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The Nature of the Interatomic Forces in Metals

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It has been generally assumed that in the transition elements (Fe, Co, Ni, Cu, etc.) the 3*d* shell is filled with ten electrons or is nearly filled, and that the *d* electrons make no significant contribution to the cohesive forces in metals. Evidence is presented here to show that about half of the *d* orbitals (2.56 of the total of 5) are involved in bond formation, through hybridization with the 4*s* and 4*p* orbitals, and that the number of covalent bonds resonating among the available interatomic positions increases from one to nearly six in the sequence K, Ca, Sc, Ti, V, Cr, remains nearly constant from Cr to Ni, and begins to decrease with Cu. The remaining 2.44 *d* orbitals, with very small interatomic overlapping, are occupied by nonbonding electrons which are mainly responsible for the ferromagnetic and paramagnetic properties of the metals. This point of view provides a qualitative explanation of many properties of the transition metals (including those of the palladium and platinum groups), such as interatomic distance, characteristic temperature, hardness, compressibility, and coefficient of thermal expansion, and it accounts satisfactorily for the observed values of the atomic saturation magnetic moments of the ferromagnetic elements iron, cobalt, and nickel and their alloys. It is also shown to provide a reason for the occurrence of the positive exchange integrals which give rise to ferromagnetism.

DURING the year 1926–1927 I had the great privilege of working as a Guggenheim Fellow in Munich under the direction of Professor Arnold Sommerfeld. At that time he was interested in the systematization of the new quantum mechanics and its application to problems of spectroscopy and atomic structure. It was not until the following year, after the pioneer work of Pauli[1] on the small temperature-independent paramagnetism of the alkali metals, that Professor Sommerfeld and his students began their development of the quantum-mechanical theory of metals.[2]

Their special field of investigation dealt with the electrical and thermal properties of metals. More recently considerable attention has been paid to the question of the nature of the interatomic forces in metals, which are significant for properties such as density, compressibility, crystal energy, and hardness; and it has been found possible to treat this problem in a reasonably satisfactory way for the case of the alkali metals, with a single valence electron per atom.[3] The extension of the theory to other elements has also been attempted.

In recent years I have formed, on the basis mainly of empirical arguments, a conception of the nature of the interatomic forces in metals which has some novel features. According to this view, the metallic bond is very closely related to the ordinary covalent or electron-pair bond; some of the electrons of an atom in a metal are involved with those of neighboring atoms in the 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* (3*d*, 4*d*, and 5*d* for the iron, palladium, and platinum transition groups, respectively), take part in bond formation. (It has been assumed by most of the investigators in this field that the *d* electrons make no significant contribution to the cohesive forces.) It is shown below that this point of view leads to a qualitative explanation of many properties of metals, including their magnetic properties.

The combination of two lithium atoms to give the molecule Li_2 is described as involving the formation of a covalent bond between the atoms. In a crystal of fluorine, F_2, the repulsion of the unshared outer electron pairs keeps the molecules spaced so that the minimum intermolecular

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[1] W. Pauli, Zeits. f. Physik **41**, 81 (1927).

[2] A. Sommerfeld, Naturwiss. **15**, 825 (1927); A. Sommerfeld, W. V. Houston, and C. Eckart, Zeits. f. Physik **47**, 1 (1928); A. Sommerfeld and N. H. Frank, Rev. Mod. Phys. **3**, 1 (1931); A. Sommerfeld and H. Bethe, *Handbuch der Physik*, Vol. 24, second edition.

[3] J. C. Slater, Phys. Rev. **35**, 504 (1930); **45**, 794 (1934); E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934); F. Seitz, Phys. Rev. **47**, 400 (1935); K. Fuchs, Proc. Roy. Soc. **A151**, 585 (1935); H. M. Krutter, Phys. Rev. **48**, 664 (1935); M. F. Manning and H. M. Krutter, Phys. Rev. **51**, 761 (1937); W. Shockley, Phys. Rev. **51**, 129 (1937).

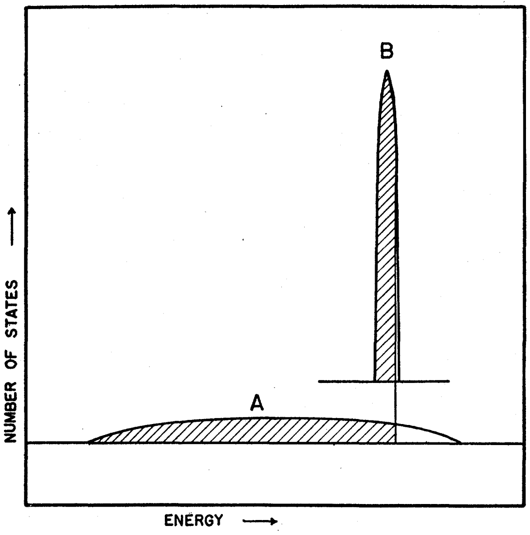

FIG. 1. Electronic states for iron-group atoms, showing number of states as qualitative function of electronic energy. Electrons in band *A* are paired with similar electrons of neighboring atoms to form bonds. Electrons in band *B* are *d* electrons with small interatomic interaction; they remain unpaired until the band is half-filled. The shaded area represents occupancy of the states by electrons in nickel, with 0.6 electron lacking from a completely filled *B* band. (States corresponding to occupancy of bond orbitals by unshared electron pairs are not shown in the diagram.)

internuclear distance is about twice as great as the intramolecular internuclear distance; there is no chance for resonance of a bond from one pair to another pair of atoms. Moreover, in fluorine all of the orbitals are occupied, so that resonance could occur only by the synchronous interaction of two or more molecules. In a crystal of lithium formed from Li_2 molecules, on the other hand, the conditions for resonance are satisfied; the molecules would be expected to approach one another closely, and each lithium atom has four *L* orbitals which might be used for bond formation. It is accordingly reasonable to think of the lithium crystal as involving covalent bonds resonating among the available positions. (Around each atom in the body-centered structure there are fourteen positions for bonds, eight at cube corners and six (with internuclear distance 15 percent larger) at cube face centers. On the average one of these is occupied by a bond.) Since the conditions for one-electron bond formation are satisfied,[4] it may be considered that these bonds also make some contribution to the structure of the crystal.

This qualitative description of the interactions in the metal is compatible with quantum mechanical treatments which have been given the problem,[5] and it leads to an understanding of such properties as the ratio of about 1.5 of crystal energy of alkali metals to bond energy of their diatomic molecules (the increase being the contribution of the resonance energy), and the increase in interatomic distance by about 15 percent from the diatomic molecule to the crystal.

The alkaline earth metals, by assuming the configuration *nsnp*, are able to form twice as many bonds as the alkalis. Similarly the succeeding elements in the periodic table can form bonds in increasing number.

The possibility that only some of the outer electrons enter into bond formation needs to be considered. There is a close relation between interatomic distance and bond type, and the values of the interatomic distances in the sequence[6] K, *A*2, 4.62A; Ca, *A*1, *A*3, 3.93–3.95A; Sc, not yet investigated; Ti, *A*3, 2.92–2.95A; V, *A*2, 2.63A; Cr, *A*2, 2.49A, as well as those in the similar sequences from Rb to Mo and Cs to W, indicate that the number of bonds resonating among the available positions increases from one to nearly six.

This conclusion is given strong support by the magnetic properties of the metals. Let us consider vanadium as an example. The configuration of the normal vanadium atom is $3d^3 4s^2$. If only the two $4s$ electrons were involved in bond formation (perhaps with promotion of one to $4p$) the core of the atom, with the configuration $3d^3$, would have a large magnetic dipole moment,[7] and in consequence the metal would show ferromagnetism or large paramagnetism, decreasing in magnitude with increasing temperature. Instead vanadium is only weakly paramagnetic (molal susceptibility at room temperature 60×10^{-6} cgsmu.) and its paramagnetism is nearly temperature-independent; there is, indeed, a small in-

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[4] L. Pauling, J. Am. Chem. Soc. **53**, 3225 (1931).

[5] See in particular J. C. Slater, Phys. Rev. **35**, 509 (1930).

[6] The symbols *A*1, *A*2, and *A*3 represent the three simple metal structures: cubic closest packed, body centered, and hexagonal closest packed, respectively.

[7] Values 3.8 to 4.0 Bohr magnetons are observed for iron-group ions with this configuration.

crease in susceptibility with increasing temperature. This behavior is that expected if all five outer electrons take part in bond formation, with pairing of spins as in the usual electron-pair bond. The observed paramagnetic properties are then explained, as in Pauli's theory of the temperature-independent paramagnetism of the alkali metals, by the assumption that some of the electrons occupy excited levels with unpaired spins (that is, that under equilibrium conditions some of the bonds are broken), the number of these unpaired electrons increasing with increasing temperature. Since diamagnetism or small temperature-independent paramagnetism is observed for all of the metals K, Ca, Ti, V, Cr, Rb, Sr, Zr, Cb, Mo, Cs, Ba, La, Ta, and W, it seems necessary to accept the conclusion that all of the outer electrons take part in bond formation.

The *d* orbitals alone are not especially well suited to use in bond formation, but hybridization of *d*, *s*, and *p* orbitals leads to the best bond orbitals known,[8] such as the d^2sp^3 orbitals in octahedral complexes ($[\mathrm{Fe(CN)_6}]^{\equiv}$, $[\mathrm{PtCl_6}]^{=}$, etc.). There are available a total of nine relatively stable orbitals: five 3*d*, one 4*s*, and three 4*p* for the iron-group elements, and corresponding sets for the other series; and there exists accordingly the possibility that as many as nine outer electrons per atom enter into bond formation. The number of bonds would then be six for chromium, seven for manganese, eight for iron, and nine for cobalt; at nickel, with ten electrons, one unshared pair would occupy one of the nine orbitals, leaving only eight bonds, and the continued decrease in the number of bonds would lead to seven for copper, six for zinc, five for gallium, four for germanium, three for arsenic, two for selenium, and one for bromine.

It is indicated by the observed interatomic distances and shown by magnetic data that there occurs some deviation from this simple and attractive scheme in the middle region of the sequence. From chromium to cobalt the interatomic distances do not continue to decrease in value, as expected with increase in the number of bonds; instead they remain nearly constant: Cr, *A*2, 2.49A; Mn, no simple structure; Fe, *A*2, 2.48A, *A*1, 2.52A; Co, *A*1, *A*3, 2.50–2.51A; Ni, *A*1, *A*3, 2.49A; Cu, *A*1, 2.55A; Zn, *A*3, 2.66, 2.91A. This indicates that there are only about six bonds per atom for iron, cobalt, and nickel, and still fewer for copper and the succeeding elements.

The values for the atomic saturation magnetization at the absolute zero, σ_A, for the ferromagnetic metals iron, cobalt, and nickel are 2.22, 1.71, and 0.61 Bohr magnetons per atom, respectively.[9] These numbers are the average numbers of unpaired electron spins in the metals (the approximation of the *g* factor to 2 found in gyromagnetic experiments shows that the orbital moment is nearly completely quenched, as in complex ions containing the transition elements).

In the past the following interpretation has been given these numbers.[10] In nickel, for example, it has been assumed that the 3*d* shell is occupied by 9.39 (on the average) of the total of ten outer electrons, with 0.61 electron in the 4*s* shell. The 0.61 *s* electron alone was assumed to interact strongly between atoms, and to give rise to the principal cohesive forces in the metal. This interaction would quench the magnetic moments of the *s* electrons almost completely. The hole of 0.61 electron in the nearly completed *d* shell was then assumed to give a corresponding magnetic moment to the atom, the interaction of *d* orbitals of adjacent atoms being considered to be small.[11] It was similarly assumed that the cohesion of cobalt is due to 0.71 *s* electron, that

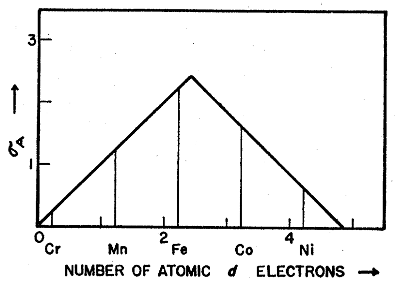

FIG. 2. Predicted dependence of atomic saturation magnetic moment σ_A as function of number of atomic *d* electrons.

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[8] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

[9] P. Weiss and R. Forrer, Ann. de physique **12**, 279 (1929); E. C. Stoner, *Magnetism and Matter* (Methuen and Co., London, 1934), p. 366.

[10] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, 1936), pp. 190, 222, 316.

[11] J. C. Slater, Rev. Mod. Phys. **6**, 272 (1934), has also concluded that the *d* electrons do not take much part in cohesion.

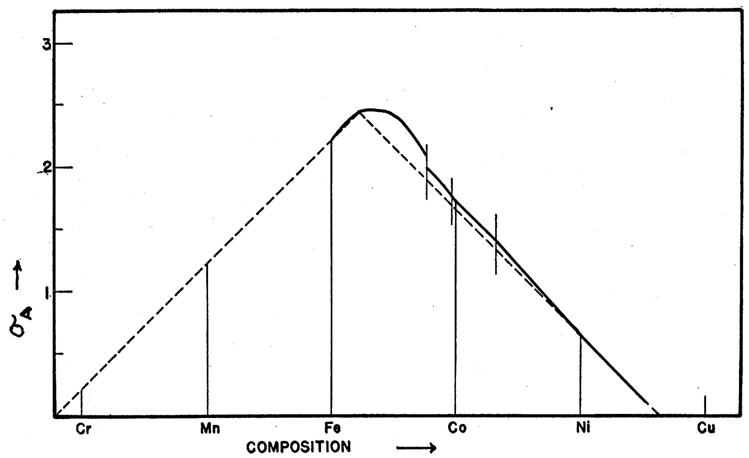

FIG. 3. Comparison of experimental values (solid curves) and predicted values (dashed lines) of σ_A for Fe-Co, Co-Ni, and Ni-Cu alloys. The short vertical lines indicate change in crystal structure.

of iron to 0.22 *s* electron, and that of copper to one *s* electron (the *d* shell for copper having its full complement of ten electrons). The difficulties of accounting for the interatomic distances and mechanical properties of the metals in this way are obvious.

Our picture, on the other hand, is that some of the 3*d* orbitals, as well as the 4*s* and 4*p* orbitals, are used for the formation of five or six bonds per atom. Instead of assuming the configuration $3d^{10}4s$ for copper, with bonding by the 4*s* electron only, we assume a configuration such as $d^2d^2d^2ddspp$ (to list the independent orbitals separately), so that each atom contains three unshared pairs in the *d* shell and five electrons used in forming bonds with surrounding atoms. This structure, involving only unshared and shared electron pairs, accounts satisfactorily for the observed diamagnetism of the metal.

Our knowledge of the properties of orbitals indicates that some of the 3*d* orbitals might be combined with the 4*s* and 4*p* orbitals to form bond orbitals in metals, the other 3*d* orbitals being unsuited to bond formation, but does not suffice to give a theoretical derivation of the number of *d* orbitals in each of these classes. Empirical evidence, outlined below, indicates that about 2.44 *d* orbitals (on the average) show only weak interatomic interactions, and that the remaining 2.56 *d* orbitals combine with the *s* orbital and the *p* orbitals to form hybrid bond orbitals.

In Fig. 1 there is indicated the division of the nine outer orbitals into these two classes. It is assumed that electrons occupying orbitals of the first class (weak interatomic interactions) in an atom tend to remain unpaired (Hund's rule of maximum multiplicity), and that electrons occupying orbitals of the second class pair with similar electrons of adjacent atoms. Let us call these orbitals *atomic orbitals* and *bond orbitals*, respectively. In copper all of the atomic orbitals are occupied by pairs. In nickel, with $\sigma_A = 0.61$, there are 0.61 unpaired electrons in atomic orbitals, and in cobalt 1.71. (The deviation from unity of the difference between the values for cobalt and nickel may be the result of experimental error in the cobalt value, which is uncertain because of the magnetic hardness of this element.) This indicates that the energy diagram of Fig. 1 does not change very much from metal to metal. Substantiation of this is provided by the values of σ_A for copper-nickel alloys,[12] which decrease linearly with mole fraction of copper from $\sigma_A = 0.61$ for pure nickel toward the value zero for mole fraction 0.6 of copper, and by the related values for zinc-nickel and other alloys.[13] The value $\sigma_A = 2.61$ would accordingly be expected for iron, if there were 2.61 or more *d* orbitals in the atomic orbital class. We conclude from the observed value $\sigma_A = 2.22$ for iron that

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[12] M. Alder, *Dissertation* (Zurich, 1916), quoted by Stoner, reference 9, p. 537.

[13] C. Sadron, Ann. de physique **17**, 371 (1932).

the number of orbitals in this class is less than 2.61, and lies between 2.22 and 2.61.

If it be assumed that one electron is removed from these atomic orbitals at each step Ni-Co-Fe, the number of orbitals is determined as 2.44 ±0.03. There is shown as Fig. 2 a diagram representing the expected change of atomic saturation moment σ_A with change in number of electrons. It is seen that σ_A is predicted to rise to a maximum value of 2.44 Bohr magnetons at a point 23 percent of the way from iron to cobalt. It is indeed observed[14] that the atomic saturation moment for iron-cobalt alloys rises to its maximum value, 2.47 Bohr magnetons, at 26 atomic percent cobalt. Curves showing measured values of σ_A for iron-cobalt, cobalt-nickel, and nickel-copper alloys are compared with the theoretical curve for 2.44 atomic *d* orbitals in Fig. 3. The experimental values are seen to indicate a tendency for the class of atomic *d* orbitals to remain half-filled with electrons (maximum multiplicity) over a small range of composition; the values of σ_A remain close to the maximum until an excess of about 0.25 electron is present, and then slowly decrease to the expected line.

There are no data available for testing the predicted numbers 0.22 and 1.22 of unpaired electron spins for chromium and manganese, respectively.

It seems probable that the palladium and platinum transition groups approximate the iron group very closely. For example, the paramagnetic susceptibility of palladium-gold alloys falls to zero at 60 atomic percent gold, the paramagnetic susceptibility of palladium containing hydrogen becomes zero at 60 atomic percent hydrogen, and the saturation moment of nickel is changed very little by the addition of palladium.[15]

It is of interest to calculate the number of bonding electrons, which we assume for the elements Cr to Ni to be all of the outer electrons except those in the atomic *d* orbitals. For chromium this number is $6-0.22=5.78$, and the same value is found for the other atoms also; this supports the evidence from interatomic distances that there is little change in bond type from chromium to nickel.

There are 2.56 *d* orbitals available for bond formation. To form 5.78 bonds these would hybridize with the *s* orbital and 2.22 of the less stable *p* orbitals. In copper, with one electron more than nickel, there is available an additional 0.39 electron after the hole in the atomic *d* orbitals is filled. This might take part in bond formation, with use of additional 4*p* orbital. However, the increase in interatomic distance from nickel to copper suggests that it forms part of an unshared pair with part of the bonding electrons, thus decreasing the effective number of bonds.

To this treatment of the metals the objection might be raised that it requires the considerable promotion of electrons to higher levels (for the separated atoms): thus, whereas Mott and Jones[16] consider that only the configurations $3d^84s^2$, $3d^94s$, and $3d^{10}$, which give states lying within an energy range of about 1.5 ev, can be considered for nickel, our treatment requires consideration of configurations such as d^7sp^2, which probably lie about 10 ev above the normal state. It is not the energy of the configuration of the isolated atom which is significant, however, but that of the metal itself, and the additional bond energy of the metal with this configuration compensates for the instability of the atom. The crystal energy (heat of sublimation) of a metal provides little information regarding the structure of the metal because it is the difference of two quantities, the energy of the metal and the energy of the separated atoms. It is properties such as interatomic distance, compressibility, and coefficient of thermal expansion, characteristic of the metal itself, which give information about the nature of the bonds.

We have mentioned that the increase in effective number of bonds from one to about six in the series of metals K to Cr, its approximate constancy to Ni, and subsequent decrease are compatible with the observed course of inter-

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[14] P. Weiss and R. Forrer, Ann. de physique **12**, 279 (1929). Mention should also be made of the moments found for iron, cobalt, and nickel by measurement of the paramagnetic susceptibility above the Curie point, the values being 3.15–3.20, 3.15, and 1.61–1.78 Bohr magnetons, respectively (W. Sucksmith and R. R. Pearce, Proc. Roy. Soc. **A167**, 189 (1938)). The root-mean-square values predicted from the magneton numbers on the assumption that the iron atoms contain either two or three unpaired electron spins, the cobalt atoms one or two, and the nickel atoms zero or one are 3.09, 2.56, and 1.35 Bohr magnetons, respectively. The reason for the only very approximate agreement is not known.

[15] Mott and Jones, reference 10, pp. 197, 199, 200.

[16] Reference 10, p. 190.

atomic distances for this sequence of elements. A similar behavior is observed for the sequences Rb to Ag and Cs to Au. In each of these three sequences the maximum or minimum values (corresponding to maximum strength of bonds) of the compressibility, coefficient of thermal expansion, characteristic temperature, melting point, and hardness occur for the metals to which we have assigned the maximum number of bonds.[17]

In the development of the quantum mechanical theory of ferromagnetism by Heisenberg, Frenkel, Bloch, Slater, and other investigators the assumption has been made that the exchange integrals between the unpaired *d* electrons of adjacent atoms are positive in sign. It has in the past been very difficult to understand why this should occur, since exchange integrals between atoms are usually negative. The situation is clarified by our picture of the structure of the transition metals. A large negative value of an exchange integral (corresponding to a strong covalent bond) results from the large overlapping of the orbitals of two atoms. Good bond orbitals can be formed by hybridization of the outer *d*, *s*, and *p* orbitals of the metal atoms, and we expect that all the *d* orbitals which are able to form strong bonds will enter into bond formation. The remaining *d* orbitals will hence be those which avoid overlapping with the orbitals of adjacent atoms. The exchange integrals of these atomic *d* orbitals will accordingly be small in absolute value, and may be positive.[18] This conclusion agrees with the observation that the transition metals may be either paramagnetic or ferromagnetic, the absolute magnitude of the exchange integrals in either case being about 1 kcal./mole.

It is obvious that many factors may enter into the determination of the sign of the exchange integral.[19] We would predict that in an atom which formed many strong bonds with its neighbors the *d* orbitals with negative exchange integrals would be drawn into bond formation, and that unpaired electrons in the remaining *d* orbitals could give rise to ferromagnetism. The condition for ferromagnetism that the metal atoms form a large number of strong bonds is satisfied by the ferromagnetic elements. We would also expect that manganese would develop ferromagnetic properties in alloys in which its atoms form more and stronger bonds with surrounding atoms than in the element itself. This may occur in the Heusler alloys (such as Cu_2AlMn and Cu_2SnMn).

In this discussion of the transition elements we have considered only the orbitals $(n-1)d\ ns\ np$. It seems probable that in some metals use is made also of the *nd* orbitals in bond formation. In gray tin, with the diamond structure, the four orbitals $5s5p^3$ are used with four outer electrons in the formation of tetrahedral bonds, the $4d$ shell being filled with ten electrons. The structure of white tin, in which each atom has six nearest neighbors (four at 3.016A and two at 3.175A), becomes reasonable if it is assumed that one of the $4d$ electrons is promoted to the $5d$ shell, and that six bonds are formed with use of the orbitals $4d5s5p^35d$.

This arrangement of bonds for white tin is not to be considered as the only one contributing to the structure of the metal. An atom in a metal shows great versatility in the formation of bonds. There is little difference in stability of structures involving not only different numbers of bonds but also varied types of coordination, and in consequence an atom in a metal can form bonds after deformation of the original structure which are approximately as strong as the original bonds. This gives a metal its ability to heal itself after deformation, which underlies such characteristic metallic properties as malleability and ductility.

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[17] The minimum reported values of the compressibility occur for the three sequences at Ni, Mo, and Pt, respectively; the minima of the coefficient of thermal expansion at Fe, Pd, and W; the maxima of the characteristic temperature at Cr, Ru, and W or Ir; those of the melting point at Ti, Mo, and W; and those of the hardness at Cr, Ru, and Os.

[18] Examination of the form of the exchange integral shows that it is necessarily positive if the two orbitals are orthogonal.

[19] This question has been discussed by J. C. Slater, Phys. Rev. **36**, 57 (1930).