals ( $\beta$ -manganese and  $\alpha$ -manganese) in which sexivalent and quadrivalent manganese occur together.

#### *The metals of the first ascending branch*

If the assumption is made that the bond orbitals and one metallic orbital (except for the state with maximum valence, which has no metallic orbital) have the same hybrid character, values of the radii for the various pure valence states of the metals of the first ascending branch, from copper to germanium, can be calculated by use of equations (10c) and (10d). These values are given in table 6. There are also given the values interpolated for resonance between the state of maximum valency (with no metallic orbital) and the next state (with valency two less, and with a metallic orbital) in the ratio 25 : 75, the number of orbitals being included in the calculation as a weight factor.

For *copper* the predicted value of  $R_1$  for the hybrid state with valency 5.5 is 1.172 Å. This is in nearly exact agreement with the observed value,  $R_{(\text{CN}12)} = 1.276$  Å, which corresponds to  $R_1 = 1.174$  for  $v = 5.50$ , and hence supports this value for the valency of copper in the elementary metal.

*Zinc* in the elementary metal has six ligates at 2.660 Å and six at 2.907 Å. If the strong bonds are assumed to have bond number  $n = \frac{1}{2}$ , the value of  $R_1$  is 1.240 Å. This is close to the value 1.229 Å predicted for Zn B, with  $v = 4$ . If this quadrivalent zinc alone is represented, the weak bonds have  $n = \frac{1}{6}$ , and the value of  $R_1$  calculated with the correction  $-0.300 \log \frac{1}{6} = 0.234$  is 1.220 Å, again in good agreement with the predicted value. On the other hand, if there were 25 % contribution of Zn A, making  $n = \frac{1}{4}$  for the long bonds, the value of  $R_1$  would be 1.273 Å, which is much larger than the predicted radius for  $v = 4.5$ , 1.214 Å. We hence conclude that elementary zinc is pure quadrivalent Zn B, and that the six strong and six weak bonds have bond numbers  $\frac{1}{2}$  and  $\frac{1}{6}$ , respectively. The strong bonds formed by each atom involve resonance of three valencies among six positions, and the weak bonds involve resonance of one valency among six positions.

TABLE 6. METALLIC RADII OF ELEMENTS OF THE ASCENDING BRANCHES

	Cu	Zn	Ga	Ge
A	1.138 (7)	1.176 (6)	1.206 (5)	1.223 (4)
B	1.185 (5)	1.229 (4)	1.266 (3)	1.253 (2)
C	1.227 (3)	1.309 (2)	1.296 (1)	
D	1.352 (1)			
	1.172 (5½)	1.214 (4½)	1.248 (3½)	1.244 (2½)
	Ag	Cd	In	Sn
A	1.303 (7)	1.343 (6)	1.377 (5)	1.399 (4)
B	1.353 (5)	1.400 (4)	1.442 (3)	1.434 (2)
C	1.396 (3)	1.485 (2)	1.477 (1)	
D	1.528 (1)			
	1.340 (5½)	1.384 (4½)	1.423 (3½)	1.423 (2½)
	1.456 (2½)			
	Au	Hg	Tl	Pb
A	1.303 (7)	1.345 (6)	1.387 (5)	1.430 (4)
B	1.351 (5)	1.403 (4)	1.460 (3)	1.540 (2)
C	1.393 (3)	1.490 (2)	1.540 (1)	
D	1.520 (1)			
	1.338 (5½)	1.388 (4½)	1.419 (4)	1.506 (2½)
		1.418 (3½)	1.439 (3½)	
			1.477 (2½)	
			1.497 (2)	

In the complex structure of *gallium* each atom has seven neighbours, at four different distances, 2.437 (1), 2.706 (2), 2.736 (2) and 2.795 Å (2). These were previously interpreted, with the assumed valency 3.44, as corresponding to bond numbers 1.21, 0.43, 0.38 and 0.31, respectively, leading to the single-bond radius 1.245 Å, and the value 1.251 Å would have been obtained if the valency had been taken as 3.50. The close agreement of this value with the predicted value 1.248 for valency 3.50 (table 6) thus supports this valency for elementary gallium.

If it is assumed that the valency 3½ is divided among one single bond, four ½-bonds, and two ¼-bonds the corresponding values of  $R_1$  are 1.219, 1.263, 1.278 and 1.217 Å. The first and last values correspond to orbitals with 16 % *d* character, and the others to *sp*<sup>3</sup> orbitals. This suggests that the 0.25 *d* orbital provided by the 25 % contribution

of Ga A is divided among the  $1\frac{1}{2}$  orbitals of the single bond and two  $\frac{1}{4}$ -bonds, giving 16.7 % *d* character to them.

The observed interatomic distance 2.446 Å for *germanium*, with the diamond structure, was used as a fixed point in formulating equation (9a), the valency 4 being assumed. Germanium seems to be quadrivalent in all of its intermetallic compounds. A representative one is  $Mg_2Ge$ , with the  $Mg_2Sn$  (fluorite) structure. The germanium atom is surrounded by eight magnesium atoms, and its four valences undergo pivoting resonance among the eight positions, leading to half bonds.

### *The radii of the heavier transition metals*

For the palladium-transition metals we write the equations

$$R_1(sp^3) = 2.001 - 0.043z, \quad (11a)$$

$$R_1(d^3sp^3) = 1.303, \quad (11b)$$

$$R_1(\delta, z) = 2.001 - 0.043z - (1.627 - 0.100z)\delta, \quad (11c)$$

$$R_1(p) = R_1(sp^3) + 0.035. \quad (11d)$$

The corresponding equations for the platinum-transition metals are

$$R_1(sp^3) = 1.850 - 0.030z, \quad (12a)$$

$$R_1(d^3sp^3) = 1.303, \quad (12b)$$

$$R_1(\delta, z) = 1.850 - 0.030z - (1.276 - 0.070z)\delta, \quad (12c)$$

$$R_1(p) = R_1(sp^3) + 0.110. \quad (12d)$$

Equations (11a) and (12a) are based upon the values 1.399 and 1.430 for  $R_1(sp^3)$  for tin and lead, respectively, with slopes as indicated by the tetrahedral radii for the heavier elements. The value 1.430 for quadrivalent lead was obtained by adding to the radius for quadrivalent tin the difference 0.031 Å between the Mg-Pb distance in  $Mg_2Pb$  and the Mg-Sn distance in  $Mg_2Sn$ . The simple form of equations (11b) and (12b) was assumed in analogy with (10b), and the equal values of the constant were obtained from the observed distances for silver and gold, both assumed to have valence  $5\frac{1}{2}$ .

Revised values† of the single-bond radii for the elements molybdenum to palladium and tungsten to platinum are given in table 5. These differ from those previously published (Pauling 1947) in that the valency is assumed‡ to be 6 instead of 5.78. The course of the radii for these sequences differs from that in the sequence chromium to nickel in that the contraction shown in the preceding sequences continues, a minimum being reached at ruthenium and osmium. It is likely that this further contraction beyond molybdenum and tungsten is due to the appropriation of an amount of *d* character greater than 42.9 % (for  $d^3sp^3$  orbitals) by the bond

† The value for technetium is from Mooney (1948):

$$Tc-Tc = 2.706(6), 2.738(6); R_1(CN 12) = 1.361 \text{ Å}.$$

‡ Possibly slightly different valencies should be assumed, especially for ruthenium and osmium, and a small change may be required when reliable magnetic data become available.

orbitals, probably at the expense of both the atomic orbitals (occupied by unpaired electrons) and the metallic orbital. The effect decreases at palladium and platinum, with atomic orbitals mainly occupied by pairs of electrons, which tend to cause them to retain 100 % *d* character. It is seen from table 5 that the amounts of *d* character calculated by application of equations (11c) and (12c) show a reasonable trend, and are almost exactly the same for the two series of elements. The *d* character is equal to that for  $d^3sp^3$  bonds at molybdenum and tungsten, and reaches its maximum of 50 % at ruthenium, rhodium, osmium, and iridium.

### *The metals of the silver and gold ascending branches*

Values of the single-bond radii for the metals of the series silver to tin and gold to lead are also given in table 6, as calculated by equations (10c) and (11c) for the pure valence states A, B, C and D and for certain intermediate valencies, corresponding to resonance among these states.

The values for *silver* and *gold* with  $v = 5\frac{1}{2}$  agree closely with the experimental values, 1.340 and 1.337 Å, respectively, upon which the equations were in part based.

For *cadmium* the observed interatomic distances 2.973 (6) and 3.287 Å (6) indicate bond numbers  $\frac{1}{2}$  and  $\frac{1}{6}$ , respectively, as for zinc, and lead to the values 1.397 and 1.410 Å for  $R_1$ , in good agreement with the value 1.400 Å given in the table for  $v = 4$ . Bond number  $\frac{1}{4}$  for the longer bonds would lead to  $R_1 = 1.463$ , in disagreement with the value 1.384 for  $v = 4\frac{1}{2}$ . Hence we conclude that in the elementary metal cadmium, like zinc, is quadrivalent.

*Mercury*, with interatomic distances 2.999 (6) and 3.463 (6), appears to have valency  $3\frac{1}{2}$ . With bond numbers  $\frac{1}{2}$  and  $\frac{1}{6}$ , respectively, these distances lead to  $R_1 = 1.410$  and 1.498, the latter being much too large for  $v = 4$  ( $R_1 = 1.403$ ), whereas bond numbers  $\frac{1}{2}$  and  $\frac{1}{12}$  lead to  $R_1 = 1.410$  and 1.408, in approximate agreement with the value 1.418 for  $v = 3\frac{1}{2}$ . The decrease in valency from cadmium to mercury conforms to a general trend toward smaller metallic valencies with increasing atomic number in a group of elements.

In *indium* each atom has four ligates at 3.242 and eight at 3.370 Å. The first of these distances leads with  $n = \frac{1}{4}$  to  $R_1 = 1.440$ , a reasonable value in comparison with  $R_1 = 1.442$  for  $v = 3$  (table 6). However, the eight longer bonds must have  $n < \frac{1}{4}$ , so that the valency is less than 3. With  $n = \frac{3}{16}$  for these bonds their value of  $R_1$  is 1.446, the weighted average of this value and that for the shorter bonds, 1.456, agreeing exactly with the value for  $v = 2\frac{1}{2}$  in table 6; the valency of indium in the elementary metal is hence indicated to be  $2\frac{1}{2}$ .

In grey *tin* the distances 3.016 (4) and 3.175 (2) lead with  $n = \frac{1}{2}$  and  $\frac{1}{4}$  to  $R_1 = 1.418$  and 1.407, respectively, in approximate agreement with the interpolated value 1.423 for  $v = 2\frac{1}{2}$ . The distances 2.980 (2) and 3.198 (6) for  $\gamma$ -tin (containing a small amount of mercury), with  $n = \frac{1}{2}$  and  $\frac{1}{4}$ , similarly give  $R_1 = 1.400$  and 1.418.

*Thallium*, with  $R(\text{CN } 12) = 1.712\text{Å}$ , seems to be approximately bivalent. With  $n = \frac{1}{6}$  the value 1.478 is found for  $R_1$ , slightly smaller than that in table 6 for  $v = 2$ , 1.497. The value  $R(\text{CN } 12) = 1.746\text{Å}$  for *lead* gives  $R_1 = 1.512$  for  $v = 2$ , and  $R_1 = 1.542$  for  $v = 2\frac{1}{2}$ ; comparison with the values in table 6 suggests that the

valency lies between these limits. The conclusions for thallium and lead are uncertain because of uncertainty in the radii for pure *p* bonds. The value of the constant in equation (11d) is indicated not only by the single-bond radius for bismuth but also by the distances in the diatomic hydrides (M-H distance minus 0.300 = 1.570 for TIH, 1.539 for PbH, 1.509 for BiH; table III of Pauling 1947). By decreasing these radii by 0.03 Å exact agreement would be obtained for both thallium and lead with valency 2.

#### INTERATOMIC DISTANCES IN INTERMETALLIC COMPOUNDS

The discussion of interatomic distances is less simple for intermetallic compounds than for pure metals; among the complicating factors are the partial ionic character of bonds, the transfer of electrons, with consequent changes in valency, and the preferential use of the valencies of an atom in the formation of strong bonds rather than weaker ones. These factors, which of course participate in minimizing the energy of the system, usually operate to decrease the interatomic distances. Their effects may be illustrated by some examples.

In a discussion of cementite,  $\text{Fe}_3\text{C}$ , it was pointed out (Pauling 1947) that the observed interatomic distances,  $\text{Fe-C} = 2.01 \text{ \AA}$  and  $\text{Fe-Fe} = 2.62 \text{ \AA}$  (average), differ from those predicted from the valencies and radii of iron and carbon,  $\text{Fe-C} = 2.04 \text{ \AA}$  and  $\text{Fe-Fe} = 2.59 \text{ \AA}$ , by  $\pm 0.03 \text{ \AA}$ , and that the lack of agreement might indicate that the structure is under some strain, compressing the Fe-C bonds and stretching the Fe-Fe bonds. An alternative and in some ways preferable explanation is that, in order to form as strong bonds as possible with the carbon atoms, the two corresponding orbitals of the iron atoms undergo a change in hybridization with increase in the amount of *d* character and decrease of the iron radius by 0.03 Å, and that a compensating decrease in the amount of *d* character (by one-half as much) occurs in the four orbitals involved in forming Fe-Fe bonds, accompanied by an increase in radius by 0.015 Å. The same explanation has been advanced (Pauling & Soldate 1948) for the observed shortening of the Fe-Si distances in the cubic crystal  $\text{FeSi}$ ; and in addition it has been suggested that in this crystal the valency of silicon is used entirely in forming bonds with iron, the Si-Si separation of 2.76 Å, which indicates bond number 0.20, being assumed rather to be a non-bonded contact required by the geometry of the atomic arrangement.

The substance  $\text{FeB}$ , which may serve as another example, forms orthorhombic crystals (Bjurström 1933) in which each boron atom has two boron ligates at 1.77 Å and six iron ligates at  $2.15 \pm 0.03 \text{ \AA}$ . These distances correspond to half bonds, for which the calculated distances are 1.78 and 2.15 Å, respectively, and the covalency of boron is hence indicated to be 4. We might thus be led to assume that, in order to allow the formation of the maximum number of strong bonds (involving boron) permitted by the number of bonding orbitals of the boron atom, an electron is transferred from iron to boron. An alternative explanation is that the B-Fe bonds have bond number  $\frac{1}{2}$ , the iron radius being decreased by 0.11 Å by an increase in *d* character of the two iron orbitals involved in these bonds, and the boron atom remaining tervalent. Such a large decrease in the iron radius seems unlikely, how-

ever, and it is instead probable that both effects operate, there being a smaller change in hybridization and also some electron transfer in this crystal.

Each iron atom in FeB has six boron ligates, six iron ligates at 2.64 Å, and four iron ligates at 2.94 Å, corresponding to valency about 5.5.

The interpretation of simple structures of intermetallic compounds is made difficult by the metrical relations between non-equivalent interatomic distances that prevent them from independently assuming the values corresponding to their bond type. The B32 structure, shown by LiGa and several other compounds of elements of groups I and III *b* of the periodic table, consists of two interpenetrating diamond arrangements: each atom is surrounded by four atoms of the same kind and four of the other kind, at the tetrahedral corners of a cube, and there is thus only one bond distance (2.68 Å in LiGa) for three kinds of bonds (Li-Li, Li-Ga and Ga-Ga), which hence are expected to be strained. Nevertheless the bond number calculated from this distance for the strongest bonds (Ga-Ga) should be approximately correct.

Several investigators have suggested that in the B32 substances the alkali metal loses its valence electron to the III *b* metalloid, which then acts as a fourth-group element, and forms four single bonds with its four similar neighbours. However, this structure would lead to interatomic distances much smaller than those observed—to 2.53 Å for LiGa, for example, instead of 2.68 Å. The corresponding Ga-Ga bond number, 0.57, calculated by equation (9), suggests instead that the bonds are half bonds, or perhaps  $\frac{5}{8}$ -bonds. Presumably the lithium atom uses its valence electron in forming bonds with gallium atoms (four Li-Ga  $\frac{1}{4}$ -bonds), the Li-Li contacts being essentially non-bonded. The valency of gallium is 3 (for Ga-Ga half bonds) or  $3\frac{1}{2}$  (for  $\frac{5}{8}$ -bonds).

The compound PtTl (Zintl & Harder 1935) illustrates the phenomenon of the increase in valency of an element (thallium) in response to a change in its environment. This substance forms hexagonal crystals, the unit containing 3 Pt, 1 TlI, and 2 TlII, with ligation as follows: Pt, 4 Pt at 2.803 Å, 2 TlI at 2.803 Å, and 4 TlII at 2.83 Å; TlI, 6 Pt at 2.803 Å; TlII, 6 Pt at 2.83 Å. The Pt-Pt distance corresponds to  $n = 0.44$ , calculated by equation (9) with  $R_1 = 1.295$ . Presumably platinum has its normal valency 6, which is used in forming Pt-Tl bonds except for the amount used in the Pt-Pt bonds. The bond number  $n = 0.44$  would lead to 4.24 as the average valency of thallium in this compound; it is likely, however, that the Pt-Pt bonds are half bonds, and that the valency of thallium is 4—twice that for the elementary substance. The predicted value of  $R_1$  for quadrivalent thallium is 1.419 Å, and the calculated bond numbers for Pt-TlI and Pt-TlII are 0.71 and 0.64, respectively. The small differences between these values and the value  $\frac{2}{3}$  corresponding to the assumed valencies and between 0.44 and  $\frac{1}{2}$  for the Pt-Pt bonds may be attributed to a change in hybridization of the orbitals of platinum, in response partially to the requirement of the structure that the Pt-Pt and Pt-TlI distances be equal and partially to the effort to use better bond orbitals (with more *d* character) for the stronger Pt-Pt bonds than for the weaker Pt-Tl bonds.

There are many interesting problems involving solid solutions that might be discussed by use of the new system of radii. Of these I select one pointed out to me by Mr E. C. Ellwood, of King's College, Newcastle-upon-Tyne. The solid solution of

zinc in aluminium, with the Al structure, extends from 0 to 66 atomic % zinc. On cooling below 365° C the phase containing approximately 40 at. % zinc separates into two phases, both of which are solid solutions with the Al structure; at 275° C one phase ( $\alpha$ ) contains only 17 at. % zinc, and the other ( $\alpha'$ ) contains 59 at. % zinc. The values of the lattice constants indicate that the effective radius of zinc is smaller in the  $\alpha'$  phase than in the  $\alpha$  phase.

An explanation that may be suggested of these facts is that solid solutions of a quadrivalent metal (zinc) in a tervalent metal (aluminium) tend to be unstable because of the difficulty of saturating the valency of isolated quadrivalent atoms by bonds to its lower-valent ligates. With zinc as the solute an increase in free energy at the lower temperatures would accompany the separation into the zinc-poor  $\alpha$  phase, in which the versatile zinc atoms tend to assume the valency 3 (less stable, however, for them than their normal valency) in order to fit into the aluminium structure, and the zinc-rich  $\alpha'$  phase, in which the concentration of zinc atoms is great enough to permit the extra valency of zinc to be satisfied through the formation of Zn-Zn bonds.

#### BRILLOUIN ZONES AND THE RESONATING-VALENCE-BOND THEORY

In the customary treatment of metals it is shown that the interaction of the metallic electrons with the atomic nuclei (and their strongly bound electrons) arranged in a crystallographic array leads to perturbations of the energy that can be described as the concentration of the one-electron energy levels into Brillouin zones. It is interesting that the same concentration into Brillouin zones results from the resonating-valence-bond theory, and, moreover, the successive zones (Brillouin polyhedra) contain the same numbers of electrons as given by the one-electron molecular-orbital theory.

Instead of formulating the wave function for a crystal as a sum of functions describing various ways of distributing the electron-pair bonds among the interatomic positions, as was done in the first section of this paper, let us formulate it in terms of two-electron functions describing a single resonating valence bond. A bond between two adjacent atoms  $a_i$  and  $a_j$  may be described by a function  $\phi_{ij}(1, 2)$  in which 1 and 2 represent two electrons and the function  $\phi_{ij}$  may have the simple Heitler-London form

$$\phi_{ij}(1, 2) = C\{\phi_i(1)\phi_j(2) + \phi_j(1)\phi_i(2)\}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}, \quad (13)$$

with  $\phi_i$  and  $\phi_j$  the appropriately hybridized bonding orbitals of atoms  $a_i$  and  $a_j$  and  $\alpha$  and  $\beta$  the one-electron spin functions, or it may include ionic terms or have a still more complex form. The  $\phi_{ij}$  could then be used in building antisymmetrized functions corresponding to the various possible valence-bond structures for the crystal. This procedure would lead to essentially the same results as those given by equations (1) and (2). However, a convenient approximation is made by neglecting the resonance energy of the bonding pairs of electrons with one another, and considering only the bond energy and the resonance energy of each bond among its

alternative positions, without correlating its resonance with that of other bonds. The wave function for the crystal (not antisymmetrized) may then be written as

$$\psi(1, 2, \dots, 2N) = \Phi_1(1, 2)\Phi_2(3, 4), \quad (14)$$

in which each of the functions  $\Phi_k$  is a two-electron function representing a valence bond resonating through the crystal. The total energy, in this approximation, is the sum of the resonating-bond energies:

$$W = \Sigma W_k. \quad (15)$$

The form of the functions  $\Phi_k$  may be closely similar to that of the molecular orbitals used in the simple theory of metals. If there are  $M$  interatomic positions in the crystal which might be occupied by any one of the  $N$  electron-pair bonds, then the  $M$  functions  $\phi_i$  may be combined into the  $M$  mutually orthogonal linear aggregates that approximate the solutions of the wave equation with inclusion of the interaction terms representing resonance. This combination can be effected with use of Bloch factors:

$$\Phi_k(1, 2) = C\phi_r(1, 2)e^{2\pi i \mathbf{P}_k \cdot \mathbf{r}/\hbar} \quad (16)$$

Here  $\mathbf{r}$  is the radius vector from the origin to a point  $R$  in the crystal,  $\phi_r$  is the electron-pair-bond function in the region near  $R$ ,  $\mathbf{P}_k$  is the momentum vector corresponding to the three quantum numbers  $k$  (the density of states being calculated in the usual way),  $\hbar$  is Planck's constant, and  $C$  is the normalizing factor.

When the momentum vector  $\mathbf{P}_k$  has such magnitude and orientation as to correspond to Bragg reflexion from an important crystallographic plane (with large structure factor for slow electrons) strong interaction between the resonating bond and the rest of the crystal will occur, leading to the displacement of energy levels and the formation of Brillouin zones. The striking agreement between the number of bonding electrons given by the new system of metallic valencies and the number of electrons contained in an important Brillouin polyhedron for the  $\gamma$ -alloys,  $\alpha$ -manganese,  $\beta$ -manganese, and some other metallic substances with properties indicating filled zones (brittleness, low electrical conductivity) has been discussed in an earlier paper (Pauling & Ewing 1948).

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