

Electron-phonon interactions and superconductivity in Si, Ge, and Sn

K. J. Chang and Marvin L. Cohen

*Department of Physics, University of California, Berkeley, California 94720
and Materials and Molecular Research Division, Lawrence National Laboratory,
Berkeley, California 94720*

(Received 10 February 1986; revised manuscript received 16 June 1986)

The pseudopotential-total-energy method is used to calculate the phonon frequency, the electron density of states at the Fermi level, and the electron-phonon coupling constant for the group-IV elements in the metallic β -Sn structure. For these elements, the normal-state behavior is similar to that found in other simple and transition metals; the phonon frequencies, force constants, and electron-phonon matrix elements increase with increasing average electron density. With use of a semiempirical treatment of the electron-phonon coupling calculated for one phonon wave vector, the superconducting transition temperatures at normal and high pressures are examined. The superconducting transition temperature decreases while the magnitude of its pressure coefficient increases in going to heavier elements. This behavior is in good agreement with experiment. For Si and Ge, the superconducting behavior is similar to that of white tin. Because of competition and compensation between the cutoff in the phonon spectrum and the electron-phonon matrix element, the electron-phonon coupling λ 's are similar for the three elements. Hence, the Debye temperature, which is the prefactor of the McMillan equation, dominates in determining the superconducting critical temperatures.

I. INTRODUCTION

High-pressure metallic phases of Si and Ge have attracted considerable attention since the transition from covalent to metallic bonding occurs at accessible pressures. Unlike carbon, Si, Ge, and Sn crystallize in the tetragonal β -Sn structure when they are first metallized. For Si and Ge, this transition occurs at pressures around 100 kbar (Ref. 1) while the β form (white tin) of Sn is stable at normal pressures and temperatures.² In contrast, for carbon, theoretical calculations indicate that crystal structures^{3,4} such as body-centered cubic with 8 atoms per unit cell (BC-8) and simple cubic are more stable than the β -Sn structure at high pressures.

The structural tendency of the group-IV elements are closely related to the details of their atomic properties which play an important role in determining the nature of the crystal bonding. At atmospheric pressures, Si, Ge, and α -Sn have strong covalent bonds. At high pressures in the metallic β -Sn phase, the covalent bonds coexist with metallic bonding and these systems become superconducting.⁵ The superconducting transition temperature T_c is highest for Si and decreases in going to Sn in this series. Usually, superconductors having high T_c are transition metals or transition-metal compounds with a high density of states at the Fermi energy arising from d electrons. For covalent systems, it was suggested⁶ that electron-phonon interactions can be enhanced by local-field effects resulting from covalent bonds and soft phonon modes. In fact, the T_c 's found in the group-IV materials are reasonably high compared to other simple metals, and the recent discovery⁷ of superconductivity at 8.2 K in simple hexagonal Si has motivated a search for higher T_c 's in high-

pressure metallic phases of strongly covalent materials.

Because Sn is stable in the β -Sn structure at normal pressures, more experimental data for the phonon spectrum^{8,9} and the heat capacity¹⁰⁻¹² are available compared to Si and Ge. Hence, there have been several calculations¹³⁻¹⁶ to compute electron-phonon couplings in this element. For Si and Ge, a lack of experimental data for the phonon spectra makes it difficult to use previous methods which involve a calculation of the band mass, a force-constant model for phonons, and an electron-phonon calculation based on the rigid-ion¹⁷ or the rigid-muffin-tin¹⁸ approximations. Recently, a new method¹⁹ has been proposed to calculate wave-vector-dependent electron-phonon interactions in metals. This approach uses a self-consistent change in potentials caused by a phonon distortion. Applications of this method to Si (Refs. 7 and 20) and Al (Ref. 19) have been successful.

Here we extend the calculations for the electron-phonon interactions to the group-IV elements Ge and Sn and compare their results for normal and superconducting states with the previous calculations for Si.^{7,20} To calculate the phonon frequency, the density of state at the Fermi level, and the electron-phonon coupling, we use an *ab initio* pseudopotential-total-energy method.²¹ For the calculations of the phonon frequencies and electron-phonon couplings, the phonon wave vector is chosen along the [001] direction. Because of computational difficulties in using supercells, we limit the wave vector to the edge of the β -Sn Brillouin zone. Based on the computed electron-phonon couplings and scaling them by the constant factor obtained from the measured superconducting critical temperature for Sn at normal pressures, the superconducting critical temperatures are estimated and their pressure dependences are calculated by varying the size of the unit

cell. For different elements in the same structure, phonon frequencies, electron-phonon matrix elements, and electron-phonon couplings are compared as a function of the average electron density. Furthermore, the valence wave functions are decomposed into angular-momentum states to compare physical properties of the group-IV elements.

Section II describes the theoretical approach and discusses the accuracy of the calculation. In Sec. III, the results of the calculations are presented and discussed. Conclusions are given in Sec. IV.

II. THEORETICAL METHOD

The present calculations are based on the *ab initio* pseudopotential-total-energy approach.²¹ The structural, electronic, and vibrational properties are calculated self-consistently using only information about atoms, i.e., the atomic number and atomic mass. The exchange-correlation potentials are approximated using the Wigner interpolation formula.²² Angular momentum dependent pseudopotentials are generated from the scheme proposed by Hamman, Schlüter, and Chiang.²³ For Si and Ge, the potentials were tested previously and found to be successful in predicting the structural and vibrational properties.^{1,24} The pseudopotentials used for Sn include a partial core correction,²⁵ and they are able to reproduce the ground-state properties. The computed equilibrium lattice constant of 5.80 Å and bulk modulus of 628 kbar, are in reasonable agreement with the experimentally measured values of 5.812 Å (Ref. 11) and 579 kbar (Ref. 26) at 4.2 K. Relativistic and spin-orbit effects are not included here since the structural properties change slightly with these modifications.

The superconducting transition temperature T_c is estimated using the McMillan equation.¹⁴ The electron-phonon interaction parameter λ in this equation is the average of the coupling $\lambda_{\mathbf{q}\nu}$ for a phonon of wave vector \mathbf{q} and phonon mode ν over the entire Brillouin zone (BZ),

$$\lambda = \frac{1}{\Omega_{\text{BZ}}} \int \sum_{\nu} \lambda_{\mathbf{q}\nu} d^3\mathbf{q}, \quad (1)$$

where Ω_{BZ} is the volume of the BZ. The wave-vector-dependent electron-phonon coupling $\lambda_{\mathbf{q}\nu}$ is proportional to the phonon linewidth²⁷ $\gamma_{\mathbf{q}\nu}$,

$$\lambda_{\mathbf{q}\nu} = \frac{\gamma_{\mathbf{q}\nu}}{\pi N(E_F) \hbar \omega_{\mathbf{q}\nu}^2}, \quad (2)$$

where $N(E_F)$ is the density of states (DOS) per atom and per spin at the Fermi level, E_F , and $\omega_{\mathbf{q}\nu}$ is the phonon frequency for wave vector \mathbf{q} and branch ν . The calculations of the electron-phonon coupling $\lambda_{\mathbf{q}\nu}$ are based on the method described in Refs. 19 and 20. This approach goes beyond the rigid-ion or rigid-muffin-tin approximations, and the crystal potentials are fully relaxed and calculated self-consistently. The coupling $\lambda_{\mathbf{q}\nu}$ is related to the Fermi-surface average of the electron-phonon matrix element¹⁷ g ,

$$\lambda_{\mathbf{q}\nu} = 2N(E_F) \frac{\langle \langle |g(n\mathbf{k}, n'\mathbf{k}', \mathbf{q}\nu)|^2 \rangle \rangle}{\hbar \omega_{\mathbf{q}\nu}}, \quad (3)$$

where $\langle \langle |g|^2 \rangle \rangle$ represents a Fermi-surface average of g . In a crystal with several ions per unit cell, the electron-phonon matrix element is defined by

$$g(n\mathbf{k}, n'\mathbf{k}', \mathbf{q}\nu) = \sum_{\tau} \left[\frac{\hbar \Omega_{\text{BZ}}}{2M_{\tau} \omega_{\mathbf{q}\nu}} \right]^{1/2} \delta(\mathbf{k} - \mathbf{k}' - \mathbf{q}) \times \left\langle \psi_{n\mathbf{k}}^0 \left| \hat{\epsilon}_{\mathbf{q}\nu}^{\tau} \cdot \frac{\delta V}{\delta \mathbf{R}_{\tau}} \right| \psi_{n'\mathbf{k}'}^0 \right\rangle, \quad (4)$$

where M_{τ} is the atomic mass of the τ -type atom in the unit cell, $\hat{\epsilon}_{\mathbf{q}\nu}^{\tau}$ is the polarization vector, and $\psi_{n\mathbf{k}}^0$ and $\psi_{n'\mathbf{k}'}^0$ are the electron Bloch wave functions for states \mathbf{k} and \mathbf{k}' in bands n and n' , respectively, for the undistorted crystal lattice. For the β -Sn structure considered here, all the atoms are the same type and $M_{\tau} = M$. The change of the potential caused by a phonon distortion is replaced by the finite difference between the self-consistent potentials of the distorted and undistorted crystals,

$$\sum_{\tau} \hat{\epsilon}_{\mathbf{q}\nu}^{\tau} \cdot \frac{\delta V}{\delta \mathbf{R}_{\tau}} = \frac{V_{\mathbf{q}\nu} - V_0}{\bar{u}_{\mathbf{q}\nu}}, \quad (5)$$

where $V_{\mathbf{q}\nu}$ and V_0 are the distorted and undistorted potentials, respectively. The average of the square of the frozen-phonon displacements per unit cell is defined by

$$\bar{u}_{\mathbf{q}\nu}^2 = \frac{1}{N} \sum_{a,\tau} u_{\tau}^2 \sin^2[\mathbf{q} \cdot (\mathbf{R}_a + \mathbf{R}_{\tau})], \quad (6)$$

where unit cells are indexed by a , N is the total number of unit cells, and the u_{τ} 's for the normal modes are

$$u_{\tau} = \begin{cases} (-1)^{\tau} u & \text{for acoustic modes} \\ u & \text{for optic modes.} \end{cases} \quad (7)$$

The frozen-phonon approximation requires supercells to calculate the phonon frequency and the finite difference of the potentials. For phonon displacements given by Eq. (6), the force constant $\kappa_{\mathbf{q}\nu}$ is obtained from the difference of the total energies

$$\kappa_{\mathbf{q}\nu} = \frac{2[E_T(u \neq 0) - E_T(u = 0)]}{N \bar{u}_{\mathbf{q}\nu}^2}. \quad (8)$$

The phonon frequency $\omega_{\mathbf{q}\nu}$ is calculated from the force constant using

$$\omega_{\mathbf{q}\nu} = (\kappa_{\mathbf{q}\nu} / M)^{1/2}. \quad (9)$$

By choosing the wave vector \mathbf{q} commensurate with the lattice such as $n\mathbf{q} = \mathbf{G}$, where n is an integer and \mathbf{G} is a reciprocal-lattice vector, a supercell for the phonon wave vector \mathbf{q} becomes n times larger. Thus, the electron state $\mathbf{k}' + \mathbf{q}$ is folded back into \mathbf{k} and then the δ function in Eq. (4) is eliminated.

In the present calculations, we choose the wave vector \mathbf{q} to be $2\pi(0,0,1)/c$. Since the supercell calculations of $\lambda_{\mathbf{q}\nu}$ and $\omega_{\mathbf{q}\nu}$ for \mathbf{q} inside the BZ require considerable computing time and memory capacity, we are limited to only one wave vector with $n=2$. Hence, only a limited knowledge of $\lambda_{\mathbf{q}\nu}$ over the BZ is obtained and we cannot accurately determine the average λ in Eq. (1).

Within the Debye model, $\omega_{\mathbf{q}\nu}$ is proportional to q . Al-

though the phonon linewidth γ_{qv} in Eq. (2) is affected²⁷ by the geometry of the Fermi surface, for small q it depends linearly on ω_{qv} for longitudinal phonons screened by a jellium.¹⁷ Hence, the parameter λ_{qv} is a decreasing function of q with $\lambda_{qv} \sim q^{-1}$, and the value of λ_{qv} at the Debye wave vector q_D is usually smaller than the average λ . To make contact with experiment, λ_q is multiplied by a scaling factor to produce the measured superconducting transition temperature for Sn (Ref. 5) at normal pressures and then the same scaling factor is used for Si, Ge, and Sn at high pressures. One justification for this approximation is that λ is dominated by couplings at the BZ edges because of the q^2 weight in the spherical approximation of Eq. (1). We note that the same structure is involved in all three materials and their normal and superconducting properties behave in a similar way.

A uniform grid of 75 \mathbf{k} points in the irreducible BZ is used for the summation over the BZ of the supercells constructed for evaluating the longitudinal and transverse modes at $2\pi(0,0,1)/c$. The axial ratio c/a is optimized using energy minimization. The Fermi-surface integrals in Eq. (3) are calculated with use of a Gaussian broadening of the δ functions to ensure good convergence.

III. RESULTS AND DISCUSSIONS

The electronic and vibrational properties, and the electron-phonon interactions are compared in Table I for the group-IV elements Si, Ge, and Sn with the same β -Sn structure. For Si and Ge, the calculated pressures of 110 and 100 kbar, respectively, are used for the β -Sn structure. Although the atomic mass and lattice constant increase in going from Si to Sn, for all three elements the axial ratio c/a lies around 0.55. The density of states at the Fermi level $N(E_F)$ is calculated using the tetrahedron method,²⁸ for Sn it is 2.85 states/Ry per atom per spin and is the highest among the elements considered here. This computed value per atom per spin is in good agreement with the Heine-Animalu model pseudopotential calculation¹³ of 2.88 states/Ry and is slightly smaller than another calculated result²⁹ of 3.1 states/Ry using a relativistic augmented-plane-wave method. From the measured specific-heat coefficient¹⁰ $\gamma = 1.75$ mJ/molK², we can derive the value of $N(E_F)$; the electron-phonon coupling $\lambda = 0.72$ measured from the tunneling data¹⁶ produces $N(E_F) = 2.94$ states/Ry while the McMillan electron-phonon coupling¹⁴ $\lambda = 0.6$ gives $N(E_F) = 3.15$ states/Ry.

The calculated phonon frequencies for Sn are compared with experimental measurements.^{8,9} The longitudinal optic and acoustic (LOA) and transverse-acoustic (TA) modes have relatively larger errors compared to the transverse-optic (TO) mode. This discrepancy is expected for two reasons. Since the frequencies for the LOA and TA modes are small, they have relatively larger calculation errors; these are less than a few percent for semiconductors and insulators while for metals they are within 10% (Ref. 30). Also, the phonon frequencies for β -Sn vary rapidly with temperature since the temperature induces the structural phase transition.^{31,32} Thus a direct comparison of the frequencies calculated at zero temperature with experiment at higher temperatures should introduce differences. However, the overall agreement of the

phonon frequencies for Sn with experiment is reasonably good, and this suggests that reasonable accuracy can be expected for Si and Ge where experimental data are not available. The Debye temperature Θ_D for Sn with the β -Sn structure is reported to be 195 K (Ref. 10) and this value is close to the transverse-optic (TO) frequency 208 K. By using the maximum TO phonon frequency as the cutoff in the phonon spectrum, we estimate the Debye

TABLE I. Comparisons of the structural and vibrational properties, and the electron-phonon interactions at $q=2\pi(0,0,1)/c$ for Si, Ge, and Sn. The symbols α and β denote the cubic-diamond and white-tin structures, respectively. Results for Si are from Ref. 7. The $N(E_F)$ is in units of states/Ry per atom and per spin. Ionic masses are 28.086, 72.59 and 118.69 for Si, Ge, and Sn, respectively. See the text for the calculations of T_c . The T_c 's are measured at pressures of 120 and 115 kbar for Si and Ge, respectively. For Sn, normal pressures are used.

	Si	Ge	Sn
a^{calc} (a.u.)	8.8930	9.272	10.9534
$(c/a)^{\text{calc}}$	0.546	0.552	0.547
P^{calc} (kbar)	110	100	0
$[N(E_F)]^{\text{calc}}$	2.42	2.17	2.85
T_c^{expt} ($^{\circ}\text{C}$) ^a	1430	958	232
θ_D^{expt} (K)	645(α) ^b	374(α) ^b	220(α) ^c 195(β) ^d
$\omega_{qv}^{\text{calc}}$ (10^{13} rad/sec)			
LOA	3.03	1.77	1.03
TA	2.60	1.36	0.74
TO	8.02	4.49	2.73
$\omega_{qv}^{\text{expt}}$ (10^{13} rad/sec)			
LOA			0.85 (110 K) ^e
TA			0.53 (110 K) ^e
TO			2.63 (110 K) ^e 2.69 (3 K) ^f
$\kappa_{qv}^{\text{calc}}$ (eV/a.u. ²)			
LOA	0.756	0.667	0.368
TA	0.550	0.391	0.192
TO	5.280	4.277	2.586
$\gamma_{qv}^{\text{calc}}$ (10^{10} sec ⁻¹)			
LOA	2.00	0.70	0.37
TA	1.00	0.20	0.11
TO	20.8	5.90	3.20
$\lambda_{qv}^{\text{calc}}$			
LOA	0.06	0.07	0.08
TA	0.04	0.03	0.05
TO	0.09	0.09	0.10
λ_q^{calc}	0.38	0.38	0.46
T_c^{calc} (K)	6.53	4.03	3.72
T_c^{expt} (K)	6.3 ^g 6.7 ^h	5.35 ^g	3.72 ^g

^aReference 35.

^eReference 8.

^bReference 33.

^fReference 16.

^cReference 34.

^gReference 5.

^dReference 10.

^hReference 7.

temperatures for Si and Ge to be 613 and 343 K, respectively.

Compared to the cubic diamond phase, the Debye temperatures for the β -Sn structures are slightly lower. The softness of the β -Sn phonon modes is particularly important for the grey (cubic diamond) to white-tin (β -Sn) transition of Sn. This transition is induced in Sn by increasing the temperature; however, for Si and Ge, pressure causes the transition. Since the pressure at the transition is zero in the case of Sn, the presence of soft phonon modes in the white tin phase yields a large entropy contribution to the free energy with increasing temperature and stabilizes this phase at 286 K (see Refs. 31 and 32). Because the phonon frequencies decrease in going from Si to Sn, the Debye temperature is also smaller as expected from the heavier atomic mass. In addition, the force constants increase in going from Sn to Si. This is consistent with the higher melting point T_m for the lighter elements as shown in Table I. For Sn, room temperature is about 60% of the melting temperature. Because of the small bonding distance for the lighter elements, the average electronic density is higher implying more attractive potentials and stronger bonds. Hence, both the Debye temperature and the electron-phonon matrix elements are likely to increase with increasing electron density.

The electron-phonon couplings λ_q 's are compared for Si, Ge, and Sn in Table I. At the same wave vector q , the value of λ_q is larger for Sn while Si and Ge have a similar value. As discussed earlier, to estimate an average λ from the calculated λ_q we use a scaling factor of 1.28 for Sn. This reproduces the measured superconducting transition temperature of 3.72 K (Ref. 5) at normal pressures when the McMillan equation¹⁴ is used with the Debye temperature approximated by the TO phonon frequency and the Coulomb interaction parameter $\mu^* = 0.1$ obtained from the tunneling data.¹⁶ With the same scaling factor for λ , the calculated T_c 's for Si and Ge are 6.53 and 4.03 K, respectively, and are reasonably close to the measured values of 6.3 to 6.7 K for Si and 5.35 K for Ge. In this case, we scale the coupling μ^* by the renormalized density of states $N(E_F)/[1+N(E_F)]$ where $N(E_F)$ is the DOS per eV per atom per spin at the Fermi level. This relation of μ^* to the DOS at the Fermi level was empirically derived by Benneman and Garland³⁶ and was successful in transition metals. The reliable first principle calculation of μ^* is difficult, and the variations in the DOS at the Fermi level may give different values for μ^* of elements considered here. If $\mu^* = 0.1$ is used for all elements, we get T_c of 5.52 and 3.09 K for Si and Ge, respectively. Thus, the value of T_c is less sensitive to the variation of μ^* since λ and T_c are not too small. Our estimate of T_c for Ge is smaller than the measured value. We expect this error arises from the lack of information on the electron-phonon coupling since one-phonon wave vector is chosen. Because T_c is considerably sensitive to λ , the values for T_c are reasonably estimated for elements where experimental inputs are absent.

The pressure dependence of λ is studied by varying the crystal volume, and the corresponding pressure is calculated by using the Murnaghan equation of state.³⁷ For Si, λ does not change for a small range of pressures⁷ where

the β -Sn structure is stable as shown in Table II. Experiments^{5,7} also reported that the variation of T_c with pressure is almost constant or has a very small negative slope. However, for the heavier elements, the pressure coefficient of T_c was found to decrease and to be -210 ± 50 for Ge and -495 mK/GPa for Sn⁵, respectively. In Table II, the pressure dependences of the phonon frequency, the DOS at the Fermi level, λ_{qv} , and λ_q for Ge and Sn are also listed for several different pressures. Assuming the same scaling factor for λ and the same cutoff in the phonon spectrum as those used in previous calculations, an estimate of the pressure coefficient of T_c can be made. We find that dT_c/dP is less sensitive to the value of μ^* . For Ge, T_c varies sublinearly with pressure; the slope is stiffer in the region of low pressures. For purposes of 100 to 180 kbar, the calculated dT_c/dP is about -140 mK/GPa and this value is lower than the measured dT_c/dP for pres-

TABLE II. Pressure dependences of the calculated density of states at the Fermi level, ω_{qv} , λ_{qv} , and λ_q at $q = \pi(0,0,1)/c$ for the β -Sn phase of Si, Ge, and Sn. The units for $N(E_F)$ are states/Ry per atom and per spin. Results for Si are from Ref. 7.

P (kbar)	$N(E_F)$	ν	ω_{qv} (10^{13} rad/sec)	λ_{qv}	λ_q
Si					
110	2.42	LOA	3.03	0.06	0.38
		TA	2.60	0.04	
		TO	8.02	0.09	
120	2.41	LOA	3.05	0.06	0.38
		TA	2.60	0.04	
		TO	8.15	0.09	
Ge					
100	2.17	LOA	1.77	0.07	0.38
		TA	1.36	0.03	
		TO	4.49	0.09	
180	2.12	LOA	1.85	0.06	0.34
		TA	1.38	0.03	
		TO	4.92	0.08	
265	2.07	LOA	1.93	0.06	0.32
		TA	1.40	0.03	
		TO	5.35	0.07	
Sn					
0	2.85	LOA	1.03	0.08	0.46
		TA	0.74	0.05	
		TO	2.73	0.10	
20	2.75	LOA	1.07	0.07	0.38
		TA	0.76	0.04	
		TO	2.92	0.08	
35	2.70	LOA	1.10	0.06	0.34
		TA	0.76	0.04	
		TO	3.07	0.07	

tures from 115 to 140 kbar.⁵ This smaller calculated coefficient is expected since T_c at 100 kbar (with use of the scaling factor of 1.28) is underestimated compared to the experiment. When a scaling factor is chosen to be 1.395 which produces the measured T_c , dT_c/dP is found to be -180 mK/GPa and this value lies within the experimental values. For Sn, the calculated value for dT_c/dP is about -700 mK/GPa for pressures up to 35 kbar and this coefficient is the largest among the elements studied here. Therefore, the magnitude of the pressure coefficient of T_c increases when going to heavier elements and this fact is in good agreement with experiment.

The decreasing behavior of T_c in going from Si to Sn appears to be caused by the decreasing Debye temperature. Since the electron-phonon coupling λ is similar for the three elements, the Debye temperature which is the prefactor of the McMillan equation, determines T_c if we assume μ^* to be constant. The electron-phonon interaction parameter λ can be written as^{14,38}

$$\lambda = \frac{\eta}{M\omega_D^2}, \quad (10)$$

where the McMillan-Hopfield parameter η is related to the Fermi-surface average of the electron-phonon matrix elements of Eq. (4). Using simple models, it can be shown³⁹ that both η and ω_D tend to increase with increasing average electron density \bar{n} . For lighter elements like Si with high \bar{n} , η is stronger because of the stronger attractive potentials which also produce higher phonon frequencies. However, this effect on η is largely compensated for by the high Debye temperature as seen in Eq. (10). Thus, the superconducting transition temperatures are mainly determined by the cutoffs in the phonon spectrum

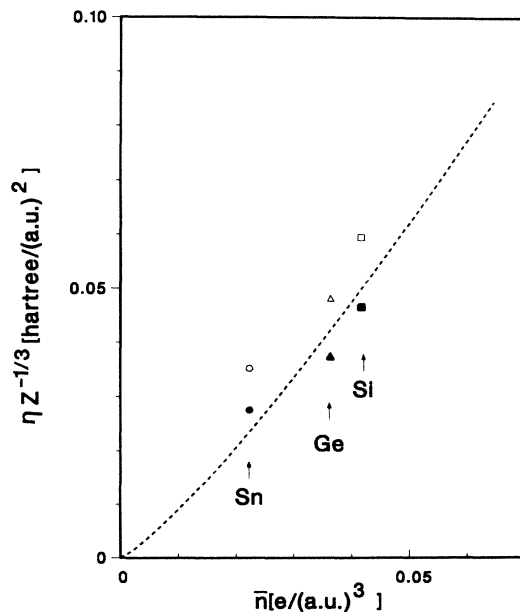


FIG. 1. Calculated electron-phonon matrix element $\eta Z^{-1/3}$ versus average electron density \bar{n} . The scaled value of 1.28 λ_q for λ is represented by the open point while the solid points are based on λ_q for $\mathbf{q}=2\pi(0,0,1)/c$. The dashed line is an empirical formula given by $\eta Z^{-1/3}=2.26\bar{n}^{1.2}$ in Ref. 39.

TABLE III. Angular-momentum decompositions of the valence charge densities for Si, Ge, and Sn in the β -Sn structure for pressures given in Table I. Units are in electrons per atom.

Symmetry	Si	Ge	Sn
<i>s</i>	1.36	1.49	1.52
<i>p</i>	2.17	2.14	2.13
<i>d</i>	0.47	0.37	0.35

for elements considered here. Based on the calculated electron-phonon couplings, the plot of $\eta Z^{-1/3}$ (Z is the valence charge) as a function of \bar{n} in Fig. 1 illustrates the correlation between the variables η and \bar{n} . Hence, the metallic group-IV elements satisfy reasonably the empirical formula $\eta Z^{-1/3}=2.26\bar{n}^{1.2}$ obtained from a study of simple and transition metals.³⁹ Furthermore, the phonon linewidths for all different phonon modes have an increasing tendency similar to the behavior of η when the electron density increases.

Although the group-IV elements are likely to form in the β -Sn structure when metallizing, their behavior under pressure differs significantly. The pressure coefficient of T_c is highest for Sn which has the smallest T_c . With increasing pressure, both Si and Ge are found to undergo a structural transition into the simple hexagonal phase at different pressures above 130 kbar (Refs. 40 and 41) and 750 kbar (Ref. 42), respectively. The higher transition pressure for Ge results from the large *d*-electron core in the Ge atom.^{1,42} Recently, the simple hexagonal phase of Si was found to be superconducting with a maximum T_c of 8.2 K.⁷ At this time a test for superconductivity in simple hexagonal Ge has not yet been made. In contrast, Sn is found to transform into the body-centered-tetragonal phase at 95 kbar and then into the body-centered-cubic phase at 350 kbar.⁴³ In analogy to Ge, the simple hexagonal phase for Sn is unstable with respect to the β -Sn phase for pressures below 350 kbar because of the large size of the *d*-electron core. In Table III, the angular-momentum decompositions of the valence wave functions are compared for Si, Ge, and Sn. Si has more *d* symmetry in the charge density of the valence electrons than Ge and Sn. For Ge and Sn, the *d* core electrons produce more repulsive *d* pseudopotentials and induce a repulsive force on the *d* valence electrons. Hence, the repulsive interaction pushes the energy for the *d* state higher and thus the *d*-symmetry state in the valence states is reduced. We found that the *s*-symmetry state increases whereas the *p*-symmetry state decreases in going from Si to Sn.

IV. CONCLUSIONS

We have shown that the pseudopotential-total-energy calculations can describe the electron-phonon interactions and superconducting properties of Si, Ge, and Sn in the β -Sn structure. With increasing electron concentration from Sn to Si, the phonon frequencies, the force constants, the phonon linewidths, and the electron-phonon interactions increase. For metallic Si, Ge, and Sn, the resulting correlation is similar to the behavior found for

other simple and transition metals. Furthermore, the electron-phonon mass enhancement parameters are similar, and assuming a reasonable μ^* , the superconducting critical temperature is highest for the element with the highest cutoff in the phonon spectrum. Based on the electron-phonon interaction calculations for one-phonon wave vector and using the constant scaling factor which gives the measured superconducting critical temperature for Sn at normal pressures, the superconducting transition temperature of Si is estimated in reasonable agreement with experiment; this value is smaller for Ge where experimental data are unavailable. We have found that the pressure dependence of the superconducting transition

temperature becomes larger for heavier elements and this behavior is in good agreement with experiment.

ACKNOWLEDGMENTS

We thank Dr. Michel Dacorogna for his collaboration on Si and for discussions. We acknowledge the support of the National Science Foundation Grant No. DMR-8319024 and support by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Cray computer time was provided by the Office of Energy Research of the Department of Energy.

- ¹See references in M. T. Yin and M. L. Cohen, *Phys. Rev. B* **26**, 5668 (1984).
- ²R. Hultgren *et al.*, *Selected Values of the Thermodynamic Properties of the Elements* (American Society of Metals, Ohio, 1973), p. 477.
- ³M. T. Yin and M. L. Cohen, *Phys. Rev. Lett.* **50**, 2006 (1983), M. T. Yin, *Phys. Rev. B* **30**, 1773 (1984).
- ⁴R. Biswas, R. M. Martin, R. J. Needs, and O. H. Nielsen, *Phys. Rev. B* **30**, 3210 (1984).
- ⁵J. Wittig, *Z. Phys.* **195**, 215 (1966).
- ⁶M. L. Cohen and P. W. Anderson, in *Superconductivity in d- and f-Band-Metals—1972, (Rochester)*, Proceedings of the Conference on Super Conductivity in d- and f-Band Metals, AIP Conf. Proc. No. 4, edited by D. H. Douglass (AIP, New York, 1972), p. 17.
- ⁷K. J. Chang, M. M. Dacorogna, M. L. Cohen, J. Mignot, G. Chouteau, and G. Martinez, *Phys. Rev. Lett.* **54**, 2375 (1985).
- ⁸J. M. Rowe, *Phys. Rev.* **163**, 546 (1967).
- ⁹J. M. Rowe, B. N. Brockhouse, and C. Svensson, *Phys. Rev. Lett.* **14**, 554 (1965).
- ¹⁰W. S. Corak and C. B. Satterthwaite, *Phys. Rev.* **102**, 662 (1956).
- ¹¹W. DeSorbo, *Acta. Metall.* **2**, 274 (1954).
- ¹²J. A. Rayne and B. S. Chandrasekhar, *Phys. Rev.* **120**, 1658 (1960).
- ¹³P. B. Allen and M. L. Cohen, *Phys. Rev.* **187**, 5205 (1969).
- ¹⁴W. L. McMillan, *Phys. Rev.* **167**, 331 (1968).
- ¹⁵J. F. Basley and J. C. Swihart, *Proceedings of the 12th International Conference on Low Temperature Physics, Kyoto, Japan, 1970*, edited by E. Kanda (Academic, Japan, 1971), Vol. 12, p. 303.
- ¹⁶J. M. Rowell, W. L. McMillan, and W. L. Feldmann, *Phys. Rev. B* **3**, 4065 (1971).
- ¹⁷G. Grimvall, in *Electron-Phonon Interaction in Metals*, edited by E. P. Wohlfarth, (North-Holland, Amsterdam, 1981).
- ¹⁸D. A. Papaconstantopoulos, L. L. Boyer, B. M. Klein, A. R. Williams, V. L. Moruzzi, and J. F. Janak, *Phys. Rev. B* **15**, 4221 (1977).
- ¹⁹M. M. Dacorogna, M. L. Cohen, and P. K. Lam, *Phys. Rev. Lett.* **55**, 837 (1985).
- ²⁰M. M. Dacorogna, K. J. Chang, and M. L. Cohen, *Phys. Rev. B* **32**, 1853 (1985).
- ²¹M. L. Cohen, *Phys. Scr.* **T1**, 5 (1982).
- ²²E. Wigner, *Trans. Faraday Soc.* **34**, 678 (1938).
- ²³D. R. Hamann, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).
- ²⁴K. J. Chang and M. L. Cohen, *Phys. Rev. B* **31**, 7819 (1985).
- ²⁵S. G. Louie, S. Froyen, and M. L. Cohen, *Phys. Rev. B* **26**, 1738 (1982).
- ²⁶S. N. Vaidya and G. C. Kennedy, *J. Phys. Chem. Solids* **31**, 2329 (1970).
- ²⁷P. B. Allen, *Phys. Rev. B* **6**, 2577 (1972); W. H. Butler, F. J. Pinski, and P. B. Allen, *ibid.* **19**, 3708 (1979).
- ²⁸We use 160 k points in the irreducible Brillouin zone of the β -Sn structure; G. Lehmann and M. Taut, *Phys. Status Solidi B* **54**, 469 (1972).
- ²⁹M. A. E. A. Ament and A. R. de Vroomen, *J. Phys. F* **4**, 1359 (1974).
- ³⁰M. T. Yin and M. L. Cohen, *Phys. Rev. B* **26**, 3259 (1982); S. Froyen and M. L. Cohen, *ibid.* **29**, 3770 (1984); P. K. Lam and M. L. Cohen, *ibid.* **25**, 6139 (1982).
- ³¹J. Ihm and M. L. Cohen, *Phys. Rev. B* **23**, 1576 (1981).
- ³²G. A. Busch and R. Kern, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1960), Vol. 11, p. 1.
- ³³P. Flubacher, A. J. Leadbetter, and J. A. Morrison, *Philos. Mag.* **4**, 273 (1959).
- ³⁴R. W. Hill and D. H. Parkinson, *Philos. Mag.* **43**, 309 (1952).
- ³⁵*Metals Handbook*, edited by T. Lyman (American Society for Metals, Ohio, 1948), p. 20.
- ³⁶K. H. Benneman and J. W. Garland, *Superconductivity in d- and f-band Metals—1972, (Rochester)*, Proceedings of the Conference on Superconductivity in d- and f-band Metals, AIP Conf. Proc. No. 4, edited by D. H. Douglas (AIP, New York, 1972), p. 103.
- ³⁷F. D. Murnaghan, *Proc. Nat. Acad. Sci.* **30**, 244 (1944).
- ³⁸J. J. Hopfield, *Phys. Rev.* **186**, 443 (1969).
- ³⁹P. K. Lam and M. L. Cohen, *Phys. Lett.* **97A**, 114 (1983).
- ⁴⁰H. Olijnyk, S. K. Sikka, and W. B. Holzapfel, *Phys. Lett.* **103A**, 137 (1984).
- ⁴¹J. Z. Hu and I. L. Spain, *Solid State Commun.* **51**, 263 (1984).
- ⁴²Y. K. Vohra, K. E. Brister, S. Desgreniers, A. L. Ruoff, K. J. Chang, and M. L. Cohen, *Phys. Rev. Lett.* **56**, 1944 (1986).
- ⁴³H. Olijnyk and W. B. Holzapfel, *J. Phys. (Paris) Colloq.* **45**, C8-153 (1984).