174. *The Nature of the Metallic Bond. I* *Structure of Metallic Crystals*

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I. *Introduction.* The individual behavior of atoms in free molecules and nonmetallic crystals was explained by the valence theory, particularly after the development of quantum mechanics.¹⁾ Almost the same procedure was applied to atoms in metallic crystals by Pauling and others who obtained many interesting results.²⁾ However, metals contain conduction electrons which have been treated collectively by the band theory. This theory explained the electric and magnetic properties of metals, but has not satisfactorily taken into account the individual nature of atoms. The concept of dislocation was very useful to account for the mechanical properties of metals which are most important from industrial point of view. However, the existing theory also has not satisfied us in taking into account the individual nature of atoms and, furthermore, the treatment is mainly based on the elastic theory.

Such being the case, several authors have attempted to improve the situation and papers have been published along this line.³⁾ We might say that emphasis has been laid too much on band theory and dislocation theory in the sense stated above and, therefore, it is necessary for the improvement of the theory to take a wider view of the whole matter, taking into account the experimental results on nonmetallic substances also. This is the reason why we presented an invited paper on the 10th anniversary of the foundation of National Research Institute for Metals, entitled "Metals and Non-metals, Members of the same family".⁴⁾ The first few papers of this series are concerned with more detailed discussion of what we reported on that occasion.

II. *Crystal Structure and Cohesive Energy.* The structure of metallic crystals evidently gives us some clue to the understanding of metallic bonds. These crystals are found generally in the f.c.c., h.c.p., and b.c.c. structures, whereas nonmetallic crystals take usually more complicated forms. On the boundary between metallic and nonmetallic elements we find many cases in which the structure is often one of the above metallic ones but is deformed considerably. This shows that there is no discontinuous change from metallic to

nonmetallic states. Even the same substance exists in both states as in the case of Sn. The crystal stable at low temperature (gray tin) has the diamond structure and is rather nonmetallic, whereas at higher temperature, the stable crystal becomes certainly metallic (white tin).

Quite a few metallic crystals assume complicated structure at lower temperature, but as the temperature is raised, they sometimes take the f.c.c. structure and finally the b.c.c. structure. In the case of iron, this structure corresponds to that of δFe , and the b.c.c. structure of αFe (which transforms to the f.c.c. structure of γFe at higher temperature) forms an exception.

αMn is one of the examples belonging to the complicated structure, the unit cell consisting of 58 atoms. However, at higher temperature it takes the f.c.c. structure (γMn) and finally the b.c.c. structure (δMn). We will show in part II of this series that the b.c.c. structure of αFe are formed by bonds with partially directional character and is different from the b.c.c. structure of δFe . This is the structure close to what we usually find in metals as alkalis. Except for such cases, the crystal structure of metals stable at room temperature shows the following regular behavior in the periodic table:

IIIa	IVa	Va	VIa	VIIa	VIII ₁	VIII ₂	VIII ₃	Ib
h	h	b	b	h	h	f	f	f

Here b, h, and f denote, respectively, the b.c.c., h.c.p., and f.c.c. structures.

Let us next consider the change of cohesive energy with atomic number in the periodic table (see Fig. 1). The general behavior of the cohesive energy is as follows: (1) In the metallic region the minima appear at Ia and IIb and the maximum at about VIa; (2) In the region consisting mainly of nonmetallic elements the minima appear at IIb and 0 and the maximum at IVb; (3) The cohesive energy becomes larger in the periods with larger atomic number for metallic elements, whereas the reverse is the case for nonmetallic elements; (4) An exceptional case of the above general behavior is formed by the transition elements in the first long period with energy minimum at Mn. This is closely related to the anomalous behavior of the crystal structure explained above.

The general behavior of the cohesive energy with maximum at W shown in Fig. 1 together with its close relation to the behavior of the crystal structure mentioned above throws great light upon the important role played by *d*-electrons of the transition elements.

However, before going into the explanation on this matter, we have to discuss the following few problems.

III. *f*-electrons and *d*-electrons. As is well known, the electric conductivity of transition metals is much lower than that of Cu or Ag. This is due to the scattering of outermost *s*-electrons to *d*-band. In addition to this problem we have to take into account *f*-electrons which begin their existence in lanthanides. Since these electrons lie in the inner part of the cores, their behavior will be simpler than that of *d*-electrons. Therefore, the change of crystal structure and cohesive energy with the number of *f*-electrons can be treated more easily than that of *d*-electrons. As is well known the chemical properties of these elements are not much different from one another, since the outer electron configuration of ions remains unchanged.

However, such is not the case for other properties. The remarkable one is the cohesive energy which changes considerably with atomic number. The behavior can be summarized as follows: (1) The cohesive energy shows maxima at La, Gd, Tb, and Lu with almost the same value which is about twice as large as the minimum value found at Eu and Yb; (2) The energy decreases gradually from La to Eu and from Gd, Tb to Yb; (3) An abrupt, almost

linear increase of the energy is observed for $\text{Yb} \rightarrow \text{Lu} \rightarrow (\text{Hf}) \rightarrow (\text{Ta})$.

Therefore, there must be some indirect contribution of f -electrons to the binding of atoms forming the crystal. Spectroscopic investigations show that La and Lu having maximum cohesive energy contain, respectively, no $4f$ - and one $5d$ -electron, and fourteen $4f$ - and one $5d$ -electrons in free atom. On the other hand Eu and Yb with minimum cohesive energy have, respectively, seven $4f$ - and no $5d$ -electrons, and fourteen $4f$ - and no $5d$ -electrons. The value of the cohesive energy of these two metals is almost the same as that of Ba without $4f$ - and $5d$ -electrons. (Here the number of d - and f -electrons of free atoms can be considered to be almost the same as those of atoms in crystals.) From what has been stated above about $4f$ - and $5d$ -electrons, it follows that $5d$ -electrons contribute to the binding of atoms in the crystal. Furthermore, the almost linear increase of the binding energy in $\text{Cs} \rightarrow \text{Ba} \rightarrow \text{La}$, and $\text{Yb} \rightarrow \text{Lu} \rightarrow \text{Hf} \rightarrow \text{Ta}$ shows that the contribution of $5d$ -electrons is not much different from that of $6s$ -electrons. It is evident that closed shell (0 or 14 f -electrons) and half shell (7 f -electrons) are stable. So we have a certain effect resulting from the tendency of f -electrons to be in one of the above stable configurations. This may be one of the factors to explain the afore-mentioned fact that the cohesive energy decreases with increasing atomic number from La to Eu.

Space does not allow us to discuss the elements of actinide series which are characterized by the existence of $5f$ -electrons. However, we would like to note that $5f$ -orbitals extend much more than $4f$ -orbitals and the cohesive energy of Th, Pa, U, and Np is larger than that of Ac. This will show the contribution of d -orbital plays a more important part in the binding of atoms in the crystals than the lanthanide elements. This results in the complicated structure and polymorphism of U, Np, and Pu. The crystal of αU has lamellar structure as in the crystals of As, Sb, and Bi. This is due, as stated above, to the contribution of d -electrons which introduces partial covalent character in the binding of atoms forming metallic crystals.

IV. *Transition Metals.* The cohesive energy of transition metals of the first long period has a minimum value at Mn with $3d$ half shell. This behavior is similar to that of lanthanides and of actinides. This shows that d -electrons participate to various extent in the binding of atoms. As mentioned before, the crystal structure of actinide elements becomes more complicated (more non-metallic), and, therefore, we have some reason to believe that the crystal of αMn is complicated because Mn atom contains $3d$ -electrons.

Here we would like to discuss a little bit about the behavior of p -electrons. In the first short period (Li→Ne), diamond with tetrahedral carbon bond has the maximum rigidity, but there is an abrupt change of binding in the neighboring atom of the periodic table which forms a molecule N_2 with strong interatomic force, but with very weak intermolecular force which can clearly be seen from the low boiling point.

The dissociation energy of N_2 molecule has the maximum value of 7.38 e.v., the energy decreasing on both sides of N in the first short period as follows: Li_2 (1.14 e.v.), B_2 (3.0 e.v.), C_2 (5.6 e.v.), N_2 (7.38 e.v.), O_2 (5.08 e.v.), F_2 (2.8 e.v.). This is due to the fact that in N_2 three p -orbitals form σ, π, π -triple-bond, in other words the cohesive energy is very much concentrated in atomic pairs even in crystalline state.

We may assume a situation similar to this for the d -orbitals of Mn, since both the p -shells of N and the d -shells of Mn are half-filled. Evidently the diatomic molecule N_2 is not the same as the atomic pair (with interatomic distance 2.24Å which is too small as interatomic distance in normal metal crystals) found in the unit cell of α Mn. However, the partial nonmetallic properties of α Mn (brittleness, low electric conductivity) will have something to do with what has been explained above. Such a change as we have seen in C→N is not observed in the parts of the periodic table with higher atomic numbers. For example, the change from Pb to Bi is continuous.

Let us further discuss the p -bonding in the Vb-group elements. The metallic properties become more pronounced in the order N→P→As→Sb→Bi. The next heavy element P also forms a molecule P_2 as N_2 , but it is much less stable than P_4 in the gaseous state. This molecule has a structure with four P atoms located at the four corners of a tetrahedron. Here P-atoms form pyramidal σ -bonds as against the triple bond of N_2 , because P has more inner electrons than N and consequently the exchange repulsion between the cores becomes so great that P_4 is much more stable than P_2 . White phosphorus has 232 atoms in unit cell. If this is composed of P_4 groups, the unit cell contains 58 of them. This may have something to do with the unit cell of α Mn which contains the same number of Mn atoms.

In As we also have pyramidal σ -bonds, but these bonds do not form small units in the crystal and, as mentioned before, the crystal has lamellar structure. Sb and Bi also have the structure similar to this, but the bonds tend to be more uniform.

From what we have described in this paper, we see that the

energy concentrated in small groups of atoms in the range of lower atomic number tends to spread uniformly over the crystal with increasing atomic numbers. Naturally this applies to the transition elements, in which we have exceptional part in the first long period, but not in the third long period with higher atomic number. An explanation for this will be made in the following paper.

V. *Summary.* In the present paper emphasis is laid on the important role of *d*-electrons in the behavior of the crystal structure and cohesive energy of transition metals.

References

- 1) See, for example, S. Mizushima and S. Nagakura: Quantum Chemistry, Tokyo (1959).
- 2) L. Pauling: The Nature of the Chemical Bond. Cornell Univ. Press (1960).
- 3) J. B. Goodenough: Magnetism and the Chemical Bond. Interscience Publishers (1963); S. L. Altmann, C. A. Coulson, and W. Hume-Rothery: Proc. Roy. Soc., **240A**, 145 (1957); W. Hume-Rothery, H. M. Irving, and R. J. P. Williams: Proc. Roy. Soc., **208A**, 431 (1951).
See also references cited in the above books and papers.
- 4) S. Mizushima: Memorial Lecture: National Research Institute for Metals (1966).