Submitted to Acta Metallurgica

LBL-2214
Preprint c.1

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September 1973

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

For Reference

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ON THE RELATIVE ENERGIES OF SIMPLE METALLIC STRUCTURES

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ABSTRACT

The asymptotic form of the two-body interatomic potentials arising from pseudopotential theory, $V(r) = V_o \cos(2k_F r)/(2k_F r)^3$, is used to discuss the relative cohesive energies of simple metallic structures. Use of this potential allows the thermodynamically preferred structure of a simple metallic element or solid solution at 0°K to be determined as a function of valence only. The appropriate lattice sums are performed exactly for the fcc, hcp (with ideal axial ratio) and bcc structures. In addition, the approximate interplanar interaction of Blandin, Friedel and Saada is summed for polytypic structures. Two modifications of the potential are also considered. First, a phase shift of 2δ is used to obtain a potential of the form, $V(r) = V_o \cos(2k_F r+2\delta)/(2k_F r)^3$. Secondly, the interplanar interaction is adjusted to reflect conditions that might hold when polytypic structures other than fcc and hcp occur. Results for the relative energies of the structures are presented. These results are compared with the observed structures of metallic elements and random solid solutions.

I. INTRODUCTION

Despite its central importance in the science of metallurgy, the problem of predicting the preferred structure of a metal alloy remains unsolved. Moreover, the complexity of the problem [1,2] is such that a viable theory of the crystal structure of alloys is unlikely to emerge for some time. In the interim the metallurgist will be forced to make do with a mixture of rough approximations and semi-empirical rules, and the development of approximate techniques in alloy theory will continue to be important.

The pseudopotential theory of simple metals has yielded several models which promise to be useful in the prediction of structure. [1,2] The simplest and most general of these follows from Harrison's [1] development of Cohen's [3] real space formulation of the pseudopotential theory. If a pseudopotential model of a simple metal is developed to second order in perturbation theory, that part of the cohesive energy which depends on the structure may be treated as if the atoms interacted in pairs according to a central, two-body potential. This two-body potential has an asymptotic form which is independent of the precise pseudopotential assumed, and which exhibits the Friedel [4] oscillations. Under suitable assumptions, discussed below, one may make a rough estimate of the relative energies of candidate structures at 0°K by simply summing the energy of two-atom interactions according to the asymptotic, or Friedel potential. This approach has been taken in several studies of the structure of simple metals and alloys [5-8] and is followed below, where we supplement prior work with new computations

to explore the results of a simple structural model based on the two-body Friedel potential.

While the approximations involved in a structural model based on the Friedel potential are drastic, the model has several attractive features. It leads to equations which are easy to use and which incorporate aspects of the more fundamental theory while avoiding the recalcitrant problem of choosing proper pseudopotentials. Moreover, the model yields a prediction of alloy structure which is based on the electron-atom ratio, in the spirit of the Hume-Rothery [9] and Engel-Brewer [10] correlations, and which is in general agreement with known structural tendencies in simple metals and alloys.

The central equations of the structural model used here are derived as follows.

Employing the real space formulation of the pseudopotential theory of a simple metal [1,3] the cohesive energy per atom may be developed in the perturbation series:

$$E = E_o + E_1 + E_2 + \ldots \tag{1}$$

whose successive terms involve perturbations of increasing order. The zeroth and first order terms in this expansion depend on the volume per atom (Ω), but are independent of structure. The second order term, E_2, is the first to show the influence of structure. It can be cast in the form

$$E_2 = \frac{1}{2N} \sum_{i,j}' V(r_{ij}) , \tag{2}$$

where N is the number of atoms, r_{ij} is the distance between the $i^{\underline{th}}$ and $j^{\underline{th}}$ atom cores, and the prime on the summation indicates that terms having i=j are to be omitted. The function $V(r_{ij})$ appearing in the summation acts as a two-body potential in a restricted sense: it governs the change of energy in a relative displacement of atoms i and j which leaves the atomic volume, and hence E_o and E_1, constant. If we fix the atomic volume and neglect higher order terms in the perturbation expansion,[1] the relative energy of a given structure is measured by E_2; that structure which minimizes E_2 will be preferred at 0°K.

Computation of the structural energy, E_2, requires a specific expression for the effective interatomic potential, V(r). This potential is sensitive to the details of the pseudopotential used.[1,2] However, irrespective of the pseudopotential, V(r) has the asymptotic form[1]

$$V(r) \rightarrow V_o \cos(2k_F r)/(2k_F r)^3 \qquad (3)$$

when $(k_F r)$ is large, where k_F is the Fermi wave number. The parameter V_o depends on fundamental quantities in a rather complicated way, but for our purposes it is sufficient to note that V_o is independent of structure. We may hence define a dimensionless two-body potential

$$v(r) = V(r)/V_o$$

which becomes the Friedel potential

$$v(r) = \cos(2k_F r)/(2k_F r)^3 \tag{4}$$

when $k_F r$ is large. If we now uniformly approximate V(r) by its asymptotic form, the structural energy, E_2, may be rewritten in a dimensionless form which is independent of the pseudopotential:

$$\varepsilon = E_2/V_o = \frac{1}{2N} \sum_{i,j}' \cos(2k_F r_{ij})/(2k_F r_{ij})^3 \tag{5}$$

In fact, the dimensionless energy, $\varepsilon = \varepsilon\ (Z)$, is a function of structure and electron-atom ratio (Z) only; since the separation distances (r_{ij}) in a given structure scale as $\Omega^{1/3}$, where Ω is atomic volume, and since the Fermi wave number, k_F, is $k_F = (3\pi^2 Z/\Omega)^{1/3}$, the set of values of the quantity ($k_F r_{ij}$) in a given structure, and hence the dimensionless energy of the structure, is determined by Z.

Equation (5) was drawn from the pseudopotential theory of simple metals. It may be generalized to estimate the relative energies of the structures of uniform random solid solutions of simple metals through use of the virtual crystal model:[11] the alloy is represented as a one-component simple metal made up of pseudoatoms whose properties average those of the atoms actually present. With this approximation the dimensionless structural energy of the solid solution is determined by its mean electron-atom ratio (Z) through Eq. (5). The preferred structure of the solid solution at 0°K may then be estimated by minimizing ε over the set of candidate structures. The result is uniquely determined by Z.

The structural model developed above depends on four specific assumptions, which we discuss in turn.

(1) The model is drawn from the second-order development of the pseudopotential theory of simple metals. It should hence be kept in mind that, in its current state of development, the second-order pseudopotential theory does not always predict a correct structure for the simple metals and is of uncertain value in treating certain of the heavy metals, the transition metals, the noble metals, and metals which have a strong tendency toward covalent bonding.

(2) The effective interatomic potential obtained from the second order pseudopotential theory is replaced by its asymptotic form, the Friedel potential. While it has been found [1] that the effective interatomic potential actually converges toward the Friedel potential rather quickly, important contributions to the structural energy due to near-neighbor interactions may be misestimated. The model is most reasonable when applied to close-packed structures having ideal axial ratios, since these differ from one another only in the third (or higher) coordination shells. The model may not yield a good value for the relative energies of structures such as fcc and bcc, which differ in the first coordination shell. As we shall show, however, it does provide an empirically reasonable estimate of the range of Z values over which the bcc structure is preferred to the close-packed structures.

(3) The variation in equilibrium atomic volume between candidate structures is ignored. Since small volume changes are observed in solid state transformations, and since these changes (at least at 0°K)

must minimize the total energy of the structure, their neglect will necessarily result in an overestimate of the energy advantage enjoyed by the preferred structure. On the other hand, since the atomic volume is left unknown in the calculation of structural energy, this approximation cannot cause an erroneous identification of the preferred structure.

(4) Alloy solid solutions are treated as if they were composed of identical pseudoatoms having average properties. While the approximations involved in this virtual crystal model are known[11] their quantitative consequences are not. The factors neglected include the tendency to short-range order, the contribution to cohesion from charge transfer between different species, the decrement to cohesion due to local lattice strain caused by size difference between species, and possible error from the second order theory if the valences of the species differ. Of course, these factors are relevant only insofar as they influence the relative energies of candidate structures. The probable error should become more important as size or valence differences become greater.

As noted above, the approach to crystal structure employed here has been used by a number of previous workers. Shaw[6] applied a method due to Epstein[12] to show how Eq. (5) may be conveniently set up for direct numerical solution for an arbitrary lattice and computed structural energies for the face centered cubic (fcc), hexagonal close-packed (hcp) and body centered cubic (bcc) structures as functions of valence. In related work, Blandin, Friedel and Saada[5] showed that when a structure is

close-packed, Eq. (3) may be recast in the form of a potential approximating the interaction between close-packed planes. Blandin, Friedel and Saada determined the energies of stacking faults in the fcc and hcp structures and found the ranges of valence over which these structures should be stable with respect to faulting. Recently, Hodges[7] suggested that the interplanar interaction might be used to simplify Eq. (5) for an arbitrary close-packed structure. He employed this formulation in a semi-quantitative discussion of the stability of the close-packed polytypic structures occasionally observed in alloy systems. Havinga, van Vucht and Buschow[8] have also discussed phase stability using interplanar interactions of a similar form. These results are summarized and supplemented in the following sections.

In the next section, the relative energies of the simple crystal structures are calculated to determine the preferred structure as a function of electron-atom ratio. Two techniques are explored. We first employ the exact summation method of Shaw and find the ranges of Z over which the fcc, hcp and bcc structures are stable with respect to one another. We then develop Hodges'[7] suggestion quantitatively so that any close-packed polytype may be handled with the interplanar interaction. Since this second method is easier to use for polytypes and is nearly as accurate as the exact summation method, it is employed to estimate the relative energies and ranges of preference of the fcc, hcp, and more complex polytypic structures.

In the third section, we explore two suggested modifications of the simple structural model. First, following several independent suggestions,[13,14] we alter the Friedel potential, Eq. (4), by adding an arbitrary phase shift, which subsequently will be referred to as the Friedel shift (2δ), to the argument of the cosine. This modification yields a two parameter model in which the dimensionless relative energy of a structure, ε, depends on the Friedel shift as well as on the valence. Second, following a suggestion by Hodges,[7] we adjust the near neighbor terms in Eq. (5) to obtain alternate criteria for the appearance of complex close-packed polytypes.

In a final section, the results of these computations are compared with the known structures of metals and alloys.

II. CALCULATIONS WITH THE UNMODIFIED FRIEDEL POTENTIAL

Two methods for performing the sums for the determination of the structure-dependent energy are presented in this section. First, the exact summation is performed for the fcc, hcp and bcc structures. The axial ratio of the hcp structure is assumed ideal. The energies of the hcp and bcc phases with respect to the fcc phase, $\varepsilon_{hcp}-\varepsilon_{fcc}$ and $\varepsilon_{bcc}-\varepsilon_{fcc}$, are then found by simple subtraction and are plotted as functions of Z.

Secondly, as mentioned above, the application of the Friedel potential is probably most appropriate to the study of the relative energies of the close-packed polytypes structures with ideal axial ratios. The polytypes are easily and accurately handled through use of the interplanar interaction of Blandin, Friedel and Saada. The method for the use of the interplanar interaction is developed and the relevant sums are performed. This second method gives directly the energy of a polytype relative to the energy of the fcc structure, $\varepsilon-\varepsilon_{fcc}$. Using the sums, the relative energies for a number of polytypes can be plotted as functions of Z.

Finally, the relative energies may be used to determine which structure is the most stable of those considered. Plots of the regions of Z for which the different structures are preferred are presented.

A. Exact Summation of the Friedel Potential

If the atoms of the metal are in crystallographically equivalent positions, as they are in the fcc, hcp, and bcc structures, one of the sums in Eq. (5) can be performed to obtain

$$\varepsilon = \frac{1}{2} \sum_{i \neq o} \frac{\cos 2k_F r_i}{(2k_F r_i)^3} \tag{6}$$

where r_i is the distance between the $i^{\underline{th}}$ atom and a reference atom.

Shaw[6] developed the summation method of Epstein[12] for exact summation of Eq. (6) and performed the appropriate sums for the fcc, hcp, and bcc structures. However, his results were not set in a form which allows a clear delineation of the regions of valence over which these structures are preferred. We have, therefore, repeated the computations.

The method of Epstein is a general technique for summing quantities like $\exp(ikr)/r^n$ over a collection of lattice points. The method involves the transformation of the sum into two rapidly converging sums. The sum in direct space remains, but an exponential damping factor appears in each term. The residue is Fourier transformed into a sum in reciprocal space; each term in this sum includes a damping factor also. Shaw obtains, for the sum of $\cos 2k_F r/(2k_F r)^3$,

$$\varepsilon = \sum_{i\neq o} \frac{\cos(kr_i)}{(kr_i)^3} = \frac{\pi}{\Omega} \sum_{q\neq o} \frac{|S(q)|^2}{k^3} \left[\left(1 + \frac{k}{q}\right) E_1(\alpha) + \left(1 - \frac{k}{q}\right) E_1(\beta)\right] \tag{6}$$

$$+ \frac{8\pi}{\Omega k^3} \left[E_1(k^2/4\omega) - 2e^{-k^2/4\omega}\right] + \sum_{i\neq o} \frac{\cos(kr_i)}{(kr_i)^3} \left[\operatorname{erfc}(\omega^{1/2} r_i) + 2\left(\frac{\omega r_i^2}{\pi}\right)^{1/2} e^{-\omega r_i^2}\right] - \frac{4}{3k^3}\left(\frac{\omega^3}{\pi}\right)^{1/2}$$

where

$$k = 2k_F ,$$

$$\alpha = (k+q)^2/4\omega ,$$

$$\beta = (k-q)^2/4\omega ,$$

$$E_1(x) = \int_x^\infty dt \{\exp(-t)/t\} ,$$

$$\mathrm{erfc}(x) = 1 - \mathrm{erf}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x dt \left[\exp(-t^2)\right] ,$$

i labels the lattice points, ω is a convergence parameter, Ω is the atomic volume, and $S(q)$ is the structure factor for the lattice in question.

The parameter ω may be chosen arbitrarily. If $\omega = \pi/s^2$ is chosen, where s is the nearest neighbor distance, the sums converge with equal rapidity.[6,15] In our computations fifty or sixty lattice vectors were used for the sums on the right hand side of Eq. (6). Then ω was adjusted so that the last terms evaluated for the sums were about equal. It was found that ω differed from π/s^2 by a small amount and the last terms in the two sums contributed less than 10^{-4} to the expression being evaluated. An accuracy of 10^{-4} is thus claimed for these sums. The difference between π/s^2 and the final values chosen for ω is evidently due to the truncation of the sums; the value $\omega = \pi/s^2$ is applicable only to a complete summation.

In Fig. 1, the quantities $\varepsilon_{hcp}-\varepsilon_{fcc}$ and $\varepsilon_{bcc}-\varepsilon_{fcc}$, as determined from exact summation, are plotted as functions of Z. These dimensionless energies have a magnitude of 5×10^{-3} or less for the range of Z considered.

This range is taken to be from 1.00 to 4.00, the range of valence which includes the simple metals to which pseudopotential theory should apply.[1] The results, shown in Fig. 1, can be used to determine which of the three structures has the lowest energy as a function of Z. Regions of preference for the different structures are shown in the third plot of Fig. 4.

B. Summation of the Interplanar Interaction of Blandin, Friedel and Saada

The computation of the relative energies of the different close-packed polytypic structures can be done without the exact evaluation of Eq. (5). The method for doing this calculation uses an approximate interplanar interaction between two parallel, hexagonal close-packed planes due to Blandin, Friedel and Saada.[5] In particular, close-packed polytypic structures can be described as the stacking of hexagonal, close-packed planes of three types, A, B, or C. When these planes are considered pairwise, they are in either equivalent (e.g., A-A) or inequivalent (e.g., A-B) positions. For example, the stacking sequence of the fcc structure is ABCABC; the first and fourth planes in the stacking sequence are in equivalent positions, while the first and second planes and the first and third planes are in inequivalent positions. The interplanar interaction of Blandin, Friedel and Saada is a rearrangement interaction which gives the change in energy when two parallel, hexagonal close-packed planes are shifted from equivalent to inequivalent positions.

Blandin, Friedel and Saada actually obtained two expressions for the interplanar interaction. The expression to be used depends on whether Z is larger or smaller than $Z_c = 1.14$. This energy (per unit area) is given to a good approximation by

$$\Delta\phi^{BFS}(nd) = \frac{V_o k_F^2 \left((Z_c/Z)^{2/3} - 1\right)^{1/2}}{(2\pi)^3 Z^2} \frac{\exp -n\theta'}{n^2}, \quad Z < Z_c \qquad (7)$$

where $\theta' = 5.67\ (Z_c^{2/3} - Z^{2/3})^{1/2}$, d is the interplanar spacing, and n denotes which near neighbor planes are being considered. Similarly,

$$\Delta\phi^{BFS}(nd) = \frac{V_o k_F^2 \left(1 - (Z_c/Z)^{2/3}\right)^{1/2}}{(2\pi)^3 Z^2} \frac{\sin n\theta}{n^2}, \quad Z > Z_c \qquad (8)$$

where

$$\theta = 5.67\ (Z^{2/3} - Z_c^{2/3})^{1/2} .$$

As is evident, the interaction goes to zero as Z approaches Z_c. This effect will be shown to be spurious below. The region near Z_c may not be treated accurately because of this defect in the interplanar interaction.

We will want to compare the results of the calculation using the interplanar interaction to the results of the exact summation, so it is useful to cast the above equations in units of energy per atom. This can be done by noting that $\sqrt{3}\ s^2/2$ is the area per atom in a hexagonal close-packed plane, where s is the nearest neighbor distance. For the energy per atom, where $Z < Z_c$,

$$\Delta\phi^{BFS}(nd) = \frac{10.44\ V_o\ ((Z_c/Z)^{2/3} - 1)^{1/2}}{(2\pi)^3 Z^{4/3}\ (2\pi)^3 Z^{4/3}} \quad \frac{\exp{-n\theta'}}{n^2} \quad , \qquad (9)$$

and for $Z > Z_c$, a similar expression holds.

Following a suggestion by Hodges,[7] the $\Delta\phi^{BFS}(nd)$ defined above can be used to calculate the structure-dependent energy and relative stability of any close-packed structure. Let c_n be the fraction of nth nearest neighbor planes in equivalent positions for some structure. For example, c_1 equals zero for any structure, since nearest neighbor planes are always in inequivalent positions. The structure-dependent energy per atom of some structure with respect to the fcc structure is just

$$\varepsilon-\varepsilon_{fcc} = \sum_{n=1}^{\infty} \Delta c_n\ \Delta\phi(nd) \quad . \qquad (10)$$

where $\Delta c_n = c_n^{fcc} - c_n$, and c_n is the coefficient of the phase in question. Table I shows stacking characteristics and stacking sequences for the polytypic structures considered in this paper.

When Eq. (7) is used in Eq. (10) the sum for $\varepsilon-\varepsilon_{fcc}$ converges rapidly for $Z < Z_c$ because of the exponentially decreasing variation of the interplanar interaction with n. Only several terms need be kept to obtain the necessary significance for $\varepsilon-\varepsilon_{fcc}$.

When Eq. (8) is used in Eq. (10) for $Z > Z_c$ one can obtain a simplification by noting that Δc_n is periodic in n. If (jd) is a common repete distance for the structure in question and the fcc structure, we can rewrite Eq. (10) as

$$\varepsilon-\varepsilon_{fcc} = \sum_{n'=0}^{\infty} \sum_{k=1}^{j} \Delta c_{jn'+k}\, \Delta\phi((jn'+k)d)$$

$$= \sum_{n'=0}^{\infty} \sum_{k=1}^{j} \Delta c_k\, \Delta\phi((jn'+k)d) \qquad (11)$$

$$= \sum_{k=1}^{j} \Delta c_k \sum_{n'=0}^{\infty} \Delta\phi((jn'+k)d) \quad ,$$

For example, it is found that the hcp structure has an energy of

$$\varepsilon_{hcp}-\varepsilon_{fcc} = \sum_{n=0}^{\infty} \Delta\phi((6n+3)d) - \Delta\phi((6n+2)d) - \Delta\phi((6n+4)d) \qquad (12)$$

with respect to the fcc structure. The terms $\sum_{n'=0}^{\infty} \Delta\phi((jn'+k)d)$ in Eq. (11) can be easily evaluated when Eq. (8) is used. It may be shown that

$$\sum_{n=0}^{\infty} \Delta\phi^{BFS}((jn+k)d) \propto \sum_{n=0}^{\infty} \frac{\sin(jn+k)\theta}{(jn+k)^2}$$

$$= \frac{1}{j} \sum_{\ell=0}^{j-1} \sin\frac{2\pi k\ell}{j}\ \beta_2(\theta + \frac{2\pi\ell}{j}) + \cos\frac{2\pi k\ell}{j}\ \alpha_2(\theta + \frac{2\pi\ell}{j}) \qquad (13)$$

where

$$\alpha_2(\theta) = \sum_{n=1}^{\infty} \frac{\sin n\theta}{n^2} = -\theta\, \ell n2\left|\sin\frac{\theta}{2}\right| + 2\int_0^{\frac{\theta}{2}} \frac{\phi d\phi}{\tan\phi}$$

and

$$\beta_2(\theta) = \sum_{n=1}^{\infty} \frac{\cos n\theta}{n^2} = \frac{\theta^2}{4} - \frac{\pi\theta}{2} + \frac{\pi^2}{6} \quad .$$

The function α_2 was obtained numerically to six digit accuracy using polynomial expansions with six terms. This accuracy is needed to assure significance in the evaluation of Eq. (13) when used in Eq. (11).

Use of Eq. (13) in Eq. (11) allows a simple calculation of $\varepsilon-\varepsilon_{fcc}$. The method does not require the calculation of reciprocal lattice vectors as in the exact summation method and is easily visualized. The results for $\varepsilon-\varepsilon_{fcc}$ using the interplanar interaction are shown in Fig. 2 as a function of the valence. The second plot of Fig. 4 displays the regions of relative stability as a function of Z.

Results for three polytype structures are also displayed in Fig. 2. Two of these, the double hexagonal (dhcp) and samarium (Sm) structures, are occasionally observed experimentally. In terms of Pauling's h-k notation (Table I) these structures have one half and two thirds hexagonal character, respectively. The final structure, designated the A structure, has one third hexagonal character and is included for completeness. These complex polytypes might be considered as compromise structures that occur when the fcc and hcp structures have nearly the same energies. Table I summarizes the stacking characteristics of these complex polytypes.

The odd behavior of the interplanar interaction near $Z = 1.14$ shows up clearly in Fig. 2. Using the results from the exact summation, the values of $\varepsilon_{hcp} - \varepsilon_{fcc}$ from the two methods can be compared and are plotted in Fig. 3. The exact summation yields $\varepsilon_{hcp} - \varepsilon_{fcc} \neq 0$ at $Z = 1.14$. This result implies that there should be non-zero terms in Eq. (10), i.e., the interplanar interaction is not always zero at $Z = 1.14$. Evidently, the approximate interplanar interaction breaks down near this value of Z.

III. MODIFICATIONS OF THE FRIEDEL POTENTIAL

Up to this point, the relative stability of different structures has been considered to be determined by one variable, the electron-atom ratio Z. The actual structures exhibited by the simple metals indicate that Z is not the only determinant of structure. In an attempt to circumvent this defect of the model, two modifications of the Friedel potential are considered in this section.

The first modification is the introduction of a new parameter into the Friedel potential. This parameter is a Friedel shift of 2δ in the argument of the cosine of the Friedel potential. The resulting potential is of the form

$$v'(r) = \frac{\cos(2k_F r+2\delta)}{(2k_F r)^3} \quad . \tag{14}$$

When Eq. (14) is used in Eq. (5), the dimensionless structure dependent energy depends on both the electron-atom ratio Z and the Friedel shift 2δ. The stability of the simple crystal structures has been determined as a function of Z and 2δ by modifying both the exact summation method and the method developed in the previous section for summing the interplanar interaction.

The second modification considered in this section pertains only to the application of the interplanar interaction to the stability of close-packed polytypes. Instead of simply using the interplanar interaction in Eq. (10), $\Delta\phi(2d)$ is adjusted to reflect conditions that might hold when the dhcp, Sm, and A polytypes occur. The regions of Z

for which the complex polytypes might appear are determined under these conditions.

A. Inclusion of a Phase Factor in the Friedel Potential

The Friedel oscillations were originally derived as oscillations in the charge density surrounding an ion in an electron gas.[4] A Friedel shift appears in the result for the charge density, as in Eq. (14). However, as usually derived from pseudopotential theory carried to second order in perturbation theory,[1] neither the charge density oscillations nor the Friedel potential contain a Friedel shift. Only in higher orders of perturbation theory does the Friedel shift occur. Friedel,[13] Seeger,[14] Heine and Weaire,[2] and Harrison[15] have also discussed the significance of the Friedel shift. Although it is not yet clear what role the Friedel shift plays in interionic potentials, the present formulation allows the Friedel shift to be incorporated into the determination of structure is a simple way, and this is done below. To sum the potential, Eq. (14), over the lattice as in Eq. (5), we note that Eq. (14) can be decomposed into the form

$$v(r) = \cos 2\delta \frac{\cos 2k_F r}{(2k_F r)^3} - \sin 2\delta \frac{\sin 2k_F r}{(2k_F r)^3} \tag{15}$$

Now just as Eq. (5) could be summed using Shaw's development of Epstein's method, the term $\sin (2k_F r)/(2k_F r)^3$ can be summed using a formula similar to Eq. (6).

The term $\sin(2k_F r)/(2k_F r)^3$ can also be cast into the form of an interplanar interaction, just as was done by Blandin, Friedel and Saada for the term $\cos(2k_F r)/(2k_F r)^3$. Instead of a singularity of the type $(k-2k_F)\ \ln|k-2k_F|$, a form like $|k-2k_F|$ appears. The final result is to simply add a Friedel shift to the interplanar interaction:

$$\Delta\phi(nd) = 10.44 \frac{V_o(1 - (Z/Z_c)^{2/3})^{1/2}}{(2\pi)^3 Z^{4/3}} \frac{\sin(n\theta + 2\delta)}{n^2} \qquad (16)$$

Expressions (14) and (16) can now be used in Eqs. (5) and (10) to determine the stable structure just as before, except that this structure will be a function of both Z and 2δ. This information can then be used to determine which structure, of those considered, is most stable as a function of the two variables. Figures 5 and 6 show the structures found to be preferred when a Friedel shift is included in the Friedel potential. Figure 5 is the result of the exact summation technique. Only the fcc, hcp and bcc structures were considered in this determination. Figure 5 shows which of the structures, fcc, hcp, dhcp, Sm, or A, are preferred as a function of Z and 2δ as determined by Eqs. (14) and (16).

B. Alternate Criteria for the Occurrence of Complex Close-Packed Polytypes

In this section, the model presented above is modified in a second way to obtain values of Z for which complex polytypes might be found. In particular, the interplanar interaction, with adjustment of $\Delta\phi(2d)$, is used to obtain the regions of Z where the polytypes dhcp, Sm, and

A might occur. What is recognized is that, since the interplanar interaction of Blandin, Friedel and Saada may be in error for small separations, $\Delta\phi^{BFS}(2d)$ may not necessarily be a good approximation to the actual interplanar interaction for second nearest neighbor planes. $\Delta\phi(2d)$ is hence adjusted to meet other requirements.

The dhcp, Sm and A structures (Table I) may be considered to be compromise structures occurring when the fcc and hcp structures have nearly the same energy. This condition can be simulated by either setting $\Delta\phi(2d) = 0$, as was done by Hodges,[7] or by requiring that $\varepsilon_{fcc} = \varepsilon_{hcp}$ and adjusting $\Delta\phi(2d)$ accordingly. These two criteria for the appearance of the complex polytypes are investigated below.

The condition that Hodges[7] used for the appearance of complex close-packed polytypes is of the form

$$\begin{aligned} \Delta\phi(2d) &= 0 \\ \Delta\phi(nd) &= \Delta\phi^{BFS}(nd) \qquad n \geqslant 3 \end{aligned} \tag{17}$$

This condition assumes that the interplanar interaction shows no preference for equivalent or inequivalent planes at the second nearest neighbor plane position. If equivalent planes are preferred at the second nearest neighbor position ($\Delta\phi(2d) > 0$), the hcp structure is favored by $\Delta\phi(2d)$, and if inequivalent planes are preferred ($\Delta\phi(2d) < 0$), the fcc structure is favored. Equation (17) expresses the condition that neither type of plane is favored, so that complex polytypes, which have both types of planes at the second nearest neighbor plane position, may appear.

The values of $\Delta\phi(nd)$ from Eq. (17) are to be inserted in Eq. (10) to determine the preferred structure and, in particular, to determine if a complex polytype is preferred. Hodges [7] did not evaluate the complete sums, Eq. (10), and therefore could not make definite conclusions about the relative energy of the samarium structure; he did not consider the A structure. The complete sums have been done and the results are included in Fig. 4. It is found that the energies of the dhcp and Sm structures are usually very close to one another, so that care must be taken in evaluating the sums.

The value of $\Delta\phi(2d)$ can be adjusted in another way. Rather than setting $\Delta\phi(2d) = 0$, one can set $\varepsilon_{hcp} = \varepsilon_{fcc}$ in Eq. (10) by adjusting $\Delta\phi(2d)$. The other terms, $\Delta\phi(nd)$, are then taken from Eq. (9). This procedure has the advantage that the condition for the appearance of complex polytypes is simply stated as a condition on the relative energies of the fcc and hcp structures. However, the term $\Delta\phi(2d)$ must still be singled out for special treatment. We take

$$\Delta\phi(2d) = \Delta\phi^{o}(2d) \tag{18}$$

$$\Delta\phi(nd) = \Delta\phi^{BFS}(nd) \quad \text{for} \quad n \geqslant 3 \quad ,$$

where $\Delta\phi^{o}(2d)$ is adjusted in Eq. (10) so that $\varepsilon_{hcp} = \varepsilon_{fcc}$. This condition with Eq. (10) can be recast in the form

$$\varepsilon - \varepsilon_{fcc} = \Delta c_2(\varepsilon^{BFS}_{hcp} - \varepsilon^{BFS}_{fcc}) + (\varepsilon^{BFS} - \varepsilon^{BFS}_{fcc}) \quad , \tag{19}$$

where the polytype with the minimum value of ε is preferred. Since $\Delta c_2^{hcp} = -1$, $\varepsilon_{hcp} = \varepsilon_{fcc}$, as promised.

Equation (19) can be interpreted in the following way. We expect the compromise polytype structures, dhcp, Sm and A to appear when $\varepsilon_{hcp} \approx \varepsilon_{fcc}$. One can then find what value $\Delta\phi(2d)$ assumes in this case. For some values of Z, polytypes will intrude when this value of $\Delta\phi(2d)$ is used. For other values of Z, the other interactions, $\Delta\phi^{BFS}(nd)$ with $n \geqslant 3$, stabilize both the fcc and hcp structures with respect to the polytypes.

In the fourth and fifth plots of Fig. 4 we have shown the regions of Z in which the polytypes might be found according to the two conditions on $\Delta\phi(2d)$ above. Of course, complex polytypes occur less frequently than the corresponding ranges of Z indicate. The plots should be interpreted as indicating what polytype would occur if the conditions for polytype formation are at all favorable. When Eq. (19) is used, the energies of the fcc and hcp structures are equal for all values of Z. This is reflected in the last plot of Fig. 4 where mutual hcp-fcc zones are indicated.

IV. DISCUSSION

The computations discussed above have allowed several determinations of structure. The results are summarized in Fig. 4 along with results obtained by Blandin, Friedel and Saada.[5] The most stable structure of those considered is plotted as a function of Z. This data is also presented in Table II. In this section we compare these results with the actual structures found among the elements and in alloy systems.

The first plot in Fig. 4 represents the results of Blandin, et.al.[5] Using the real space formulation of pseudopotential theory, they discussed the stability regions for the fcc and hcp structures. Specifically, they determined the regions of Z for which the fcc and hcp structures are stable against the formation of stacking faults, using the unmodified interplanar interaction. This criterion for stability is not strictly the same as that used in this paper; we are here concerned with the relative stability of specific alternate structures.

The results which follow from the formulae of Section II are shown in the second and third plots of Fig. 4. These results complement those of Blandin, Friedel and Saada, as can be seen by comparing the first and second plots of Fig. 4. Over the range $2.10 < Z < 2.20$ the fcc phase is stable against faulting for the model considered here, but is metastable with respect to the hcp phase. Similarly, the hcp phase is stable against faulting from $Z = 2.20$ to 2.29, but is metastable with respect to the fcc structure. On the other hand, over the range $1.27 < Z < 1.30$ the model predicts that hcp is

stable relative to the fcc structure, but unstable to faulting, while for $1.30 < Z < 1.36$ the fcc structure is preferred to hcp, though both are unstable with respect to formation of a fault. Since the close-packed polytypes may be derived from the simple fcc or hcp structure through periodic faulting, polytype intrusion is likely near $Z = 1.30$, as discussed below. At $Z = 1.66$ and 3.53 the fcc-hcp phase boundaries coincide with the limits of stability with respect to faulting.

The results obtained from the exact summation of the Friedel potential are given in the third plot of Fig. 4, which includes the predicted range of the body centered cubic structure.

The results shown in the first three plots of Fig. 4 are complementary, and express structural tendencies which are at least roughly reflected in the periodic table for Z in the range 1 to 3. The model prefers the hcp structure when $Z = 1$, as do the simplest monovalent metals, lithium and sodium, in their low temperature forms. At $Z=2$ the model shows a very slight preference for the bcc structure over an hcp structure with ideal axial ratio; the possibility of a non-ideal axial ratio was not considered. The hcp structure is clearly preferred to fcc. Empirically, the divalent metals beryllium, magnesium, zinc, and cadmium are hcp; all except magnesium have axial ratios which are far from ideal. At $Z=3$ the model prefers the fcc structure. Among the trivalent elements, aluminum is fcc and indium is nearly fcc. Gallium has a distorted structure which was not considered.

The application of the results summarized in Fig. 4 appears to be successful in alloy systems for at least one value of Z. At Z = 2.20, there is a boundary between the fcc and hcp stability regions. Corresponding to this value of Z, there are several systems with large solid solubilities that also assume a phase boundary at or near this value of Z. The fcc phase of aluminum is stable with up to 66.5 a/o additions of zinc, and similarly the fcc phase of indium is stable with additions of up to 77 a/o magnesium.[17] Also, results from splat-cooling experiments[18] indicate that fcc or fcc-like phases are observed down to Z = 2.20 in a number of systems. These experimental results for elements and alloys are in agreement with the determination of the relative stability of the fcc and hcp structures with the Friedel potential, especially in the region of Z = 2 to 3.

The region of Z for which the bcc structure is preferred is $1.48 \leq Z \leq 2.03$. This range includes the electron-atom ratios of the beta brasses, the bcc-like Hume-Rothery alloys.[9]

Besides the fcc, hcp and bcc structures, several polytypic structures were considered in Section II. In particular, results from the use of the unmodified interplanar interaction to determine the stability of the fcc, hcp, dhcp, Sm and A structures against the formation of the other structures are shown in the second plot of Fig. 4. There is a polytype intrusion near Z = 1.30. In fact, there is strong evidence[19,20] that at least the dhcp phase is found in this region of valence. At Z = 2.20 the Friedel potential yields a transition between the fcc and hcp structures with no polytype intrusion. In fact,

complex polytypes do not seem to intrude at or near this value of Z in alloy systems.

The considerations above relate to a model in which the valence is the only determinant of structure. Since simple metals from a particular group of the periodic chart, i.e., with a particular value of Z, display different structures, this type of determination is bound to fail. The flexibility necessary to allow several structures to be stable at a particular value of Z is obtained by the introduction of a Friedel shift of 2δ into the Friedel potential, as can be seen from Figs. 5 and 6.

To draw clear conclusions from the modified model we would require a method for selecting an appropriate Friedel shift for a given material. One available quantitative suggestion,[15,21] that the Friedel shift be computed from the phase shifts on scattering from the pseudopotential, has been criticized on theoretical grounds by Heine and Weaire.[23] We computed Friedel shifts from the phase shifts on scattering from several suggested model potentials and found, in agreement with Seeger,[14] that the resulting values of 2δ are so large that they destroy the reasonable agreement between the simple structural model and empirical trends in structure. Reasonable agreement can only be maintained if one accepts the conclusion of Heine and Weaire[23] that 2δ is small.

Leaving aside the computation of the Friedel shifts the accuracy of the model may be improved if 2δ is allowed to assume values of magnitude $\pi/4$ or less. Reference to Fig. 5 shows that at Z=3 this range of 2δ permits the fcc and hcp structures, which are empirically observed, but does not permit the bcc structure, which is not observed.

At Z=2 all three structures, hcp, bcc, and fcc, occur over a small range of 2δ; all are, in fact, found in the divalent metals. At Z=1 the hcp and bcc structures occur with a moderate Friedel shift; these are the structures found in the monovalent alkali metals. Reference to Fig. 6 shows that polytypic phases may be stabilized by a small Friedel shift when $1.25 \leqslant Z \leqslant 1.60$ and when $3.00 \leqslant Z \leqslant 3.60$. These are the ranges of electron-atom ratio over which the close-packed polytypes are commonly found.[8]

The second modification to the Friedel potential that we consider is actually a class of modifications to the interplanar interaction. The value of $\Delta\phi(2d)$ is adjusted to find ranges of Z where the complex polytypes, dhcp, Sm and A, might occur in the case that $\Delta\phi(2d)$ is not given correctly by the expression of Blandin, Friedel and Saada, $\Delta\phi^{BFS}(2d)$. More distant interactions are still assumed to be given by Eq. (9).

The last two plots in Fig. 4 show the regions where the complex polytypes might occur according to the modifications discussed in Section III. In both of these plots, polytype intrusions occur at Z = 1.30, as was the case for the results from the unmodified interplanar interaction. It is interesting to note that the A structure appears in the last plot only and there the A structure is stable only in relatively small regions of Z. Experimentally, the A structure is rarely found.

The last plot in Fig. 6, which shows where polytypes might occur if $\varepsilon_{fcc} = \varepsilon_{hcp}$, gives results close to those listed by Havinga, et.al.[8] who used a criterion even more general than the criteria described above to discuss polytypes. These authors did not use complete summations, Eq. (10), in their determination of polytype stability, but inserted a factor which damped the interplanar interaction at large distances. In contrast, the technique used in this paper treats the long range part of the Friedel potential explicitly. However, we note that there are experimentally observed polytypes listed by Havinga, et.al. which fall outside the stability zones found in their paper and in Fig. 4.

The size of the relative energies of the candidate structures can be estimated from Eq. (5) and the computations discussed above. The dimensionless energies, $\varepsilon_{hcp} - \varepsilon_{fcc}$, etc, have a magnitude of 2×10^{-4} for the monovalent metals and 5×10^{-3} or less for the polyvalent metals. Typical values of V_o of 10 and 50 electron volts for monovalent and polyvalent metals yield relative energies of 0.002 and 0.25 electron volts per atom, respectively. As expected, energy differences of these magnitudes are also obtained with the more complete computations[1,2] of pseudopotential theory.

ACKNOWLEDGMENT

The authors are grateful to Professor W. A. Harrison for helpful discussions. The work reported here was supported by the Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Berkeley Laboratory.

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Table I. Stacking Characteristics of Polytypes

Structure	Stacking	Symmetry	
fcc	ABCABC	kkkk	3R
hcp	ABABAB	hhhh	2H
dhcp	ABACABAC	hkhk	4H
Sm	ABABCBCAC	hhkhhk	9R
A	ABCBAC	kkhkkh	6H

Table II. The regions of Z for which structures are stable against the formation of the other structures considered.

Exact Summation: fcc, hcp and bcc		Interplanar Interaction: fcc, hcp, dhcp, Sm and A	
Z	Structure	Z	Structure
1.00-1.28	hcp	1.00-1.24	hcp
1.28-1.48	fcc	1.24-1.26	Sm
1.48-2.03	bcc	1.26-1.34	dhcp
2.03-2.21	hcp	1.34-1.66	fcc
2.21-3.53	fcc	1.66-2.20	hcp
3.53-4.00	hcp	2.20-3.53	fcc
		3.53-4.00	hcp

$\Delta\phi(2d) = 0$: fcc, hcp, dhcp, Sm and A		$\varepsilon_{fcc} = \varepsilon_{hcp}$: fcc, hcp, dhcp, Sm and A	
Z	Structure	Z	Structure
1.00-1.21	fcc	1.00-1.17	fcc-hcp
1.21-1.26	Sm	1.17-1.20	Sm
1.26-1.35	dhcp	1.20-1.23	A
1.35-1.37	hcp	1.23-1.25	Sm
1.37-1.66	fcc	1.25-1.36	dhcp
1.66-1.84	hcp	1.36-1.53	fcc-hcp
1.84-1.87	dhcp	1.53-1.66	Sm
1.87-2.08	Sm	1.66-1.95	dhcp
2.08-2.56	fcc	1.95-2.11	Sm
2.56-2.68	dhcp	2.11-2.52	fcc-hcp
2.68-2.95	hcp	2.52-2.92	dhcp
2.95-3.53	Sm	2.92-2.96	A
3.53-3.67	hcp	2.96-3.53	Sm
3.67-4.00	fcc	3.53-4.00	fcc-hcp

FIGURE CAPTIONS

Fig. 1. Results for the dimensionless relative energies, $\varepsilon_{chp}-\varepsilon_{fcc}$ and $\varepsilon_{hcp}-\varepsilon_{fcc}$, as determined by exact summation of the reduced Friedel potential as a function of Z.

Fig. 2. Results for the dimensionless energies of the polytypic structure hcp, dhcp, Sm and A relative to the fcc structure as determined from the BFS interplanar interaction as a function of Z. See Table I for the description of the packing of these structures. The region $Z < 1.14$ has been omitted for clarity.

Fig. 3. Comparison of the dimensionless energy difference $\varepsilon_{hcp}-\varepsilon_{fcc}$ as determined with the exact summation and the BFS interplanar interaction as of function of Z. The results from the BFS interplanar interaction are a good approximation to those from the exact summation, except near $Z = 1.14$.

Fig. 4. Values of Z for which various structures are stable: A) stability against faulting of fcc and hcp after Blandin, Friedel, and Saada, B) relative stability of polytypes from interplanar interaction, C) relative stability of fcc, hcp and bcc from exact summation, D and E) polytype stability using the modified interplanar interactions given in Eq. (17) and (19), respectively.

Fig. 5. Results from the determination of the most stable structure among fcc, hcp and bcc from the exact summation of the Friedel potential as a function of Z and a phase factor, 2δ. Legend for identification of structures as in Fig. 4.

Fig. 6. Results from the determination of the most stable structure from among fcc, hcp, dhcp, Sm and A using the interplanar interaction as a function of Z and 2δ. Legend for identification of polytypic structures as in Fig. 4.

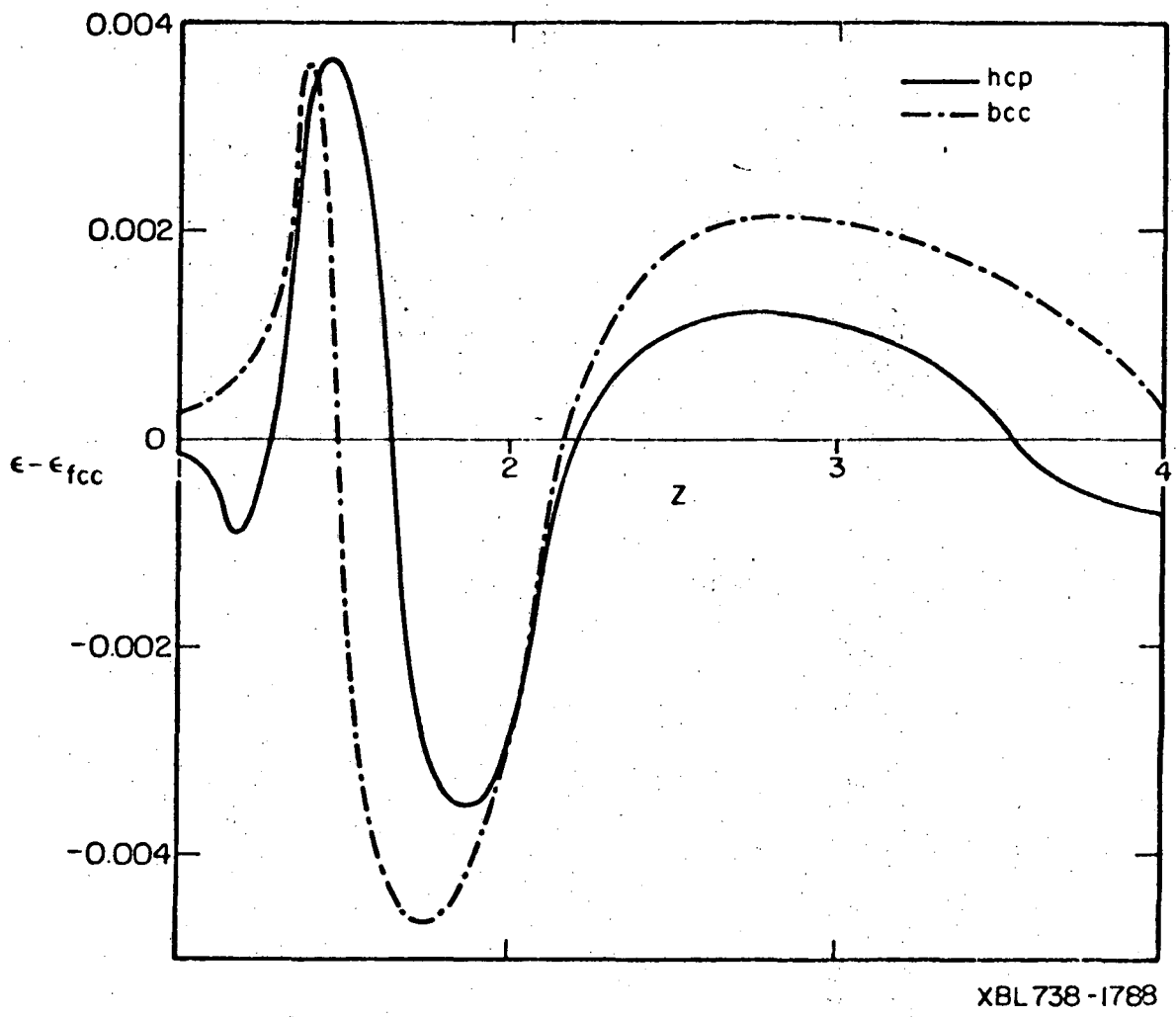
0.004
0.002
0
-0.002
-0.004
$\epsilon - \epsilon_{fcc}$
2
3
4
Z
hcp
bcc
XBL 738-1788

Fig. 1

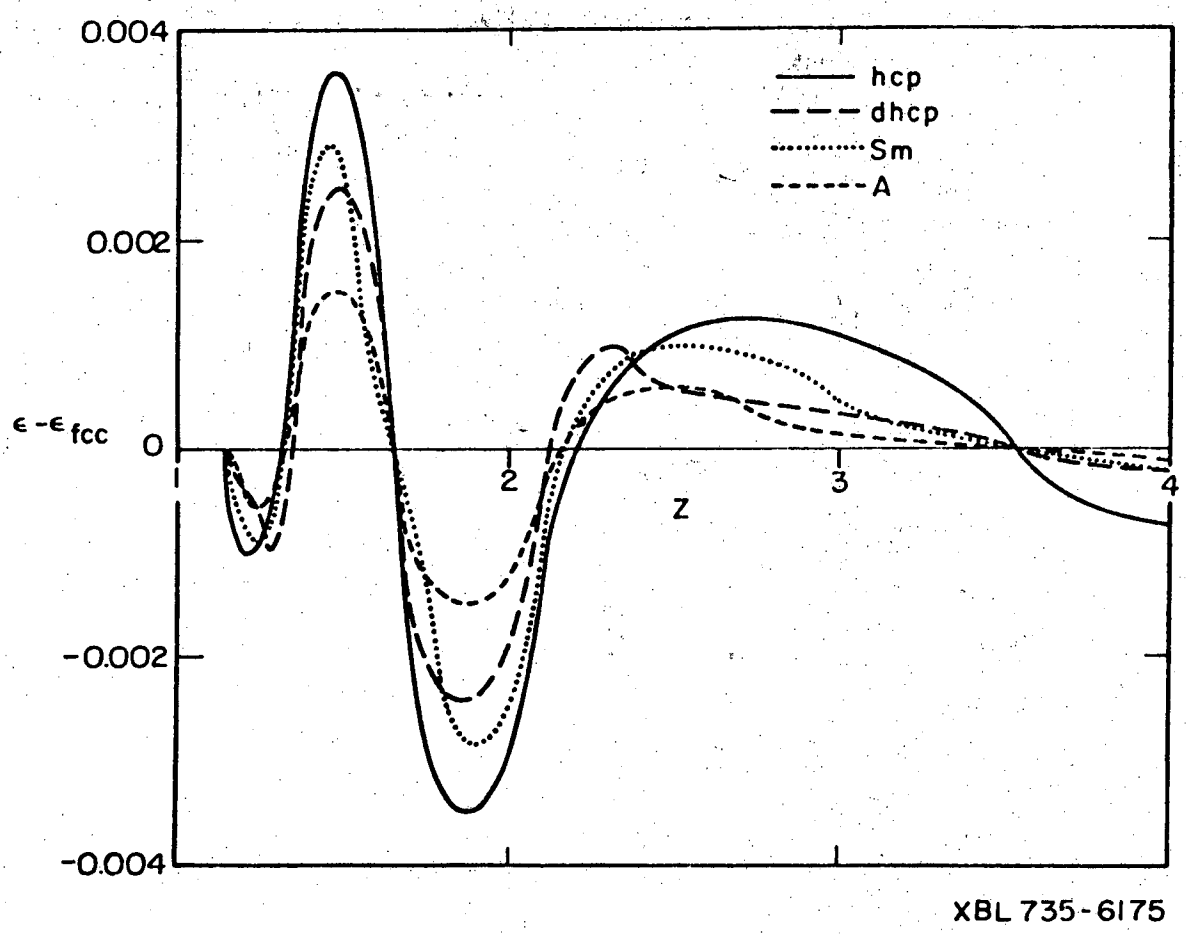

Fig. 2

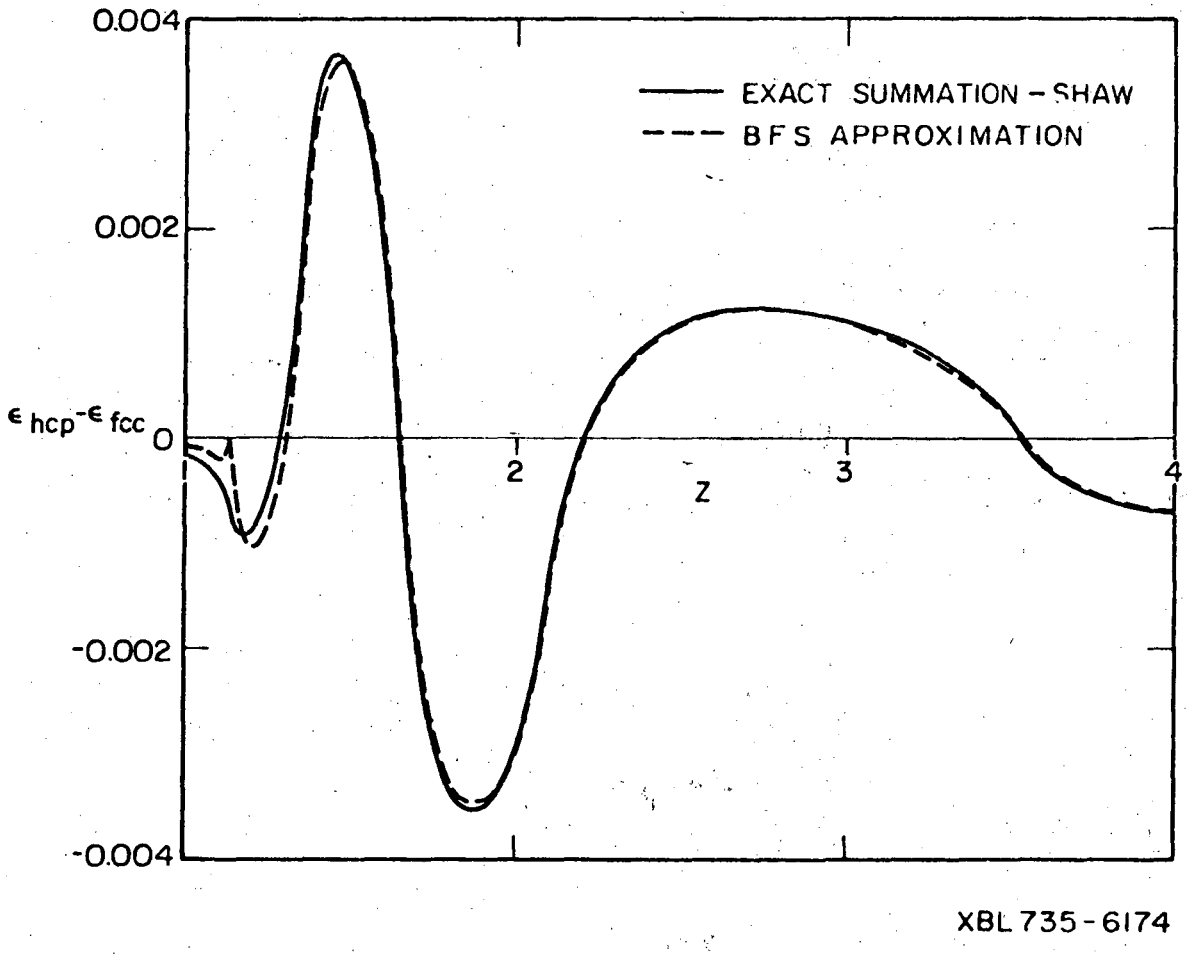
0.004
0.002
0
-0.002
-0.004
$\epsilon_{hcp}-\epsilon_{fcc}$
2
3
4
Z
EXACT SUMMATION - SHAW
BFS APPROXIMATION
XBL 735-6174

Fig. 3

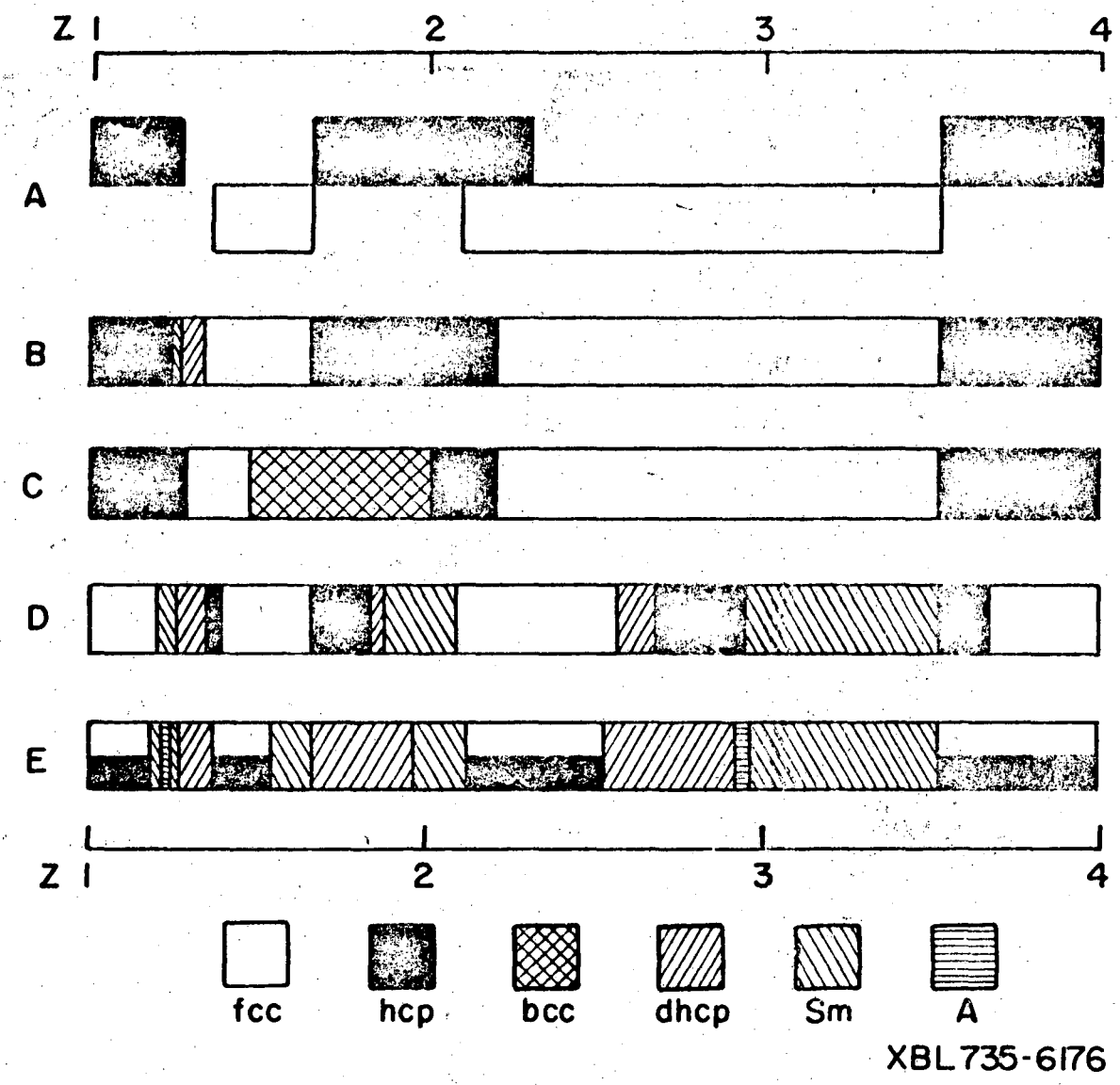

Fig. 4

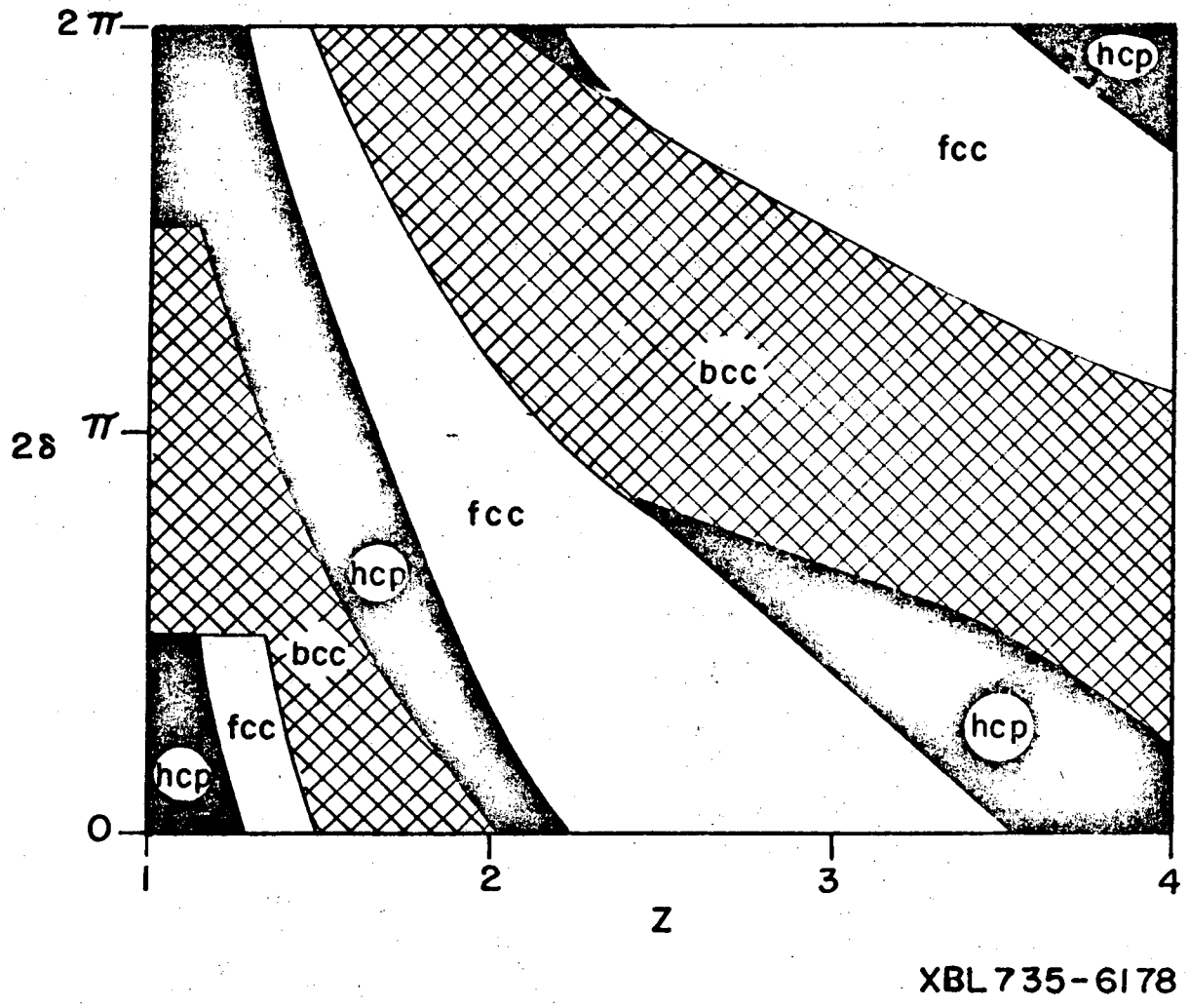

Fig. 5

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