Relation of Antiferromagnetic Structure to the Binding Energies of Some b.c.c. Transition Metals*

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Zener's theory of antiferromagnetic structure for V, Cr, Nb, Mo, Ta, and W is discussed from the point of view of binding energy. According to such a picture the large binding energies must come from coulomb interaction between cores. The importance of the outer d electrons in achieving large coulomb attraction is pointed out. A mathematical scheme for treating binding energy in the case of extensive overlap of cores is discussed. By dismissing the contribution of a Wigner-Seitz type calculation, the remaining contributions to the binding energy of tungsten are calculated at the observed lattice constant. Results obtained demonstrate the importance of the coulomb attractive energy in an antiferromagnetic structure.

I

IN a recent paper by Zener[1] the body-centered cubic structure of certain transition metals like V, Nb, Ta, Cr, Mo, and W is explained by the following two assumptions: (1) The interaction between the incomplete d shells of the transition elements is insufficient to disrupt the coupling between the d electrons in the same shell, in which the spins of the d electrons are aligned in such a manner as to attain the largest possible net spin. (2) The exchange interaction between adjacent d shells always has the same sign as in the case of the H_2 molecule, thus favoring an antiferromagnetic arrangement of d spins. In these two columns of elements maximum net d spin is achieved. This large net spin results in a big exchange interaction between adjacent d shells of parallel spins. Since the b.c.c. lattice is of such a structure that nearest neighbors of an atom cannot themselves be nearest neighbors to each other, atoms of parallel d spins can be kept as far apart as possible in such a lattice if we assume an antiferromagnetic structure for such metals. According to this theory, the binding energy of these metals must come primarily from the classical coulomb interpenetration.

By assuming the interactions between tungsten atoms to be short range interactions, Isenberg[2] has been able to show that it is possible to get some information from the elastic constants regarding the interactions between neighboring atoms and between atoms next nearest to each other. He finds that it is not inconsistent with the observed elastic constants to say that the interaction of an atom with its nearest neighbor is attractive, while the interaction of an atom with its next nearest neighbor is repulsive. This substantiates Zener's theory.

The band theory of transition metals is roughly as follows.[3] When atoms are put together, the outer d and s electrons are strongly perturbed by the proximity of other atoms. The result is that all the outer electrons can move more or less freely to all parts of the crystal. Corresponding to the case of molecular orbitals it is now appropriate to use crystal orbitals, that is, Bloch wave functions. These wave functions represent a piling-up of an electron cloud in the regions halfway between the cores, thereby resulting in a binding.

In the Pauling resonating valence bond theory[4] of the transition metals it is necessary to take into consideration np orbitals in addition to $(n-1)d$ and ns orbitals. On the average, for each atom 2.44d orbitals show only weak interatomic interactions. They are considered to be atomic orbitals. The remaining 2.56d orbitals combine with s and p orbitals to form hybrid bond orbitals. Taking tungsten as an example, one can say that of the four 5d electrons and two 6s electrons, 0.44 electron are in the atomic d orbitals, while 5.56 electrons are engaged in bonding. The introduction of 6p orbitals means promotion of electrons to higher energy levels. Pauling's contention is that the bonding energy obtained through hybridization more than compensates for the energy of promotion.

These three theories represent three different approaches to the understanding of the binding of the transition metals. An actual transition metal probably does not conform precisely to any one of these three models, but rather has certain features characteristic of each model. The purpose of the present paper is to find whether the simple antiferromagnetic model of the b.c.c. transition metals is adequate to give the major part of the binding energy, and thereby to explain the position of these non-close-packed lattices in the periodic table. We use the word "non-close-packed" here because at least in the case of the diamond structure and the simple cubic lattice an antiferromagnetic arrangement can also be realized.

We are therefore led to the question of binding energy in an antiferromagnetic b.c.c. crystal. In such a model the attraction between two nearest neighbors is mainly the electrostatic interaction between two rigid charge

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[1] C. Zener, Phys. Rev. **81**, 440 (1951).

[2] I. Isenberg, private communication.

[3] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 430–432. M. F. Manning and M. I. Chodorow, Phys. Rev. **56**, 787 (1939).

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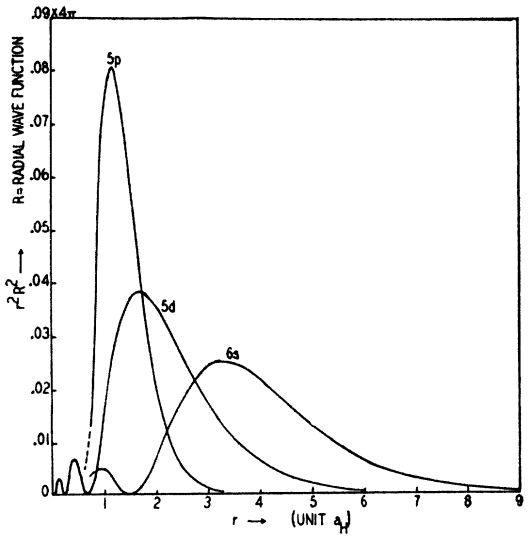

FIG. 1. Plot of r^2R^2 as a function of r for tungsten. The radial wave function R is obtained from Manning and Millman's calculation for W.

distributions. There is no additional piling-up of negative charge clouds. Accordingly, we would like to have a large coulomb attractive energy along with a small exchange repulsive energy so as to account for the large binding energies of metals like Mo and W. In Sec. II we discuss qualitatively how this is achieved via the charge distribution of the d electrons and the antiferromagnetic arrangement.

To carry out some quantitative calculation we want to formulate the mathematics in such a manner as to permit easy handling. If we assume that in the column Cr, Mo, W a single s electron per atom goes into the conduction band, we must carry out a Wigner-Seitz calculation for this electron. Since we are mainly interested in evaluating the contribution of the electrostatic attraction, we want to separate, in our mathematical formulation, the Wigner-Seitz type contribution from all other contributions. Unlike the case of alkali metals, the cores (containing electrons of the incomplete d shells) of neighboring atoms overlap quite appreciably. As a result, near the surface of a Wigner-Seitz sphere the s electron is subjected to a field deviating appreciably from the field owing to its core alone. Such an effect provides for additional electrostatic attraction. A detailed discussion is given in Sec. III.

Quantitative support to the qualitative discussion in Sec. II can be obtained only through calculation for special elements. In Sec. IV, tungsten is treated as an example because a self-consistent field calculation of the Hartree type has been carried out for free tungsten atoms by Manning and Millman.[5] Since their calculation is for the configuration $(5d)^4(6s)^2$, we have not taken into consideration the possible demotion of a $6s$ electron into the $5d$ shell. Also, since we are interested only in comparing the various contributions to the binding energy, calculation is made for the observed lattice constant. The numerical results so obtained indicate that the classical electrostatic attraction between neighboring cores is the major contributor to the binding energy. The antiferromagnetic interpretation of the b.c.c. transition metals is thereby placed upon a satisfactory quantitative basis.

II

To discuss the source of binding in an antiferromagnetic structure we can, without loss of generality, take the case of tungsten and investigate the various kinds of interaction involved. It must be emphasized that we do not know the degree of demotion of $6s$ electrons. We shall consider that no demotion has taken place. Allowing for demotion would, of course, increase the calculated binding energy.

It seems advantageous to begin our discussion by presenting the charge distributions of $5p$, $5d$, and $6s$ electrons of a W atom. From Fig. 1, in which r^2R^2 (R=radial wave function) is plotted instead, one sees that the charge distribution of the $6s$ electrons extends to a very large distance from the nucleus. In the formation of a crystal the $6s$ electrons are first subjected to strong perturbation. They can therefore be more appropriately represented by crystal orbitals.

Now let us consider an idealized crystal consisting of idealized atoms each of which contains a nucleus of charge $4e$ and only four $5d$ electrons. Suppose this crystal has an antiferromagnetic structure. The interaction between two nearest neighbors is then a pure coulomb interaction. At sufficiently large separation this is attractive. To see how large this attractive energy may be, we may mention the coulomb attraction in Heitler-London's calculation[6] for an H_2 molecule. At the optimum separation of $2a_H$ this attractive energy is 0.04 ry. It is expected that in the present case of four electrons per atom the coulomb attractive energy between two atoms would be an order greater (4^2) than this value through a certain range of separation. The contribution of the coulomb interaction to the binding energy per atom in a b.c.c. lattice will be four times this interaction. The observed heat of vaporization is 0.68 ry per atom. In the absence of all other types of interaction, the coulomb interaction between nearest neighbors would therefore give rise to a binding energy far greater than is observed.

In an antiferromagnetic b.c.c. lattice next-nearest neighbors have a parallel alignment of d shell spins. An exchange repulsion therefore acts between next-nearest neighbors. This exchange repulsion would, by itself, prevent nearest neighbors from coming so close as to attain their maximum coulomb attraction.

In real tungsten atoms we have also electrons inside the $5d$ shell. While these inner electrons of one atom

[5] M. F. Manning and J. Millman, Phys. Rev. 49, 848 (1936).

[6] W. Heitler and F. London, Z. Physik 44, 455 (1927).

do not overlap appreciably with those of a neighboring atom, they do overlap appreciably with the 5*d* electrons of neighboring atoms. This overlap gives rise to a second exchange repulsive interaction which keeps the atoms so far separated as to prevent the coulomb interaction from attaining its maximum value.

III

According to our present picture, in a metal like W the outermost *s* electrons go into the conduction band, while the incomplete *d* shells remain localized. To treat the outer *s* electrons by means of the Wigner-Seitz method, it is necessary to bear in mind several features not shared by the alkali metals, for which this method is highly successful. In the first place, the antiferromagnetic structure requires us to consider a b.c.c. lattice as a composite lattice obtained by the superposition of two simple cubic lattices. It is therefore incorrect to say that we can introduce a Wigner-Seitz sphere around each atom. All we can hope is that the spin interaction between *s* and *d* electrons can be taken into account using a wave function obtained by Hartree's method. This wave function is obtained by neglecting the exchange effect and by introducing a Wigner-Seitz sphere around each atom. In what follows the exchange effect between conduction and core electrons has been neglected.

Secondly, when one applies the Wigner-Seitz method to alkali metals, one usually argues in the following manner. Since in each cell the total charge of free electrons is just equal to the net charge of the core, the total potential due to such a cell for an electron moving in an adjacent cell is essentially zero. So when we limit ourselves to considering the motion of an electron in a cell, it is necessary to use only the potential due to the core. This contention is true only when the core is so small that the charge density due to the core electrons does not extend to the outside of the cell. In the present case the charge distribution of the incomplete *d* shell extends far outside of the Wigner-Seitz cell assigned to a tungsten atom at the observed lattice constant. As a result, the screening of the effect of a neighboring core by the almost uniform distribution of conduction electrons is rather incomplete. This necessarily complicates the calculation.

Perhaps the following is the easiest way to take such an effect into consideration. Let us first work out a Wigner-Seitz calculation using the potential due to the core of a free atom. The energy of the whole system is then calculated with this approximate wave function. It is expected that a first-order error in the wave function used will give rise to a second-order error in the energy calculated. The effect on the conduction electrons due to the overlap of cores, being a first-order one, is therefore properly taken into account in this type of calculation. The correction term so obtained for the total energy can be visualized in the following manner. Let us divide the whole space into Wigner-Seitz cells. In each cell we have an almost uniform distribution of conduction electrons with a core, which extends to the outside of the cell. The energy correction is then obviously the electrostatic interaction of the almost uniform charge distribution of conduction electrons in one cell with the conduction electrons as well as the core of another cell. This can be calculated readily if the distribution of the conduction electrons is assumed to be uniform.

The above-mentioned correction occurs whenever the overlap of cores becomes not negligible. In Fuchs' calculation for the binding energy of copper,[7] exchange repulsion between cores is taken into consideration. This is of sizable amount only when there is appreciable overlap. But then we must also take into account the electrostatic correction. At the theoretical lattice constant 4.2A the contribution to binding energy by this correction term is 0.5 ev per atom. This changes the calculated binding energy from 1.45 ev per atom to 2.0 ev per atom. The observed heat of vaporization is 3.1 ev per atom.

The case of two conduction electrons has been studied by Herring and Hill[8] for Be and recently by Raimes[9] for Mg. According to the latter, since electrons with parallel spins rarely approach each other within a distance of smaller than the radius of the Wigner-Seitz sphere,[10] it is reasonable to assume that in each sphere an electron is moving only in the field of another electron of opposite spin in addition to the field due to the core. To obtain the wave function for the conduction electron a self-consistent field calculation is therefore required.

Now we are ready to write down the formula for the binding energy per atom. The formulation, except for the above-mentioned correction and the core-core interactions, is the same as that given in Raimes' paper.[9] The binding energy per atom is found to be[11]

$$E_b = -E_I - 2\epsilon - 2E_k - 2E_{\text{ex}} - \frac{1}{2N}\sum_{a\neq b}^{N}\left(V_{ab} - \frac{4}{r_{ab}} - 2V_{ab}'\right). \quad (1)$$

The summation is to be carried over all the N lattice points. Here E_I means the energy required to ionize the two 6*s* electrons; ϵ, the eigenvalue obtained in the Wigner-Seitz method; E_k, the average Fermi kinetic energy per conduction electron; E_{ex}, the average exchange energy per conduction electron. V_{ab} represents the interaction between two cores, one situated at lattice point a, the other at point b. V_{ab}' represents the electrostatic correction due to the overlap of cores. The presence of the term $4/V_{ab}$ can be understood in

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[9] S. Raimes, Phil. Mag. **41**, 568 (1950).
[10] E. Wigner and F. Seitz, Phys. Rev. **46**, 509 (1934).
[11] The units used here are: length, a_{H} Bohr radius; energy, 2 Rydberg.

TABLE I. Contributions to the binding energy for tungsten.

	Nearest neighbors (antiparallel spins)	Next-nearest neighbors (parallel spins)
r_{ab}	$5.17a_{\mathrm{H}}$	$5.97a_{\mathrm{H}}$
C_{ab}	−0.149 ry	−0.038
$2V_{ab}'$	−0.120 ry	−0.039
K_{ab}	+0.223 ry	+0.137
X_{ab}	−0.061 ry	−0.057
Total	−0.107 ry	+0.003

the following manner. If we say that the correction term V_{ab}' is zero and that the core interaction V_{ab} can be represented by the coulomb repulsion between two positive centers each of charge +2, then every term in the summation becomes zero and we obtain the usual formula for the binding energy.

The task now reduces to the calculations of V_{ab} and V_{ab}'. Assuming a uniform distribution for the conduction electrons it can be shown that

$$V_{ab}'=\frac{2}{\Omega_0}\int_{\Omega_0}\frac{Z_p(|\mathbf{r}-\mathbf{r}_a|)}{|\mathbf{r}-\mathbf{r}_a|}d^3r. \tag{2}$$

In this expression the lattice point b is taken as the origin, and $\mathbf{r}_a$ represents the position vector of point a with respect to b. The integration is to be carried over the space bounded in the Wigner-Seitz sphere around b, its volume being Ω_0. $Z_p(r)/r$ is the potential due to a nuclear charge of Z_0-2 as well as the core electrons surrounding it, Z_0 being the total nuclear charge of the atom. Since Z_p is usually tabulated in the self-consistent field calculation for a free atom, V_{ab}' can be evaluated easily by numerical integration.

To calculate the interaction V_{ab} between the cores, we shall use the Thomas-Fermi-Dirac gas model, the charge density of the cores being regarded as superposed without any redistribution. The charge density of the cores will be taken as identical to that given by the Hartree solution for the isolated atom.

The calculation of the coulomb electrostatic contribution to V_{ab} is straightforward. The noncoulombic interaction consists of two parts. The first part, a repulsive interaction, arises from the increase in kinetic energy which comes from the superposition of two Thomas-Fermi distributions. The second part arises from the exchange interaction between electrons of parallel spin. This exchange interaction, which is of a negative sign, always increases when two charge distributions are superposed. There is no necessity for writing down the formula. We shall write only

$$V_{ab}=(4/r_{ab})+C_{ab}+K_{ab}+X_{ab}, \tag{3}$$

where $4/r_{ab}$ takes care of the net positive charge of the core, C_{ab} represents the rest of the electrostatic interaction, and K_{ab} and X_{ab} represent, respectively, the interactions arising from Fermi kinetic energy and exchange energy. $K_{ab}+X_{ab}$ is equivalent to the exchange repulsion usually understood in a quantum-mechanical calculation of the interaction between cores. It is to be noticed that, owing to the antiferromagnetic arrangement, K_{ab} and X_{ab} assume different forms for nearest neighbors and for next-nearest neighbors. For nearest neighbors they are due to the overlap of d orbitals of one atom with inner orbitals of the other. For next-nearest neighbors they are due mainly to the overlap of incomplete d shells.

For later use let us write

$$\begin{aligned}E_B'&=-\frac{1}{2N}\sum_{a\neq b}^{N}\left(V_{ab}-\frac{4}{r_{ab}}-2V_{ab}'\right)\\&=-\frac{1}{2N}\sum_{a\neq b}^{N}(C_{ab}+2V_{ab}'+K_{ab}+X_{ab}).\end{aligned} \tag{4}$$

Since all the interactions drop rapidly with increasing r_{ab}, we need to carry out the summation over nearest and next-nearest neighbors, obtaining

$$\begin{aligned}E_B'&=-4(C_{ab}+2V_{ab}'+K_{ab}+X_{ab})\text{ nearest}\\&=-3(C_{ab}+2V_{ab}'+K_{ab}+X_{ab})\text{ next nearest.}\end{aligned} \tag{5}$$

IV

To illustrate in a quantitative way the importance of the electrostatic energy, tungsten is chosen as an example. As mentioned before, to make use of Manning and Millman's calculation for the configuration $(5d)^4(6s)^2$, we assume that two electrons per atom go into the conduction band. In the expression

$$E_B=\{-E_I-2-2E_k-2E_{\mathrm{ex}}\}+E_B',$$

the first part $\{-E_I-2-2E_k-2E_{\mathrm{ex}}\}$ may be regarded as essentially the same in W as in Hg, which has, in fact, two electrons in the conduction band. Now in Hg the $5d$ shells are so small as to have no appreciable interaction, so that the binding energy may be taken as given by the first part of E_B. Since this binding energy is very small compared with that of W, we shall hereafter neglect this first part of E_B, and thus consider only that part of the binding which arises from the extension of the $5d$ shells outside of the Wigner-Seitz cells.

E_B' has been evaluated through numerical integrations. The following table gives the various contributions calculated at the observed lattice constant $5.97a_{\mathrm{H}}$. Using Eq. (5) we get $E_B'=0.42$ ry/atom. The observed heat of vaporization is 0.68 ry/atom. Considering the crudeness of our method, the agreement is quite satisfying.

In Table I one may notice that the term C_{ab}, arising from the coulomb interaction between cores, is indeed the major contributor to the calculated binding energy. In the formation of tungsten crystal this source of energy must be fully explored. The demotion of a $6s$ electron into the $5d$ shell will certainly increase the

attractive term C_{ab}; but the attractive energy $2V_{ab}'$, being proportional to the density of the conduction electrons, will be decreased to approximately half its present value. Further, the repulsive energies will be increased. It is difficult to say what will be the over-all effect. Such considerations must be preceded by a calculation of the wave functions using the Hartree-Fock method. In all cases the coulomb energy arising from the overlap of d shells will continue to play an important role in the binding energy consideration for tungsten.

From the table one sees that the exchange repulsion $K_{ab}+X_{ab}$ between nearest neighbors is quite large, being 0.162 ry. Assuming nearest neighbors to have parallel spins we obtain for $K_{ab}+X_{ab}$ a value of 0.260 ry. Comparing the two values, one can see that the antiferromagnetic arrangement is really quite effective in minimizing the repulsive energy. As the binding energy calculated from this model is of the right order of magnitude, one may be inclined to believe that the preference of b.c.c. lattice over the common close-packed lattice is coupled to the tendency of such atoms toward antiferromagnetic arrangement.

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Stability of Short Arcs in Oxygen, Hydrogen, and Helium

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An arc drawn between separating contacts is known to be very unstable, in the absence of oxygen, in the usual power circuit. To study this instability experiments have been made in which a four-ampere arc in a 125-volt dc resistive circuit was repeatedly restruck between separating contacts. Various metals were used as cathodes, with spectroscopically pure carbons as anodes, in various gases.

Data have been obtained showing the dependence of average arc duration after ignition on the cathode material and on the pressure and kind of surrounding atmosphere for a number of metals in oxygen, hydrogen, and helium. Oxygen exhibits an extraordinary stabilizing influence for most metals, whereas in hydrogen the mean life of the arc is generally less than ten milliseconds even at atmospheric pressure.

ELECTRIC arcs have been used by engineers for many years. The conduction of electricity in gases is as old as electricity itself, yet no one has developed a generally accepted theory of the physics of the concentrated cathode arc spot. Welding engineers desire stable arcs; circuit breaker engineers want unstable arcs; designers of rectifiers strive to eliminate cathode arc spots from their anodes at all times.

As long ago as 1932, Professor G. E. Doan[1–3] reported extreme instability for arcs drawn in very pure argon, between electrodes of very pure iron. Yet none of the theories proposed to describe the cathode spot suggests the influence of oxygen. Doan observed instabilities at low currents of a few amperes and also at welding currents of more than 100 amperes. Besides the reports of Doan and his collaborators, other references can be found to the difficulty of arc spot formation in the absence of oxygen.[4] Fan[5] found glow discharges between copper electrodes in hydrogen to exist for currents above ten amperes before transition to the low voltage arc occurred. When oxygen is present in even small amounts, the transition occurs at currents of the order of one ampere.

This paper presents the results of a study of the relative stability of dc arcs as a function of the composition and pressure of the surrounding gas atmosphere. Tests were made with cathodes of aluminum, carbon, cobalt, chromium, copper, iron, molybdenum, nickel, tungsten, titanium, and zirconium. These cathodes were used with spectroscopically pure carbon anodes. Observations of arc stability were made for each electrode pair in atmospheres of tank oxygen, tank hydrogen, and tank helium.

The phenomenon under investigation involves the cathode. When a source of electrons is provided, as with a thermionic cathode, no difficulty is experienced in maintaining a discharge through a gas under conditions similar to those of this experiment. Arcs in gas-filled thermionic diodes or in thyratrons are extremely stable. The instability we have observed seems to be peculiar to the self-maintaining concentrated cathode spot.

The instabilities observed in this investigation are found at high currents as well as low currents. A momentary improvement in stability is found when the arc current is increased. However, after the cathode spot has roamed over the available cathode material,

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