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Theoretical prediction of the high-pressure phase Ge-*Cmca*

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Ab initio pseudopotential total energy density-functional theory–local-density approximation calculations were performed to study the crystalline structures of Ge under pressure. Following the well established sequence of structural phases (diamond→β-Sn→*Imma*→sh) under increasing pressure, we predict a transition into a new phase, with *Cmca* space-group symmetry, at 90 ± 2 GPa. We estimate the superconducting transition temperature T_c for this phase to be in the range 2 to 7 K, the same range obtained previously by detailed calculations for the Ge-sh phase. The *Cmca* phase should remain stable up to 137 ± 10 GPa where a transition to the hcp structure is predicted to occur. The same path is followed by Si although at lower pressures.

I. INTRODUCTION

Recently, the high-pressure crystalline phases of Si and Ge became the subject of a great deal of experimental and theoretical research. For Si the currently accepted pressure induced phase path starts with a *cubic diamond* to β-Sn transition around 11 GPa,[1–4] followed by a transition to a *Imma* space-group phase at 13 GPa.[5,6] Raising the pressure to about 16 GPa induces a transition to a *simple hexagonal* (sh) (Refs. 5 and 6) phase. All of these experimental results have been examined theoretically, and in some cases the transitions were predicted prior to the experiments.[7–15] Above 38 GPa, the sh phase of Si changes to the Si-VI phase. This phase was known to exist since the work of Olijnyk *et al.*[2] Only recently was Si-VI identified by Hanfland *et al.*[16] as an orthorhombic structure having 16 atoms per cell and space-group symmetry *Cmca*. The same structure also corresponds to the Cs-V phase, found by the same group,[17] with similar structural parameters. A further increase of pressure leads to a transition into the hcp phase at 43 GPa.[2,4,16,18] Theoretical calculations on the transition sh→*Cmca*→hcp have been performed[19,20] in good agreement with the experimental results. Finally, around 80 GPa, Si changes into the fcc structure[18,21] which is observed to remain stable up to 248 GPa,[18] in agreement with theoretical calculations.[10,14]

The first structural transitions of Ge are similar to those of Si, but they occur at higher pressures. The experimental pressure for the diamond→β-Sn transition is about 10 GPa,[2,22] in agreement with theoretical calculations.[7,15,22–24] For the transition β-Sn→*Imma*→sh it is necessary to raise the pressure to 75 GPa,[25] and the *Imma* phase remains stable up to at least 81 GPa. An argument involving the *d*-core states in Ge (nonexistent in Si) given by Chang and Cohen[24] and Lewis and Cohen[26] accounts for an extra repulsion resulting in a shift of the energy curves to higher volume giving rise to a higher transition pressure in Ge than in Si. Theoretical calculations by Lewis and Cohen[27] predict a smooth transition for this sequence.

Motivated by the similarities between the structural transitions of Ge and Si, and by the recently discovered *Cmca* phase, we have performed calculations for the high-pressure phases of Ge and focus on the sh→*Cmca*→hcp transition.

II. METHOD

We performed *ab initio* pseudopotential total-energy calculations within density-functional theory (DFT) and the local-density approximation (LDA)[28] using the Ceperley-Alder functional[29] for the exchange-correlation energy. The interaction of the ionic cores with the valence electrons is modeled by a separable[30] norm-conserving, nonlocal, Troullier-Martins[31] pseudopotential with reference configuration $4s^{2.0}4p^{1.5}4d^{0.0}$. The cutoff radii (in a.u.) for the *s*, *p*, and *d* potentials are 1.89, 1.98, and 2.19, respectively. For sampling the Brillouin zone we use 1500 *k* points for the β-Sn, *Imma*, and sh, 216 *k* points for the *Cmca* structure (8 atms/unit cell), 2744 for hcp, and fcc, and 1372 for dhcp. The wave functions are expanded in plane waves[32] up to a cutoff of 40 Ry. With these parameters, the total-energy precision is better than 0.2 mRy/atom.

Some of the structures studied have lattice parameters and/or internal degrees of freedom that were relaxed using a quasi-Newton method.[33]

To find the stable structures as a function of pressure requires finding the structure having the minimum Gibbs free energy. For zero temperature, the Gibbs free energy is identical to the enthalpy, and one can calculate the transition pressure between two phases by constructing the common tangent to the two total energy curves.

III. STRUCTURES

The *Imma* structure has a body-centered orthorhombic Bravais lattice with four atoms per cell (two atoms per irreducible unit cell). It can be characterized by two lattice-vector parameters (b/a and c/b) and one internal degree of freedom (Δ). When $b/a=1$ and $\Delta=1/4$ the β-Sn structure is obtained; with $b/c=\sqrt{3}$ and $\Delta=1/2$ we get the sh struc-

TABLE I. Calculated transition reduced volumes (V_0 is the volume/atom in the *diamond* phase at zero pressure) for the studied structures and the corresponding calculated transition pressures. The last column shows some experimentally obtained pressures for comparison.

Calculated V_t/V_0					P_t (GPa)	
β-Sn	*Imma*	sh	*Cmca*	hcp	(calc.)	(expt.)
0.561	0.559				70(3)	~75[a]
	0.533	0.532			89(5)	~85[a,b]
		0.531	0.524		90(2)	102[c]
			0.475	0.473	137(10)	

[a]Reference 25.
[b]Estimated value (see text).
[c]Reference 22. Reported as a transition to dhcp.

ture. A picture and more detailed discription of the *Imma* structure can be found in Refs. 5, 6 and 13.

The *Cmca* structure has an orthorhombic Bravais lattice with 16 atoms per cell (8 in the irreducible unit cell). It is characterized by two lattice parameters (a/c and b/c) and three internal degrees of freedom (y_1, z_1, and x_2). Details about the *Cmca* structure can be found in Refs. 16 and 17.

IV. RESULTS

A. β-Sn→*Imma*→sh transition

First, we analyze the transition β-Sn→*Imma*→sh. This transition has been studied theoretically in the past for both Si and Ge by Lewis *et al.*[13,27] In the experimental study of Nelmes *et al.*[25] it was shown that β-Sn transforms into *Imma* at 75 GPa, and remains stable up to at least 81 GPa. Based on the rate of change of diffraction peaks between 79 and 81 GPa, Nelmes *et al.* estimate that the transition to the sh phase should occur at ~85 GPa. At this time, there are no detailed experimental results for the *Imma*→sh transition in Ge. We studied the β-Sn, *Imma*, and sh structures using the same unit cell to eliminate systematic errors in the total-energy difference. In our present calculation we compute a pressure of 70(3) GPa and a volume change of about −0.4% for the β-Sn→*Imma* transition and a pressure of 89(5) GPa with a volume change of −0.2% for the *Imma*→sh transition (see Table I). Table II shows a comparison of the calculated and measured internal parameters of the three structures.

TABLE II. Comparison between the calculated and experimentally reported structural parameters for β-Sn, *Imma*, and sh. The parameter c/a shown for the sh structure (unit cell with *Imma* symmetry) corresponds to $a/2c$ in the standard sh unit cell. Values within brackets are exact.

		c/a	b/a	Δ
β-Sn	calc.	0.546	[1.0]	[0.5]
	expt.[a]	0.550(8)	[1.0]	[0.5]
Imma	calc.	0.535	0.937	0.430
	expt.[b]	0.538(1)	0.959(1)	0.390(4)
sh	calc.	0.535	$[\sqrt{3}\,c/a]$	[0.25]
	expt.[a]	0.538(4)	$[\sqrt{3}\,c/a]$	[0.25]

[a]Reference 22.
[b]Reference 25.

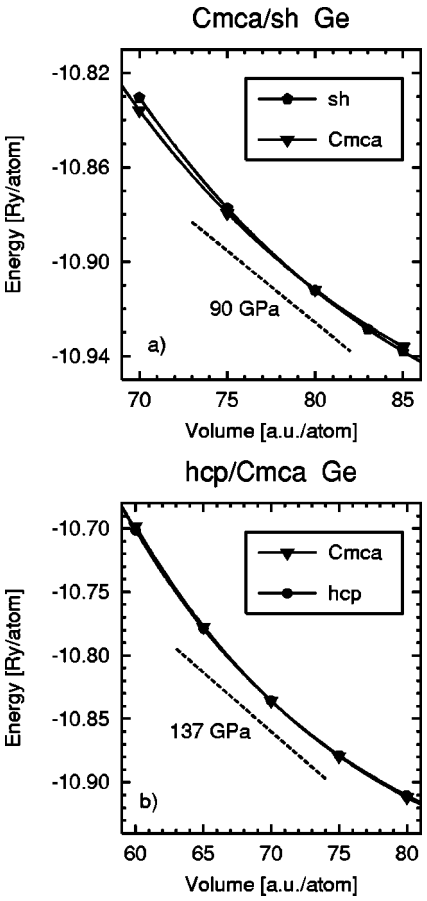

FIG. 1. Total-energy curves and common tangent construction (dashed line) for phase transitions of Ge: (a) the sh→*Cmca* transition and (b) the *Cmca*→hcp transition.

B. sh→*Cmca*→hcp transition

In 1986 Vohra *et al.*[22] studied Ge up to 125 GPa. At that time, neither the *Imma* nor the *Cmca* phases were known, and it was thought that the Si-VI phase was a dhcp structure, despite the theoretical prediction that dhcp should be metastable relative to hcp.[22] Our calculations now suggest that the

TABLE III. Comparison between the structural parameters for the *Cmca* phase of Ge for the present calculation and the experimental values for the Si-VI and Ce-V phases. For our calculation the values in parenthesis give the spread of the parameters along the accessible volume region of the structure ($0.524 < V_t/V_0 < 0.475$), while for the experimental results we include the error bar for the specific pressure/volume.

	Ge-*Cmca* Present calc.	Si-VI Expt. (Ref. 16)	Cs-V Expt. (Ref. 17)
a/c	1.685(6)	1.676	1.699
b/c	1.002(2)	1.004	1.005(1)
y_1	0.169(3)	0.172(5)	0.1729
z_1	0.321(1)	0.328(5)	0.327
x_2	0.2176(9)	0.219(5)	0.2161

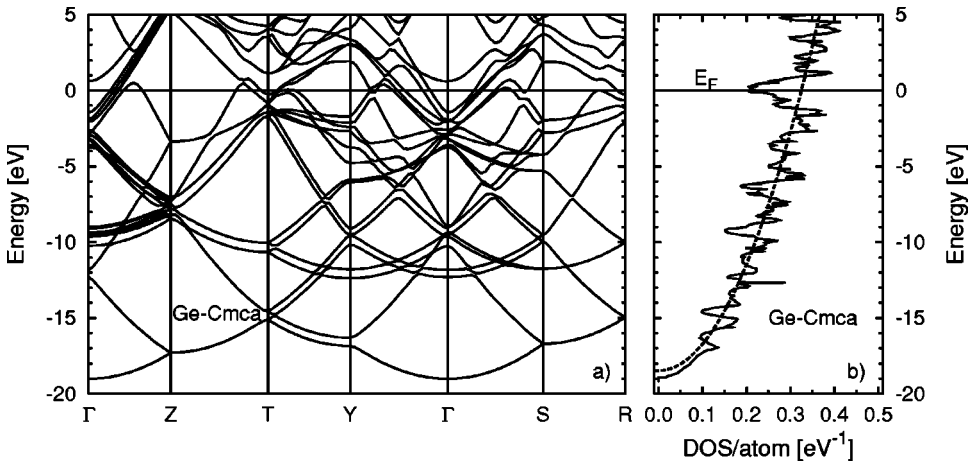

FIG. 2. Calculated (a) band structure and (b) density of states per atom for the Ge-*Cmca* phase at a volume of 75 a.u./atom (110 GPa). In (a) the high-symmetry points in the Brillouin zone follow the convention of Ref. 34. In (b) the dashed line represents a free electron DOS for the same electronic density.

102 GPa transition observed by Vohra *et al.* from sh to dhcp was actually a sh→*Cmca* transition, which we predict to be at 90(2) GPa [see Table I for detailed values and Fig. 1(a) for total energy curves]. In Table III we present a comparison of the relaxed five structural parameters of the *Cmca* structure and, for comparison, the experimentally obtained parameters for Si-VI (Ref. 16) and Cs-V.[17] The similarity is encouraging and suggests that this structure exists for Ge. In Fig. 2 we present the band structure of Ge in the *Cmca* phase and the corresponding density of states at a volume of 75 a.u./atom (110 GPa). These plots show the almost free electron metallic character of the Ge-*Cmca* phase, and are similar to the band structure and density of states (DOS) for Si-VI obtained by Schwarz *et al.*[34] Comparing the band structures of Si-VI (Ref. 34) and Ge-*Cmca* we see that they are very similar except for a wider energy separation (of the order of 0.5 eV) between some of the bands. Also, we show the electron density plot in Fig. 3, which is similar to the equivalent plot for Si,[19,34] as one would expect. Therefore the conclusions regarding the differences between the bonding properties of Si-VI and Cs-V reached by Christensen *et al.*[19] can be extended to Ge-*Cmca*.

Detailed first-principles calculations of the electron-phonon coupling for the Ge-sh phase done by Martins and Cohen[35] predict a superconducting transition temperature T_c in the range 2–7 K. In their work the calculated Fermi level density of states per spin for Ge-sh was $N_\uparrow(E_F) = 0.12$ eV^{-1} compared to a free-electron value of 0.17 eV^{-1}. The corresponding values for the Ge-*Cmca* structure are $N_\uparrow(E_F) = 0.11$ and 0.16 eV^{-1} for the free-electron system. This shows that the reduction in density of states at the Fermi level relatively to the free-electron system is roughly the same in the two systems. Since no calculations were done in the electron-phonon coupling for the *Cmca* phase we shall assume that the values of the electron-phonon coupling λ and electron-electron Coulomb repulsion μ^* are approximately the same as in the sh phase. In a continuum mechanics model, the Debye temperature is proportional to the square root of the bulk modulus. From the second derivative relatively to the volume of the total-energy curve of *Cmca* and sh we get a bulk modulus of about 400 GPa (at 90 GPa) for both phases within 1%. Since the mass densities of both phases are very close together, the Debye temperature for sh and *Cmca* should be roughly the same. We then conclude that the superconducting transition temperature for the *Cmca* phase should be in the same range (2–7 K) as the sh phase.

According to our calculations, the Ge-*Cmca* phase should remain stable up to 137(10) GPa, the pressure at which it should change into the hcp structure. In Si this transition occurs around 43 GPa. In Fig. 1(b) we show a plot of the total-energy curves and the common tangent construction for the *Cmca*→hcp transition. In Si, the hcp phase ultimately becomes unstable (at 80 GPa) and transforms into fcc. In Fig. 4 we show a plot of the total-energy curves of the fcc, dhcp, and hcp structures for high pressures. Close inspection of the curves reveals that both fcc and dhcp remain thermodynamically unstable relatively to hcp up to at least 500 GPa. At this density the core electrons may start to play an important role in the transitions, making our pseudopotential approximation questionable.

From Figs. 1 and 4 it is apparent that the energy differences between the various phases are very small. For the transitions sh→*Cmca* and *Cmca*→hcp (Fig. 1) the total-energy difference between phases on the left and right edges of the plots always exceeds 2 mRy/atom. The energy difference between the hcp, dhcp, and fcc phases (Fig. 4) is again

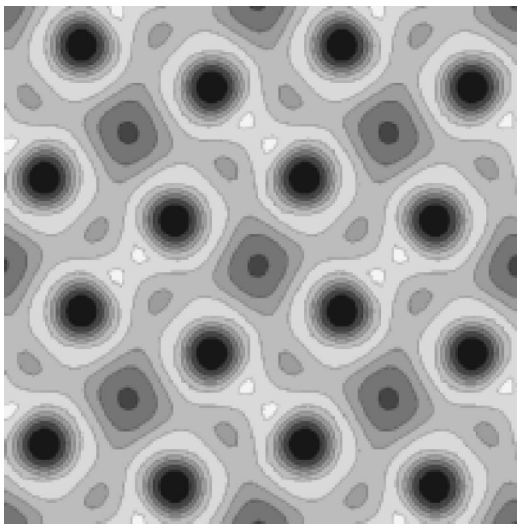

FIG. 3. Contour plot of the electron density in the $x=0$ plane intersecting the atoms in the $8f$ Wyckoff position. Black areas: less than 0.025 bohr^{-3}; gray areas: increasing steps of 0.010 bohr^{-3}; white areas: more than 0.075 bohr^{-3}.

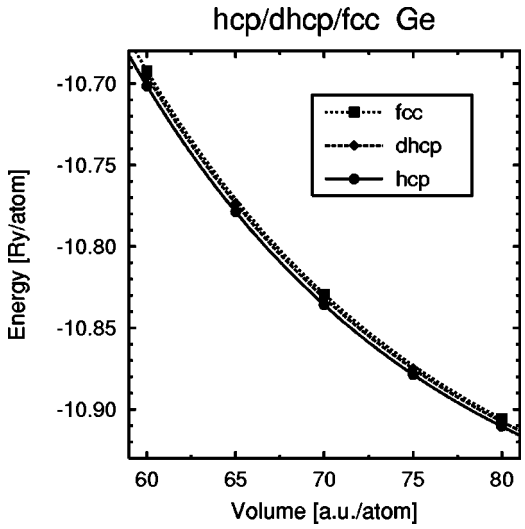

FIG. 4. The total-energy curves for the stable hcp phase of Ge (solid line), and the metastable dhcp and fcc phases (dashed lines).

larger than 2 mRy/atom for the range of volumes studied. This value is well above the precision of our calculation (better than 0.2 mRy/atom).

V. CONCLUSION

We conclude that the phase transitions of Ge on increasing pressure are similar to those of Si. The recently identified Si-VI and Cs-V phases (space-group symmetry *Cmca*) should also be present in Ge above 90 GPa and remain stable up to about 137 GPa. The band structure and corresponding density of states for Ge-*Cmca* show an almost free-electron metallic behavior. The structural parameters for *Cmca* in Ge are similar to those of Si-VI and Cs-V. This suggests that this structure might exist in other systems as well. The superconducting transition temperature should be in the range 2–7 K, the same range as for the previously calculated T_c for the Ge-sh phase.

We predict that Ge undergoes a transition to the hcp phase at about 137 GPa (the Si transition is at 43 GPa). Above 80 GPa, Si changes from the hcp to the fcc structure. According to our calculations Ge should not change into the fcc phase for pressures below 500 GPa.

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