The nature of metals

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ABSTRACT - The resonating-valence-bond theory of metals was first
developed in 1938 and further advances were made in the years 1947-49.
This theory explains the nature of the bonding in metals and alloys and
the characteristic properties of such substances. One of the principal
ideas in this theory, that on average 0.72 of an outer orbital per atom
must be unoccupied by bonding electrons in order to permit the
unsynchronized resonance that confers metallic properties on a substance,
was based largely on empirical evidence. Substantial theoretical advances
have been made in the development of this approach during the past few
years. Among other things, the origin of this orbital (the "metallic
orbital") has been found through the use of a statistical treatment,
rooted in the principles of quantum mechanics, of unsynchronized resonance
of covalent bonds in a metallic substance with atoms restricted by the
electroneutrality principle to forming $\underline{v} - 1$, $\underline{v}$, or $\underline{v} + 1$ bonds, with $\underline{v}$
the valence. Recent applications of the theory have been the development
of a multiple twinning explanation of the so-called icosahedral quasi-
crystals and the development of a set of principles determining the
structures of metals under high pressures.

In 1938 I formulated a resonating-covalent-bond theory of metals. John C. Slater,
in 1934, and also N. F. Mott and H. Jones, in 1936, had assumed that the electronic
structure of the iron-group transition metals, from chromium to copper, could be
satisfactorily discussed on the assumption that six orbitals are available for occupancy
by unshared electron pairs, bonding electrons, and ferromagnetic electrons. These six
orbitals are the five 3d orbitals and the 4s orbital. I concluded, for reasons discussed
below, that the three 4p orbitals should also be taken into consideration. The resonating-
covalent-bond theory of metals was extended and refined in 1947 and 1948, and further
extended and refined during the past five years, when a statistical theory of resonating
covalent bonds was developed.

My interest in metals began in the summer of 1919, when I was working as a paving engineer,
building a highway through the mountains in southern Oregon. During my free time I thought
about the properties of substances in relation to their composition. My chief reference
book was an early edition of the Handbook of Physics and Chemistry. Organic compounds and
ordinary inorganic compounds seemed to me to have reasonable properties and compositions, in
relation to the valences of the elements and such structural principles as the tetrahedral
structure of the carbon atom, the ionic structure of salts, and the Werner coordination
theory. The metals, however, showed great ranges of values of their properties, such as
melting point and boiling point, hardness and strength, and magnetic properties. Moreover,
the formulas of intermetallic compounds showed no relationship, in general, to positions of
the metals in the periodic table. My interest in metals increased during the year 1920-1921,
when I studied metallography and metallurgy with Professor Sam Graf, in the Oregon
Agricultural College. For two years I served as a part-time assistant in metallography and
strength of material, with Professor Graf. I also worked, during my fourth year at Oregon
Agricultural College on a research problem that I had formulated, that of determining the
orientation of crystals of iron deposited electrolytically in a magnetic field.

When I became a graduate student in the fall of 1922 I was taught the technique of
determining the structure of crystals by the x-ray diffraction method by one of the earliest
workers in this field in the United States, Roscoe Gilkey Dickinson, who had been the first
person to obtain a Ph.D. degree from the California Institute of Technology (1920). My
first scientific paper, published with Dickinson in 1923, was on the structure of the
mineral molybdenite, MoS_2. In the meantime, in the fall of 1922, I had made single crystals
of two intermetallic compounds, and had determined the structure of one of them, Mg_2Sn, the
first intermetallic compound to have its structure determined. The second compound, $NaCd_2$,
turned out to be extremely complicated in structure, with more than 1000 atoms in a cubic

unit with cube edge over 30 Å. I worked for 40 years in the effort to determine the structure of NaCd$_2$, without success. The structure was finally determined, in 1962, by my associate Sten Samson.

I now present the argument that led to the formulation of the resonating-covalent bond theory of metals. By 1938 I felt that I had a good understanding of the properties of many substances in relation to the shared-electron-pair chemical bond, as discussed by Gilbert Newton Lewis in 1916, Irving Langmuir in 1919, and Heitler and London in 1927. I had formulated the concepts of hybridization of bond orbitals, partial ionic character in relation to difference in electronegativity, resonance of molecules among two or more valence-bond structures, and other aspects of chemical bonding in molecules and crystals. It seemed clear to me that the increase in hardness, strength, melting point, and other properties of metals in the sequence K, Ca, Sc, Ti, V, Cr could be attributed to the increase from 1 to 6 of the number of covalent bonds formed by the metal atom, and I assumed that the physical properties of other metals would give a good indication of the number of covalent bonds that their atoms were forming.

Because the ligancy of the atoms in the crystals was usually 8 or 12, much greater than the valence, the covalent bonds had to be assumed to be resonating among alternative positions.

With the assumption that the following metals, Mn, Fe, Co, Ni, Cu, have structures involving only six orbitals, and the conclusion reached by Slater in 1934 that the d electrons do not take much part in cohesion, Slater, Mott, and Jones had concluded that the cohesive forces in the metal are the result of bonding by 0.22 s electron in iron, 0.71 in cobalt, 0.61 in nickel, and 1 in copper. If this were the case, I argued, these metals should be soft, weak, low-melting substances, comparable to potassium, whereas in fact their properties indicate that the bonding is about the same as that for chromium, involving six resonating covalent bonds. I noted that metallic valence of about 6 for these metals could be achieved by the assumption that the 4p orbitals, as well as 3d and 4s could be used for occupancy by unshared pairs, paramagnetic electrons, or bonding electrons.

The argument is then extended by consideration of the so-called Slater-Pauling curve of the saturation magnetic moment per atom of Fe, Co, Ni, and Cu and their alloys with one another. In fact, consideration of these values led to the conclusion that only about 8.28 orbitals, rather than 9, were being used by the metal atoms.

For nine years I remained puzzled by the fact that 0.72 orbital per atom seemed to remain unused. Finally, in 1947, I realized that this 0.72 orbital per atom was in fact required to give metals their characteristic properties, especially that of electronic conductivity of electricity, with the conductivity increasing as the temperature is lowered. There are two conceivable kinds of resonance of covalent bonds in a crystal. One is synchronized resonance, involving two bonds or more shifting at the same time in such a way that every atom retains the number of bonds equal to its valence, v. This may be called Kekulé resonance: It is the kind of resonance assumed to occur between the two Kekulé structures of the benzene ring. The other is unsynchronized resonance, that permits a single bond to shift. The number of resonance structures and the amount of resonance stabilization are far greater for unsynchronized resonance than for synchronized resonance. With unsynchronized resonance an atom can form one bond less than its valence v, giving it a positive charge, M$^+$, or a number equal to its valence, M^0, or a number one greater than its valence, M$^-$. If we consider three adjacent atoms, with a bond between the first and the second and all three having valence v, a bond can rotate about the first atom from the position to the second atom to that to the third atom. The second atom then becomes M$^+$, and the third atom M$^-$. In order that M^0 (the third atom) be able to pick up an additional bond, it must have an additional orbital, remaining unused until it is occupied through the shift of a bond. Similarly, in order that M$^+$ be able to change its valence from v-1 to v, it must have an orbital that is not occupied until the covalent bond has shifted. The atom M$^-$, however, has no need for an extra orbital, because the electroneutrality rule (the rule that atoms in stable molecules and crystals may have resultant electric charges +1, 0, or -1, but not +2 or -2) prevents M$^-$ from picking up an additional bond. Accordingly the number of orbitals per atom needed in the metal is the sum of the fractions representing M$^+$ and M^0. The value 0.72 for this sum is given by the composition of the Cu-Zn alloy at the foot of the Slater-Pauling curve, Cu$_{56}$Zn$_{44}$. It corresponds to 28% M$^+$, 44% M^0, and 28% M$^-$. Because of the requirement of this extra orbital for metallic properties, I named it the metallic orbital. In general, a substance with available metallic orbitals is a metal, and a substance without the metallic orbital is a metalloid or nonmetal. A metalloid (semiconductor) has small electrical conductivity, increasing with increase in temperature, rather than decrease in temperature.

In 1949 I published in Proceedings of The Royal Society a paper on the resonating-valence-bond theory of metals and intermetallic compounds. In a footnote in this paper there is a brief discussion of a statistical theory of resonating covalent bonds of metals, leading to the conclusion that for lithium metal there are 28.5% Li$^+$, 43% Li^0, and 28.5% Li$^-$, and

0.715 metallic orbitals per atom for this metal and other alkali metals. For some reason I did not continue the development of the statistical resonating-covalent-bond theory of metals for 35 years. At first the reason may have been that I was much involved in the discovery of the alpha helix and the two pleated sheets, the principal ways of folding polypeptide chains in fibrous and globular proteins. I also was involved in the discovery of molecular diseases and in the formulation of the principles of orthomolecular medicine. In 1984 and the following years, however, I developed the theory further, partially in collaboration with Professor Barclay Kamb. The development of this statistical theory has made the theory of metals more powerful. For example, its application to the Ni-Cu alloys has led to the conclusion that the number of metallic orbitals for the alloy at the foot of the Slater-Pauling curve is 0.722, in exact agreement with the observed value 0.72.

In 1947 I formulated an equation showing the dependence of bond length on bond number, and applied this equation to obtain a set of metallic radii for the metallic element. Nearly 40 years later it became possible to formulate a set of single-bond radii for metal atoms in clusters and in organo-metallic compounds. These values were surprising, in that for the transition metals they were about 0.10 Å larger than the single-bond values of the metallic radius that had been formulated in 1947. An explanation for the discrepancy was then found by Barclay Kamb and me. It is that a correction to the bond length should be made with consideration of the number of resonating-covalent-bond structures per atom. This correction is about 0.10 Å for the transition metals. On the basis of this correction, a revised set of single-bond metallic radii was formulated by Kamb and me.

Among other contributions to the theory, I may mention a study of Brillouin zones by Fred Ewing and me in 1948, a study of compressibilities, force constants, and interatomic distances of the elements in the solid state, including metals, by Jurg Waser and me, my study of electronic transfer in intermetallic compounds and the description of metals as hypoelectronic, buffer, and hyperelectronic in 1950, a theory of paramagnetism in 1953, several recent papers on icosahedral, decagonal, and octagonal quasicrystals as twins of cubic crystals or crystals with lower symmetry, and the theory of superconductivity. During recent months I have been working on the analysis of the factors determining deviations from additivity of atomic volumes when metallic elements combine to form intermetallic compounds and on the various structural factors that determine the nature of the phase diagrams of binary alloys. I have found that the most important factor determining the nature of the phase diagrams is the difference in electronegativity of the two metals composing the binary alloy. Other factors, such as the ratio of the metallic radii and the relative values of the valence and bond numbers, are also important.

The resonating-valence-bond theory of metals is a quantum mechanical theory. There is no ·aspect of it that is not compatible with quantum mechanics. In fact, there is nothing that I have published since 1925 that is incompatible with quantum mechanics. I began the study of quantum mechanics as soon as Heisenberg had published his first paper, and I continued it, in 1926, while Schrödinger was publishing his papers on wave mechanics. My first paper on quantum mechanics was published in 1926, and in the following ten years I published about 50 papers in this field, many of them relating to the nature of the chemical bond. In 1935, with my student E. Bright Wilson, I published a textbook on this subject, Introduction to Quantum Mechanics, which is still in print, without revision.

Many solid-state physicists discuss the structure and properties of metals and alloys with use of the band theory, in its several modifications. This theory is also a quantum-mechanical theory, which starts with a solution of the wave equation for a single electron, and introduces electron-electron correlation in one or another of several ways. The resonating-valence-bond theory introduces electron-electron correlation in several stages, one of which is by the formation of covalent bonds between adjacent atoms, and another the application of the electroneutrality principle to restrict the acceptable structures to those that involve only M^+, M^0, and M^-. It should be possible to find a relationship between the band-theory calculations and the resonating-covalent-bond theory, but I have been largely unsuccessful in finding such a correlation. I have, for example, not been able to find any trace of the metallic orbital in the band-theory calculations, which thus stand in contrast to the resonating-valence-bond theory, in which the metallic orbital plays a predominant role.

It may be noted that in the foregoing paragraphs I have referred almost entirely to work done by me and my close associates during the past 50 years. In doing so, I am not doing an injustice to other investigators, because, in fact, other investigators interested in metals and intermetallic compounds have for the most part refrained from making use of the resonating-covalent-bond theory or from referring to it. During this 50-year period I have not seen any papers, by other authors, on this theory in Physical Review or Physical Review Letters, and only a couple in other journals.. Textbooks of general chemistry and inorganic chemistry usually ignore metals and intermetallic compounds. The authors may be embarrassed by chemical formulas such as $NaZn_{13}$, Na_2Cd_{11}, Cu_5Zn_8, $Ag_{51}Tb_{14}$, and so on. Some textbooks of solid-state physics include a sentence or two about an alternative explanation of the

shape of the Slater-Pauling curve, but ignore the resonating-valence-bond theory in its other aspects.

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