

Theory of the hcp-fcc Transition in Metals

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A theory is developed for the hcp-fcc structural phase transition in close-packed metals as a function of the average electron concentration per atom. It is found that the transition can be *continuous* at low temperatures. Ordered polytypic stacking sequences are found near the transition point. Short-period structures are stabilized by Fermi-surface effects, but long-period structures result from elastic distortion of the lattice. Unusual “staircase” crystallographic data for Mg-based Friauf-Laves alloys are accounted for successfully and the structure of rare-earth intermetallic alloys is discussed.

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Many metals crystallize into structures which can be described as regular stackings of close-packed triangular lattice planes.¹ Each layer can occupy one of three positions commonly denoted by *A*, *B*, and *C*. The two simplest stacking sequences lead to the familiar hexagonal close-packed structure (hcp), *ABABAB*... , and the face-centered cubic structure (fcc), *ABCABC*... However, several classes of metals are known² where the crystal adopts a structure which can be regarded as a “compromise” between fcc and hcp. A convenient way to visualize these structures employs an alternative notation³ that labels each plane by the letter *h* if its nearest neighbors are identically stacked (e.g., *B* in *ABA*) or the letter *c* if the nearest neighbors differ in stacking (e.g., *B* in *ABC*). One then can imagine an infinite set of interpolating structures which effect the transition from hcp to fcc by the systematic introduction of *c* stacking faults into the pure *hh*... structure. A particularly detailed experimental study of this phenomenon has been carried out by Komura and Kitano⁴ for quench-cooled, magnesium-based, Friauf-Laves-phase ternary alloys. A summary of their data is shown in Fig. 1. The vertical axis identifies a crystal structure by the fraction of *h* layers per stacking direction repeat unit. The horizontal axis labels the average number (*Z*) of valence electrons per atom for the alloy in question. The remarkable staircase appearance of these polytypic data is, at present, without explanation.

The purpose of this Letter is to develop a microscopic theory of the hcp-fcc transition in metals and show that the appearance of highly modulated structures is a feature to be expected quite generally. The physical picture derives from the seminal work of Hume-Rothery and Raynor⁵ who first identified the electron concentration as a controlling factor in structural phase transformations. The simplest argument^{1,6} applied to the present case notes that as the average

valence increases above the fcc stability limit, near $Z = 1.67$ in Fig. 1, the free-electron Fermi wave vector increases towards half the magnitude of the second reciprocal lattice vector (*g*) of the hcp structure in the stacking direction. Hence, when k_F just touches the Brillouin-zone boundary, electron “condensation” energy can be gained by a transition to the hcp structure. A simple extension of this idea would consider that even if k_F does not reach this point some electronic energy can still be gained by modulating the lattice

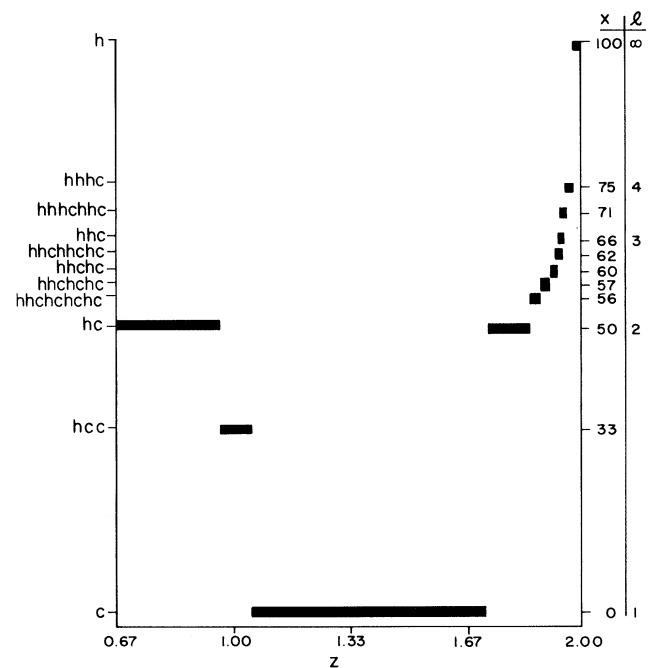


FIG. 1. Crystal structure data for Mg-based ternary alloys from Ref. 4. The percentage fraction, x , of *h* stacking layers is related to l by $x = 100(1 - 1/l)$. See text for further discussion.

with a wave vector $q = g - 2k_F$ at the cost of distorting the hcp structure. In the simplest case, this may be accomplished by inserting c layer stacking faults separated by a distance $2\pi/q$. The situation is analogous to the case of a $2k_F$ charge-density-wave lock-in transition with the c layer playing the role of a discommensuration.⁷

Our inquiry begins with the stability analysis of the hcp and fcc structures in simple metals performed by Blandin, Friedel, and Saada⁸ (BFS). These authors noted that any two layer planes, separated by a distance z , in a close-packed structure are either precisely lined up (e.g., A - A) or are shifted with respect to one another by a fixed distance (e.g., A - C). Since the two alternative stackings conserve the crystal volume, the structural energy difference per unit area between them, $\phi(z)$, can be computed from the pair potentials of pseudopotential theory.⁹ Using a point-ion version of this theory, BFS found an asymptotic expression for the planar interaction energy difference:

$$\phi(z) \approx a \frac{\sin(z\theta/d)}{(z/d)^2}. \quad (1)$$

Here, d is the separation between adjacent planes, $\theta(Z)$ is a smooth function of Z (through k_F), and the prefactor, a , sets the Z -dependent energy scale (~ 100 ergs/cm²). The sinusoidal nature of $\phi(z)$ reflects the long-range Friedel oscillations of the screened ion-ion interaction. Of course, the phenomenon of Friedel oscillations is much more general than rigid-band pseudopotential theory. Hence, we approximate the true planar potential by Eq. (1) supplemented by a phase shift δ and a correction $\Delta\phi(2d)$ to the potential at the shortest structure-sensitive separation. These two quantities may be treated as adjustable parameters within calculable bounds.¹⁰

The total structure-dependent electronic contribution to the cohesive energy of L rigidly stacked close-packed layers then is given by

$$E = -\frac{1}{3L} \sum_{|i-j| \geq 2}^L \phi(|i-j|d) \times \left[\cos\left\{ \frac{2\pi}{3} (n_i - n_j) \right\} - 1 \right], \quad (2)$$

where $n_i = 1, 2,$ or 3 for $A, B,$ or C layers, respectively. This is a $T=0$ one-dimensional three-state Potts model with long-range interactions for which we seek the ground-state stacking configuration as a function of valence. Our analysis of this model will consider low-energy defects of the uniform ground state and their mutual interactions.¹¹ We begin in the hcp phase and introduce a single c fault into the structure. The chemical potential of this defect can be computed⁸

from Eq. (2):

$$\gamma_\Delta = \sum_{n=1}^{\infty} n \phi(2nd) + \Delta\phi(2d). \quad (3)$$

If, following BFS, we ignore the interaction between stacking faults, the hcp phase becomes unstable when γ_Δ becomes negative. For $\delta = \Delta\phi(2d) = 0$ this happens when θ is a multiple of $\pi/2$. However, two such defects actually have an interaction energy $V(z)$ which is also calculable from Eq. (2):

$$V(md) = \begin{cases} -2 \sum_{k=1}^{\infty} k \phi[(m+2k)d], & m \text{ even,} \\ -\sum_{k=1}^{\infty} k \phi[(m+2k)d], & m \text{ odd.} \end{cases} \quad (4)$$

The asymptotic form of the potential can be found using the Euler-Maclaurin formula. For m even we find

$$V(md) = \frac{a}{4} \frac{\sin(m\theta + \delta)}{m^2 \sin^2\theta} \quad (m \gg 1). \quad (5)$$

The oscillatory form of $V(z)$ suggests that two stacking faults can have an attractive interaction, and hence the hcp phase can be unstable for small positive values of γ_Δ . If we neglect interactions between c layers, which are greater than nearest neighbors, the exact Potts expression can be simplified to the energy of a one-dimensional model "solid" of stacking faults,

$$E \approx \frac{1}{L} \sum_{j=1}^N \{ \gamma_\Delta + V((k_{j+1} - k_j)d) \}, \quad (6)$$

where $k_j d$ is the position of the j th stacking fault and N is the total number of faults. This class of Hamiltonian is known¹¹ to support a small number of stability intervals separated by first-order discontinuities ("harmless staircase"). Using the asymptotic form of $V(z)$, we find that Eq. (6) does not yield stability for periodic defect arrays with stacking fault separation greater than $4d$ for experimentally realizable values of Z . Shorter-period structures are most easily studied numerically.¹⁰ We find (Fig. 2) a phase diagram in qualitative agreement with Komura's: The fcc, $4H$, and $9R$ polytypes are present.

The polytypes of longer period ($6H, 21R, 10H$, etc.) are missing. A clue to their origin is provided by the fact that there is infinite structural degeneracy right at the first-order transition points. Consider two shorter-period polytypes with defect separations md and $(m+1)d$, respectively (e.g., $4H$ to $9R$). Any intermediate structure with mean defect separation ld ($m < l < m+1$) has an energy

$$E_m(l) = V((m+1)d) - V(md) + \mu_m/l, \quad (7)$$

where

$$\mu_m = \gamma_\Delta + (m+1)V(md) - mV((m+1)d).$$

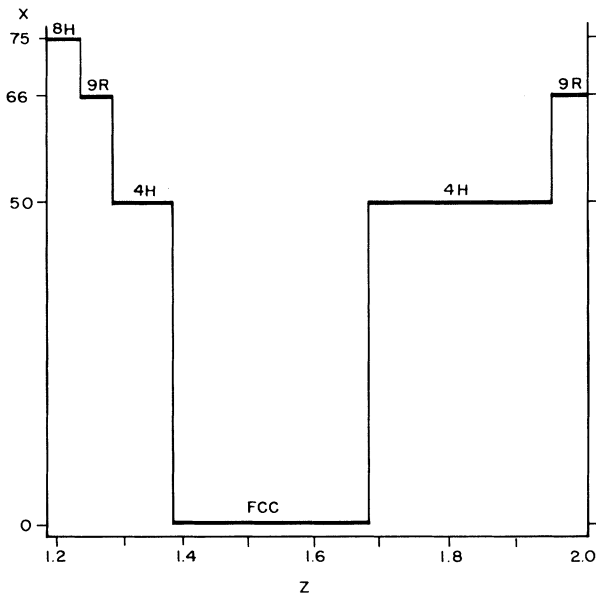


FIG. 2. Crystal-structure polytypism using BFS electronic planar interaction energy. Although the details of the stability interval locations and widths is sensitive to the choice of $\Delta\phi(2)$ and δ , the overall first-order staircase structure is not. Here, $\Delta\phi(2d) = -0.18a$ and $\delta = -\pi/4$.

Note that $E_m(l)$ is independent of l at the phase transition point: $\mu_m = 0$. Hence, a very small energy can break this degeneracy and stabilize a longer-period structure. One source of this energy could be the direct defect-defect interaction beyond nearest neighbors. Indeed, Kitano, Ohba, and Komura¹² have attempted to reproduce the entire observed structural sequence by treating each of the $\phi(nd)$ in the original Potts expression as independent fitting parameters up to $n = 6$. However, we find that their fitted values are completely inconsistent with any BFS potential.

We suggest that the structural degeneracy is lifted by an elastic distortion of the lattice. This identification is supported by x-ray diffraction data¹³ which indicate that stacking faults of the highly modulated structures are appreciably ($\sim 1\%$) displaced from their ideal positions of $z_j = k_j d$. Let u_j denote the true position of the j th fault. The energy cost associated with this additional lattice distortion¹⁴ can be added to the electronic energy to yield a Hamiltonian which describes the transition from $l = m$ to $l = m + 1$:

$$H_m = \frac{1}{L} \sum_{j=1}^N \left\{ \mu_m + \frac{1}{2} V_m (u_{j+1} - u_j - b_m)^2 + \frac{1}{2} \kappa (u_j - k_j d)^2 \right\} + C_m. \quad (8)$$

In this expression, V_m is a simple combination of the expansion coefficients of $V(z)$ around $z = md$ and $z = (m+1)d$, $b_m^2 = m(m+1)$, and κ is related to the velocity of sound along the stacking direction. C_m is a constant which guarantees that $H_m \rightarrow E_m(l)$ as $\kappa \rightarrow \infty$.

This model has been studied by Aubry¹⁵ for the case of a fixed number of defects. The stacking structures which intervene between the short-period $l = m$ and $l = m + 1$ phases are obtained from an equation of state:

$$dU_m(l)/dl = -p_m(l) + \mu_m/l. \quad (9)$$

$U_m(l)$ is the internal energy/defect and $p_m(l)$ is an effective, Z -dependent pressure exerted on the stacking fault "solid." In general, Eq. (9) admits a set of solutions for each Z near the nominal first-order point. However, for c -defect densities less than 50%¹⁶ in the stiff-lattice limit ($\kappa/V_m \gg 1$), the right-hand side of Eq. (9) becomes nearly independent of l and the phase diagram is obtained readily.¹⁵ As illustrated in Fig. 3 (plotted as a function of μ_m/mV_m rather than Z), there is actually a finite stability interval for every ra-

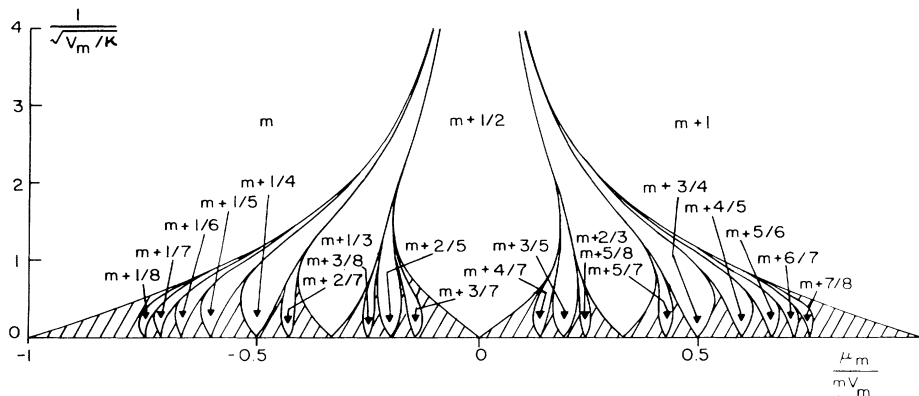


FIG. 3. Crystal structure polytypism taking account of both electronic and elastic contributions to the structural energy for the transitions from $l = m$ to $l = m + 1$ in Fig. 2. The parameter μ_m/mV_m is a smooth function of Z . Longer-period stacking structures are found in the shaded regions.

tional fraction l between m and $m + 1$ which implies that at least a portion of the hcp-fcc transition is a continuous function of Z .

This "devil's staircase"^{7,17} arises from the competition between $V(z)$, which favors $u_{j+1} - u_j = b_m$, and the elastic energy, which favors $u_{j+1} - u_j = md$ or $(m + 1)d$. The most stable intervening phase occurs at $l = m + \frac{1}{2}$ and the next most stable at $l = m + \frac{1}{3}$ and $l = m + \frac{2}{3}$, etc. Comparing our results with those of Komura between the $4H$ and $9R$ phases, we correctly obtain the $l = \frac{9}{4}$, $\frac{7}{3}$, $\frac{5}{2}$, and $\frac{8}{3}$ polytypes ($18H$, $21R$, $10H$, and $16H$). In addition, the $l = \frac{7}{2}$ polytype ($14H$) is seen at higher valence between the short-period $9R$ and $8H$ structures. It would be quite interesting if further investigation revealed additional steps in this system, although other stacking materials¹⁸ may also be good candidates for study.

An hcp-fcc transition sequence is observed in the rare-earth elemental metals as a function of decreasing atomic number. Duthie and Pettifor¹⁹ identified the $5d$ -electron "valence" as the parameter which established crystal stability among the considered structures. In the view espoused in this paper, we note that the asymptotic part of the planar interaction will consist of a sum of terms similar to Eq. (1), one for each partial wave, phase shifted in accordance with the nonlinear screening of the ion.²⁰ Neglecting hybridization, we can define a Fermi wave vector for the d electrons and another for the s electrons, each of which favors a different configuration of defects. However, the amplitude of the $l = 2$ derived Friedel oscillation is much larger than its s -wave counterpart. The " d -valence" analog of Fig. 2 for this case produces precisely the same phase diagram as obtained in Ref. 19. Long-period polytypes must be sought in the narrow range of d count between those represented by the elemental metals. They are found²¹ in intermetallic alloys of rare-earth metals with simple metals.

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⁶See, for example, H. Sato, R. S. Toth, and G. Honjo, *J. Phys. Chem. Solids* **28**, 137 (1967).

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¹⁴This is a very restricted class of lattice distortions. For example, displacements of the h layers are not considered in this model.

¹⁵S. Aubry, in *Solitons and Condensed Matter Physics*, edited by A. Bishop and T. Schneider (Springer, Berlin, 1978), p. 264, and *J. Phys. C* **16**, 2497 (1983). This analysis, and ours, assumes that $V_m > 0$.

¹⁶The fcc- $4H$ transition cannot be analyzed accurately with a stability analysis which begins in the hcp phase. Our model must be complemented by study of h defects in the uniform fcc phase. These results and details of the current study will appear in a future publication.

¹⁷Similar "staircase" polytypism has been studied in insulators [G. D. Price and J. Yeomans, *Acta Crystallogr. Sect. B* **40**, 448 (1984)] and long-period antiphase domains in alloys [J. Kulik and D. de Fontaine, in *Phase Transformations in Solids*, edited by T. Tsakalacos (Elsevier, Amsterdam, 1984), p. 225.] using an Ising model with competing first- and second-neighbor interactions (ANNI model, see Ref. 7). Therein, modulated structures are entropy stabilized at degeneracy points by thermal fluctuations of the appropriate defects. In the present case, this mechanism is ruled out since high-resolution electron-microscope lattice images [Y. Komura, S. Takeda, and M. Takata, *Trans. Jpn. Inst. Met.* **24**, 413 (1983)] clearly show that the stacking-fault boundaries of long-period close-packed structures are quite flat.

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