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On the Lattice Stability of Metals

I. A Uniform Treatment of NFE and Transition Metals*

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The success of perturbation calculations of second order for the NFE ("Nearly Free Electron") metals and that of the two-parameter model of Pettifor for the transition elements show that the lattice-stability of the metals has simple physical reasons. Using the results of Harrison, Heine and Weaire, Deegan, and Pettifor, a model is developed which allows to explain the stability of the three metal lattices in terms of differences in the potentials. Only those potential differences are considered which are caused by the different packing of the lattices. With the aid of the virial theorem the band structure energy is connected with the potential bandstructure energy. The sequence of stability is predicted to be body centered cubic (*bcc*), hexagonal close packed (*hcp*), face centered cubic (*fcc*) with increasing valence electron concentration. The ranges of stability can be expressed in simple numbers. This simple model holds in principle for NFE as well as for transition metals because it contains no assumptions restricted to only one of these metal types. Deviations of the observed lattice stability from the model can be understood from the approximations involved.

Key words: Metals – Lattice stability

1. Introduction

The first type of chemical bond which was understood, was the ionic bond. In simple cases the structure of heteropolar compounds can be explained with the aid of the Coulomb model and the ratio of the ionic radii (e.g. Krebs [1]). Quantum mechanics explained the covalent bond, and the concept of hybridization (e.g. Krebs [1]) helped to understand a variety of systems. In 1957 Altmann, Coulson, and Hume-Rothery [2] tried to give an explanation of the structure of the transition metals using directed hybrids. But this picture is not sufficient. A tight-binding calculation for chromium (Asdente and Friedel [3]) has shown that the energy varies over the whole width of the *d*-band along several symmetry lines (e.g. Λ,F) without any variation in hybridization. Therefore the understanding of lattice stability in metals can not be based on directed orbitals.

By means of the pseudopotential method (for a short review see e.g. Brauer [4]), Harrison [5] could explain the lattice stability of sodium, magnesium, and aluminium. Using second order perturbation theory, Heine and Weaire [6] and

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Blandin [7] made considerable progress in understanding simple metals which have only *s* and *p* valence and conduction bands. To a good approximation they can be treated with the "Nearly-Free-Electron" method (NFE) (compare e.g. [4]).

Hubbard, Dalton [8, 9] and Pettifor [10] simplified the Korringa-Kohn-Rostoker Method (KKR), [12] to the Hybrid-Nearly-Free-Electron-Tight-Binding method (H-NFE-TB). Pettifor [11] applied this scheme to the transition metals and predicted the observed lattice stability, when using only the two resonance parameters ε_d and Γ_d of the virtual *d*-states (see Sect. 2). In 1968, Deegan [13] has shown already for the transition metals that the stability of the body-centered cubic lattice (bcc) compared to that of the face-centered cubic lattice (fcc) has a maximum for the half filled *d*-bands.

Today it is possible to calculate the stability of some phases by complicated *ab initio* calculations (e.g. [14]).

In 1968 Brewer [15] proposed a general explanation of the lattice stability on the basis of spectroscopic data.

Based on the work of Harrison [5], Heine and Weaire [6], Blandin [7], Deegan [13], and Pettifor [11], a model of the lattice stability of the metals should provide the following properties:

1. It should comprehend both NFE- and transition metals.
2. It should be simple. Actually the success of perturbation theory of second order for NFE-metals with plane waves and that of the two-parameter model of Pettifor for the transition metals show that the physical reasons for the lattice stability in principle cannot be too complicated. Both methods cannot involve more than what is provided by Hamiltonians, the potential of which differ only in the arrangement of the atomic potentials. This simplicity is also suggested by the wide distribution of the three metal lattices in the periodic system of elements (PSE) or the chemical differences. Although metals such as potassium and tungsten show large chemical and physical differences, they crystallize in the same lattice.

   Let us consider as an example the difference in the hardness between potassium and tungsten in more detail. As it holds for other physical properties too, this difference is caused by the bulk of the cohesive energy which does not influence the structure. Thus, as far as we are dealing with the structure energy differences of one and the same metal, we should not worry about differences like that in hardness.

   But even if one could argue that if the hardnesses are very different one cannot treat two compounds in the same way, one could treat *K* and *W* together: the hardness of *W* is about 250 to 500 times that of *K* [16, 17]. These numbers have to be divided by the numbers of valence electrons. Then the factor for *W* is about 40 to 80. For iron we would find about 6 to 25. Now we look which factors we find for ionic and covalent compounds. For example for MgO and KJ we find 70. Actually the structure of these compounds can be treated as ionic because in both cases we have a ratio of the ionic radii determining the structure to be that of NaCl. As covalent compounds with the same type of bond system we take CdTe and BN. The hardness factor here is 200!

3. As in chemistry it is usual (see e.g. Krebs [1]) there should be a picture of the charge distribution and the potential which accounts for the energy differences between different lattices.

In Sect. 2 the necessary terms are explained and the essential suppositions of this work are summarized. In Sect. 3 a picture of the connection between band structure energy differences and potential differences is developed. In Sect. 4 the valence- and conduction bands which form the basic mechanism of the lattice stability are described and their properties are discussed. The connection between the lattice stability and the changes in the density of states curve is analyzed in Sect. 5. The general sequence of the stability of the metal lattices is given in Sect. 6 and is applied to the NFE-metals in Sect. 7 and to the transition metals in Sect. 8. The differences between the predictions of the model and observation and calculations of Pettifor are discussed in Sect. 9. In Sect. 10 a summary is given.

2. The Essential Suppositions

After Deegan [13] and Pettifor [11] the total energy of a crystal may be written:

$$E_{\text{total}} = E_{\text{bs}} + E_r$$

E_{bs} is the band structure energy, which is the sum of the energy of the occupied one particle states. E_r contains the energy contributions of the electrostatic energy minus the self energy of the valence electrons, the contribution of the ion cores and the exchange and correlation effects. After Harrison [5] and Heine and Weaire [6] for the NFE-metals, and Deegan [13] and Pettifor [11] for the transition metals, it can be assumed that for the highly symmetric metal lattices the band structure energy E_{bs} determines to a very good approximation the energy difference between the lattices. For two metal lattices A and B this means:

$$E^{AB} = E^{A}_{\text{total}} - E^{B}_{\text{total}} \approx E^{A}_{\text{bs}} - E^{B}_{\text{bs}} = E^{AB}_{\text{bs}}$$

The metal lattices are the body centered cubic (bcc), the hexagonal close packed (hcp) and the face centered cubic (fcc) lattice. Their band structure energies are calculated and compared at constant atomic volume. Applying pseudopotential theory for NFE metals this can be done by perturbation theory of second order [5, 6]. Only those members of the reciprocal lattice sum are of importance, which have a distance $\bar{K}$ smaller or equal to the six second-nearest neighbours of bcc.

$$E^{A}_{\text{bs}} \approx \sum_{K^A \leqslant \bar{K}} KN^A(K^A)\mathrm{X}(K^A/2k_F)(V^A(K^A))^2$$

K^A is the length of a vector of the reciprocal lattice. KN^A is the number of equivalent reciprocal lattice neighbours and $V^A(K^A)$ are the associated Fourier components of the pseudopotential. The pseudopotential consists of the crystal potential, and the repulsion potential which is caused by the overlap of the atomic valence orbitals and the core orbitals of neighbouring atoms. The effect of the repulsion potential is to push the charge density out of the core region (e.g. [6]). $X(K^A/2k_F)$ is the perturbation characteristic:

$$X(K^A/2k_F) \equiv \sum_{\mathfrak{k}}^{\mathfrak{k}_F} \frac{1}{\mathfrak{k}^2-(\mathfrak{k}+\mathfrak{K}^A)^2}$$

After Heine and Weaire [6] all the low lying Fourier components of the pseudopotentials of the light NFE-metals are constant to a very good approximation. Therefore one can put

$$V^A(K^A)=V^B(K^B),\ K^A \approx K^B$$

Using this approximation the lattice stability which is given by the sign of $\Delta E_{\mathrm{bs}}^{AB}$, is independent of the specific light NFE-metal and depends only on the valence electron concentration (VEC) [6].

After Deegan and Pettifor [13, 11] the same statement holds for the transition metals. By the angular momentum part of the potential, the d states are strongly localized in the inner part of the atom. (For an explanation see the book of Ziman [17].) Only the weakly bound, unscreened parts of the d band eigenfunctions reach into the flat portion of the potential between the atoms. The situation for the d electrons is similar to that of the pseudo-eigenfunctions: changing from one lattice to another only the change of this flat region of the potential plays an important role. Variations of the Fourier components of the potential corresponding to longest wavelength are most important. The part of the d states which are localized in the inner region of the atoms can be treated as virtual states [18] which are in resonance with the delocalized states. This resonance is determined by the resonance energy ε_d and the resonance width Γ_d. These two parameters appear in Pettifor's calculations [10] only in form of the ratio γ_d

$$\gamma_d \equiv \frac{\Gamma_d}{K_d j_2^2(K_d r_i)},\ K_d \equiv \sqrt{|\varepsilon_d|}$$

which is constant for all transition elements (r_i is the radius of the muffin-tin sphere).

As these considerations show, the core region of the atoms is in effect independent of the lattice. For the s-p bands of NFE and transition metals this is a natural consequence of the pseudopotentials. Because the atomic d orbitals are more localized than the s and p orbitals the changes of the core parts of the d band states are smaller than those of the s and p band states. The resonance energy ε_d depends essentially on the inner parts of the atomic potential, while the resonance width Γ_d depends more on the portion of the potential in the region beyond the core. The quantity γ_d combines these two parameters ε_d and Γ_d and is found to be independent of the lattice. By similar arguments, it can be shown that the mean value of the potential is lattice independent.

$$\bar{\bar{V}}=\frac{1}{\Omega_0}\int_{\Omega_0} V(\mathrm{r})\,d\tau$$

Ω_0 is the volume of the unit cell. For the NFE-metals $\bar{\bar{V}}$ is the term corresponding to first order perturbation theory which does not enter $\Delta E_{\mathrm{bs}}^{AB}$.

3. Lattice Stability and Potential Differences

The Virial theorem gives us a convenient connection between the total energy E and the total mean potential energy $\overline{V}$ (Slater [20])

$$E=\tfrac{1}{2}\overline{V}-\tfrac{3}{2}p\Omega_0$$

Ω_0 is the volume of the unit cell. We assume that this equation holds for all lattices. The rearrangement of the atoms going from one lattice to the other can only happen by performing disordered structures. Because we observe almost only the crystalline state for metals we can assume that the lattices have a lower energy than any disordered structure. Therefore all outer forces [20] vanish besides that one caused by the pressure p, and we are left with the above equation.

As was pointed out in the foregoing section we have to compare different structures for equal atomic volume and vanishing differences in the energy contributions E_r. Therefore we obtain for the differences in the bandstructure energy and the potential bandstructure energy of two lattices A and B:

$$\Delta E_{\mathrm{bs}}^{AB}=\tfrac{1}{2}\Delta\overline{V}_{\mathrm{bs}}^{AB}$$

This equation gives us the possibility to discuss the lattice stability by the potential differences of the lattices. We may use it in two ways:

a) We change the valence electron concentration (VEC) by going from one metal to another, for example in the row sodium, magnesium, aluminium. Here we cannot vary VEC continuously.
b) We change the VEC for one and the same metal. There arise especially electrostatic forces which change E_r. But because they vanish in the neutral case we neglect them here too for reasons of consistency. Besides this reason we may ignore electrostatic forces because we are only interested in the dependence of $\Delta E_{\mathrm{bs}}^{AB}$ on $\Delta\overline{V}_{\mathrm{bs}}^{AB}$ which is for the electrical neutral case only important.

Because of the independence of the shape of the bands from VEC (Sect. 2) both ways *a* and *b* lead to the same conclusion concerning the dependence of the lattice stability on the VEC.

We are treating the metallic bond in a completely general way. Therefore we cannot consider the effects of special types of the atomic potentials $V_0(\mathrm{r})$ on the lattice potential $V(\mathrm{r})$

$$V(\mathrm{r})=\sum_j V_0(\mathrm{r}-\mathrm{j})$$

and the bandstructure energy. j is a lattice vector. For an appropriately chosen $V_0(\mathrm{r})$ one may always have any lattice most stable for any VEC. This is because the reciprocal lattice vectors are always different or at least they can be chosen to differ infinitesimally. Thus the Fourier components of $V_0(\mathrm{r})$ and of the lattice potential can be completely arbitrary.

In our general treatment we discuss the lattice stability only so far as it is determined by the potential differences caused by the different packing of the lattices.

It is not selfevident that the virial theorem holds for a one particle potential.

Generally it holds only for the case of a many-particle potential, for example a self consistent Hartree-Fock potential. But we may stay with a one particle picture because we can always assume that our one-particle potential is adapted to the many-particle potential. This is possible, at least in principle, by determining the coefficients v_m of an Ansatz for the atomic potential $V_0(\mathfrak{r})$

$$V_0(\mathfrak{r}) = \sum_{m=1}^{\bar{m}} v_m g_m(\mathfrak{r})$$

with localized and spherically symmetric orbitals $g_m(\mathfrak{r})$ so that we obtain for a certain VEC the same energies and potential energies for the three metal lattices as in the many particle picture. The accuracy of this adaptation is only a question of the number $\bar{m}$ of the coefficients in the Ansatz for $V_0(\mathfrak{r})$.

The lattice potentials $V(\mathfrak{r})$ represented by a superposition of atomic potentials $V_0(\mathfrak{r})$ as shown above are called overlap atomic potentials (OAP). We notice that their mean values $\bar{\bar{V}}$ are lattice independent:

$$\bar{\bar{V}} \equiv \frac{1}{N}\int_\Omega V(\mathfrak{r})d\mathfrak{r} = \frac{1}{N}\sum_j \int_\Omega V_0(\mathfrak{r}-\mathfrak{j})d\mathfrak{r} = \int_\Omega V_0(\mathfrak{r})d\mathfrak{r}$$

4. The Valence Function Space (VFS)

If the structure of a compound changes, only a few atomic-like and appropriately chosen orbitals or hybrids are necessary to build up the occupied eigenfunctions of any crystal by Bloch sums (e.g. [4, 18]). This is explicitly shown by the tight-binding calculations for lithium of Lafon, Lin, Chaney, and Tung [19, 20]. For simplicity we may imagine that the occupied states together with a sufficiently large number of conduction states play the role of a closed function space with a lattice-independent energy center of gravity ($\bar{\bar{E}}$). But because this independence of the energy center is not exactly fulfilled in the real case, it is necessary to consider the upper part of our function space as a buffer zone which only provides the lattice dependent changes of $\bar{\bar{E}}$. The whole function space will be called valence function space (VFS) and the part of it below the buffer zone will be called the occupation part. The buffer zone prevents the lattice dependent energy changes of the occupation part to be influenced by the changes of the states above VFS.

This model should be especially appropriate for metals because the effective changes of their potentials are small and therefore the buffer zone must be small too. In the case of free electrons as well as in the tight-binding limit the buffer zone vanishes. A very nice example for a VFS is the *d* band without *s*-*p* hybridization given by Pettifor [11].

5. Lattice Stability and Changes of the Density of States

According to Sect. 2 the lattice stability depends only on the valence electron concentration (VEC). Now let us assume that for small VEC(z_A) lattice A is stable while for a large value of VEC(z_B) the lattice B is more stable. Which differences in the densities of states of A and B could account for the stability within our model? First, for small VEC, A must have more states with lower energy than B.

These are the states I in Fig. 1. Second, to make *B* more stable than *A*, in the notion of Figs. 1 and 2 the states II of *A* must be elevated enough in energy. Would this happen only on account of the energy decrease of the states I of *A*, *B* could never become more stable than *A*; it could only reach an equal stability. The states II of *A* must be elevated on account of the states III which therefore must be decreased. Generally this means: to invert the lattice stability, the states in a certain region must be elevated on account of the deeper states as well as the higher states.

We subdivide the density of states into groups of states so that the energy movement of each group changes (under a lattice change) its direction going from one group to the next. If it would be impossible to find more than two groups (the energy change of which are opposite), in the higher of these groups an infinite number of states would see the same direction of potential changes – in spite of the fact that the arrangement of atoms changes completely with the lattice. Therefore we have more than two such groups. And groups far apart do not interact as it was already discussed in the foregoing section. This means that the three lowest of these groups display the stability mechanism shown in Figs. 1 and 2, and that we have always to expect a lattice stability change when VEC varies sufficiently. For all valence electron concentrations possible for NFE respectively transition metals we could find one and only one lattice stable if all the Fermi energies would fall in one and the same group. But this would mean that this group would be extremely large.

As has been shown in Sects. 3 and 4 the change in the density of states is caused by the change in the potential energy. What does this mean for the lattice potentials?

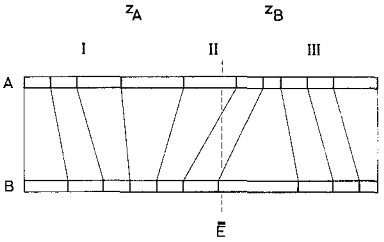

Fig. 1. Two typical density of states distributions (schematic) of two crystals *A* and *B* for which the stability changes with increasing VEC from left to right

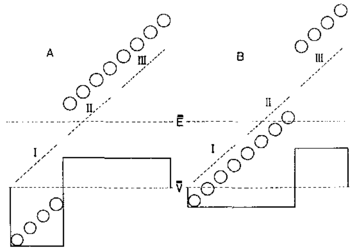

Fig. 2. Schematic representation of the potentials of the crystals *A* and *B* and their effect on the electronic states indicated by circles. These potentials are produced by the different arrangements of the atoms in the two crystals

Because the low energy states of A lie deeper than those of B, A has deeper potential valleys than B. This must be so because it is impossible to have the deeper potential energy for a charge density localized in regions of higher potentials. Imagine two overlap atomic potentials (OAPs, Sect. 3). Although the mean value $\bar{\bar{V}}$ of the potentials remains constant (Sects. 2 and 3) the different arrangements of the atomic potentials $V_0(\mathrm{r})$ cause larger potential differences in A than in B. In A there are regions in which two or more atomic potentials approach each other more than it happens in B. As the atomic volume is constant, in A there must be other regions in which fewer atomic potentials participate than in B. We may say in short that A is more sperry than B. A compared to B has regions of smaller extent with effectively deeper potential valleys and others of broader extent which have the effect of higher potential mountains. As illustrated in Fig. 2, these potentials cause for the energy of the states I, II, and III, which are represented schematically by circles, the same movement as in Fig. 1. For example, the lattice stability changes in Fig. 2 from A to B at the occupation of eight states.

If for any valence electron concentration the less sperry lattice is stable, there exists a smaller VEC where the more sperry lattice is stable. Therefore we have to expect that the stability sequence of the metal lattices, as far as it depends on the packing of the lattices, is that of decreasing sperryness with increasing valence electron concentration.

6. The Model of the Lattice Stability

In order to study the relative stability of bcc, hcp, and fcc let us consider their space filling. If one goes from bcc to fcc or hcp the coordination number of the nearest neighbours changes. However, for hcp and fcc the first difference occurs in distance and coordination number of the third nearest neighbours. Therefore there is a significant difference between bcc and both hcp and fcc, but only a small difference between hcp and fcc. bcc has the smaller coordination number and smaller distances to nearest neighbours. It is more sperry and plays the roll of the lattice A of Figs. 1 and 2 compared with hcp and fcc. For example for bcc and fcc overlap atomic potentials have been calculated using Gaussian orbitals as $V_0(\mathrm{r})$. Compared to fcc, bcc had always the deeper potential value $V(\mathrm{r})$. Therefore we expect bcc to be stable for small values of VEC and the dense packed lattices (hcp, fcc) for high values of VEC.

Perpendicular to the hexagonal plane hcp and fcc have trigonal channels. In hcp they are empty or twice as full as in fcc. Therefore hcp is more sperry and plays the role of lattice A and fcc that of B. With increasing VEC the sequence of stability is hcp-fcc. In terms of the potential, hcp is a compromise between bcc and fcc. Therefore if there are changes in the lattice stability at all, the general stability sequence is bcc-hcp-fcc for increasing valence electron concentration. The reason why this sequence is not only bcc-fcc is that because of the decreasing sperryness of the three lattices the VEC, for which fcc is more stable than bcc, is larger than the one for hcp. Thus there exists a VEC range between that of bcc and fcc for which we expect hcp to be stable.

Now we estimate the division of VFS into the ranges for which one of the three

Table 1

	Stability Range in Parts of VFS
bcc	2
hcp	1
fcc	1
Buffer zone	1

lattices is most stable. The lower bound of VFS is the lowest valence state. The upper bound is taken from the light NFE metals for which the metallic state is possible up to three electrons per atom. For four electrons, the light elements have covalent bonds. Therefore their buffer zone of VFS cannot be greater than one electron per atom. Consequently for NFE metals the maximum VFS has the upper limit of four electrons per atom. For the transition metals ten *d* electrons per atom have to be added and VFS consists of fourteen electrons per atom.

Because the lattice difference between bcc and the densely packed lattices is much stronger than that between hcp and fcc the stability range of bcc is larger than that of one of the densely packed lattices. The stability range of the densely packed lattices we may divide into two almost equal parts, the first for hcp and the second for fcc. The buffer zone of VFS (Sect. 4) only needs to interact with the upper region of the occupation part and should not be larger than the stability range of hcp or fcc. According to these arguments we choose simple numbers to divide VFS as given in Table 1. In the following two chapters these numbers are tested for NFE and transition metals.

7. Stability of the Light NFE Metals

For the NFE metals the total VFS corresponds to four electrons per atom. The parts of VFS as mentioned above lead to the following stability limits:

Table 2

VEC	0.0		1.6		2.4		3.2		4.0
Lattice		bcc		hcp		fcc			
Metal		(Li) (Na)		Be Mg		Al			

Although lithium and sodium have hcp structure at room temperature, they show a phase transition to bcc at 36°K and 78°K respectively.

Heine and Weaire [6] replaced the perturbation characteristic X by a jump-function and got the following sequence of stability:

Table 3

VEC	1.0	1.5	2.0	3.0
Lattice	hcp	bcc	hcp	fcc

Except for the occurrence of hcp at VEC 1.0, this is the same sequence of stability as above.

Blandin [7] compared the stability of hcp with that of fcc without any assumption on the perturbation characteristic and obtained the following lattice sequence:

Table 4

VEC	1.0	1.5	2.0	3.0
Lattice	hcp	(fcc)	hcp	fcc

For VEC two and three this is also consistent with our results. The stability of hcp at VEC one, will be discussed in Sect. 9.

8. The Stability of Transition Metals

For the transition metals VFS corresponds to fourteen electrons per atom. The stability limits are:

Table 5

VEC	0.0		5.6		8.4		11.2
Lattice Group of PSE		bcc (Sc) (Ti) V		hcp (Cr) Mn Fe		fcc Co (Ni) (Cu)	

The chromium group has bcc. The simple choice of dividing VFS cannot account for this stability. In the scandium- and titanium group hcp dominates. This will be discussed in Sect. 9. However, it should be mentioned that the high temperature form in the titanium group is bcc. Nickel and copper have fcc as predicted. But Pettifor's calculations have shown that this is rather due to the hard-core effect [11] than to the band structure energy which gives bcc instead of fcc. Here nothing can be said about the zinc group and the metals below the scandium group. For these groups the lattice stability is not determined only by the degree of occupation of the density of states by electrons. If this is the case we are leaving the suppositions of Sect. 2.

9. The Deviations from the Model

The deviations from the predicted lattice stability are understandable as consequences of the simple suppositions of the model. Especially the following points have not been taken into account:

1) Peculiarities of special lattices (as e.g. lattice symmetry).
2) The lattice dependence of the potentials.
3) The different symmetries of the atomic orbitals.

9.1. Peculiarities of Special Lattices

In fcc and bcc there are respectively twelve and eight nearest neighbours which are connected by symmetry operations of the point group of the crystal.

This is not the case for the next nearest neighbours of hcp which is the consequence of the much lower symmetry of D_{3h} compared with O_h. If the neighbours were equivalent it would not be possible that there is, in the reciprocal lattice, a splitting in three different sets of neighbours the distances of which have only little differences. For hcp it happens that the smallest nearest neighbour distance of the reciprocal lattice is shorter ($2\sqrt{2/3}$) than that of bcc ($\sqrt{2}\cdot\sqrt[3]{2}$) and fcc ($\sqrt{3}$).

With increasing energy the deviation of the *s*-*p* bands from free particle bands increases. In the same direction the localization of the *d* states in the atomic region increases. In both cases the contributions of the higher Fourier components grow. For the deepest states the contribution of the lowest Fourier components dominates. If only the states lowest in energy are occupied these long-wavelength Fourier components favour hcp in comparison to the cubic lattices. After Heine and Weaire [6] actually the shortest Fourier component of hcp is responsible for the stability of this lattice at VEC equal one. For the transition metals a similar situation is found, especially for the scandium group which has hcp again.

9.2. *The Lattice Dependence of the Potentials*

The distances 1.782 (bcc), 1.848 (hcp), 2.000 (fcc) are the largest possible ones of those lattice vectors which play an essential role for the band structure energy of the NFE metals. They increase in the row bcc, hcp, fcc. If the Fourier components to these K vectors do no longer fall in the flat part of the Fourier transform of the pseudopotential $V(K)$ but in the negative and increasing part, the stability of the lattices decreases in the above sequence. This is the case for the row caesium, barium, thallium and lead. Caesium, barium and thallium above 330°C have bcc. Thallium in the low temperature form has hcp. Lead has fcc. If the atomic weight increases, the first zero of $V(K)$ runs through the low reciprocal lattice vectors to larger K. Compared with the light NFE-metals the heavy NFE-metals need a higher VEC to make hcp or fcc stable. With increasing atomic weight the repulsion potential decreases. The eigenstates are increasingly localized in the inner part of the atoms. Potential changes in the outer region of the atoms influence higher states in VFS.

9.3. *The Different Symmetries of the Atomic Orbitals*

After Pettifor [11] in the scandium group fcc (and hcp) is favoured versus bcc, and bcc versus the dense packed lattices in the nickel and copper group. This is partly the consequence of the well-known fact that the density-of-states function of bcc consists essentially of two peaks with a deep valley between them. There can be no doubt that this will be favoured by the considerably higher degeneracy of eigenstates for bcc in the points H and P of the Brillouin zone compared with the points X and L in fcc. This degeneracy allows only for small distances between the branches of the bands. Such a strong effect is not possible for states with predominant s or p character.

10. Summary

Starting from a consideration of the work done by Asdente and Friedel [3], Harrison [5], Heine and Weaire [6], Blandin [7], Pettifor [11], Deegan [13] and Lafon, Lin, Chaney and Tung [19, 20] the following statements concerning the metallic bond and the lattice stability can be made:

The energies of different structures have to be compared at the same atomic volume. The energy difference can be approximated by the band structure energy. The lattice stability depends only on the valence electron concentration VEC. The core region of the atoms and the mean values ($\bar{V}$) of the potential are lattice independent.

Using the virial theorem the lattice stability can be connected with the difference in the potential band structure energy. There may be two kinds of potential differences:

One depends on the particular shape of the atomic potential and is characteristic for a special metal. We are not concerned with it. The other is caused by the difference in the packing of the lattices. This allows a general discussion of the lattice stability of NFE- and transition metals. It does not depend on interaction between nearest neighbours only or on the use of directed orbitals.

Especially for metals one can do as if there were a closed valence function space VFS with a lattice independent energy center of gravity. To change the lattice stability with increasing VEC the energy of states in a certain region of the density of states distribution has to be elevated on account of the energy of lower and higher states.

The energy change can be explained by two potentials with different regions of low and high values but equal mean values. The smaller and deeper the regions of low potential in a lattice are, the higher and wider are the regions of high potential.

The connection of the metal lattices and the two potential types is found by consideration of the differences in the packing of these lattices. A more sperry lattice has smaller atomic distances with deeper potential mountains. If for any VEC a less sperry lattice is stable there exists a smaller VEC for which the more sperry lattice is more stable. Therefore, if there are lattice changes at all, the sequence of stability should be bcc, hcp, fcc for increasing VEC.

The model holds for NFE-metals as well as for transition metals. The region of VEC in which one of these lattices is favoured can be expressed by simple numbers. This is proved for NFE and *d* metals.

Deviations of the model from the observed lattice stabilities can be shown to be the consequence of the simple suppositions of the model. Important are the peculiarities of the lattices such as the lattice symmetry, the lattice dependence of the potential and the differences of the atomic orbitals.

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