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Theory of the crystal structures of transition metals

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MS. received 27th August 1969

Abstract. The structure trend that is observed across the transition metal series as the number of valence electrons N increases from 3 to 11 is explained quantitatively. The difference in the total one-electron band structure energy between the close-packed structures face-centred cubic and hexagonal close-packed is shown to determine completely which structure is favoured, whereas an additional hard-core repulsive contribution is necessary when comparing the body-centred cubic and close-packed structures at the noble metal end of the series. The calculations were performed assuming a model transition metal characterized by only the two d-resonance parameters ϵ_d and Γ , from which the densities of states for the three structures were obtained using energy levels calculated by the hybrid nearly-free-electron tight-binding scheme of Pettifor. The present results indicate that it should be possible to calculate accurately other properties of the transition metals using this simple two-parameter model.

1. Introduction

All three periods of the transition metal series show the same very definite structure trend as the d-shell is progressively filled with electrons, as is clearly illustrated in table 1. This trend has been *qualitatively* explained using a number of different models—for example Brewer (1967) has taken the chemists' viewpoint of the importance of Engel correlations between the electrons in a valence bond, Kaufman (1967) has worked with a semi-empirical thermodynamic approach, and Beeby (1966) has assumed that the main contribution arose from an interaction energy between anti-parallel spin electrons. However, in the present paper we shall extend the *quantitative* work of Deegan (1968) and Dalton and Deegan (1969) who showed that the differences in the total one-electron band structure energy could successfully account for the occurrence of the body-centred cubic structure in the region of $N = 5$ and 6, where N is the number of d- and outer s-electrons per atom. Our present numerical calculations show that the entire structure trend between body-centred cubic, face-centred cubic and hexagonal close-packed can be explained correctly using this one-electron band structure approach, provided some hard-core contribution is also included when comparing body-centred cubic with the close-packed structures towards the noble metal end of the series.

In § 2 we write the total energy of a transition metal as the sum of three terms, namely a one-electron band structure contribution, an electrostatic contribution, and an exchange and correlation term that includes all those many body effects not included implicitly in the band-structure energy. We shall assume that the third term is of secondary importance when dealing with non-magnetic systems—an assumption certainly justified by the results of our present calculations (see for example figure 4). The electrostatic contribution will be shown to be very weakly structure dependent and has therefore been neglected. We are, therefore, left with the first term, which we write in two parts, firstly that part which gives the absolute energy of the mean position of the d-band and secondly that part which gives the band structure energy relative to this mean position. The first part will be shown to include all the energy difference between b.c.c. and the close-packed structures that arises from hard-core effects. The second part is obtained from the sum of the one-electron energy levels, which are calculated using the hybrid nearly-free electron tight-binding (H-NFE-TB)

model Hamiltonian discussed in Pettifor (1969). Both the tight-binding overlap parameters and the hybridization matrix element can be expressed analytically in terms of the two parameters ϵ_d and Γ , defining the resonance scattering of the $l = 2$ component of a plane wave from the atomic potential in the crystal. Γ is the width of this resonance when ϵ_d is measured relative to the bottom of the conduction band. We shall show that ϵ_d and Γ taken together are good constant parameters for calculating the band-structure energy under changes of volume or structure.

The structure trend shown in table 1 is observed in all three periods of the transition metals, even though the d-band width may vary by as much as a factor of two or three between the first and third period. We believe, therefore, that this trend is not due to some specific set of atomic scattering phase shifts, but can be reproduced using any arbitrary set of resonance parameters ϵ_d and Γ , ignoring all pseudopotential contributions as being of secondary importance. We have, therefore, chosen *model* resonance parameters $\epsilon_d = 0.5$ ryd (a value typical for the first period) and $\Gamma = 0.03$ ryd (a width slightly larger than that for nickel) unlike Dalton and Deegan (1969) who performed their f.c.c. and b.c.c. calculations using the complete set of $l = 0, 1$ and 2 phase shifts obtained from the muffin tin potential for iron. In § 3 we calculate the densities of states for the three structures f.c.c., b.c.c. and h.c.p. using this simple two-parameter scheme. Our results for $N \geq 3$ show all the structure and shape that previous more complicated densities of states calculations have observed. The differences in band-structure energies between the three structures, obtained from these densities of states, is drawn in figure 2 as a function of the number of valence electrons N . The h.c.p. against f.c.c. trend is determined primarily by this band-structure term alone, whereas the b.c.c. against f.c.c. trend requires an additional hard-core contribution, which we have semi-empirically calculated for the noble metal end of the series.

In § 4 we conclude.

2. The total energy of the crystal

As the d-electrons are of primary importance in determining the cohesive energy of a transition metal (see for example Friedel 1969, p. 361), it is sensible to write the total energy per atom (containing N d- and outer s-electrons) as follows

$$E_{\text{total}} = N\epsilon_d^{\text{abs}} + E_{\text{bs}} + E_{\text{es}} + E_{\text{core}} + E_{\text{xc}}. \quad (1)$$

We shall consider these terms individually.

ϵ_d^{abs} is the absolute position of the d-electron resonance level. This energy is very sensitive to the form of the crystal potential used in the band-structure calculations, even when they are carried through self-consistently (see for example Snow 1968, table 2). We know, however, that it cannot lie far from the atomic d-level, for otherwise the cohesive energies would be much larger than are observed experimentally. For example the noble metals cannot have their mean d-level lying more than about 0.03 ryd below their free atomic level. We shall see later that the *differences* in the hard-core effects between b.c.c. and f.c.c. are included in this term alone.

E_{bs} is the total one-electron band-structure energy measured relative to ϵ_d^{abs} and is obtained from summing over all the occupied energy levels. We shall calculate these values using the hybrid nearly-free-electron tight-binding scheme proposed in Pettifor (1969).

E_{es} is the electrostatic potential energy of the ion lattice from which is subtracted the self-energy of the d- and outer s-electrons (E_{bs} has counted this latter term twice). However, since in the present paper we are interested solely in the differences in structural energy, we shall neglect E_{es} because it is only very weakly structure dependent for such symmetrical structures at the same atomic volume. For example if we set up the crystal charge-density using Mattheiss' (1964) model of simply bringing together free atoms, then we have estimated that the maximum difference in electrostatic energy between f.c.c. and b.c.c. is less than 0.001 ryd/atom for the value of the resonance width Γ used in our present calculation.

E_{core} is the contribution of the ion core to the total energy. The only part of this term which might be noticeably structure dependent would be the hard-core repulsion between the filled s^2p^6 shells. Yet, even if we take b.c.c. tungsten which has the largest repulsive energy of all the transition metals, the difference in this energy between b.c.c. and f.c.c. amounts to only 0.0003 ryd/atom. Therefore, it is a very good approximation to neglect the structure dependence of this term.

E_{xc} contains all the exchange and correlation effects not included implicitly in the resonance parameters ϵ_d^{abs} and Γ . It is our hope that when dealing with non-magnetic transition metals, this term will be of secondary importance only (provided we are working at approximately constant atomic volume), as is true for non-transition metals (Heine and Weaire 1970, to be published). Our present results on the structural trend seem to indicate that this is indeed the case.

From the above discussion, therefore, we see that it is a very good approximation to write the difference in energies between any two structures at the same atomic volume at absolute zero as follows:

$$\Delta E(N) = N\Delta\epsilon_d^{\text{abs}} + \Delta E_{\text{bs}}(N). \quad (2)$$

Let us first consider $\Delta E_{\text{bs}}(N)$. We have chosen the band-structure energy to be measured relative to the resonance level ϵ_d^{abs} so that its value will be determined primarily by the tight-binding overlap parameters and by the hybridization matrix element (see for example Pettifor 1969, equations (26), (13), and (45)), all of which depend on the resonance parameters Γ and ϵ_d through the ratio $\Gamma/\kappa_d \{j_2(\kappa_d r_i)\}^{1/2}$, where κ_d is the square root of the resonance energy ϵ_d measured relative to the bottom of the conduction band, Γ is the corresponding resonance width, and r_i is the muffin tin radius. Now, although the slightly different scattering potential of b.c.c. compared with f.c.c. at the same atomic volume gives rise to a different set of resonance parameters ϵ_d and Γ , they are nevertheless such that the above ratio remains constant to a high degree of accuracy on passing from the one structure to the other. For example Davis *et al.* (1968) have computed the changes in the band structure of copper under compression, during which ϵ_d and Γ taken individually alter appreciably. However, we have fitted the width of their d-band at the centre of the Brillouin zone exactly by an inverse fifth power law of the lattice parameter, which thereby implies from equation (45) of Pettifor (1969) that the above mentioned ratio has remained constant throughout the compression. Therefore, the band structure energy is well described by treating the parameters ϵ_d and Γ , combined together as above, as constants for all three structures f.c.c., h.c.p. and b.c.c.

The shift in the mean position of the bands on change of structure (or volume) is included explicitly in the first term $\Delta\epsilon_d^{\text{abs}}$ of equation (2). We expect ϵ_d^{abs} to differ negligibly between h.c.p. and f.c.c. structures at the same atomic volume, because both have 12 nearest neighbours identically distanced. However, this will not be the case for b.c.c. where there are 8 neighbours closer and 6 further away than the 12 nearest neighbours of the close-packed structures. Yet, although we expect ϵ_d^{abs} to differ for the b.c.c. structure, it is not at present possible to discuss quantitatively how $\Delta\epsilon_d^{\text{abs}}$ (b.c.c.-f.c.c.) changes as we fill up the d-shell with electrons. Nevertheless, much useful insight can be gained by considering the noble metals with their completely full d-shells, where hard-core forces are important to the extent that only close-packed structures are found in nature.

This problem of the interaction between closed shells has been carefully studied for the case of helium (see for example Slater 1963). From the mathematics Dick and Overhauser (1958) have extracted the essential physics of the repulsive interaction and have proposed an exchange charge model in which the diminution of electronic charge midway between the atoms, brought about by the Pauli exclusion principle as the outer shells begin to overlap, is represented by a positive exchange charge. Hafemeister (1969) has applied this simple model to the noble metals and has obtained the radial dependence of the repulsive Born-Mayer potential to within 25% of the value estimated from compressibility, cohesive energy and lattice parameter data. Moreover, he found that the exchange charges were well

localized midway between the atoms and could approximately be replaced by *point* charges.

We are now in a position to answer the question as to how much hard-core repulsion is included in the first-principle Hartree-Fock band-structure calculations. Firstly, because these calculations are equivalent to the molecular-orbital approach which has been shown to work very well for the full-shell 'molecules', we should expect to obtain the correct variation of ϵ_d^{abs} with structure or with volume, provided that the band-structure calculations are performed self-consistently and with no approximations. However, such a calculation is not feasible at present; to reduce the problem to computational manageability, both a spherically averaged muffin-tin potential and a Slater-type exchange potential must be used. But the exchange charge model discussed above has shown that the interaction between the atoms can be simply described in terms of *point* exchange charges lying midway between the atoms. Therefore, although we might expect a large amount of their contribution to be retained for the close-packed structures even when the potential is spherically averaged, we do not expect a simple muffin-tin approximation to be capable of accurately yielding $\Delta\epsilon_d^{\text{abs}}$ (b.c.c.-f.c.c.), where the directional nature of the hard-core forces will be important.

Because of the present impossibility of accurately calculating $\Delta\epsilon_d^{\text{abs}}$ from first principles if a muffin-tin approximation is used, we shall treat the two contributions to the total structural energy difference given by equation (2) independently: ΔE_{bs} will be treated as previously outlined using the parameters ϵ_d and Γ obtained by scattering from a spherical muffin-tin potential, whereas $\Delta\epsilon_d^{\text{abs}}$ will be estimated semi-empirically as follows. Jaswal and Girifalco (1967) have calculated the repulsive potential for copper from the experimentally determined values of the cohesive energy, compressibility, and lattice parameter. However, this potential must be suitably scaled for our model calculation, because the width of the copper resonance is approximately half that which we have used (see for example Burdick's (1963) potential with $\Gamma = 0.015$ ryd). Therefore, the copper lattice needs to be compressed linearly by 15% before the probability of finding a d-electron midway between the atoms is the same as that in our model calculation (c.f. Heine 1967, equation (26)), from which we deduce that the repulsive energy per atom in the f.c.c. lattice is about 0.3 ryd for $\Gamma = 0.03$ ryd. Then, assuming a Lennard-Jones power law variation of the potential with distance, we find the difference in repulsive energy between the b.c.c. and f.c.c. lattices to be about 0.02 ryd/atom, that is

$$\Delta\epsilon_d^{\text{abs}} (\text{b.c.c.-f.c.c.}) \simeq 0.002 \text{ ryd.} \quad (3)$$

This fixes $\Delta\epsilon_d^{\text{abs}}$ at the noble metal end of the transition metal series. Unfortunately, it is not at all clear how we should expect it to change as the number of electrons decreases, because as the shell becomes less full Hartree-Fock molecular orbital theory becomes less capable of accurately describing the energy levels (see for example Slater 1963, p. 112). However, as the repulsive potential in the exchange charge model is proportional to the number of electrons in each shell (see Hafemeister 1969, equation (25)), we shall in the present paper simply assume a linear dependence on the number of electrons N and shall assume that equation (3) describes the difference in the mean position of the d- bands between b.c.c. and the close-packed structures sufficiently accurately for all values of N . It should be possible to make the two separate contributions to the total structural energy difference given by equation (2) self-consistent, since we should be able to express the exchange charges in terms of our resonance parameter Γ . We are investigating this problem at present.

3. Results and discussion

The structure trend shown in table 1 should be capable of being reproduced using any arbitrary set of resonance parameters ϵ_d and Γ , because, as mentioned in the introduction, the trend is found in all three periods. We have chosen $\epsilon_d = 0.5$ ryd (a typical value for the first period) and $\Gamma = 0.03$ ryd, the latter being deliberately chosen not too large, as the removal of the energy dependence from our hybrid nearly-free-electron tight-binding

matrix elements (c.f. equations (21) and (26) of Pettifor 1969) requires that the bands be narrow; this value of Γ is slightly larger than that for nickel. The values of the muffin tin and Wigner-Seitz radii have been taken to be those of b.c.c. iron, namely $r_i = 2.341$ A.U. and $r_{ws} = 2.662$ A.U. respectively. The same values were used for all three structures.

Table 1. The structures of the transition metals

Period	N	3	4	5	6	7	8	9	10	11
3d, 4s		Sc	Ti	V	Cr	(Mn)	(Fe)	Co	Ni	Cu
4d, 5s		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
5d, 6s		(La)	Hf	Ta	W	Re	Os	Ir	Pt	Au
Structure		h.c.p.	h.c.p.	b.c.c.	b.c.c.	h.c.p.	h.c.p.	f.c.c.	f.c.c.	f.c.c.

We shall see later (figure 4) that the differences in energy between f.c.c. and h.c.p. are extremely small, being only about 0.002 ryd/atom, which is an order of magnitude smaller than the differences between f.c.c. and b.c.c. Therefore, in order that the total band-structure energy might converge to an accuracy much better than this, it is necessary to sample over a large number of points in the Brillouin zone, which means that we must be able to evaluate the energy levels (obtained by diagonalizing the model Hamiltonian matrix) as rapidly as possible. Because the size of the d-block is fixed, we must therefore choose as few a number of reciprocal lattice vectors in the conduction block as is feasible. By keeping only first nearest neighbours in k -space for the f.c.c. structure, we obtain a 4×4 conduction block which describes the nearly-free-electron energy levels accurately up to about 1.70 ryd (for the value of r_{ws} mentioned above). By looking at the nearly-free-electron energy levels for b.c.c. and h.c.p. (see Slater 1965, pp. 254 and 263), we see that an equivalent set of reciprocal lattice vectors to that of f.c.c. can be achieved by having a 7×7 block for b.c.c. (accurate up to 2.02 ryd) and an 11×11 block for h.c.p. (accurate up to 1.86 ryd). Since the d-block size is determined by the number of atoms in the unit cell (5×5 for f.c.c. and b.c.c., 10×10 for h.c.p.), the order of the model Hamiltonian matrix to be diagonalized is, therefore, 9 for f.c.c., 12 for b.c.c. and 21 for h.c.p. The h.c.p. matrix is complicated further by Hermiticity, a property which cannot be transformed away by suitable choice of the basis vectors because the H-NFE-TB model Hamiltonian is in a mixed k - and R -space representation. (It is not difficult to carry over our hybrid H-NFE-TB scheme to structures containing more than 1 atom per unit cell with the aid of a paper by Segall 1957.)

The size of the conduction block now determines what value of the splitting parameter, β , must be chosen in order to obtain energy levels that are accurate to better than 0.001 ryd (within the approximations of our scheme; these inherent approximations, such as the removal of the energy dependence from the matrix elements, will be discussed later). From table 2 of Pettifor (1969) we see that all degeneracy splitting will be removed if we choose $\beta = 0.5$ for the value of $\Gamma = 0.03$ ryd. With this value of the splitting parameter, we require up to third nearest neighbours for f.c.c. (which, thereby, includes 42 neighbouring atoms), up to fourth nearest neighbours for b.c.c. (50 atoms), and up to fourth nearest neighbours for h.c.p. (38 atoms). We have taken h.c.p. to have the ideal axial ratio. The values of the overlap parameters for all these neighbours were calculated using equation (45) of Pettifor (1969). With the H-NFE-TB model Hamiltonian optimized as mentioned above, we can now proceed to calculate the energy levels and hence the densities of states for these three different structures f.c.c., b.c.c., and h.c.p.

Figure 1 shows the computed densities of states for f.c.c., b.c.c., and h.c.p. corresponding to $\epsilon_d = 0.5$ and $\Gamma = 0.03$ ryd. They were calculated using for the f.c.c. structure 916 k -points in $1/48$ of the Brillouin zone (32 032 points altogether in the complete zone), for b.c.c. 819 k -points (27 586 points altogether), and for h.c.p. 585 k -points in $1/24$ of the Brillouin zone (10 704 points altogether, but there are twice as many eigenvalues at each k -point than for either f.c.c. or b.c.c.). Such a large number of points was demanded if an accuracy to much better than 0.002 ryd/atom was to be achieved. For example, if we consider h.c.p., then

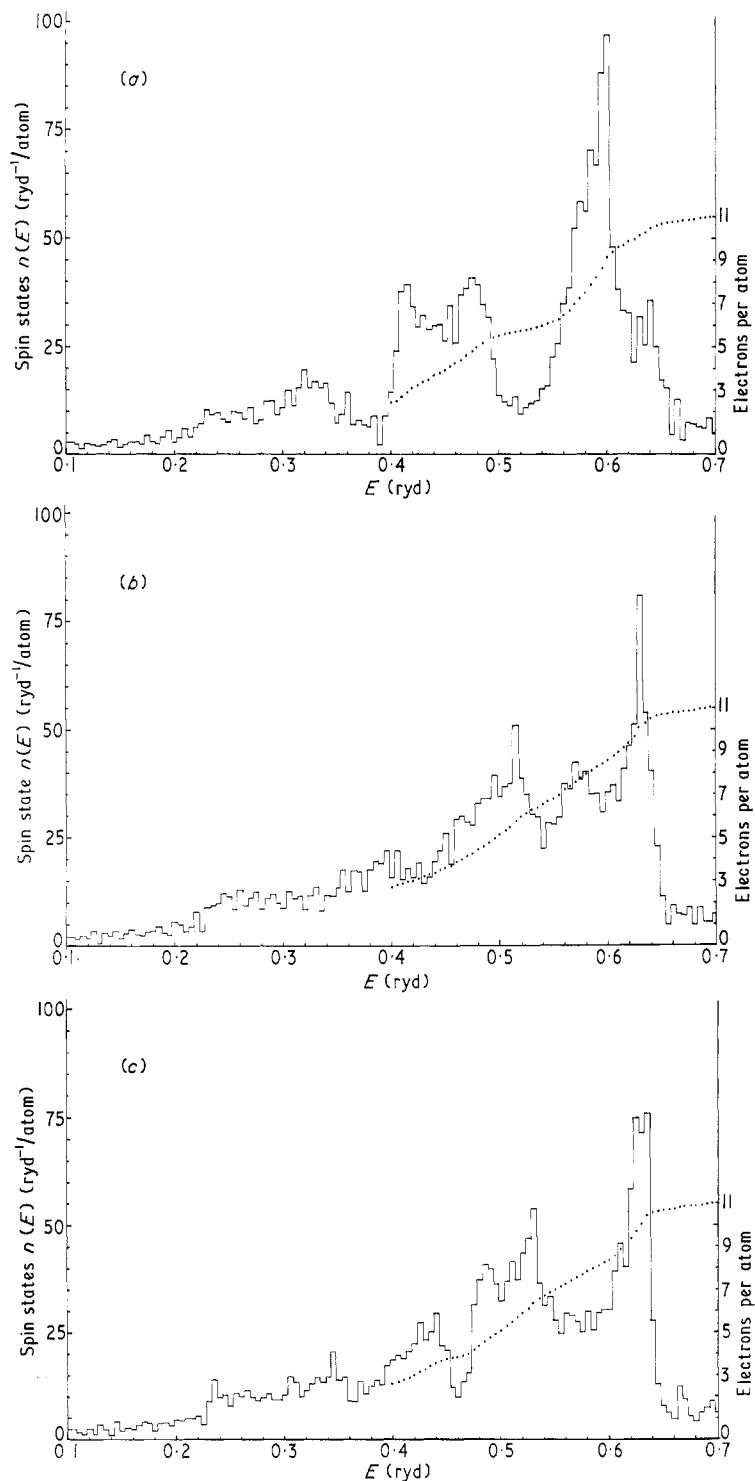


Figure 1. The densities of states for the three structures (a) b.c.c., (b) f.c.c. and (c) h.c.p. calculated using $\epsilon_d = 0.5$ ryd and $\Gamma = 0.03$ ryd. The broken curves represent the integrated density of states.

95 k -points in $1/24$ of the Brillouin zone (1 320 points altogether) gave rise to convergence errors in the total band structure energy of about 0.002 ryd/atom and 0.005 ryd/atom for $N = 1$ and 11 respectively. Therefore, in order to obtain the desired accuracy we halved the mesh size, thereby giving rise to a total of 585 points in the reduced Brillouin zone and good convergence. The other two structures gave rise to similar convergence errors for equivalent numbers of eigenvalues sampled. The width of the histogram channels used in calculating the densities of states was taken to be 0.005 ryd. The total structural energy remained unaltered when this was changed to a value of 0.001 ryd.

These densities of states, computed using only two parameters, show all the structure that previous first-principle or interpolation calculations have obtained. For example, compare our f.c.c. results with figure 7 of Mueller (1967) for copper, our b.c.c. results with figure 1 of Cornwell *et al.* (1968) for iron, and our h.c.p. results with figure 5 of Mattheiss (1966) for rhenium. The good agreement with the copper and iron results is perhaps not surprising, but the very close agreement between our model h.c.p. calculation and rhenium both in the density of states and in the integrated number of electrons is remarkable considering that their band widths differ by a factor of nearly three. This clearly justifies our underlying assumption that the *shape* of the density of states is basically independent of which transition metal is considered. A further interesting observation is that the densities of states for f.c.c. and h.c.p. are practically identical for $N \geq 4$, except that h.c.p. does not possess the f.c.c. peak around $N = 7\frac{1}{2}$, which in fact causes f.c.c. to become favoured over h.c.p. at the larger values of N . The b.c.c. peaks occur at entirely different energy levels.

Unfortunately, the densities of states in figure 1 all show a very marked broadening for $N < 3$, when compared with the other above mentioned calculations. This is to be expected from table 3 of Pettifor (1969), which shows that the lowest levels of the d-band are not given accurately by our H-NFE-TB scheme, essentially because of the removal of the energy dependence from the matrix elements (and in particular from the hybridization block). But although these lowest energy levels affect our total band structure energy and give rise to an appreciable error between f.c.c. and h.c.p. (compare figures 2 and 4; we shall discuss this point in much more detail later), they do not influence our densities of states in the region of greatest physical interest, namely at the Fermi surface. Therefore, since all transition metals have $N \geq 3$, we can confidently use our two parameter curves drawn in

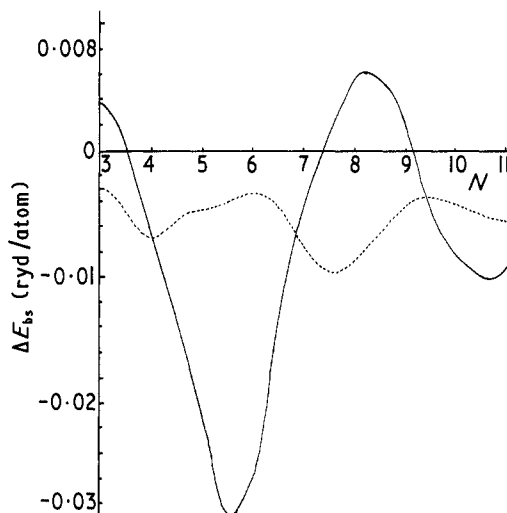


Figure 2. The differences in band structure energy of b.c.c. (full curve) and h.c.p. (broken curve) relative to f.c.c. as a function of the number of valence electrons N , computed from the densities of states in figure 1.

figure 1 when dealing with properties that depend primarily on the behaviour of the density of states about the Fermi level only.

In figure 2 we show the band structure energy difference between b.c.c. and f.c.c. (full curve) and h.c.p. and f.c.c. (broken curve), as computed using the densities of states presented in figure 1. We shall discuss the two cases separately.

3.1. *h.c.p. against f.c.c.*

The shape of the h.c.p.–f.c.c. curve in figure 2 shows very conspicuous minima around $N = 4$ and $N = 7$ and 8, just as we would expect from the structure trend observed in table 1. However, the entire curve lies below the zero line, so that f.c.c. is nowhere favoured. We have already mentioned in § 2 that we do not expect ϵ_d^{abs} to be appreciably different for these two structures and we must, therefore, look for the explanation of this discrepancy elsewhere. We saw in figure 1 that the lowest d-levels were reproduced badly by our H-NFE-TB scheme, basically because of the removal of energy dependence from the hybridization block (compare for example, equations (21) and (26) of Pettifor 1969). We have, therefore, studied the dependence of the total band-structure energy on the energy at which the hybridization block is evaluated. If this block is evaluated at the resonance energy, then $E_{\text{bs}} = 0.924$ ryd ($N = 3$) with respect to the bottom of the conduction band for the f.c.c. structure, whereas it is 0.06 ryd larger when the hybridization is evaluated at the bottom of the d-band.

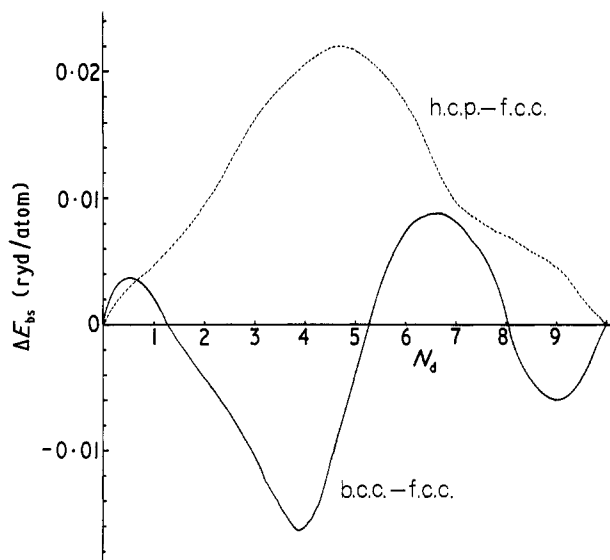


Figure 3. The differences in band-structure energy for pure d-levels, containing no hybridization with the conduction electrons.

We must now consider how we expect this fairly sensitive energy dependence of the hybridization block to influence the *differences* in band structure energy. The hybridization couples states of similar symmetry and therefore we expect b.c.c. and f.c.c., which have high cubic symmetry, to be coupled differently from the less symmetric hexagonal close-packed structure. Figure 3 demonstrates this very clearly. It is a plot of the energy difference between pure d-bands, in which there is no coupling via the hybridization to the conduction block. In this case we have set the splitting parameter $\beta = 1.0$ so that only first nearest neighbours are required for the close-packed structures, and first and second nearest neighbours for b.c.c. (Note that the energy difference between all three structures is zero at $N = 10$, since then the d-bands are full and the total energy must be given mathematically by the mean position of the d-bands.) From figure 3 we see that the b.c.c.–f.c.c. curve has almost exactly

the same shape as that found when the hybridization is included (figure 2), whereas the h.c.p.-f.c.c. curve is large and positive and of an entirely different shape from that drawn in figure 2. Thus the hybridization lowers the energy of h.c.p. much more than it does for f.c.c.

This somewhat surprising result is not altogether unexpected, considering that the h.c.p. lattice with two atoms in the unit cell gives rise to energy levels that are of a distinctly different form from those of the b.c.c. and f.c.c. lattices with only one atom in the unit cell. Along the symmetry axes of the Brillouin zone the b.c.c. and f.c.c. band structures exhibit similar features in that only *one* d-level hybridizes strongly with the nearly-free electron band in the region where they cross, leaving the other four d-levels virtually pure and unmixed; also the five d-states at the centre of the Brillouin zone are unaffected by hybridization. On the other hand, the h.c.p. band structure is quite different, for practically *all* the d-levels in the symmetry directions show strong mixing (for example, half-way along the ΓK -axis only two of the ten d-levels remain pure, the other eight of symmetries T_1 , T_2 and T_4 hybridizing strongly with the nearly-free-electron levels of similar symmetries) and even at the centre of the Brillouin zone there is hybridization, the d-level Γ_4 -mixing strongly with the corresponding nearly-free-electron level. Therefore, although the *difference* in energy between b.c.c. and f.c.c. might be expected not to be determined critically by the exact value of the hybridization, the same will not be true between h.c.p. and f.c.c., where the hybridization affects the two band structures in fundamentally different ways, because of their different crystal symmetries. Thus, the hybridization is very important when comparing these two close-packed structures; it is not a good approximation to ignore the hybridization or to treat it as a small perturbation on the pure d-levels.

The densities of states in figure 1 have been calculated with the hybridization block evaluated at the resonance energy ϵ_d . This leads to the energy levels corresponding to $N < 3$ being given inaccurately, basically because at these low energies the energy-independent hybridization matrix element used in the present calculations (see equations

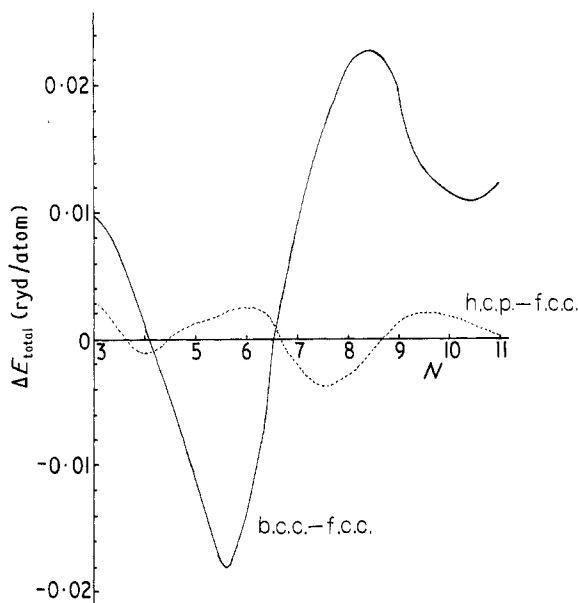


Figure 4. The differences in total energy between the three structures. The h.c.p.-f.c.c. curve was obtained from figure 2, shifted upwards by an amount 0.006 ryd/atom. The b.c.c.-f.c.c. curve was obtained from figure 2 by adding the hard-core contribution of 0.002 ryd/electron. (0.001 ryd/atom = 314 cal/g atom).

(26) and (13) of Pettifor 1969) is quite a bit larger than its energy-dependent counterpart (see equation (21) of Pettifor 1969). But we have seen from figures 2 and 3 that the effect of the hybridization is to favour the h.c.p. structure over f.c.c., and therefore the introduction of too large a value of the hybridization for $N < 3$ will cause the h.c.p.-f.c.c. curve to be pushed down by too much. This is in fact what we observe in figure 2, where the h.c.p.-f.c.c. curve is everywhere negative. If the smaller correct energy-dependent hybridization matrix elements had been used, then this curve would have been higher. We have, therefore, *arbitrarily* raised the energy of h.c.p. with respect to f.c.c. at $N = 3$ by an amount 0.006 ryd. For larger values of N we believe that our densities of states are given sufficiently accurately for no further correction to be made. This adjustment shifts the broken curve in figure 2 bodily upwards by 0.006 ryd to the position given in figure 4. The size of this adjustment is not unexpected, considering that we found as discussed earlier a change of 0.06 ryd in $E_{bs}(N = 3)$ for the f.c.c. structure on altering the energy at which the hybridization block was evaluated. The broken curve in figure 4 predicts correctly the h.c.p. against f.c.c. structure changes, except for $N = 3$. For this small value of N we might have expected the simple two resonance parameter scheme to break down because the Fermi energy lies far away from the resonance. The non-ideal axial ratios of the real h.c.p. transition metals (for example, $c/a = 1.59$ for scandium and titanium as compared with 1.63 for the ideal case) must make h.c.p. even more energetically favourable than is shown in figure 4.

3.2. b.c.c. against f.c.c.

The full curve in figure 2 shows a very marked minimum between $N = 5$ and 6, just as we would have expected from table 1. However, it also predicts the incorrect structure for $N > 9$; Dalton and Deegan (1969) found a similar trend in their calculations on f.c.c. and b.c.c. iron. That this discrepancy resides in the neglect of hard-core terms and not in any inherent approximation in the H-NFE-TB scheme nor in the sampling over the Brillouin zone can be seen from figure 3, where for $N > 8$ b.c.c. is favoured over f.c.c., which is clearly not to be expected for a nearly full pure d-band. In figure 4 we have added the effect of this hard-core interaction to the b.c.c.-f.c.c. curve of figure 2, using the semi-empirical value of $\Delta\epsilon_d^{abs}$ given by equation (3). Figure 4 now predicts the structure trend correctly for all three structures everywhere except at $N = 3$. We must stress, however, that although we expect the b.c.c.-f.c.c. curve to show the deep minimum between $N = 5$ and 6 and to have approximately the correct value at $N = 11$, the exact form it takes in between is uncertain owing to the uncertainty in $\Delta\epsilon_d^{abs}$ at the present time. In addition, the magnitude of our energy differences appears to be about two to three times *larger* than that proposed recently by Kaufman (1967 and private communication), whose results were based on the judicious use of thermodynamic data and observations of phase equilibria in binary systems. It is not clear at present where this discrepancy arises, although perhaps in the neglect of the electrostatic contribution to $\Delta E(N)$.

4. Conclusion

Our calculations have clearly demonstrated that the band-structure contribution to the total energy is the term that primarily determines which structure is energetically favoured at absolute zero. For example, in figure 2 we found very definite minima occurring at $N = 4$ and $N = 7$ and 8 for h.c.p. against f.c.c. and a deep minimum between $N = 5$ and 6 for b.c.c. against f.c.c. We have argued that the h.c.p. against f.c.c. trend is determined solely by this one-electron band-structure term, whereas the b.c.c. against f.c.c. trend requires the contribution of the hard-core effects to be included as well. Many body effects which have not been included implicitly in the resonance parameters ϵ_d^{abs} and Γ are of secondary importance in determining this transition metal structure trend, provided of course that magnetism is not present.

We are hopeful that a lot of the properties of the transition metals can now be calculated simply and accurately by developing and extending the basic ideas underlying this paper. Firstly, the band-structure contribution to the total energy is well described by the two

resonance parameters ϵ_d and Γ , which can be treated accurately as constants (in the sense outlined in § 2) for small volume changes or changes in structure. Secondly, the variation of the mean position of the bands with volume or with structure should be calculable at the noble metal end of the series by using techniques based on the exchange charge model. Our aim is to develop a simple scheme whereby the changes in energy of the system with volume or with structure may be calculated directly without having to resort to lengthy density of states computations at each step.

Acknowledgments

I wish to thank my supervisor, Dr V. Heine, for his help and encouragement during the course of this work. I am grateful to the University of the Witwatersrand and the Ministry of Technology for financial support.

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