ADVANCES
IN
CATALYSIS

VOL. VII

ADVANCES IN CATALYSIS

AND RELATED SUBJECTS

VOLUME VII

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NICOLAI DMITRIEVICH ZELINSKY

1861–1953

It was my very good fortune to study and work with two great chemists. In succession it is now my honorable but sad duty to write their obituaries.

One of them was well known to us; the Willard Gibbs medalist, Vladimir Nicholaevich Ipatieff, who passed away in November, 1952.

The other is Nicolai Dmitrievich Zelinsky, whose death at the age of ninety-three was announced on July 31st, 1953 in Moscow.

The first scientific publication of Zelinsky's was presented in 1884, the last one in 1953, which makes it nearly seventy years of productive research work. This certainly must represent some kind of a record.

During his long and successful scientific career, Zelinsky published more than five hundred papers mostly devoted to catalysis, and raised to scientific maturity scores of successful pupils who became famous on their own accord.

Among the numerous collaborators and pupils of Zelinsky such names as Chugaev, Schilov, Reformatsky, Nametkin, Chelinzev, Stadnikoff, Lebedev and Balandin, to mention only a few, speak for themselves.

In his famous book "Grosse Männer," Ostwald separates famous scientists in two classes. One is "Romanticists"; the representatives of this type are brilliant researchers who study a certain problem with vigor and energy, and who very quickly make valuable discoveries and immediately pass to another problem, sometimes of an entirely different nature, leaving the details of the first to other investigators.

The "classicists" after making an important discovery, continue to investigate the problem systematically and carefully.

It is interesting to note that both of these great men belonged to the two different classes. Ipatieff was a typical "Romanticist," Zelinsky a typical "Classicist." It might also be of interest that their major contributions were in the study of two opposite reactions; Ipatieff—the reaction of hydrogenation. Zelinsky—the reaction of dehydrogenation.

After graduation from the Novorossiisk University in Odessa, Zelinsky was sent by the faculty to Germany where he worked and studied under Victor Meyer (Göttingen) and Wilhelm Ostwald (Leipzig). While in the laboratory of Victor Meyer, Zelinsky was the first to prepare the mustard gas (β-β'-dichlorodiethylsulfide) and was the first victim of its toxic properties.

The first period of scientific work upon returning to Odessa was devoted to study of stereoisomerism of dibasic carboxylic acids, resulting in the discovery of the known Hell-Volgard-Zelinsky method of α-bromination of fatty acids.

The major work of Zelinsky was devoted to petroleum and catalysis. This work was started in the laboratories of the University of Moscow where he moved in the year 1893 as associate professor and where, with the exception of a six year interval, carried out all his research until his death.

The classical studies of Zelinsky in dehydrogenation catalysis started with the discovery of platinum (and later of palladium and nickel-alumina) catalyst in the dehydrogenation of cyclohexane, its homologues and derivatives, to aromatics. This work was the foundation of a systematic study of hydrocarbon reactions in the presence of metal catalysts, belonging to the 8th group of the periodic system, which resulted in the discovery of decyclohydrogenation of cyclopentane and its homologues to paraffins; hydrogen disproportionation of cyloolefins and cyclodiolefins to aromatics and cycloparaffins, and cyclization of paraffins. All these reactions served as excellent tools in the study of the nature of petroleum hydrocarbons and became of tremendous importance in aromatization of petroleum. This work laid the foundation for the modern processes of catalytic reforming of napthas.

One cannot forget the leading role of Zelinsky in development of the gas mask, which saved many thousands of lives of Russian and Allied soldiers during the first World War.

As a matter of fact, the Zelinsky mask (Activated charcoal) was so good that it was accepted by the Germans and masks with the sign "Nach Zelinsky" could be found on the German soldiers.

It will also be important to mention the successful work of Zelinsky in the field of proteins. This method of hydrolysis of proteins with dilute acids under pressure resulted in the production of clean hydrolyzates and helped the development of the diketopiperazine and polypeptide theory of protein structure.

Professor Zelinsky's devotion to his beloved science was unique. His work was his life and hobby and his home was in his laboratory. He had the satisfaction to see the results of much of his research work be transferred to industrial practice. He received numerous decorations and prizes for the Russian Government and was elected an honorary member of the Chemical Society (London).

With the passing away of Professor Zelinsky, we are losing another pioneer and great Master of catalysis.

V. I. Komarewsky

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The Electronic Factor in Heterogeneous Catalysis

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I. Introduction

The theoretical approach to the subject of surface catalysis was first considered in a series of classical papers by Langmuir (1), who suggested that the adsorbed particles are held to the surface by chemical forces, and applied the theory to interaction of adsorbed species at adjacent adsorption sites on the surface. Langmuir pointed out that steric hindrance effects between molecules might play a prominent part, and the role of the geometric factor in catalysis was greatly emphasized by Balandin and others. The importance of this factor has already been reviewed in this series by Trapnell (2) and Griffiths (3).

As early as 1928, Roginskiĭ and Schul'tz (4) stressed the importance of electronic considerations, and Rideal and Wansbrough-Jones (5) related the work function of metals to the activation energy for their oxidation. Brewer, 1928 (6), Schmidt, 1933 (7), and Nyrop, 1935 (8) proposed that the surface must be capable of effecting ionization of the adsorbed species in some catalytic processes. Lennard-Jones (9) in his

theory of chemisorption on metal surfaces considered the possibility of covalent bond formation due to the pairing of a valence electron of the adsorbed atom and an electron from the conduction band of the metal.

Further developments in the fundamental approach to the electronic structure of catalysts were made possible by the development of the quantum mechanical treatments of solids which followed the work of Sommerfeld, Bloch and others. Similarly, Pauling's resonating valence bond treatment has lent further impetus to consideration of metallic catalysts.

II. THEORIES OF THE SOLID STATE

1. Quantum Mechanical Theory

The molecular orbital treatment of a crystalline solid considers the outer electrons as belonging to the crystal as a whole (10,11). Sommerfeld's early free electron theory of metals neglected the field resulting
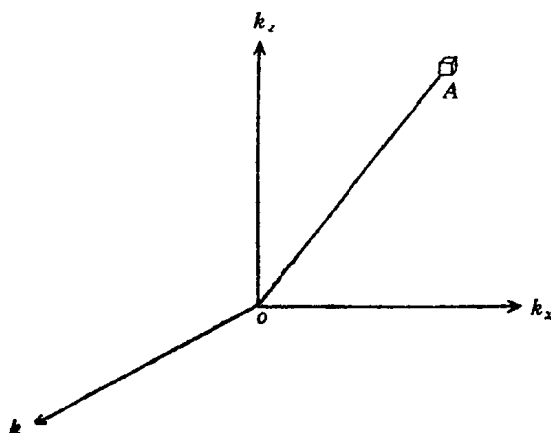
FIG. 1. Momentum diagram.

from the array of metallic nuclei. A great advance was made by Bloch and others who assumed that the electrons move in a field whose periodicity is that of the crystal lattice. The possible energy states for the electrons can be obtained from the solutions of the Schrödinger equation

$$\nabla^2\psi + \frac{2m}{h^2}(E - U)\psi = 0 \tag{1}$$

In the consideration of the momentum of a large number of particles restricted to a volume V, it is often convenient to describe the system by an assembly of points in a momentum diagram (Fig. 1). The length OA represents the magnitude of momentum of the particle A, and its direction is $\overrightarrow{OA}$. The application of Heisenberg's uncertainty principle leads to the

restriction that the momentum of any particle cannot be represented by a point, but must be associated with a volume h^3/V (h is Planck's constant). This means effectively that momentum space must be divided into cells of volume h^3/V, each cell corresponding to an energy state, and from Pauli's Principle each of these states can contain two electrons. Furthermore, the energy of the assembly will be a minimum when the occupied states are clustered about the origin. The wavelength of a free electron is given by $1/\lambda = mu/h$. Since the wave number $k = 2\pi/\lambda$, it is obvious that a k-diagram may be constructed in a manner similar to that
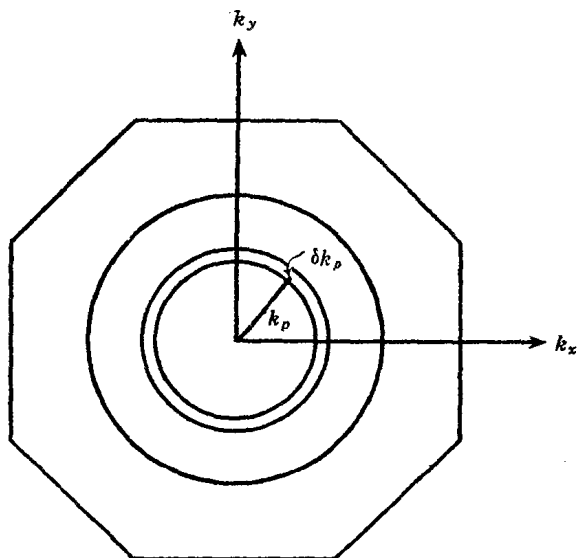
Fig. 2. Brillouin zone for a two dimensional crystal.

used for the momentum diagram. The boundary between occupied and unoccupied states in k-space is referred to as the Fermi surface. When the periodic field of the lattice is taken into account, the wave number is no longer simply related to the momentum (mu). The wave mechanical examination of the equation for the motion of an electron in a periodic field shows that the energy does not vary continuously with the wave number. This means that in any one direction in k-space, there will arise energy discontinuities as the states are filled. These regions can be represented in the k-diagram by surfaces; the regions bounded by such surfaces are usually termed Brillouin zones. Figure 2 represents a Brillouin zone for a two-dimensional crystal; in the figure, the Fermi surface is circular and the states are not completely occupied by electrons up to the boundary of the Brillouin zone.

A typical energy distribution curve is represented by Fig. 3. An elec-

tron state, value k_p in k-space, will have an energy E_p. The number of states $N(E)$ in the energy band dE_p is related to the volume of the spherical shell, and it can be seen that $N(E)$ in a range dE_p will increase with E_p. The maximum at E_2 occurs at the point where the Fermi surface first touches the Brillouin zone. A rapid decrease of $N(E)$ then occurs because there are no energy states available for some directions of the wave number k. If the first and second Brillouin zones do not overlap, on completion of the first band, the next available electron state will involve an increase in energy of $(E_4 - E_2)$. If the first and second zones overlap, the addition of electrons will fill the first zone to the point where the
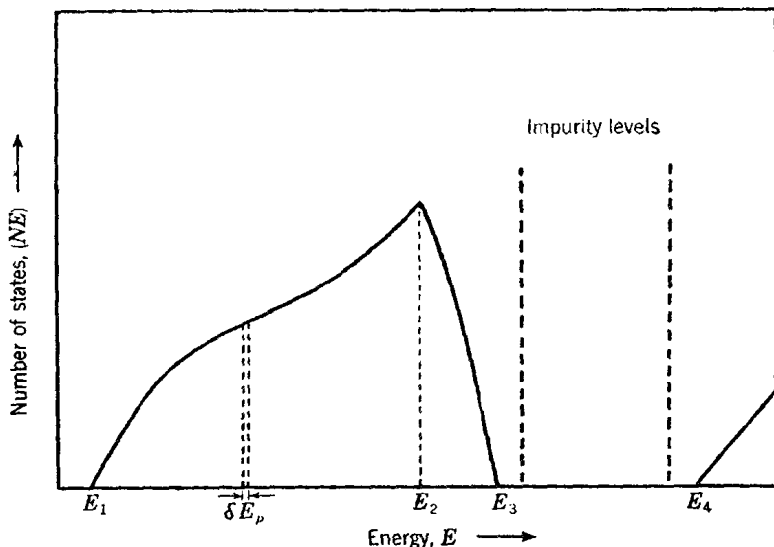
FIG. 3. Typical electron bands.

highest filled states of the first zone have the same energy as the lowest filled states of the second zone. More electrons will then enter the states of both zones. The resulting $N(E)$ curve has the form shown in Fig. 4.

The effect of an external electric field is to produce an acceleration of the electrons in the direction of the field, and this causes a shift of the Fermi surface. It is a necessary condition for the movement of electrons in the k-space that there are allowed empty states at the Fermi surface; hence electrical conductivity is dependent on partially filled bands. An insulating crystal is one in which the electron bands are either completely full or completely empty. If the energy gap between a completely filled band and an empty band is small, it is possible that thermal excitation of electrons from the filled to the empty band will result in a conducting crystal. Such substances are usually referred to as intrinsic semiconductors. A much larger class of semiconductors arises from impurities

in the crystal. The introduction of foreign atoms generally creates additional energy levels, and these impurity levels may lie within the energy gap, as shown in Fig. 3. At temperatures above absolute zero there are two possible processes which may occur: either electrons may be thermally excited from the impurity levels to the empty band, or electrons from the filled band may be excited into the impurity levels. In both cases partly occupied bands are produced, and the crystal becomes conducting.

(a) *Alloys.* In the formation of simple alloys, the progressive substitution of one type of metal atom by another type with different valency
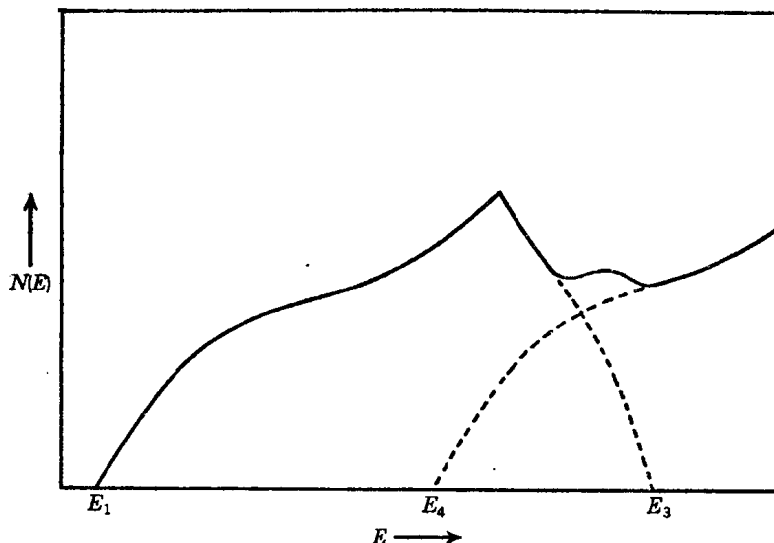

FIG. 4. Overlapping electron bands.

changes the ratio of valence electrons to metal atoms of the crystal. This ratio has been termed the electron concentration. The Fermi level of the solvent metal will be either raised or lowered depending on whether the solute metal has a higher or lower valency. Many properties of alloys can be related to the electron concentration.

Hume-Rothery (12,13) has pointed out that in some alloys the structure of the intermetallic phases are determined by the electron concentration (E.C.). The work of Hume-Rothery and others has shown that the series of changes (i.e. α phase $\rightarrow \beta$ phase $\rightarrow \gamma$ phase $\rightarrow \epsilon$ phase), which occurs as the composition of an alloy is varied continuously, takes place at electron–atom ratios of 3/2, 21/13, and 7/4, respectively. The interpretation of these changes in terms of the Brillouin zone theory has been made by H. Jones (14) and can be understood from the $N(E)$-curves for typical face centered cubic (a) and body centered cubic (b) structures as

shown in Fig. 5. The alloying of univalent metals, such as copper, silver, and gold, with higher valence elements is considered to be a process in which the solute elements merely serve to increase the electron concentration. The higher the $N(E)$-curve, the greater is the number of electrons which may be accommodated in states within the energy range concerned, and hence the lower will be the energy necessary to accommodate a given number of electrons. In Fig. 5 it can be seen that up to the point A the face centered cubic structure has the lower energy and will be the stable phase of the alloy. Beyond point A the number of states decreases rapidly, and addition of more electrons into the band causes a rapid increase in energy. At some point, the body centered cubic structure
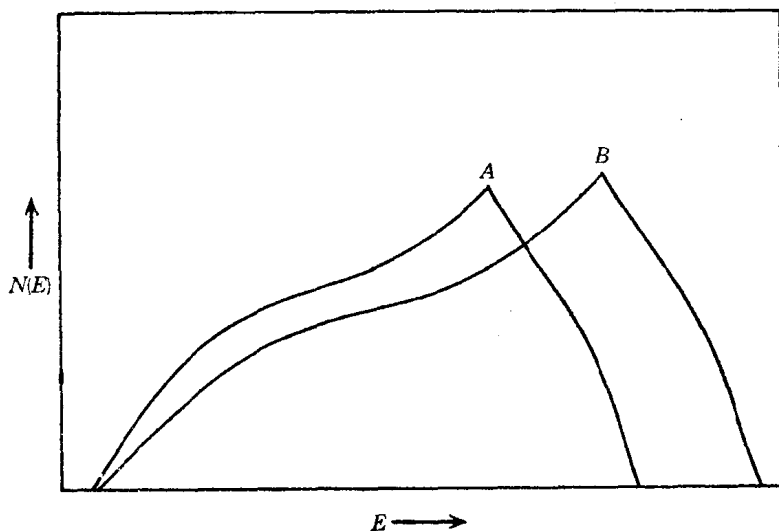

FIG. 5. Interpretation of Hume-Rothery alloys in terms of Brillouin zone theory.

becomes more stable than the face centered cubic structure, since the electron band in the former can accommodate the same number of electrons with a lower energy. H. Jones has calculated the electron–atom ratios corresponding to the maximum $N(E)$-peaks for each of the four phases, and has obtained the values $\alpha = 1.362$, $\beta = 1.480$, $\gamma = 1.538$. These values for the α-, β-, and γ-phases agree quite well with the Hume-Rothery values for the corresponding phase changes.

(b) *Transition Metals*. The transition metals are characterized by ferromagnetism or strong paramagnetism and by their comparatively low electrical conductivity. According to Mott and Jones (10), the outermost electrons are considered to occupy two bands. In the first long period of the periodic table these bands arise from the $3d$ and $4s$ atomic states. The broadening of the $3d$-band is much less marked than that of the

s-band, since the smaller 3d-orbitals overlap to a lesser extent. The broadening process can be seen from Fig. 6(a). The density of states is five per atom in the d-band and is one per atom in the s-band. The actual $N(E)$-curves for some transitional elements may be complex, but it is more convenient in this discussion to represent the s- and d-bands in their general form (Fig. 6(b)). Considering nickel as a typical example, the ten outermost electrons per atom must be shared between the two bands. There is strong evidence that there are 9.4 electrons per atom in the 3d-band and 0.6 in the 4s-band. The electron bands of copper will not
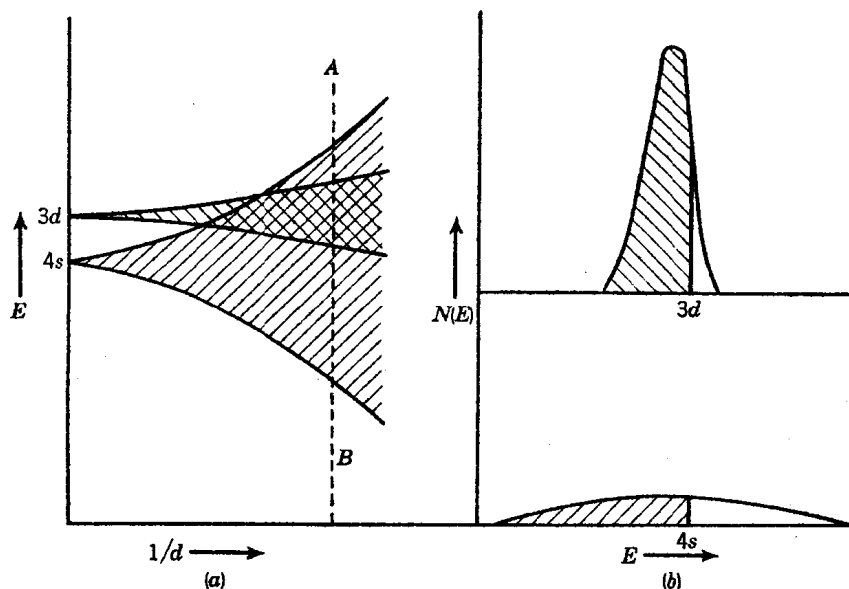

FIG. 6. Electron bands of transition metals.

differ appreciably in energy from those of nickel, but the addition of another electron will completely fill the d-band and half fill the s-band, in agreement with its monovalent nature. From this point of view, the ferromagnetism of iron, cobalt, and nickel is almost entirely due to the spins of the d-electrons and the saturation magnetization intensity expressed in Bohr magnetons per atom is approximately equal to the number of "holes" in the d-band (Fe, 2.2; Co, 1.7; Ni, 0.6). The noninteger number of electrons in the d-band can be understood if they are considered as average values for a crystal containing the configurations $(3d)^{10}$, $(3d)^9$, and $(3d)^8$. Mott and Jones consider that only the $(3d)^{10}$ and $(3d)^8$ configurations are important, the two holes in the shell of the $(3d)^8$-ion having the same spin. The strong paramagnetism of platinum and palladium, which is probably also due to electron spin, and the physical

properties of their alloys can be explained by this theory if there are about 0.55–0.6 holes in the d-band.

(c) *Transition Metal Alloys.* The theoretical consideration outlined above readily explains the changes in properties accompanying alloy formation of transition metals with other metals. If we take as an example the Cu–Ni alloys, the replacement of nickel atoms by copper atoms will add extra electrons to the lattice. Since the density of states in the d-band is much greater than in the s-band, the added electrons will enter the d-band until it is filled. As the atomic percentage of copper in the alloy increases, the saturation magnetic moment decreases; extrapolation to zero magnetic moment shows that the d-band is just full at 60%. The addition of an atom of palladium, zinc, or aluminium will increase the number of electrons in the d-band by 0, $+2$, or $+3$ respectively. Similarly, for the palladium and platinum alloys with copper, silver, and gold, the atomic susceptibility drops as the percentage of solute increases, the susceptibility becoming negligible at a concentration of about 55% of the monovalent metal (10,11). This confirms the assumed number of d-"holes" in these two metals.

The solution of hydrogen in palladium must be considered as a different type of alloy system, because the hydrogen cannot replace palladium in the lattice structure. The fall in susceptibility to zero at a hydrogen–palladium ratio of 0.55 suggests that all the electrons of the hydrogen atoms enter the $4d$ palladium levels (11).

2. Resonating Valence Bond Theory

Pauling (15–17), in an approach more easily described in language familiar to chemists, considers that metal bonds resemble ordinary covalent bonds, all or most of the outer electrons of the metal atoms taking part in bond formation. He suggests that when the number of possible positions at which bonding can occur is greater than the number of bonds, resonance occurs about the available positions.

This approach explains satisfactorily the decrease in bond length with increasing valency in the sequences of elements K $\rightarrow$ Cr, Rb $\rightarrow$ Mo, and Co $\rightarrow$ W. The number of electrons available for bond formation in these metals increases with valency, and therefore, according to the resonating valence bond theory, the number of bonds resonating about the available positions increases, resulting in smaller bond lengths.

The magnetic properties of these elements also fit into this concept. In metallic vanadium for example (atomic configuration $3d^3 4s^2$), if the $4s^2$ electrons only were involved in bond formation, the cores of the atoms would have a large dipole moment with the result that ferromagnetism or strong paramagnetism decreasing with increasing temperature should

be exhibited. Contrary to this, vanadium is only weakly paramagnetic, the paramagnetic moment being almost temperature independent. This indicates that all its outer electrons are involved in bond formation. Similarly, all elements in the sequences mentioned above are either diamagnetic or weakly paramagnetic.

Lithium may serve as an example for illustrating the general picture of resonance structures in metals. Pauling points out that it is unlikely that synchronized resonance, i.e. resonance of two bonds simultaneously, of the type

$$
\begin{array}{ccc}
\text{Li—Li} & \text{Li} & \text{Li} \\
& | & | \\
\text{Li—Li} & \text{Li} & \text{Li}
\end{array}
$$

could give the stabilization necessary to explain the strength of metallic bonding. He shows that a much greater resonance stabilization can be achieved by resonance of one bond involving electron transfer.

$$
\begin{array}{cc}
\text{Li} & \text{Li}^{\oplus} \\
& | \\
^{\ominus}\text{Li—Li}
\end{array}
$$
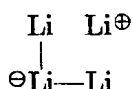
According to this concept, the metallic properties are based on the possession by some or all of the atoms in a given metal of a free orbital (the "metallic orbital"), in addition to the orbitals required for bonding and nonbonding electrons, thus permitting uninhibited resonance of valence bonds. For the case of tin, the following scheme illustrates these relationships for three electronic structures (A, B, and C) of this metal:

		3d	4s	4p	
Sn (A) $v = 4$	Kr	⇅ ⇅ ⇅ ⇅ ⇅	•	• • •	⇅ atomic electrons
(B) $v = 2$	Core	⇅ ⇅ ⇅ ⇅ ⇅	⇅	• • ○	• valence electrons i.e. electrons occupying bonding orbitals
(C) $v = 0$		⇅ ⇅ ⇅ ⇅ ⇅	⇅	⇅ ○ ○	○ metallic orbitals

where v is the valency of the metal atom in each electronic structure. In Sn (A) there is no metallic orbital and therefore no metallic phase; the four electrons are hybridized to give sp^3 tetrahedral bond orbitals. The nonmetallic form of tin, gray tin, does in fact have the diamond tetrahedral structure. Pauling suggests that the metallic form of tin (valency 2.44) consists of Sn (B) resonating with Sn (A), the Sn (B) configuration having the larger statistical weight. The loss in energy due to a decreasing number of bonds is largely compensated by the resonance energy gained.

Although the number of electrons theoretically available for bond formation increases with increasing atomic number in the series, Cr, Mn,