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NOTE ON AN EXPLANATION OF CRYSTAL STRUCTURES OF ELEMENTARY SUBSTANCES

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SVMMARIVM — Sententia, quae christallinas corporis structuras ex atomicis interactionibus interpretatur, magis recepta est quod attinet ad nonmetallica corpora, quam quod ad metallica. De his autem Auctores systematicam quamdam proponunt interpretationem, cuius hoc sit exemplum: in transitionis metallis electrones *d*, qui sunt statim interius quam electrones *s*, haberi possunt ut electrones qui ita se gerant prout se gerunt electrones *p* in christallis non metallicis.

INTRODUCTION

The crystals of both typically nonmetallic and metallic elementary substances exhibit structures simpler than those on the boundary between them. The atomic interactions in the former are generally well understood, but those in the latter (metallic crystals) are not explained satisfactorily, even though they exhibit simple structures.

In contrast to nonmetallic substances, valence electrons

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responsible for bonding in metals are able to move through the crystal. The band theory has made a great contribution to the understanding of the behavior of these conduction electrons, particularly those near the FERMI surface. Thus several interesting properties of metals, such as electric and thermal properties have been explained. Furthermore, for some kind of alloys, the HUME-ROTHERY rule [1] was explained in a similar way by JONES [2]. However, the crystal structure of transition metals cannot be explained by the mere extension of this kind of concept, nor by PAULING's resonating-valence bond treatment [3]. Such being the case, we want to discuss in this note some problems to be solved or partially solved in order to obtain a systematic view on this subject.

CRYSTAL STRUCTURE AND COHESIVE ENERGY

The structure of crystals and cohesive energies evidently give us some clue to the understanding of the nature of bonds. In the case of metallic elements which occupy the major part of the periodic table, they show generally the following behavior:

I*a*	II*a*	III*a*	IV*a*	V*a*	VI*a*	VII*a*	VIII_1	VIII_2	VIII_3	I*b*
b	(*f*)	*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.

On the other hand the cohesive energy of these elementary substances in the crystalline state changes with atomic number as shown in Fig. 1 [4]. It is to be noted that for transition metals the cohesive energy decreases in the order: *b.c.c.*→ *h.c.p.*→*f.c.c.* As we will show in the following, the behavior of cohesive energy has generally a close relation with the change of crystal structure mentioned above.

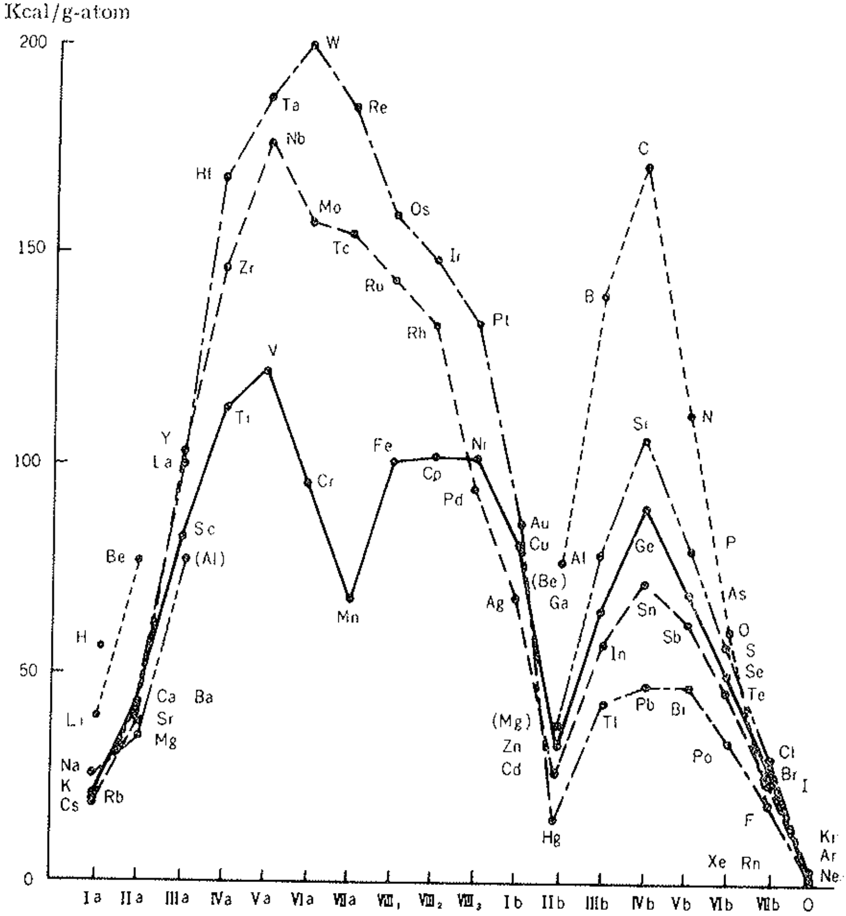

Fig. 1 — Cohesive energy

Let us first consider I*a* and I*b* elements, both of which consist of atoms with the closed core and one valence electron. The fact that I*b* elements have the cohesive energies much higher than I*a* elements can be understood easily, since the $s-d$ exchange (in I*b*) plays a more important role than the $s-p$ exchange (in I*a*) [5]. As the bonds are non-directional and the cohesive energies are much higher, I*b* crystals exhibit the *f.c.c.* structure (or a close-packed structure). This is not generally the case for I*a* elements with lower cohesive energies, although the bonds are also non-directional. They exhibit the *b.c.c.* structure except for L*i* and N*a* with the close-packed structures at low temperature. This exceptional behavior of L*i* and N*a* was explained by BARRETT [6] as follows: The stability of a structure is determined by the value of the free energy $F = H - TS$, where H denotes the enthalpy, T the absolute temperature and S the entropy. According to him the entropy S of the *b.c.c.* structure is greater than that of the *f.c.c.* structure and the free energy of the former increases more rapidly than that of the latter, as the temperature is lowered. Therefore, the *b.c.c.* structure should transform to closest-packed one at sufficiently low temperatures where TS becomes less significant.

In II*a* elements with overlapped $s-p$ bands, each atom can afford two valence electrons and the cohesive energies of the II*a* crystals are higher than that of I*a*, but not so high as those of I*b*, because the nuclear charge of II*a*-atoms is stronger than that of I*a*-atoms and the $s-d$ exchange is much higher than the $s-p$ exchange as mentioned above. Therefore, we may regard II*a* elements such as C*a* and S*r*, are as intermediate between I*a* (entropy term predominant) and I*b* (enthalpy predominant) elements. Thus we can understand the structure change of C*a* and S*r* (*f.c.c.*→*h.c.p.*→*b.c.c.*) taking place at temperatures much higher than that of I*a* elements. It is to be noted that although we have used the concept of thermodynamical stability, we want to explain the quantities of states in terms of atomic interactions. Such a point of view becomes more important in the understanding of the behavior of transition metals.

Before entering into this problem, we should like to refer to the crystal structures of the rare gas elements. The crystals are formed by the van der Waals forces which are also non-directional as in typical metals mentioned above. Since they exist at low temperatures where TS is very small, it is quite natural that they exhibit the *f.c.c.* structure. In H*e* crystal, however, the interatomic forces are so weak and the atomic mass is so small that the closed-packed structure is observed at very low temperature only under high pressure. As the pressure is lowered at a proper temperature, the crystal finally exhibits the *b.c.c.* structure [7] which is quite reasonable from the above point of view. (We might add that L*i*, the lightest alkali metal exhibit the *h.c.p.* structure at low temperature and then the *f.c.c.* structure by cold working) [6]. Thus we see that even if the nature of forces is quite different, the crystals show behaviors similar to each other, so far as the forces are non-directional.

Generally speaking in the case of polymorphic metals, the highest temperature form is the *b.c.c.* structure which is understandable from what we explained above, comparing the values of enthalpy and that of entropy term.

TRANSITION METALS

The crystal of F*e* transforms as: $\alpha(b.c.c.)\rightarrow\gamma(f.c.c.)\rightarrow\delta(b.c.c.)$ with rising temperature and the *b.c.c.* structure of δF*e* and the *f.c.c.* structure of γF*e* are understandable from what we discussed above. However, the *b.c.c.* structure of αF*e* which is less densely packed than the *f.c.c.* structure of γ*Fe* cannot be stable at lower temperature, if the crystal force were typically metallic.

It is well known that gray tin with diamond structure is a semi-conductor, whereas white tin stable at higher temperature is a metallic crystal. Here by raising the temperature, the less densely packed structure transforms to the more densely packed one. Taking into account such kind of things, we see that the *b.c.c.* structure of α*Fe* cannot be explained only by the usual metallic bond. This is also the case for the transition elements belonging to V*a* and VI*a* groups, which have cohesive energies much higher than I*a* elements.

We propose to explain these structures by the behavior of *d*-electrons lying just inside of outermost *s*-conduction electrons. Since the extension of the wave functions of $(n-1)$ *d*-electrons is much narrower than that of *ns*-electrons, the *d*-bands are considered to have an atomic orbital character to a considerable extent. In the free state the atomic *d*-level is fivefold degenerate and this can be divided into two groups: doubly degenerate d_γ and triply degenerate d_ε. By suitable combination, d_ε can form body-diagonal orbitals which can overlap those of neighboring F*e*-atoms to form a kind of the framework of the F*e* crystal. The *b.c.c.* structure of this crystal can be understood in this way as was done by GOODENOUGH from the magnetic investigations [8].

Thus we understand approximately that the *d*-framework will be most stable, when we have three *d*-electrons per atom. This seems that V*a* and VI*a* elements exhibit the *b.c.c.* structure with high cohesive energies.

III*a* and IV*a* elements have, respectively, one or two *d*-electrons in the free state. Therefore, they tend to exhibit the close-packed structure, but not the less densely-packed one as *b.c.c.* However, there will be some contribution of a *d*-electron or electrons to the bonding of atoms in the crystals. This can be seen that the cohesive energies of III*a* and IV*a* elements are higher than those of I*a*, II*a*, but lower than those of V*a*, VI*a* elements. The smaller contribution of *d*-orbitals is compatible with the *h.c.p.* structure of those elements, which has no center of symmetry in contrast to the cubic closest packing (*f.c.c.*).

The *h.c.p.* structure of *Mg*, *Ca* and *Sr* has an axial ratio $c/a = 1.633$ which corresponds to the closest-packed structure. However, this ratio of all the transition metals is less than this value [9]. This means that the bonding along the *c*-axis is stronger than the in-plane bonding. We should like to explain this fact of the transition metals as mainly due to the presence of d_{z^2}-orbital, since this is considerably extended in one direction which can be the direction of the *c*-axis.

Evidently the extension of *d*-orbitals is reduced with increasing atomic number (or with increasing effective nuclear charge) and, therefore, in $VIII_3$ atoms the *d*-orbitals are too contracted to form the above structure, but exhibit the *f.c.c.* structure.

In VII*a* and $VIII_1$ elements (lying between V*a*, VI*a* elements with the *b.c.c.* structure and $VIII_2$, $VIII_3$ elements with the *f.c.c.* structure) the *d*-orbitals are not so contracted that the d_{z^2}-orbital again play an important part. For this reason they exhibit the *h.c.p.* structure with the c/a ratio less than 1.633.

As mentioned above, $VIII_1$ elements have the *h.c.p.* structure show no transformation except for *Fe*. The density of electron clouds in 3*d*-orbitals is higher than those in 4*d* and 5*d*-orbitals and consequently, the 3*d*-orbitals (with rather strong atomic orbital character) can overlap each other effectively to exhibit the *b.c.c.* structure, although $VIII_1$ group elements generally exhibit the *h.c.p.* structure.

The thermal motion can easily affect the overlapping of rather sharp electron clouds, so that at higher temperature α*Fe* of the *b.c.c.* structure transforms to γ*Fe* of the f.c.c. structure with non-directional bonding. This means that the overlapping of orbitals of αFe exhibiting the *b.c.c.* structure is not so stable as that of V*a* and VI*a* elements (e.g. T*a* and W). Similarly we may understand C*o* belonging to $VIII_2$ elements exhibits both the *f.c.c.* and *h.c.p.* structures in a certain temperature range.

LANTHANIDES

So far we have discussed the behavior of *s*-, *p*- and *d*-electrons. In lanthanides we have *f*-electrons inside of *d*-electrons. However, since the energy levels of 4*f*-electrons are close to those of 5*d*-electrons in the free state, we have to take into account the relations between these two states much more seriously. Fig. 2 [4] afford one of the clues to this problem.

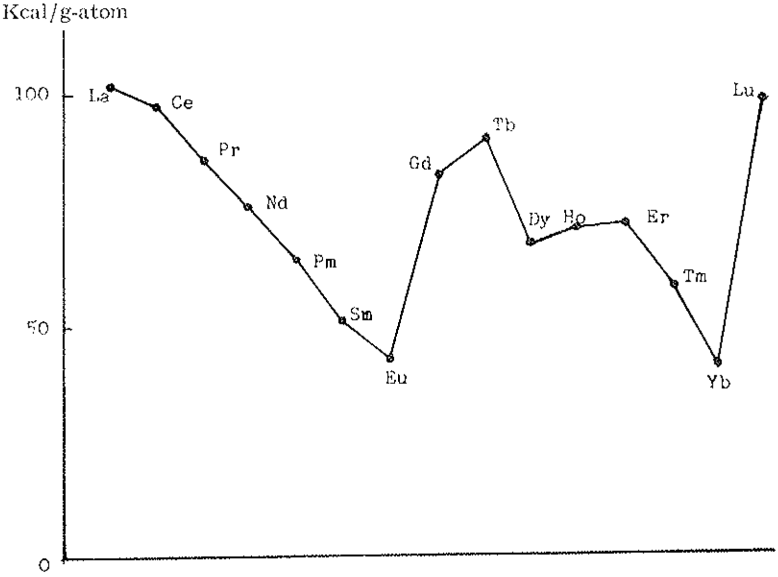

FIG. 2 — Cohesive energy of Lanthanides

Spectroscopic investigations show that atoms of lanthanides in the free state probably have no *d*-electron except for those of L*a*, C*e*, G*d*, T*b* and L*u*, each of them having one *d*-electron. As the cohesive energies of these elements show values larger than those of other elements, we may consider that *d*-electrons play a part in atomic bonding. This will be seen from Fig. 2 that the cohesive energies of E*u* and Y*b* (with no *d*-electron in the free state) show the minimum value. The atoms of E*u* and Y*b* have, respectively, stable half *f*-shell and closed *f*-shell and, therefore, no *f*-electron will be changed to a *d*-electron even in the crystalline state.

Since half shell (E*u*) and closed shell (Y*b*) of *f*-electrons will not directly contribute to the cohesive energy and, furthermore, since B*a* with no *d*-electron has a cohesive energy as low as E*u* and Y*b*, we have another reason to believe that *d*-electrons play an important part in cohesive energy.

From Fig. 2 we see gradual lowering of cohesive energies from L*a* to E*u*. Although P*r*, N*d*, P*m* and S*m* has no *d*-electron in the free state, we consider some contribution of *d*-electrons to cohesive energies in the crystalline state, because the bonding energy may overbalance the energy of elevation of an atomic state. The contribution of *d*-electrons to cohesive energies will decrease in the order P*r*, N*d*, P*m*, and S*m*, because the elevation of a *f*-state will become more difficult as it approaches to the stable half shell (E*u*). We see a situation similar to what has been stated above in the latter group of lanthanides (G*d* to Y*b*).

Thus we see that in lanthanides which exhibit the *h.c.p.* structure (with $c/a < 1.633$) or a related one [9, 10], *d*-electrons also play an important part in the crystal structures as well as in the cohesive energies. Thus it seems understandable that E*u* and Y*b* with no *d*-electrons do not exhibit the *h.c.p.* structure.

REMARKS

As mentioned in the beginning the explanation of atomic interactions in metallic crystals is much less satisfactory than that in non-metallic crystals. Therefore in this note, stress is laid on a preliminary explanation of the nature of bonding in metallic crystals from a systematic point of view. In transition metals which occupy the majority of metallic elements, *d*-electrons lying just inside of outermost *s*-electrons can be considered to behave something like *p*-electrons of non-metallic crystals.

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