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The Metallic Orbital and the Nature of Metals*

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In 1938 it was noticed (L. Pauling, *Phys. Rev.* **54**, 899, 1938) that about 0.72 of the nine outer *spd* orbitals per atom of a transition metal remain unoccupied by bonding electrons, unpaired ferromagnetic electrons, or unshared electron pairs. In 1948 this 0.72 orbital per atom was identified (L. Pauling, *Nature* (*London*) **161,** 1019, 1948; *Proc. Roy. Soc. A* **196,** 343, 1949) as required for the unsynchronized resonance that confers metallic properties on a substance, and it was named the metallic orbital. A statistical theory of unsynchronized resonance of covalent bonds in a metal with atoms restricted by the electroneutrality principle to forming bonds only in number $v - 1$, v, and $v + 1$, with v the metallic valence, has now been developed. This theory leads directly to the value 0.70 ± 0.02 for the number of metallic orbitals per atom, in reasonable agreement with the empirical value, and to the conclusion that M^+, M^0, and M^- occur in the ratios near 28 : 44 : 28. It leads also to the conclusions that stability of a metal or alloy increases with increase in the ligancy and for a given value of the ligancy is a maximum for valence equal to half the ligancy. These results with consideration of the repulsion of unshared electron pairs on adjacent atoms go far toward explaining the selection of different structures by different elemental metals and intermetallic compounds.

Introduction

Mike Sienko's interest in the question of the nature of the structural features that confer metallic properties on a substance (*1*) has stimulated me to renew my interest in this question.

Forty six years ago, on the basis mainly of empirical arguments, I formulated a description of the interatomic forces in metals (*2*) that had some novel features. I pointed out that according to this view the metallic bond is very closely related to the ordinary covalent (shared-electron-pair) bond: some of the electrons in each atom in a metal are involved with those of neighboring atoms in an interaction described as covalent-bond formation, with the bonds resonating among the available positions in the usual case that the number of positions exceeds the number of bonds. Moreover, all or most of the outer electrons of the atom, including for the transition elements the *d* electrons, take part in bond formation.

One of the reasons for my having attacked this problem in 1938 was that I was thoroughly dissatisfied with the claim of some physicists that only the *s* electrons were involved in the cohesion of the transition metals: the observed magnetic properties were said to show that the bonding in Ni involves 0.61 *s* electrons per atom, that in Co involves 0.71, that in Fe involves 0.22, and that in Cu involves 1 (the *d* shell for copper having its full complement of 10 electrons). The physical properties of these

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* Dedicated to Dr. M. J. Sienko.

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metals seemed to me to show clearly that the bonds involve interaction of a larger number of electrons. I knew, of course, that the quadrivalence of carbon is not based on the normal state $2s^2 2p^2$ of the carbon atom, but requires $s \rightarrow p$ promotion of one electron, to give the configuration $2s2p^3$, and it seemed possible to me that the cobalt atom in the metal might be promoted from its normal configuration $3d^7 4s^2$ to $3d^5 4s 4p^3$, with nine unpaired electrons which might enter into the formation of as many as nine covalent bonds.

I feel now that I was influenced to some extent by my knowledge that in 1926 Goldschmidt had formulated a set of "atomic" radii that represented reasonably well the interatomic distances in both covalent crystals and metals (*3*). I was also impressed by a discussion of the properties of metals by Bernal, who, however, rejected the idea that covalent bonds are present in metals (*4*). Bragg also rejected this idea (*5*).

The Discovery of the Metallic Orbital

In order to explain the observed saturation ferromagnetic moment of Fe, $2.22\mu_B$, I assumed that the Fe atom in the metal has two kinds of $3d$ orbitals: 2.22 "atomic" (contracted) orbitals, and 2.78 bonding $3d$ orbitals, which can hybridize with $4s$ and $4p$ to form bond orbitals. Thus 2.22 of the 8 outer electrons could occupy the atomic orbitals to provide the ferromagnetic moment, with the other 5.78 outer electrons forming 5.78 covalent bonds.

At that time I was handicapped by my remembering a misinterpretation that I had made of some results obtained in 1932 by one of my students, Ralph Hultgren (*6*). He had begun to make a thorough study of sets of equivalent *spd* hybrid bond orbitals, and soon found that he could not handle the computational problem in those precomputer days. I pointed out that the best hybrid orbitals have cylindrical symmetry about the bond direction and suggested that he assume cylindrical symmetry for his orbitals. With this assumption he treated several sets of equivalent orbitals, and found that the bond strength decreased rapidly for more than six orbitals. Only much later was it found that this decrease does not occur when the requirement of cylindrical symmetry is not imposed. In 1938, however, it seemed reasonable to assume that the number of bonding electrons remained constant at 5.78 from Cr to Ni.

With this assumption, and with 3.22 other orbitals available for occupancy by odd electrons or electron pairs, the ferromagnetic moment would be predicted to rise to a maximum of $3.22\mu_B$ at Co and then to decrease steadily with slope -1 to 0 for the alloy $Zn_{78}Ga_{22}$. This prediction agrees only in part with observation: the values of μ_B for alloys Fe–Co, Co–Ni, and Ni–Cu (Fig. 1) reach a rounded-off maximum of about 2.50 and then decrease to 0 at $Ni_{44}Cu_{56}$.

The obvious conclusion to be reached is that there are *three* kinds of *spd* orbitals: hybrid bond orbitals, contracted *d* orbitals, and about 0.70 other orbitals. In 1938 I considered this 0.70 unstable orbital per atom to be unsuited for either bond formation or

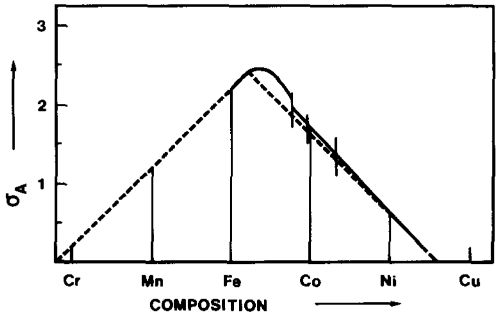


FIG. 1. Comparison of experimental values (solid curves) and predicted values (dashed lines) of the saturation ferromagnetic moment per atom, in Bohr magnetons, for Fe–Co, Co–Ni, and Ni–Cu alloys. The short vertical lines indicate change in crystal structure (from Ref. (*2*)).

occupancy by an "atomic" electron; only 10 years later did I recognize its significance and name it the metallic orbital (*7*, *8*).

The argument was originally presented (*7*, *8*) with Li as an example. The value of ΔH_f^0 (at 298 K) for the reaction $Li^+ + e^- \rightarrow Li(c)$ is -164 kcal mole^{-1} and that for $Li^+ + e^- \rightarrow Li(g)$ is -126 kcal mole^{-1}. Accordingly we might consider 77% of the binding energy of Li^+ and e^- in lithium metal to result from the formation of normal lithium atoms in the metal, and only 24% to result from the interaction of these atoms with one another. Moreover, the enthalpy change for the reaction $Li(g) \rightarrow \frac{1}{2}Li_2(g)$ is -13 kcal mole^{-1} and that for the reaction $\frac{1}{2}Li_2(g) \rightarrow Li(c)$ is -25 kcal mole^{-1}. If we consider four atoms in a square in a lithium crystal, there are two ways in which the bonds can be drawn to form Li_2 molecules:

$$\begin{array}{cc} \mathrm{Li} & \mathrm{Li} \\ | & | \\ \mathrm{Li} & \mathrm{Li} \end{array} \quad \text{and} \quad \begin{array}{c} \mathrm{Li}\text{—}\mathrm{Li} \\ \\ \mathrm{Li}\text{—}\mathrm{Li} \end{array}$$

The energy of the synchronized resonance between structures of this sort would contribute to the stabilization of the crystal, but far greater stabilization would result if there were also unsynchronized resonance to structures such as

$$\begin{array}{ll} \mathrm{Li}^-\text{—}\mathrm{Li} & \\ | & \\ \mathrm{Li} & \quad \mathrm{Li}^+ \end{array}$$

in which one bond resonates independently from one position to another. The electroneutrality principle permits M^+, M^0, and M^- in a crystal or molecule, but not charges larger than ±1.

However, this uninhibited resonance requires that the atom receiving a bond (M^+ or M) have an orbital available for its reception (occupied in M^-). *It is the possession of this orbital (the metallic orbital), in addition to the orbitals required for occupancy by unshared electron pairs and bonding electrons, by all or many of the atoms in a condensed phase that permits the unsynchronized resonance of covalent bonds that gives rise to metallic properties.*

Electric Conductivity

The unsynchronized resonance of covalent bonds through a metal provides a simple explanation of their characteristic electric conductivity. The valence bonds resonate from one position to another at electronic frequencies, as determined by the resonance energy, which is comparable in magnitude to the bond energy and is only about an order of magnitude less than the binding energy of a valence electron to the atom. In the presence of an applied electromagnetic field the electrons tend to move in the appropriate direction from atom to atom, as indicated in the diagram of Fig. 2, in which by a succession of shifts by single bonds a negative charge is seen to move toward the anode. In a similar way positive charges (electron holes) can move toward the cathode. The negative temperature coefficient of the electric conductivity is accounted for by the effect of thermal agitation in temporarily lengthening some bonds

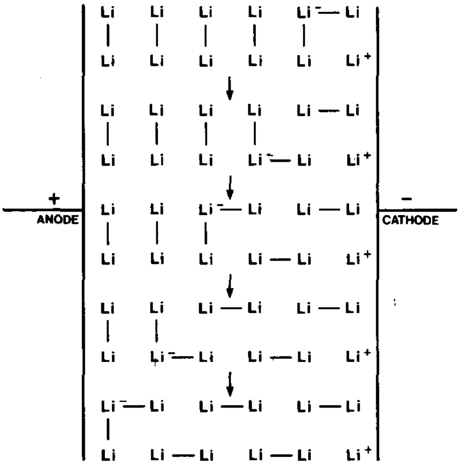


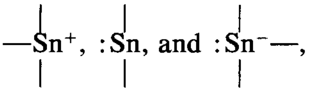
FIG. 2. Diagram illustrating motion of a negative charge (an electron) from the cathode to the anode by successive pivoting resonances of a covalent bond.

and shortening others, thus interfering somewhat with the resonance of the bonds, which takes place less often between nonequivalent positions than between equivalent (equienergetic) positions. This explanation is, of course, compatible with the usual explanation involving the scattering of electron waves by phonons.

An Example: White Tin

Hypoelectronic atoms, with fewer outer electrons than stable outer orbitals, do not provide a test for the metallic orbital, because such an orbital is necessarily available. The metallic orbital was discovered through the analysis of the values of the saturation ferromagnetic moments of the alloys of the hyperelectronic elements, from cobalt to copper, as shown in Fig. 1. Another test is provided by gray and white tin. Gray tin is not metallic; it is instead a metalloid, a semiconductor, with a positive temperature coefficient of its electric conductivity. It has the diamond structure, with each atom forming four covalent bonds, with bond length 2.80 Å. These bonds make use of all four of the stable outer orbitals, $6s6p^3$, leaving no metallic orbital and accordingly not permitting the substance to be a metal.

White tin, on the other hand, has metallic properties. Each atom in the crystal forms six bonds, four with length 3.016 Å and two with length 3.175 Å. When I first made a thorough study of bond lengths in metals (*9*) I interpreted these values as showing the valence to be 2.44; later (*8*) the value was recalculated to be 2.50, and then (*10*) to be 2.56. This value is explained by use of the metallic orbital. The atoms Sn^+, Sn, and Sn^- have the structures



$$-\overset{|}{\underset{|}{\mathrm{Sn}}}{}^{+},\ :\overset{|}{\underset{|}{\mathrm{Sn}}},\ \text{and}\ :\overset{|}{\underset{|}{\mathrm{Sn}}}{}^{-}-,$$

with Sn^+ and Sn having a metallic orbital and all other stable orbitals used either for bond formation or for occupancy by an unshared pair. (Sn^- has no need for a metallic orbital, because it is prevented by the electroneutrality principle from accepting another electron.) With Sn^+ and Sn^- tricovalent and Sn^0 bicovalent, the resultant valence 2.56 is achieved by 28% Sn^+, 44% Sn^0, and 28% Sn^-. The amount of metallic orbital (Sn^+ + Sn^0) is 0.72 per atom, in agreement with the value given by the magnetic moment measurements.

A Comment on the Magnetic Moments

When the magnetic moments were first analyzed (*2*) the conclusion was reached that the metal atoms from Cr to Ni use 5.78 orbitals for bond formation and 2.44 for occupancy by unshared atomic electrons. The deviation of the values 5.78 and 2.44 from integers was not understood; moreover, the slope of the curve of Fig. 1 from $Fe_{72}Co_{28}$ to $Ni_{44}Cu_{56}$ was not -1, as expected, but was about -1.10. These difficulties were eliminated in 1953, when I pointed out (*11*) that the Zener theory of ferromagnetism (*12*) clarifies our understanding of the phenomena. In this theory the interaction between atomic moments that stabilizes their parallel orientation is the resultant of the polarization of the conduction electrons, some electron pairs becoming decoupled in order that each of the two electrons be able to orient its spin parallel to the spin of the atomic electrons, in accordance with Hund's first rule. This effect is equivalent to converting a shared-electron-pair bond into two one-electron bonds, with the spins of the two electrons then contributing to the ferromagnetic moment. This adds about 11% to the moment. The moment for Fe is $2.22\mu_B$, of which 0.22 is contributed by polarized one-electron bonds and 2.00 is the corrected atomic moment. The total metallic valence of Fe, and also of adjacent elements, thus becomes 6, and the amount of metallic orbital given by the foot of the curve at $Ni_{44}Cu_{56}$ becomes 0.72 per atom.

A Simple Theory of Resonating Covalent Bonds in Metals

The significance of unsynchronized resonance can be assessed by a simple theoretical treatment.

Let us consider a crystal containing N atoms in which each atom has ligancy L and covalence v. The average occupancy of each bond position by a bond is v/L, and the average nonoccupancy is $(L - v)/L$. There are $W = (LN/2)!/\{(L - v)N/2\}!\,(vN/2)!$ ways of distributing $vN/2$ bonds among $LN/2$ positions, with multiple occupancy excluded. The total number of ways $w = W^{1/N}$ in which bonds are arranged around each atom is found with use of Stirling's approximation $x! = (2\pi x)^{1/2}(x/e)^x$ to be

$$w = \frac{L^{L/2}}{v^{v/2}(L - v)^{(L-v)/2}}. \qquad (1)$$

The number of ways in which n bonds are arranged around an atom with average valence v in a crystal involves a binomial coefficient:

Number of structures per atom with n bonds, average valence v

$$= w\,\frac{v^n(L - v)^{(L-n)}\,L!}{L^L\,n!\,(L - n)!} \qquad (2)$$

The number of structures for synchronized resonance is given by Eq. 2 with $n = v$:

Number of structures for synchronized resonance

$$= \frac{v^{v/2}(L - v)^{(L-v)/2}\,L!}{L^{L/2}\,v!\,(L - v)!} \qquad (3)$$

For a metal crystal, with unsynchronized resonance, the electroneutrality principle (*13*) permits the number of bonds per atom to be $v - 1$, v, and $v + 1$, corresponding respectively to M^+, M^0, and M^-. With Eq. 2 we calculate the number of structures with $n = v - 1$ and $v + 1$ to differ from the number with $n = v$ by the factors $(L - v)/(L - v + 1)$ and $v/(v + 1)$, respectively. The numbers of M^+ and M^- must of course be equal. With the assumption that the electrostatic interactions give the mean probability for M^+ and M^- to each, the number of unsynchronized resonance structures is found to be given by the equation:

Number of unsynchronized resonance structures per atom

$$= \frac{v^{v/2}(L - v)^{(L-v)/2}\,L!}{L^{L/2}\,v!\,(L - v)!}\left(\frac{L - v}{L - v + 1} + 1 + \frac{v}{v + 1}\right). \qquad (4)$$

The equation for synchronized resonance with $L = 4$ and $v = 2$ gives $R \ln 3/2$ for the residual entropy of ice (*14*). This value differs by only 1.1% from that given by calculations that do not involve the approximations made in our simple treatment. It is likely that the accuracy of Eq. 4 is also reasonably high.

The Amount of Metallic Orbital

The amount of metallic orbital per atom is given by this theory as $(2v + 1)/(3v + 1)$, for $v = L/2$, with values decreasing from 0.714 for $v = 2$ to 0.684 for $v = 6$, in good agreement with the value 0.72 given by the magnetic moments.

A Comparison of Synchronized and Unsynchronized Resonance

The ratio of the number of structures per atom for unsynchronized resonance to that for synchronized resonance is given by the expression in parentheses in Eq. 4. Its value increases from 2.33 for $L = 6$, $v = 1$ to 2.78 for $L = 16$, $v = 8$, with average about 2.65. The amount of resonance stabilization for unsynchronized resonance is thus far greater than that for synchronized resonance. Accordingly we should expect that *every element with an extra orbital to serve as the metallic orbital should be a metal.*

This expectation is in fact realized, with a single apparent exception. Boron, with three valence electrons and four outer orbitals ($2s2p^3$), is not usually classed as a metal.

Boron

Boron as an element and in some of its high-boron compounds assumes crystalline arrangements in which all or most of the boron atoms are present as icosahedral clusters B_{12}. For example, the unit of structure of the tetragonal form has four B_{12} icosahedra and two other tetraligating B atoms. The ligancy of the icosahedral borons is 6, being accordingly greater than the number of orbitals, as is customary for electron-deficient substances. The average bond number is 0.506.

The calculated number of resonance structures per atom (Eq. 4) is 2.50 for synchronized resonance and 6.25 for unsynchronized resonance. The second number is so much greater than the first that there is no doubt that the structure is one involving unsynchronized resonance, with 28% B^+, 44% B^0, and 28% B^-.

We may now ask why boron does not show the properties of large electric conductivity, high malleability, and high ductility characteristic of metals. The total number of structures per B_{12} icosahedron is $6.25^{12} = 3.55 \times 10^9$ and the number involving interactions between B_{12} groups is only 32.7, smaller by the factor 10^{-8}. Moreover, the usual mechanism of unsynchronized resonance involves pivoting of a bond about one atom (Fig. 2). There are no atoms in the B_{12} groups that have neighbors such as to permit pivoting resonance to transfer a charge from one B_{12} group to another, and the electric conductivity would accordingly be very small. The reported values of the conductivity for various samples of doped and undoped boron have minima usually around 10^{-10} to 10^{-13} ohm^{-1} cm^{-1} at $T \sim 100$ K, but with indication that at lower temperatures the conductivity increases, as is characteristic of metallic conduction.

We may now ask why boron does not crystallize with ligancy 12. The answer is that the bond lengths for Li and Be are large enough that the repulsion of the K-shell electron pairs is so small as to be overcome by the extra resonance energy associated with high ligancy, whereas for B to F this repulsion is large enough to require that the ligancy be kept small, decreasing the number of K-shell contacts.

Some Conclusions about Metal Structures

Some calculated values of the number of resonance structures are given in Table I. It is seen from the values for ligancy 12 that the number of structures per bond is roughly constant from $v = 1$ to $v = 6$, and then decreases rapidly from $v = 7$ to $v = 11$. Also the number of resonant structures per bond increases rapidly from 4.17 at $L = 6$ to 34.91 at $L = 16$. It is found that the following equation holds reasonably well for $v \leq L/2$ g with L not greater than 12:

$$\text{Number of resonance structures per bond} = 0.90\,L^2,\ v \leq L/2. \quad (5)$$

The resonance energy stabilizing a metal can be taken to be proportional to the number of resonating structures per atom. (This number is less by 1 than the number of structures, in that there is no resonance energy for a single structure, but we may ignore this correction in our approximate treatment.) *Accordingly the most stable atomic arrangement, in the absence of conflicting effects, should be that in which the atoms have the maximum ligancy.* If the atoms are all equivalent this arrangement

TABLE I

NUMBER OF RESONANCE STRUCTURES FOR UNSYNCHRONIZED RESONANCE

		Number	
L	v	Per atom	Per bond
6	3	6.25	4.17
8	4	11.38	5.69
10	5	21.00	8.40
12	6	39.19	13.06
14	7	73.73	21.07
16	8	139.65	34.91
18	9	265.89	59.09
12	1	5.19	10.38
12	2	11.39	11.39
12	3	19.97	13.31
12	4	29.21	14.61
12	5	36.44	14.58
12	6	39.19	13.06
12	7	36.44	10.41
12	8	29.21	7.30
12	9	19.97	4.44
12	10	11.39	2.28
12	11	5.19	0.94

has $L = 12$, as found in cubic and hexagonal closest packing, A1 and A3. These arguments show why 80% of all metals crystallize with closest packing, $L = 12$.

About 24% of all metals crystallize in the body-centered arrangement A2 (some metals have more than one modification). In this arrangement the ligancy L may be said to lie somewhere between $L = 8$ and $L = 14$, in that each atom has 8 neighbors at one distance and 6 others at a distance 15% greater, which is short enough to count as a position for a bond, but with smaller probability than the shorter positions. I have in the past considered the effective ligancy in A2 to be about 10, but it might be as great as 12 in contributing to the resonance stabilization in a statistical treatment.

With atoms of two different sizes arrangements are known for which the smaller atoms have $L = 12$ and the larger ones have $L = 13$, 14, 15, 16, or even larger values. Our statistical analysis explains why many alloys crystallize with these arrangements, which are stabilized by the large values of the resonance energy, as given by Eq. (4). Manganese is an example of an element that crystallizes in arrangements of this sort, involving two different kinds of manganese atoms, with different valences and different sizes.

Metal Arrangements with Smaller Ligancy

From Table I we see that the amount of resonance stabilization is small if the valence v is larger than one-half the ligancy. For a metal with valence v the ligancy should accordingly be equal to or greater than $2v$. The resonance energy increases with increase in the ligancy. There is another interatomic interaction that opposes increase in the ligancy. This is the repulsion that operates between electrons that are not paired with each other (*15*). This repulsion is especially strong between two unshared electron pairs. Unshared electron pairs appear in the outer shells of electrons in the right-hand side of the periodic table, starting with the Cu, Ag, Au column.

All of the metals to the left of Cu, Ag, Au have the A1, A2, or A3 arrangement (including Cu, Ag, and Au) except Mn, mentioned above, and U, which has an unusual structure with $L = 12$. To the right, however, we have a number of metals with values of L less than 12, as predicted by these arguments.

The next elements are Zn, Cd, and Hg. Each of these metals crystallizes with an arrangement such that each atom has six neighbors at one distance and six others at a distance corresponding to bonds about half as strong. The effective ligancy might accordingly be considered to be 9, rather than 12, and the maximum stability would thus be achieved for these elements, which have metallic valence 4.56, about one-half as great, together with a minimization of the repulsion of the unshared electron pairs by keeping the number of contacts as small as possible.

The next metals are Ga, In, and Tl, with metallic valence 3.56. Maximum stability, with minimum ligancy and minimum repulsion of unshared electron pairs, would be expected for ligancy 7. Gallium has an atomic arrangement in which each atom has 7 near neighbors, as expected from the foregoing considerations. Indium has a tetragonal structure in which each atom has 4 near neighbors and 8 more distant neighbors, perhaps representing an effort to achieve ligancy 7. Tl has the A3 structure, indicating that unshared pair repulsion is less important for it than for its lighter congeners.

Of the next elements, Ge, Sn, and Pb, Sn, and Ge (at high pressure) have metallic phases with $L = 6$, as discussed above, and Pb has the Al structure.

Our consideration of Eq. 5 accordingly accounts in a general way for the atomic arrangements of most of the metals, in addition to providing a criterion for metallic character.

Interatomic Distances

In 1947 I formulated the equation

$$D(n) - D(1) = -0.60\ \text{Å} \log n \qquad (6)$$

for the relation between the difference in bond length for fractional bond number n (between 0 and 1), $D(n)$, and the bond length $D(1)$ for a single bond, taken as the sum of the single-bond metallic radii R_1 for the two atoms (*9*). With use of this equation I formulated sets of single-bond metallic radii R_1 and also of R (ligancy 12). It has become clear in recent years that the system based on Eq. 6 fails when the ligancy is much smaller or larger than 12. In intermetallic compounds with ligancy greater than 12 the bond lengths are shorter than the calculated values, and in those with low ligancy they are longer. Especially striking is the difference of about 0.07 Å between the enneacovalent radii of the transition metals in the organometallic cluster compounds (1.23 Å for cobalt, for example (*16*)), and the single-bond metallic radii (1.162 Å for cobalt (*9*)). There is some evidence that when the nature of the hybrid bond orbitals is essentially the same the value of the single-bond radius does not change. For Fe and Co the enneacovalent radii are 1.24 and 1.23 Å, and the radii for ligancy 6 are 1.23 and 1.22 Å, the same to within their uncertainty of about ±0.01 Å.

I conclude that the 1947 values of the metallic single-bond radii are in error because of the neglect of the increasing stabilizing and bond-shortening effect of resonance. The number of resonance structures over the region of interest can be taken as $0.9\,L^2$, and the energy of resonance stabilization is expected from quantum mechanical principles to be proportional to this number. The decrease in single-bond radius should be proportional to this number. The observed difference for cobalt gives the relation

$$\Delta R_1 = -L^2 \cdot 0.0005\ \text{Å} \qquad (7)$$

This correction of R_1 for ligancy, together with the bond-number equation and a set of values of the new single-bond metallic radii, provides an improved system of correlating interatomic distances not only in metals and alloys but also in other crystals and molecules.

The Metallic Valence of the Heavier Transition Metals

In 1938 I concluded (*2*) from the consideration of the values of their saturation ferromagnetic moments that the elements of the first transition sequence from Cr to Ni have the constant metallic valence 5.78, later revised (*8*) to 6. Despite their lack of ferromagnetism, I assumed (*9*) in 1947 that their heavier congeners Mo to Pd and W to

Pt also have the same metallic valence, 5.78 or 6. Then in 1977 I reconsidered this question (*17*) with consideration of the observed enneacovalence of transition metals in some of their organometallic compounds and concluded that the metallic valence could become as large as 8.3 for Ru–Rh and Os–Ir alloys. This conclusion was reached by an argument based on the observed bond lengths that I now believe to have been misleading.

Values of the reciprocal of the covalent radius for ligancy 12 are shown in Fig. 3. It is seen that the points for each sequence can be represented by three curves. The first curve for each sequence represents the effect of the increase in valence from 2 to 6 and the corresponding increase in binding energy for Co to Cr, Sr to Mo, and Ba to W. Each of these curves is extrapolated to a maximum at $v = 8.3$, corresponding to nine *spd* orbitals with 0.7 metallic electron. It is seen that for all three sequences the values deviate from the extrapolated curves. From Cr to Ni they are represented by a straight line, interpreted as corresponding to the constant value 6 for the metallic valence. For the other two sequences, however, the curves indicate a continued increase in the valence, although not so great as indicated by the extrapolated curves.

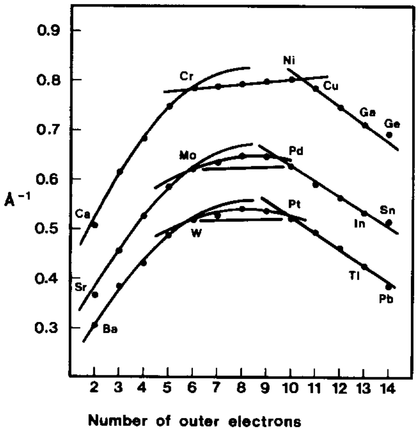


FIG. 3. Curves showing values of the reciprocal of the metallic radius for ligancy 12 of metals of the sequences Ca to Ge, Sr to Sn, and Ba to Pb. The vertical scale has been shifted down for the second and third sequences by 0.1 and 0.2, respectively.

The Valence of Pd and Pt

Information about the structure of Pd and Pt is provided by the paramagnetic susceptibility of the metals, interpreted by the Weiss equation

$$\chi = \frac{C}{T - \Theta} \tag{8}$$

with

$$C = \frac{N\mu^2}{kT}. \tag{9}$$

In Fig. 4 there are shown the lines representing χ^{-1} as a function of T for Ni, Pd, and Pt. It is seen that the slopes, which give the values of C^{-1}, are essentially the same, and that accordingly Pd and Pt have the same number of unpaired electrons as Ni. We accordingly conclude that they have the same valence, 6.

The Curie temperature Θ has the value 680 K for Ni, corresponding to the Zener interaction that tends to keep the electron spins parallel and that below this temperature gives rise to ferromagnetism. For Pd and Pt the values of Θ are negative (−100 K, −650 K). These negative values correspond to a dominating interaction that tends to keep the electron spins antiparallel, and which we may describe as the formation of a weak shared-electron-pair bond. We might accordingly conclude that Pd and Pt have metallic valence slightly greater than 6.

Application of the Theory of Unsynchronized Resonance

We may apply the statistical theory to determine the number of outer electrons involved in bond formation by determining

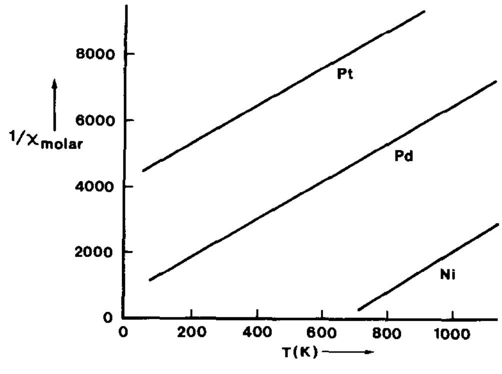


FIG. 4. Curves showing the reciprocal of the molar paramagnetic susceptibility of Ni, Pd, and Pt as a function of the temperature.

the derivative with respect to v of the number of resonating structures per atom (presumably proportional to the stabilizing resonance energy). Values of the increase in the number of resonating structures per atom with $L = 12$ as v increases by unit steps from 0 to 9, obtained by subtracting successive numbers in the third column of Table I, are shown in Fig. 5. It is seen that the value 0 comes at $v = 6.5$, which may be considered the maximum expected metallic valence for ligancy 12.

Here I have ignored the energy of the bond itself and of other contributions to the energy of cohesion of the metal. Some justification for this neglect is provided by some rough calculations (*8*) indicating that for the alkali metals the nonresonating bond energy contributes only about one-third and the resonance energy two-thirds of the cohesion energy.

The Metallic Valences of Tc, Ru, Rh, Re, Os, and Ir

From Fig. 5 we might predict that the values of v for the metals Tc, Ru, Rh, Re, Os, and Ir would be close to 6.5. From Fig. 3 we make the estimates $v = 6.5$ for Tc and Re, 7.0 for Ru and Os, and 6.6 for Rh and Ir. Consideration of the values of the paramagnetic Curie constant in comparison with those for the elements Mu to Co might permit the determination of more precise values.

The Metallic Orbital and the Band Theory of Metals

It was pointed out in my 1949 paper (*8*) that resonance of electron-pair bonds among the bond positions gives energy bands similar to those obtained in the usual band theory by formation of Bloch functions of the atomic orbitals. There is no incompatibility between the two descriptions, which may be described as complementary. It is accordingly to be expected that the 0.72 metallic orbital per atom would make itself clearly visible in the band-theory calculations for the metals from Co to Ge, Rh to Sn, and Pt to Pb; for example, the decrease in the number of bonding electrons from 4 for gray tin to 2.56 for white tin should result from these calculations. So far as I know, however, no such interpretation of the band-theory calculations has been reported.

Conclusion

Since 1938 there has been recognition of

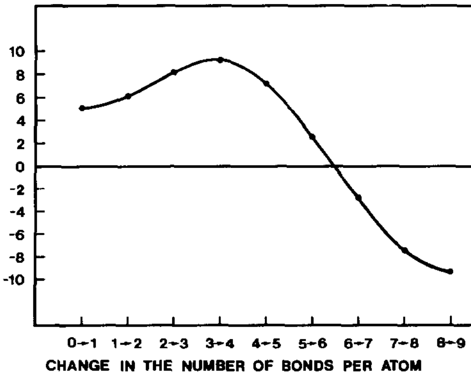


FIG. 5. Increase in the number of resonance structures per atom with unit increase in the average number of bonds formed by an atom; ligancy 12.

the existence of the metallic orbital and of its significance in conferring metallic properties on a substance. The amount of metallic orbital per atom, about 0.72, given by the values of the saturation ferromagnetic moments of the alloys from Fe to Cu agrees well with values from 0.684 to 0.714, average 0.70, given by the statistical theory of unsynchronized resonance of bonds. Also, for the elements Mo to Pd and W to Pt the values of R_{12}^{-1} (Fig. 3) indicate a maximum at 8.3 outer electrons, 0.7 less than the possible number 9 of *spd* orbitals.

The value 0.72 for the number of metallic orbitals per atom corresponds to the distribution 28% M^+, 44% M^0, and 28% M^-, with the electric charges moving from atom to atom with electronic frequencies, as determined by the magnitude of the resonance energy. This distribution is given in a straightforward way by the statistical theory, together with the electroneutrality principle. The statistical theory, described in earlier sections of this paper, provides strong support for the resonating-covalent-bond theory of metals that has been developed over the last 45 years on a largely empirical basis.

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