Hybridization and the fcc-bcc Phase Transitions in Calcium and Strontium*

John A. Moriarty

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544
(Received 22 September 1972)

The effect of s-d hybridization on the phase stabilities of calcium and strontium is studied as a function of temperature and pressure within the context of the generalized pseudopotential theory. The inclusion of hybridization is found to favor the fcc structure at all pressures and, in particular, is necessary to explain the observed fcc structure in these metals at zero temperature and pressure. Phase boundaries are calculated by equating the free energy of the fcc structure to that of the bcc structure. Temperature-induced phase transitions are predicted to occur at 555 °K in calcium and 625 °K in strontium, as compared with the experimentally observed values of 721 and 830 °K, respectively. The transition temperature T_c is found to increase with pressure P for both metals. The predicted dT_c/dP is qualitatively correct but quantitatively too large for calcium, while of the wrong sign for strontium. However, in the simple-metal limit of no hybridization, dT_c/dP is calculated to be negative in both cases. This suggests that the experimental behavior at nonzero pressures can be explained by an appropriate balance of pseudopotential and hybridization contributions to the free energy.

I. INTRODUCTION

In an earlier paper[1] (hereafter referred to as Paper I), we made a detailed application of the generalized pseudopotential theory[2,3] to the alkaline-earth metals calcium, strontium, and barium. The motivation for that work was to investigate the influence, through hybridization, of the empty d band above the Fermi level upon the properties of these metals. One of the more interesting findings of that work was that the hybridization plays an important role in stabilizing the (observed) fcc structure at zero temperature and pressure in both calcium and strontium. In this paper we shall pursue this matter further and consider the phase stabilities of these metals as a function of both temperature and pressure.

Experimentally,[4] both calcium and strontium undergo a temperature-induced transition from the fcc to the bcc structure at zero pressure. This occurs at 721 and 830°K, respectively. In calcium the transition temperature T_c increases with pressure, while in strontium T_c decreases with pressure and goes to zero at about 35 kbar.

From a theoretical point of view, the fcc-bcc phase transitions in calcium and strontium were investigated by Animalu[5] in the context of the second-order simple-metal pseudopotential theory. Using a local approximation to evaluate the energy-wave-number characteristic and taking the effective valence equal to the true valence, he calculated and compared free energies of the fcc and bcc structures for two model pseudopotentials. His model A pseudopotential was taken to be the Heine-Abarenkov model potential,[6] referred to as HAA-II in Paper I; his model B pseudopotential was constructed from model A by an *ad hoc* adjustment in the model-potential parameters designed to pro-

duce a more realistic phonon spectrum and free energy. With both models he found the bcc phase of calcium to be always more stable than the fcc phase. For strontium, on the other hand, his model B pseudopotential led to a qualitatively correct pressure-temperature phase diagram.

One might suspect the inadequacy of the simple-metal theory for calcium and strontium, however, simply by examining the experimental trend in the stable structures of the alkaline-earth metals at zero temperature and pressure. Both beryllium and magnesium are stable in the hcp structure with axial ratios near the ideal value, but there is an abrupt change to a stable fcc structure in calcium. The second-order simple-metal theory correctly predicts[7] the hcp structures of beryllium and magnesium, but as our calculations show, it also predicts this trend to continue in calcium and strontium. The obvious physical feature which sets calcium and strontium apart is the hybridization of the otherwise free-electron-like bands with the empty d band above the Fermi level in these metals. This hybridization, of course, is missed by the second-order simple-metal theory.

In the generalized pseudopotential theory of calcium and strontium, an enlarged basis set consisting of plane waves and localized d states is used to calculate the total energy of the electron system. The result is a more rapidly convergent expansion in which both pseudopotential and s-d (i.e., plane-wave d) hybridization terms enter directly. Because the hybridization matrix elements are small in comparison to $E_d - E_F$ (the position of the d band minus the Fermi energy) for calcium and strontium, it is possible to order the hybridization terms and combine them with pseudopotential terms of the same magnitude.[1,3] The final total energy expression thus retains much of the mathematical sim-

plicity of the simple-metal result, while at the same time, it takes direct account of the s-d hybridization.

We proceed with the phase-stability calculation in much the same spirit as did Animalu. The free energy of the metal is determined from its effective valence and its energy–wave-number characteristic, where the latter is now a function of both a pseudopotential and a hybridization potential. In the simple-metal limit of no hybridization our calculation of the free energy parallels that of Animalu, although, unlike Animalu, we always compute the effective valence and energy–wave-number characteristic rigorously from first principles. After briefly reviewing the relevant formalism in Sec. II, we consider the phase stabilities of calcium and strontium both with and without hybridization included in Sec. III.

II. THEORETICAL APPROACH

At a fixed temperature T and pressure P, the most stable phase of a metal is that which has the lowest Gibbs free energy

$$G = F + P\Omega \, , \tag{1}$$

where Ω is the volume of the metal and F is the Helmholtz free energy

$$F = E - TS \, . \tag{2}$$

The quantities E and S are, respectively, the total internal energy and the entropy. At the phase boundary separating the bcc and fcc phases of a metal, therefore, one must have

$$\Delta G = \Delta F + P\Delta\Omega = 0 \, , \tag{3}$$

where $\Delta X = X_{bcc} - X_{fcc}$ for any quantity X. For $\Delta G < 0$ the bcc structure is stable, while for $\Delta G > 0$ the fcc structure is stable.

In order to calculate ΔG for a metal, we employ the adiabatic principle to uncouple the electron and phonon systems. To second order in the pseudopotential, the hybridization potential squared, and $(k_B T/E_F)$, the Helmholtz free energy per ion of the electron system can be written

$$F_{el} = E_{fe} + E_{bs} + E_{es} + E_{ol} - ZE_F \left(\tfrac{1}{2}\pi\right)^2 (k_B T/E_F)^2 \, , \tag{4}$$

where Z is the valence of the metal, E_F is the free-electron Fermi energy, and k_B is the Boltzmann constant. The first four quantities on the right-hand side of Eq. (4) are, respectively, the free-electron energy, the band-structure energy, the electrostatic (or Ewald) energy, and the overlap energy. These terms make up the familiar internal energy at $T = 0$, which was discussed in Paper I. The final term in Eq. (4) is the Helmholtz free energy of the free-electron gas minus the zero-temperature kinetic energy, which has already been

included in E_{fe}. Both this free-energy term and E_{fe} depend only on the volume Ω and not on the configuration of the ions. As a consequence, these terms will make essentially no contribution to ΔG. As demonstrated in Paper I, the overlap energy can be made vanishingly small by a proper choice of d basis functions and may also be dropped in the present analysis. If Ω is taken to be the atomic volume of the metal, then the remaining band-structure energy and electrostatic energy per ion can be written

$$E_{bs} = - \sum_{\vec{q}_0}' (4\pi Z^{*2}/q_0^2 \Omega) F_N(q_0) \tag{5}$$

and

$$E_{es} = - \alpha_{es} Z^{*2}/R_{WS} \, , \tag{6}$$

where Z^* is the usual effective valence of the metal, F_N is the normalized energy–wave-number characteristic, and R_{WS} is the Wigner-Seitz radius $(\Omega = \tfrac{4}{3}\pi R_{WS}^3)$. The sum in Eq. (5) runs over all reciprocal-lattice vectors $\vec{q}_0$, excluding the $\vec{q}_0 = 0$ vector. The geometrical constant α_{es} is 1.79186 for the bcc structure and 1.79175 for the fcc structure.

The phonon system is treated in the harmonic approximation, in which the Helmholtz free energy per ion is given by the well-known expression

$$F_{ph} = (k_B T/N) \sum_{\vec{q}} \ln[2 \sinh(\hbar\omega_q/2k_B T)] \, , \tag{7}$$

where N is the number of ions in the metal, $\hbar$ is Planck's constant, and ω_q is the phonon frequency for wave vector $\vec{q}$. The sum in Eq. (7) runs only over the first Brillouin zone. At zero temperature F_{ph} reduces to the familiar zero-point vibrational energy:

$$F_{ph} = E_{ph}^0 \quad \text{at } T = 0$$

$$= (1/2N) \sum_{\vec{q}} \hbar\omega_q \, . \tag{8}$$

In the harmonic approximation the ω_q are independent of the temperature and depend only on the atomic volume and crystal structure of the metal. The ω_q may be calculated entirely within the pseudopotential framework once Z^* and $F_N(q)$ are specified.

One may use Eqs. (3), (4), and (7) to obtain an explicit formula for ΔG. First note that the volume change accompanying the fcc-bcc phase transformation is very slight; typically, $\Delta\Omega/\Omega$ is 1% or less. If one expands the Helmholtz free energy for the bcc structure in powers of $\Delta\Omega$, then ΔF can be written

$$\Delta F = (F_{bcc} - F_{fcc})_\Omega + \left(\frac{dF_{bcc}}{d\Omega}\right)_\Omega \Delta\Omega + O((\Delta\Omega)^2) \, , \tag{9}$$

where the terms on the right-hand side of this equation are to be evaluated at constant volume Ω.

TABLE I. Atomic volumes and associated quantities for calcium and strontium used in the present calculations. Both Ω and R_{WS} are in a.u. while P is in kbar.

Quantity	1.10	1.00	Ω/Ω_0 0.90	0.80	0.70
			Calcium		
Ω	319.0	290.0	261.0	232.0	203.0
R_{WS}	4.239	4.106	3.964	3.812	3.646
P^a	...	0	20	50	100
			Strontium		
Ω	411.0	373.6	336.3	298.9	261.5
R_{WS}	4.612	4.468	4.314	4.148	3.967
P^a	...	0	15	35	70

[a]Values taken from the experimental pressure-volume curves of F. P. Bundy and H. M. Strong, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1963), Vol. 13, p. 116.

By the first law of thermodynamics, the second term on the right-hand side of Eq. (9) is (to lowest order) $- P \Delta \Omega$, which cancels the $P \Delta \Omega$ term in Eq. (3). Thus to first order in $\Delta \Omega / \Omega$, one has

$$\Delta G = \Delta E_{bs} + \Delta E_{es} + \Delta F_{ph} , \qquad (10)$$

where again the terms on the right-hand side in this equation are to be evaluated at constant volume. At zero temperature, the leading correction term to ΔG is $\frac{1}{2}\Omega B(\Delta\Omega/\Omega)^2$, where B is the bulk modulus. For $\Delta\Omega/\Omega = 0.01$ this term is of the order of 10^{-5} Ry (and negligible) for both calcium and strontium.

We have now reduced the task of calculating ΔG at temperature T and pressure P to that of determining Z^* and $F_N(q)$ at the appropriate volume Ω and then evaluating the right-hand sides of Eqs. (5)–(7) and (10). Utilizing the formalism of Paper I, we have calculated Z^* and $F_N(q)$ for calcium and strontium both with and without hybridization
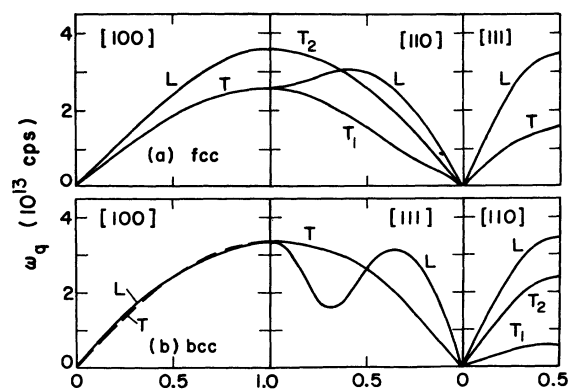

FIG. 1. Phonon frequencies for calcium along principal symmetry directions for $\Omega/\Omega_0 = 1.00$: (a) fcc structure, (b) bcc structure.

TABLE II. Zero-point vibrational energies (10^{-4} Ry) as a function of volume for calcium.

Structure	1.10	1.00	Ω/Ω_0 0.90	0.80	0.70
		Without hybridization			
fcc	14.5	16.4	18.6	21.3	24.6
bcc	13.8	15.9	18.2	21.0	24.4
		With hybridization			
fcc	14.9	16.9	19.1	21.8	25.1
bcc	14.2	16.2	18.5	21.2	24.5

at volumes ranging from $\Omega/\Omega_0 = 1.10$ to 0.70, where Ω_0 is the normal atomic volume at zero pressure. The precise values of Ω used in these calculations are listed in Table I. The localization potential used to construct the d basis states was taken to be a square well of radius R_{WS} and depth $100Z/R_{WS}$ for each volume Ω. This procedure is essentially equivalent to requiring that the d state vanish at R_{WS} and beyond, and provides a consistent method of calculating the hybridization at each atomic volume.

The formulas for calculating the phonon frequencies ω_q from Z^* and $F_N(q)$ can be found in a number of places, including Animalu's paper.[5] With each set of Z^* and $F_N(q)$, we have computed ω_q along the three principal symmetry directions for both the fcc and bcc structures. Figure 1 shows the phonon spectra obtained for calcium at $\Omega/\Omega_0 = 1.00$ when hybridization is included. In general, the qualitative features of these curves are preserved as the volume is varied and also in the simple-metal limit of no hybridization. One qualitative difference which does occur is that the transverse branch of the bcc spectrum does not cross above the longitudinal branch for $\Omega/\Omega_0 \le 0.80$ nor in the simple-metal limit for any volume. This behavior, however, does not have any noticeable effect on ΔF_{ph}.

Quantitatively, the phonon spectrum may be characterized by the zero-point vibrational energy E_{ph}^0, which is a measure of the average value of ω_q. In Table II we have listed the E_{ph}^0 that we calculated here for calcium. Note that E_{ph}^0 always increases when either Ω is decreased or hybridization is included at a fixed volume. Also note that ΔE_{ph}^0 is always negative, which means that the average bcc frequency is lower than the average fcc frequency. In the simple-metal limit $|\Delta E_{ph}^0|$ approaches zero as Ω decreases, while it remains almost constant when hybridization is included.

The same over-all qualitative picture emerges for strontium, and in Table III we have listed our calculated E_{ph}^0 for this metal. We point out, however, that some of the transverse bcc phonon frequencies become imaginary for $\Omega/\Omega_0 = 0.70$ when

TABLE III. Zero-point vibrational energies (10^{-4} Ry) as a function of volume for strontium.

Structure	Ω/Ω_0				
	1.10	1.00	0.90	0.80	0.70
Without hybridization					
fcc	9.1	10.2	11.6	13.3	15.3
bcc	8.7	10.0	11.4	13.1	15.2
With hybridization					
fcc	9.5	10.7	12.1	13.7	15.8
bcc	8.9	10.1	11.5	13.1	...[a]

[a]Some phonon frequencies were calculated to be imaginary.

hybridization is included. This means that the bcc structure cannot be stable at this volume. We also comment that our simple-metal values for E_{ph}^0 of 10.2×10^{-4} Ry for the fcc phase and 10.0×10^{-4} Ry for the bcc phase of strontium compare favorably with Animalu's (model B) values of 10.5×10^{-4} and 10.2×10^{-4} Ry, respectively.

In calculating the above quantities two approximate numerical procedures have been used. The first of these concerns the evaluation of sums over reciprocal-lattice vectors which occur in the formulas for both the band-structure energy and the phonon frequencies. In all cases, we have performed such sums out to a sphere of radius $8.15q_D$, where q_D is the Debye wave number. Within this sphere there are 536 reciprocal-lattice vectors for the fcc structure and 554 for the bcc structure. This procedure seems to provide more than adequate convergence. In a test case, increasing the sphere radius from $7.15q_D$ to $8.15q_D$, which increases the number of reciprocal-lattice vectors summed over by about 50%, changed ΔE_{bs}, ΔE_{ph}^0, and ΔG by about 6%, 0.1%, and 6%, respectively.

The second procedure concerns the integration over the first Brillouin zone required in Eqs. (7) and (8). To perform such integrations, we have replaced the first zone by the Debye sphere and have used the so-called three-direction Houston's method, as described by Animalu.[5] This was done as a matter of convenience rather than strict necessity. Any small quantitative error this approximation may introduce into ΔE_{ph}^0 or ΔF_{ph} will not affect our final conclusions.

III. PHASE STABILITY CALCULATIONS

A. Pressure-Induced Transitions

We first consider the phase stabilities of calcium and strontium in the limit of zero temperature. In that limit Eq. (10) reduces to

$$\Delta G = \Delta E_{bs} + \Delta E_{es} + \Delta E_{ph}^0 \ . \tag{11}$$

Both ΔE_{ph}^0 and ΔE_{es} give predictable contributions to ΔG. As noted above, ΔE_{ph}^0 is always negative

and thus this contribution always favors the bcc structure over the fcc structure, although only slightly. From Tables II and III it can be seen that $|\Delta E_{ph}^0|$ has a maximum value of 0.7×10^{-4} Ry for calcium and 0.6×10^{-4} Ry for strontium at Ω/Ω_0 = 1.10. The electrostatic-energy contribution ΔE_{es} is also always negative, as can be inferred from Eq. (6). The quantities Z^* and $(R_{WS})^{-1}$, and hence $|\Delta E_{es}|$, increase as the volume is decreased. The effective valence Z^* also increases slightly upon the inclusion of hybridization at a given volume. The approximate upper and lower limits on Z^* over the volume range under consideration here are, respectively, 2.55 and 2.33 for calcium and 2.69 and 2.40 for strontium. Over this volume range, $1.4 \leq |\Delta E_{es}| \leq 2.0$ (10^{-4} Ry) for both calcium and strontium. In contrast to ΔE_{ph}^0 and ΔE_{es}, the band-structure energy contribution ΔE_{bs} will depend in detail on the form of the energy–wave-number characteristic.

We have calculated band-structure and electrostatic energies for nine different crystal structures as a function of Ω. In addition to the fcc and bcc structures, we have considered seven hcp structures with axial ratios ranging from 1.5 to 2.0. In all cases, it was found that the ideal axial ratio (1.63) minimizes the hcp energy. Apart from the zero-point vibrational energy, Fig. 2(a) shows the zero-temperature Gibbs free energy of the bcc and ideal hcp structures relative to that of the fcc structure for calcium as a function of volume in the simple-metal limit of no hybridization. Figure 2(b) shows the corresponding result for strontium. Note that for both metals the ideal hcp structure is stable at Ω/Ω_0 = 1.00, while at a sufficiently compressed volume the bcc structure becomes stable. In general, these findings are not consistent with experimental observation, although our simple-metal model does permit the observed pressure-induced transition from fcc to bcc in strontium. We should also point out that the negative slope of the bcc curve in Figs. 2(a) and 2(b) is in qualitative agreement with Animalu's calculations.[5] However, only in strontium (with model B) did he find the fcc energy to be lower than the bcc energy at Ω/Ω_0 = 1.00.

In Figs. 3(a) and 3(b) we have plotted the results of the above calculations repeated with hybridization included. Note that the fcc structure is now stable at Ω/Ω_0 = 1.00 for both metals, and that it becomes more stable as the volume is decreased. This latter behavior is qualitatively correct for calcium, but not for strontium.

B. Temperature-Induced Transitions

We next consider the case of zero pressure and finite temperature. Because ΔE_{bs} and ΔE_{es} are now constant, the sign of ΔG can only be changed
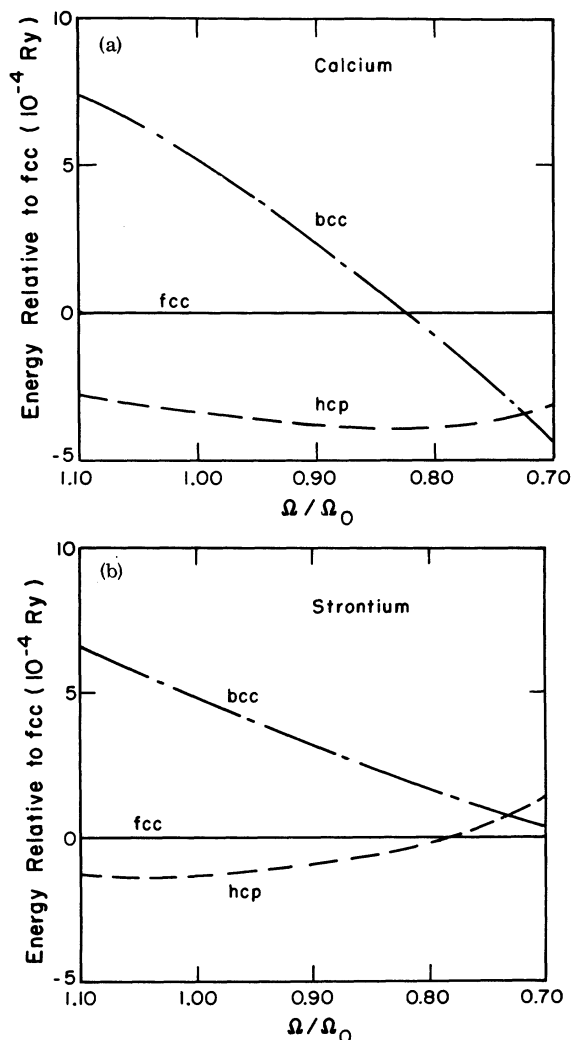
FIG. 2. Band-structure energy plus electrostatic energy of the bcc and ideal hcp structures relative to that of the fcc structure as a function of volume in the simple-metal limit of no hybridization: (a) calcium, (b) strontium.

by the phonon contribution to the free energy ΔF_{ph}. As indicated above, ΔF_{ph} is small and negative at $T = 0$. As the temperature is increased, the sign of ΔF_{ph} must remain negative because the phonon frequencies are not altered. The magnitude of ΔF_{ph} will increase, however, as can be inferred from Eq. (7). Thus if ΔG is positive at $T = 0$, there will be some temperature T_c where $\Delta G = 0$ and an fcc-bcc phase transition is possible. In contrast, no fcc-hcp transition is expected because the ideal hcp structure, being close-packed like the fcc structure, should have a zero-point vibrational energy above that of the bcc structure by an amount comparable to $|\Delta E^0_{ph}|$.

In Fig. 4 we have plotted ΔG for calcium calculated both with and without hybridization. The values of T_c determined (to ± 5 °K) from the condition

$\Delta G = 0$ are, respectively, 555 and 245°K. These values are to be compared with the experimental transition temperature of 721°K. Also note that the slopes of the two ΔG curves in Fig. 4 are almost identical. This means that hybridization has had virtually no effect on ΔF_{ph}.

Figure 5 shows the corresponding results for strontium. The predicted values of T_c are 625 and 260 °K, with and without hybridization, respectively, as compared with Animalu's 150 °K value[5] and the experimental value of 830 °K. Also, note that hybridization has steepened the (negative) slope of ΔG somewhat.

C. Phase Diagrams

The calculation of T_c at nonzero pressure again proceeds by requiring that $\Delta G = 0$ at the appropriate
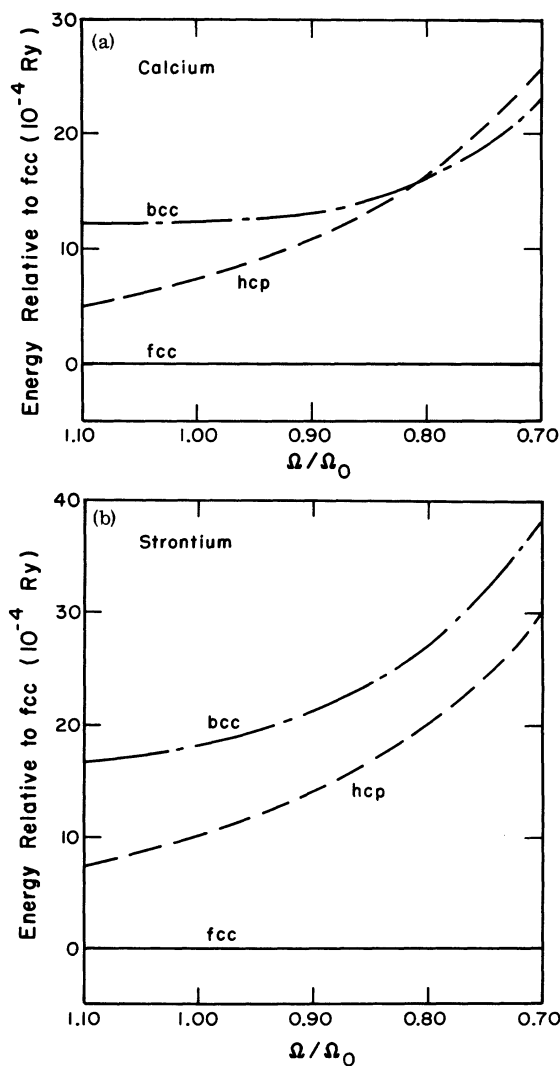

FIG. 3. Band-structure energy plus electrostatic energy of the bcc and ideal hcp structures relative to that of the fcc structure as a function of volume with hybridization included: (a) calcium, (b) strontium.
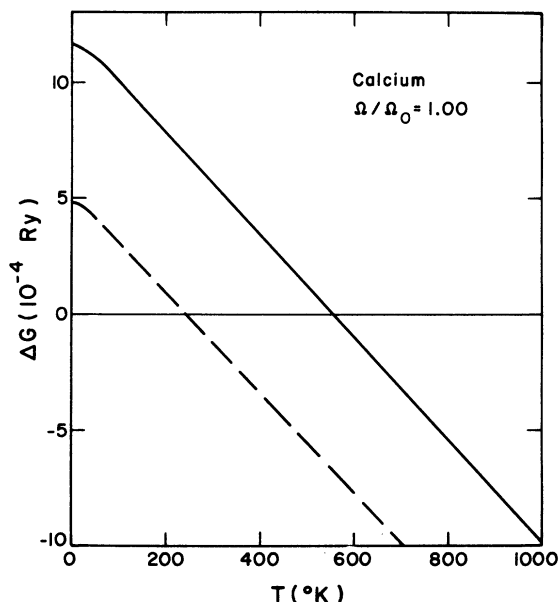
FIG. 4. bcc-fcc difference in free energy vs temperature for calcium as calculated from Eq. (10) at Ω/Ω_0 = 1.00. The solid line refers to the calculation done with hybridization and the dashed line to that done without hybridization.
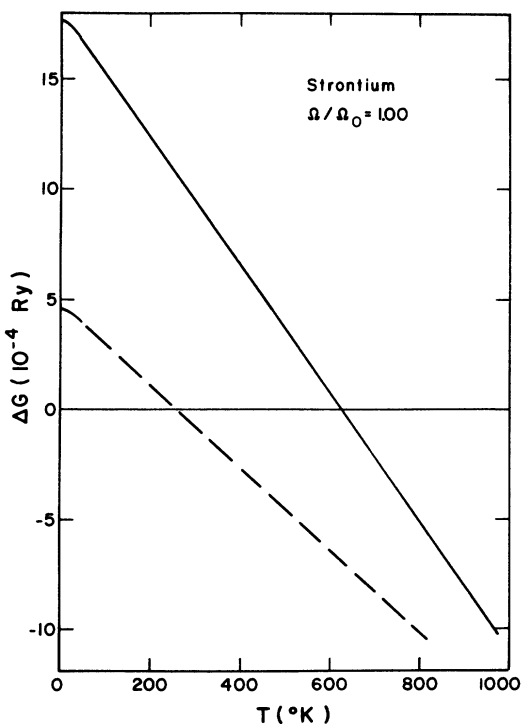

FIG. 5. bcc-fcc difference in free energy vs temperature for strontium as calculated from Eq. (10) at Ω/Ω_0 = 1.00. The solid line refers to the calculation done with hybridization and the dashed line to that done without hybridization.
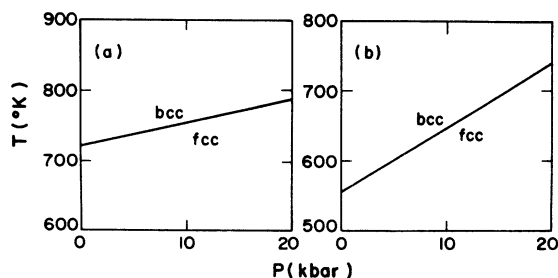

FIG. 6. Pressure-temperature phase diagram for calcium: (a) experimental from Ref. 4, (b) present calculation with hybridization included.

atomic volume. The values so determined for calcium are listed in Table IV and those for strontium in Table V. It is interesting and important to note that the trends in T_c could have been inferred from our earlier results. In the simple-metal limit, T_c decreases as the volume is decreased, in accord with Fig. 2. When hybridization is included, T_c increases as the volume is decreased, as one would expect from Fig. 3.

We may use the experimental pressure-volume relationships (Table I) and the values of T_c given in Tables IV and V to calculate pressure-temperature phase diagrams. In Figs. 6 and 7 we have plotted both the experimental phase diagram and our result with hybridization included for calcium and strontium, respectively. The agreement for calcium is satisfactory, although clearly the theoretical slope dT_c/dP is too large. For strontium our calculated dT_c/dP has the wrong sign.

IV. DISCUSSION

Several clear trends have emerged from our calculations. There is first the strong tendency for the hybridization to stabilize the fcc structure in the alkaline-earth metals at all pressures. The positive dT_c/dP slopes that we have calculated reflect the increase in the strength of the hybridization as the atomic volume is decreased. The pseu-
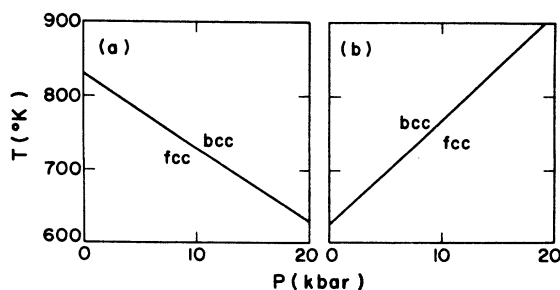

FIG. 7. Pressure-temperature phase diagram for strontium: (a) experimental from Ref. 4, (b) present calculation with hybridization included.

TABLE IV. fcc-bcc transition temperatures T_c (°K) predicted from Eq. (10) for calcium.

1.10	1.00	Ω/Ω_0 0.90	0.80	0.70
		Without hybridization		
235	245	160	$0 <$ [a]	$0 <$ [a]
		With hybridization		
420	555	740	1070	1635

[a] bcc structure already has a lower free energy at $T = 0$.

dopotential contribution, on the other hand, tends to favor the bcc structure at high pressures, as is evidenced by the negative values of dT_c/dP we have found in the limit of no hybridization. Furthermore, the hybridization is operative primarily through the band-structure energy and not the phonon Helmholtz free energy. The strong influence of the hybridization on E_{bs} can be traced to the local maximum in $F_N(q)$ which consistently occurs near $q = 2k_F$. (See Fig. 6 of Paper I.) For $Z = 2$ the fcc structure has six reciprocal-lattice vectors at 2.03 k_F, and, hence, the magnitude of E_{bs} tends to be maximized for this structure.

The strength of the hybridization is governed primarily by two quantities: the mean position of the empty d band, E_d, and the hybridization matrix element $\langle \vec{k} | \Delta | \varphi_d \rangle$. [Note that Δ here refers to the hybridization potential and is not to be confused with the symbol defined in Eq. (2).] The effective strength of the hybridization can be roughly characterized by the function

$$M_{hyb} = (\langle \vec{k} | \Delta | \varphi_d \rangle_{av})^2 / (E_d - E_F) , \tag{12}$$

where the average is over the free-electron Fermi sphere. In Tables VI and VII, respectively, we have listed our values of E_F, E_d, $E_d - E_F$, and M_{hyb} for calcium and strontium as a function of volume. Note that all four quantities increase as Ω decreases, although E_d/E_F remains almost constant for both metals. The behavior of E_d and $E_d - E_F$ is in qualitative agreement with the band-

TABLE V. fcc-bcc transition temperatures T_c (°K) predicted from Eq. (10) for strontium.

1.10	1.00	Ω/Ω_0 0.90	0.80	0.70
		Without hybridization		
250	260	235	150	50
		With hybridization		
445	625	840	1145	$\cdots$ [a]

[a] No transition temperature. Some phonon frequencies for the bcc structure were calculated to be imaginary.

TABLE VI. Quantities associated with the hybridization for calcium, in Ry.

Quantity	1.10	1.00	Ω/Ω_0 0.90	0.80	0.70
E_F	0.325	0.347	0.372	0.402	0.440
E_d	0.593	0.640	0.688	0.741	0.805
$E_d - E_F$	0.268	0.293	0.316	0.338	0.365
M_{hyb}	0.0816	0.0907	0.1021	0.1184	0.1393

structure results of Kmetko[8] on calcium and strontium.

A significant omission in our calculational technique, however, is a realistic volume dependence for the ion-core potential, from which E_d, the d basis states, and the pseudopotential itself are directly obtained. In a formal sense, our core potential is constructed in the infinite volume limit. (See Paper I.) The smaller the volume ratio Ω/Ω_0 and the greater the amount of core, the larger the error one expects to make in calculating both the pseudopotential and the hybridization terms. It is not surprising, therefore, that our calculated results show the best over-all agreement with experiment at zero pressure and the worst agreement in the case of strontium at high pressures. It seems clear that the experimental behavior in strontium at pressures greater than zero could be explained, at least within the context of the generalized pseudopotential theory, if an appropriate admixture of pseudopotential and hybridization contributions to the energy–wave-number characteristic were achieved. In particular, a decrease in the effective strength of the hybridization potential and/or an increase in the effective strength of the pseudopotential could change the sign of dT_c/dP.

Another possible complication in the phase stability calculation is the effect of (neglected) higher-order terms in the band-structure energy. At the present time, it is not possible for us to make a meaningful evaluation of such terms. However, we have attempted here to optimize the convergence of our total energy expansion both through the use of a fully nonlocal pseudopotential and the use of an expanded basis set. The significance of the choice of pseudopotential to the validity of ne-

TABLE VII. Quantities associated with the hybridization for strontium, in Ry.

Quantity	1.10	1.00	Ω/Ω_0 0.90	0.80	0.70
E_F	0.275	0.293	0.314	0.340	0.372
E_d	0.613	0.653	0.702	0.760	0.829
$E_d - E_F$	0.338	0.360	0.388	0.420	0.457
M_{hyb}	0.0982	0.1089	0.1228	0.1400	0.1637

glecting terms beyond second order can be illustrated by the following example. The phonon spectrum and the stable structure of the alkaline-earth metal magnesium can be successfully described in two distinct ways: first by the second-order optimized nonlocal model potential theory of Shaw[7,9] and second, by the third-order local empirical pseudopotential theory of Brovman *et al.*[10] A comparison between the two treatments shows that the quantitative effect of including full nonlocality in second order is nearly the same as that of including local third-order terms. Our nonlocal pseudopotential, of course, is the orthogonalized-plane-wave (OPW) analog of Shaw's model potential.

The importance of the d states in optimizing the convergence of the total energy expansion is also quite clear. When hybridization is included directly, ΔE_{bs} is typically 10–15% of E_{bs}, as compared with only 2–3% when it is omitted. Thus unless the contribution to ΔE_{bs} from higher-order terms is the same order of magnitude as their contribution to E_{bs} itself, we expect these terms to be of secondary importance. Moreover, the degree of convergence, at least at $\Omega/\Omega_0 = 1.00$, is not highly sensitive to small changes in the d states, and hence, to the exact choice of the localization po-

tential. Using the d states from models D and E of Paper I, for example, we obtain transition temperatures of 575 and 515 °K for calcium and 605 and 555 °K for strontium, respectively.

It remains to be seen whether or not improvements in calculating pseudopotential and hybridization contributions to the band-structure energy will have a significant impact on the theoretical phase diagrams of calcium and strontium. In the high-pressure region, at least, this is certainly conceivable and we do expect that some improvement can be made there. We do not wish to speculate beyond this point, however, as a good deal of additional work will be necessary to clarify the situation further. But regardless of what future developments may bring, it is now clear that a careful account of s-d hybridization will be an essential ingredient to any complete theoretical description of the structures and phase transitions in the heavy alkaline-earth metals.

ACKNOWLEDGMENT

*Work performed under the auspices of the U. S. Atomic Energy Commission.

[1]J. A. Moriarty, Phys. Rev. B **6**, 4445 (1972).

[2]W. A. Harrison, Phys. Rev. **181**, 1036 (1969).

[3]J. A. Moriarty, Phys. Rev. B **5**, 2066 (1972).

[4]A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, Phys. Rev. **132**, 1620 (1963).

[5]A. O. E. Animalu, Phys. Rev. **161**, 445 (1967).

[6]V. Heine and I. Abarenkov, Philos. Mag. **9**, 451 (1964); A. O.

E. Animalu, Proc. R. Soc. A **294**, 376 (1966).

[7]R. W. Shaw, Jr., J. Phys. C **2**, 2335 (1969).

[8]E. A. Kmetko, in *Electronic Density of States* (U. S. GPO, Washington, D.C., 1971).

[9]R. W. Shaw, Jr., Phys. Rev. **174**, 769 (1968); and J. Phys. C **2**, 2071 (1969).

[10]E. G. Brovman, Yu. Kagan, and A. Kholas, Zh. Eksp. Teor. Fiz. **61**, 737 (1971) [Sov. Phys.-JETP **34**, 394 (1972)].