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GENERALIZED PSEUDOPOTENTIAL THEORY OF d-BAND METALS

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Generalized Pseudopotential Theory of d -Band Metals

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ABSTRACT

The generalized pseudopotential theory (GPT) of metals is reviewed with emphasis on recent developments. This theory, which attempts to rigorously extend to d -band metals the spirit of conventional simple-metal pseudopotential perturbation theory, has now been optimized and fully integrated with the Kohn-Sham local-density-functional formalism, allowing for systematic first-principles calculations. Recent work on the problems of cohesion, lattice dynamics, structural phase stability, pressure- and temperature-induced phase transitions, and melting is discussed.

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1. Introduction

The use of pseudopotentials in solid-state theory has enjoyed widespread popularity for nearly two decades, with numerous specialized techniques having been developed [1-11]. All such methods share in common the initial step of replacing a true Schrödinger equation for the valence electrons in the solid by a pseudo-Schrödinger equation, in which the deep potential and oscillatory valence wavefunctions in the core region are replaced by a relatively weak pseudopotential and nodeless pseudowavefunctions. Moreover, once a pseudopotential has been established, the resulting pseudo-Schrödinger equation can be treated in one of two general ways. The first is by heavy nonperturbative methods in which a basis set (e.g., plane waves) is chosen, a large pseudo-Hamiltonian matrix is set up and diagonalized, and all desired eigenvalues and eigenfunctions are obtained. The empirical pseudopotential method [2] and the more recent *ab initio* pseudopotential (AP) methods [3-5] pioneered by Cohen and others are prime examples of this approach, and have been well-developed for semiconductors, simple metals, and *d*-band metals alike. Alternatively, one can seek to capitalize on the weakness of the pseudopotential and develop perturbation expansions. The focal point of such an approach is usually not the eigenvalue spectrum itself, but rather integrated quantities such as the electron density and total energy from which physical properties can be directly obtained. Straightforward perturbative

methods [1] are confined to simple metals, but over the past decade it has become possible to treat d -band metals as well through more intricate procedures [6-11] based on the narrow width of the d bands. The generalized pseudopotential theory (GPT) [7-10] which we have developed is such a method.

To a large extent, the relative strengths and weaknesses of nonperturbative and perturbative pseudopotential methods tend to be complementary. Nonperturbative methods have the advantage of being able to treat exactly systems with potentials of general shape and magnitude, including systems with extreme variations in environment such as surfaces. At the same time, such methods must rely heavily on crystal symmetry to be tractable and computational effort increases rapidly as this symmetry is lowered. Perturbative methods, on the other hand, can treat analytically the crystal-structure dependence of the bulk electron density and total energy, so that systems of arbitrary symmetry, including completely disordered ones such as liquid metals, can be efficiently handled. The presence of sufficiently weak potentials is always required, however, with the neglect of higher-order terms in the perturbation expansions being the main additional approximation.

In recent years, there has been a great deal of emphasis on the use of first-principles pseudopotentials [3-5, 7-10] and methodologies derived from the Kohn-Sham local-density-functional formalism [12], in contrast to most early formulations in terms of empirical model

pseudopotentials [1,2] and *ad hoc* treatments of exchange and correlation. Both the nonperturbative AP methods [3-5] and the perturbative GPT method [9,10] have now been formulated in this way and have permitted calculation of physical properties from the barest of essentials: the atomic number and weight of the element(s) in question. We review below the GPT method and recent work on its application to problems of current interest in both simple and *d*-band metals.

2. Theoretical Framework of the GPT

The basic theoretical foundations for the GPT are discussed at length in early papers by Harrison [6] and the present author [7], while the systematic development of this theory within the framework of the local-density-functional formalism is treated in detail in more recent papers by the author [9,10]. Briefly, one begins with the local-density Schrödinger equation

$$(T + V)|\psi_\alpha\rangle = E_\alpha |\psi_\alpha\rangle \quad (1)$$

for all the electrons in the metal, where V includes both a direct Coulomb or Hartree potential plus a local exchange-correlation potential. Conceptually, one can divide the electrons governed by Eq. (1) into three broad categories: (i) very tightly-bound inner-core electrons, which are amenable to a purely atomic-like treatment (the

small-core approximation); (ii) less tightly-bound outer-core electrons (i.e., the d -electrons), which are amenable to a tight-binding or LCAO (linear-combination-of-atomic-orbitals) treatment; and (iii) loosely-bound s and p valence electrons, which are amenable to a nearly-free-electron treatment. Invoking the small-core approximation allows one to exactly transform Eq. (1) to the pseudo-Schrödinger equation

$$(T + W)|\phi_a\rangle = E_a |\phi_a\rangle \quad (2)$$

for the remaining s , p , and d electrons, where in optimized form W is the nonlocal pseudopotential operator

$$W = (1-P)V, \quad (3)$$

with

$$P = \sum_c |\phi_c\rangle\langle\phi_c| \quad (4)$$

the inner-core projection operator. In metals, the pseudopotential W is weak for the valence s and p electrons, but not for the outer-core d electrons. A suitable basis set for expanding ϕ_a in a d -band metal then is one including both plane waves $|\underline{k}\rangle$ and localized d -states ϕ_d . The latter are chosen to be exact eigenstates of a suitable atomic-like reference Hamiltonian:

$$(T + v_{at})|\phi_d\rangle = E_d |\phi_d\rangle . \quad (5)$$

A second effectively weak potential is then

$$\Delta = v_{at} - V - \langle \phi_d | v_{at} - V | \phi_d \rangle . \quad (6)$$

In the present formulation of the GPT, we take $v_{at} = v_{pa} + v_{loc}$, where v_{pa} is the zero-order (pseudoatom) potential in the metal and v_{loc} is a convenient barrier localization potential [8-10]. For an optimum choice of v_{loc} , the d -state hybridization potential Δ is small in the interior region of the atomic site on which it is centered and only becomes large in the exterior region. Thus the product $\Delta|\phi_d\rangle$ is everywhere small. The entire structure of the d -bands in the metal and its hybridization with the nearly-free-electron s and p bands can be fully characterized in terms of E_d , d -state overlap matrix elements

$$\langle \phi_d^j | \phi_d^i \rangle \quad \text{and} \quad \langle \phi_d^j | \Delta | \phi_d^i \rangle \quad (7)$$

between states centered on atomic sites i and j , and plane-wave- d -state matrix elements

$$\langle \underline{k} | \phi_d \rangle \quad \text{and} \quad \langle \underline{k} | \Delta | \phi_d \rangle , \quad (8)$$

as detailed comparisons with independent local-density band-structure calculations [13] have verified [10].

For the central theoretical quantities of interest, namely, the electron density $n(\underline{r})$ and the total energy E_{tot} , it is possible to carry out simultaneous perturbation expansions in terms of matrix elements of W and Δ . This is, however, an extremely intricate procedure and becomes progressively more complex as one proceeds from simple metals to metals with empty-, filled-, and partially-filled d bands, respectively. We distinguish these four cases as follows:

(i) *simple metals*. A simple metal is considered to be one with either no d states of interest to consider ($\phi_d = 0$) or d states so tightly bound that they may be absorbed into the inner core ($\Delta = 0$). In the simple-metal limit, the GPT reduces to a refined version of the conventional nonlocal pseudopotential perturbation theory [1]. The prototype simple metals are the third-period elements Na, Mg, and Al.

(ii) *empty- d -band metals*. An empty- d -band metal is one with completely unoccupied d states above but in close proximity to the Fermi level E_F . The band structure and physical properties of such metals can be strongly influenced by these d states through hybridization effects at and below E_F . There are, however, two major simplifications which are possible for this category of materials. First, the effective strength of Δ is small relative to $E_d - E_F$, so that, for example,

$$\frac{\Delta^2}{|\epsilon_k - E_d|} \quad (9)$$

for $\epsilon_k = \hbar^2 k^2 / 2m < E_F$, is also a weak potential for expansion purposes.

Second, it is possible to use nonoverlapping d -basis states ϕ_d since only the hybridization [i.e., Eq. (8)] and not the full internal structure of the d bands [i.e., Eq. (7)] must be described in this case. The heavy alkali and alkaline-earth elements qualify as empty- d -band metals, with Ca and Sr being the prototype materials.

(iii) *filled- d -band metals*. A filled- d -band metal is one with fully-occupied d states below but again in close proximity to E_F . Equation (9) is now small for $\epsilon_k > E_F$, which turns out to be appropriate for expansions purposes in this case. Unlike empty- d -band metals, however, it is not possible to use nonoverlapping d states here because both the hybridization and the internal structure of the d bands must be adequately described. The nominal filled- d -band materials are the noble metals and the group-IB metals, with Zn and Cd being the prototype elements. In practice it has turned out that terms like Eq. (9) are actually somewhat too large for an accurate description of the noble metals in this category and the slight partial-unfilling of the d bands must be taken into account [10].

(iv) *partially-filled- d -band metals*. This is the most general class of metals considered and includes all the remaining transition-series elements with partially-filled d states. No direct simplifications are possible in this case and the perturbation expansions involving Δ solely reflect the weakness of the interatomic d -state couplings [i.e., Eqs. (7) and (8)]. Development of the partially-filled- d -band GPT as a

full computational scheme has only recently begun [10] and is currently being actively pursued.

A key feature of the perturbation expansions developed for $n(\underline{r})$ and E_{tot} in the GPT is the analytical separation of the volume- and structure-dependence of each quantity in the general form

$$A(\underline{R}_1, \dots, \underline{R}_N) = A_0(\Omega) + \sum_i A_1(\underline{R}_i) + \frac{1}{2} \sum_{i,j} A_2(\underline{R}_i, \underline{R}_j) + \frac{1}{6} \sum_{i,j,k} A_3(\underline{R}_i, \underline{R}_j, \underline{R}_k) + \dots, \quad (10)$$

where A_0 , A_1 , A_2 , A_3 , etc. are volume, one-body, two-body, three-body, etc. functionals of W and Δ , all of which may depend on the volume of the metal Ω but not on the individual atomic positions $\underline{R}_i$. Such volume-dependent, but structure-independent *characteristic functions* then determine A for any arbitrary arrangement of atoms. The state of the art in the GPT is to carry the electron-density expansion through one-body terms (i.e., linear screening) and the total-energy expansion through two-body terms (i.e., central-force interactions). This provides internal self-consistency while retaining the dominant structural terms in $n(\underline{r})$ and E_{tot} . The electron density then assumes the form

$$n(\underline{r}) = n_{\text{unif}} + \sum_i n_{\text{core}}(|\underline{r}-\underline{R}_i|) + \sum_i \delta n(|\underline{r}-\underline{R}_i|), \quad (11)$$

where the characteristic functions n_{unif} , n_{core} , and δn are, respectively, the uniform, inner-core and occupied- d -state, and screening plus orthogonalization-hole electron densities [10]. For the total energy, one may write

$$E_{\text{tot}} = E_{\text{vol}} + E_{\text{struc}}, \quad (12)$$

where the large volume contribution E_{vol} includes both the volume and one-body terms in Eq. (10) and the small structural energy E_{struc} takes the form of a lattice sum over a central-force pair potential between atoms. This volume-dependent interatomic pair potential is given by

$$v_{\text{pair}}(r) = (Z^*e)^2 \left[\frac{1}{r} - \frac{2}{\pi} \int_0^\infty F_N(q) \frac{\sin(qr)}{qr} dq \right] + v_{\text{ol}}(r), \quad (13)$$

where the characteristic functions Z^* , F_N , and v_{ol} are the effective valence, normalized energy-wavenumber characteristic, and d -state overlap potential, respectively [10]. The first term in Eq. (13) is the direct Coulomb repulsion between ions of charge Z^*e , the second term is the indirect ion-electron-ion attraction which screens the Coulomb interaction, and the final term represents the remaining interaction of the overlapping d states. At small separation r between atoms, less than the nearest-neighbor distance, the direct Coulomb interaction is

dominant and a strongly repulsive pair potential results. At separations on the order of interatomic spacings, however, the repulsive and attractive contributions are comparable in magnitude and an oscillatory potential typically is obtained. At very large separations, these become the familiar Friedel oscillations. These features are all clearly evident in the interatomic potentials of Ca and Zn shown in Figures 1 and 2, respectively. Shown for comparison in Figures 1 and 2 are the corresponding results calculated in the simple-metal limit. In both cases the effects of the d -state hybridization potential is seen to be large, deepening v_{pair} in the vicinity of the close-packed nearest-neighbor distance in Ca, while suppressing this minimum in Zn.

3. Applications

We have made a variety of recent applications of the GPT to the properties of cohesion, lattice dynamics, crystal phase stability, pressure- and temperature-induced phase transitions, and melting in prototype simple, empty- d -band, and filled- d -band metals.

A. Cohesion

Cohesion in metals is dominated by the volume rather than the structural components of the total energy, but is a subject of fundamental interest in connection with local-density-functional

formalism itself [13,14]. As we have previously demonstrated [10,14], the GPT-calculated cohesive energy in the 22 nontransition metals shows good systematic agreement with both experiment and local-density band-structure calculations [13]. More recently, we have been investigating the volume dependence of the total energy and in particular the zero-temperature pressure-volume relation or equation of state. The equation of state for Ca, calculated in both the simple-metal and empty-*d*-band-metal limits of the GPT, is shown in Figure 3 and compared with experiment [15]. The effect of the *d*-state hybridization is again seen to be large, uniformly lowering the calculated pressure at each volume, and is clearly quite essential to the good agreement achieved between theory and experiment.

B. Lattice Dynamics

The calculation of the phonon spectrum [1] is one of the most revealing tests of the characteristic functions contributing to the structure-dependent part of the total energy. A problem of current interest is the phonon spectrum in Ca, which has only recently been measured experimentally [16,17]. Figure 4 compares the empty-*d*-band GPT spectrum we have calculated with the experimental data of Buchenau et al. [16]. The agreement is clearly very good, especially for the transverse branches. The role of the *d*-state hybridization in achieving this agreement is somewhat more subtle in this case, generally lowering

the calculated frequencies, but in a nonuniform way with the longitudinal branches affected more strongly than the transverse ones. This is shown in Table I for the zone-boundary frequencies. In addition, the small remaining discrepancies for the longitudinal phonons near the zone boundary appear to be explainable as a slight underestimate in the present GPT calculations of the d -state hybridization. In this regard, if the effective strength of the hybridization is increased (by lowering the d -state energy E_d by a small amount E_d^{shift}) to produce optimum agreement between the GPT electron band structure and independent LMTO (linear-muffin-tin-orbital) calculations of the same [18,19], the phonon frequencies are lowered by about the amount needed to reconcile theory and experiment. This is also demonstrated in Table I.

C. Phase Stability and Phase Transitions

Based on calculated total-energy differences at fixed volume, the GPT generally gives a good account of the observed crystal structures in prototype metals [10]. In particular, it is found that d -state hybridization is essential to explaining the normal fcc structures of Ca and Sr and the high c/a axial ratios in the hcp metals Zn and Cd. Some insight into the role of the d states in this regard can be gained by examining the interatomic potentials for Ca and Zn in Figures 1 and 2. The fcc stability in Ca, for example, is clearly aided by the deep

minimum in $v_{\text{pair}}(r)$ produced by the d -state hybridization at the fcc nearest-neighbor distance. In the case of Zn, on the other hand, the suppression of this minimum makes it energetically favorable to increase the c/a axial ratio above its ideal value, primarily because the large group of second and fourth neighbors then move towards the secondary minimum in v_{pair} near $r/R_{\text{WS}} = 3.0$.

More generally, one can examine elemental crystal phase stability as a function of pressure and temperature. In collaboration with A. K. McMahan, an extensive study of the third-period elements Na, Mg, Al, and (metallic) Si has recently been performed in the volume range from normal density ($\Omega/\Omega_0 \approx 1.0$) to about ten-fold compression ($\Omega/\Omega_0 = 0.1$) [20]. This study, which included parallel sets of calculations with both the GPT and the (nonperturbative) LMTO methods, has led to a number of interesting conclusions:

(i) Under pressure all of the third-period elements eventually become d -band metals, as the initially empty free-electron-like $3d$ bands, lower, narrow, and eventually hybridize with the s and p bands below under compression. Up to at least five-fold compression, these metals appear to be well described by the empty- d -band limit of the GPT.

(ii) A wealth of new, yet unobserved, high-pressure structural phase transitions are predicted. These results are summarized in Table II. Most of these transitions occur at very high pressures, but several are predicted to occur below 1000 kbar and these could be accessed with

existing diamond-anvil-cell technology. In Mg, Al, and compressed Si, at least, all of these transitions are controlled by *d*-state effects.

(iii) In Mg, Al, and Si the same qualitative predictions are obtained with both the GPT and LMTO methods. Moreover, in the case of Al, independent AP calculations of Lam and Cohen [21] have confirmed our results. The quantitative correspondence of the LMTO, GPT, and AP results in Al is also quite good, as shown in Table 11 and Figure 5. In the special case of Na, on the other hand, the LMTO method fails due to the very tiny energy differences between structures in that metal, while the GPT results still appear to be reliable [20].

Temperature-induced phase transitions can be addressed in the context of the GPT by adding to E_{tot} the appropriate phonon free energy and considering total free-energy differences at fixed volume [24]. The observed hcp $\rightarrow$ bcc transition in Na [10] and the fcc $\rightarrow$ bcc transitions in Ca and Sr [10,24] are reasonably well accounted for in this manner. The most recent empty-*d*-band GPT calculation of the pressure-temperature phase diagram of Ca is shown in Figure 6 and compared with experiment [24]. The overestimate of the positive slope in the fcc-bcc phase line is likely an effect associated with the neglect of the partial-filling of the *d* bands under pressure. In this regard, a direct pressure-induced fcc $\rightarrow$ bcc transition at 210 kbar and room temperature has now been observed experimentally in Ca [26] and theoretical LMTO

calculations [27] suggest that this transition is indeed driven by the filling of the $3d$ bands.

D. Melting

Pseudopotential calculations of liquid-metal thermodynamic properties [28] require as input information on the structure factor and the entropy of the fluid, which in principle, can be provided by statistical mechanics. The state of the art in this regard is to use so-called fluid perturbation theory, in which the structure factor and entropy are approximated as those for a simplified model reference system containing a single variational parameter constrained to minimize the Helmholtz free energy of the real system. For simple-metal liquids, hard-sphere [28], soft-sphere [29,30], and one-component-plasma [30,31] reference systems have been proposed and studied. In the case of Al, the soft-sphere model of Ross [29] appears to be optimum in the sense of producing the lowest overall Helmholtz free energy. We have calculated the GPT melting curve for Al based on this reference system by equating solid and liquid Gibbs free energies as a function of pressure and temperature. This result is plotted in Figure 7 and compared with experiment [32]. The good agreement obtained is quite encouraging and bodes well for similar investigations on d -band metals.

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Bibliography

- [1] V. Heine and D. Weaire, Solid State Phys. 24, 249 (1970); W. A. Harrison, *Pseudopotentials in the Theory of Metals*, (Benjamin, New York, 1966).
- [2] M. L. Cohen and V. Heine, Solid State Phys. 24, 37 (1970).
- [3] A. Zunger and M. L. Cohen, Phys. Rev. B 18, 5449 (1978) and 20, 4082 (1979).
- [4] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. 43, 1494 (1979).
- [5] M. T. Yin and M. L. Cohen, Phys. Rev. B 25, 7403 (1982) and references therein.
- [6] W. A. Harrison, Phys. Rev. 181, 1036 (1969).
- [7] J. A. Moriarty, Phys. Rev. B 5, 2066 (1972).

- [8] J. A. Moriarty, Phys. Rev. B 10, 3075 (1974).
- [9] J. A. Moriarty, Phys. Rev. B 16, 2537 (1977).
- [10] J. A. Moriarty, Phys. Rev. B 26, 1754 (1982).
- [11] L. Dagens, J. Phys. F 6, 1801 (1976) and 7, 1167 (1977);
Phys. Status Solidi B 84, 311 (1977).
- [12] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
- [13] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals*, (Pergamon, New York, 1978).
- [14] J. A. Moriarty, Phys. Rev. B 19, 609 (1979).
- [15] *American Institute of Physics Handbook* (McGraw-Hill, New York, 1972), p 4-99.
- [16] U. Buchenau, H. R. Schober, and R. Wagner, J. Phys. (Paris),
Colloque C6, 395 (1981).
- [17] J. Zarestky, C. Stassis, B. N. Harmon, and R. M. Nicklow,
Bull. Am. Phys. Soc. 27, 274 (1982).
- [18] J.-P. Jan and H. L. Skriver, J. Phys. F 11, 805 (1981).
- [19] A. K. McMahan (private communication).
- [20] J. A. Moriarty and A. K. McMahan, Phys. Rev. Lett. 46, 809 (1982);
A. K. McMahan and J. A. Moriarty, Phys. Rev. B (in press).
- [21] P. K. Lam and M. L. Cohen, Phys. Rev. B (in press).
- [22] M. T. Yin and M. L. Cohen, Phys. Rev. Lett. 45, 1004 (1980) and
Phys. Rev. B (in press).
- [23] J. Hafner, Phys. Rev. B 10, 4151 (1974).
- [24] J. A. Moriarty, Phys. Rev. B 8, 1338 (1973).

- [25] A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, Phys. Rev. 132, 1620 (1963).
- [26] W. B. Holzapfel (private communication).
- [27] H. L. Skriver, Phys. Rev. Lett. 49, 1768 (1982).
- [28] N. W. Ashcroft and D. Stroud, Solid State Phys. 33, 1 (1978).
- [29] M. Ross, J. Chem. Phys. 73, 4445 (1980).
- [30] M. Ross, H. E. DeWitt, and W. B. Hubbard, Phys. Rev. A 24, 1016 (1981).
- [31] K. K. Mon, R. Gann, and D. Stroud, Phys. Rev. A 24, 2145 (1981).
- [32] J. Lees and B. H. J. Williamson, Nature 208, 278 (1965).

TABLE 1. GPT zone-boundary electron band energies (in Ry) and longitudinal (L) and transverse (T) phonon frequencies (in THz) for Ca calculated in the simple-metal limit with no hybridization, in the empty-d-band-metal limit with hybridization included, and in the latter limit with the d-state energy E_d lowered by E_d^{shift} .

Hybridization	No	GPT		LMTO ^a	Expt
E_d^{shift}	0.0	Yes	Yes	Yes	-
		0.0	-0.06	-	-

Band energies:

$X_4-\Gamma_1$	0.36	0.36	0.36	0.37	
$X_1-\Gamma_1$	0.37	0.29	0.27	0.25	
$L_2-\Gamma_1$	0.28	0.28	0.28	0.28	
$L_1-\Gamma_1$	0.27	0.23	0.22	0.22	

Phonon frequencies:

L [100]	6.0	5.3	5.0	4.9 ^b	4.5 ^c
T [100]	4.0	3.9	3.7	3.6	3.6
L [111]	6.0	5.2	4.7	4.8	4.6
T [111]	2.4	2.3	2.3	2.3	2.4

^aMcMahan [19]. Same as Fig. 4(b) of Jan and Skriver [18].

^bBuchenau et al. [16].

^cZarestky et al. [17].

TABLE II. A summary of predicted zero-temperature structural phase transitions in the third-period simple metals from LMTO [20], GPT [20], and AP [21,22] calculations. Also given are the atomic volume (Ω) and pressure (P) at the indicated transitions, with significant volume change across a transition is denoted by two values for Ω separated by a comma. Ω_0 is the observed one-atmosphere atomic volume except as indicated. Note that 1 GPa = 10 kbar.

element	Ω_0 (a.u.)	transition	Ω (a.u.)			P(GPa)		
			LMTO	GPT	AP	LMTO	GPT	AP
Na	255.2	hcp $\rightarrow$ bcc ^a		219			1	
		bcc $\rightarrow$ hcp ^a		71			104	
		hcp $\rightarrow$ fcc ^b	42			435		
Mg	156.8	hcp $\rightarrow$ bcc	88	91		57	50	
		bcc $\rightarrow$ fcc	63	37		180	790	
Al	112.0	fcc $\rightarrow$ hcp	65	48	54 ^c	120	360	240 ^c
		hcp $\rightarrow$ bcc	57	41	46 ^c	200	560	420 ^c
Si	135.1	dia $\rightarrow$ β -tin			125.97 ^d			10 ^d
		β -tin $\rightarrow$ hcp			82.76 ^e			41 ^e
	97.0 ^f	hcp $\rightarrow$ fcc	67	65		76	80	
		fcc $\rightarrow$ bcc	21	24		360	250	

^aGPT-predicted only.

^bLMTO-predicted only.

^cLam and Cohen [21].

^dYin and Cohen [22].

^eBased on extrapolations of the total-energy results of Yin and Cohen [22]. Does not take into account the possibility of an intermediate bct structure (see, for example, Hafner [23]).

^fLMTO predicted P=0 volume of the bcc phase, the most stable amongst the fcc, hcp, and bcc phases at this volume [20].

Figure Captions

- Figure 1. Interatomic pair potential of Ca as calculated in the simple-metal and empty-d-band-metal limits of the GPT. Location and number of the fcc first neighbors and the bcc first and second neighbors are indicated. R_{WS} is the Wigner-Seitz radius.
- Figure 2. Interatomic pair potential of Zn as calculated in the simple-metal and empty-d-band-metal limits of the GPT. Location and number of the ideal hcp near neighbors are indicated. Horizontal arrows show the direction these locations move as the c/a axial ratio is increased above ideal. R_{WS} is the Wigner-Seitz radius.
- Figure 3. Zero-temperature equation of state for Ca as calculated in the simple-metal and empty-d-band-metal limits of the GPT and compared with experiment [15].
- Figure 4. Phonon spectrum for fcc Ca as calculated in the empty-d-band-metal limit of the GPT vs. the experimental results of Buchenau et al. [16]. Longitudinal (L) and transverse (T or T_1 and T_2) branches are indicated.
- Figure 5. Comparison of (a) bcc-fcc and (b) hcp-fcc total energy differences for Al vs. volume, as calculated from the simple-metal and empty-d-band-metal limits of the GPT (dashed

and solid lines, respectively) [20], the LMT0 method (long-short dashed line) [20], and the AP method (dotted line) [21].

Figure 6. Pressure-temperature phase diagram for Ca as calculated in the empty-d-band-metal limit of the GPT vs. experiment [25].

Figure 7. Theoretical GPT melting curve for Al based on the soft-sphere liquid-metal reference system of Ross [29] vs. experiment [32].

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7