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Superconductivity in primitive hexagonal germanium

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We present a first-principles calculation of the electron-phonon coupling constant λ (mass enchancement parameter) for the primitive hexagonal, high-pressure structural phase of Ge ($75\ \mathrm{GPa} \lesssim p \lesssim 105\ \mathrm{GPa}$). Using the calculated value of λ, we estimate the superconducting transition temperature T_c to be in the range of 2 to 7 K. We discuss the contributions to λ from the different phonon modes and its dependence on the phonon frequency, electron-phonon matrix elements, and Fermi-surface nesting. The results are compared with previous calculations for primitive hexagonal Si.

INTRODUCTION

The tetrahedrally bonded semiconductors Si and Ge are known to transform under pressure into metallic structures with higher coordination number.[1-4] In both Si and Ge the coordination increases with pressure from the fourfold coordinated diamond structure which is stable at zero pressure, to the sixfold coordinated β-Sn structure, to the eightfold coordinated primitive hexagonal (ph) structure (these are the only elements known to have a stable primitive hexagonal phase), and at very high pressures to the twelvefold coordinated closed-packed structures hcp and fcc. The fact that the sequence of phases is the same for Si and Ge is not surprising since these elements have similar chemical properties. However, the pressures at which the phase transitions occur are remarkably different. While the transition from diamond to β-Sn occurs at similar pressures for both Si and Ge, all the other transitions occur at higher pressures in Ge than in Si (Table I). This difference in behavior at very high pressures between otherwise similar atoms was explained[4] in terms of the influence of *d* electrons on the Si and Ge metallic phases. The high-pressure metallic phases have a fair amount of *d* character in the occupied states, but Si does not have *d* electrons in the core (i.e., the Si *d* pseudopotential is less repulsive than in Ge) and thus transforms at lower pressures.

When a covalent material like Si transforms into the metallic state, the bonding retains a large amount of covalent character. Hence the distribution of the valence electrons is inhomogeneous and some directionality of the bonds can still be recognized. It has been argued[5] that in such a material local-field effects enhance the electron-phonon interaction and therefore enhance the superconducting transition temperature. The primitive hexagonal phase of high-pressure Si was predicted and observed[6,7] to be superconducting, with T_c as high as 8.2 K, which is a relatively high transition temperature for an *s*-*p* bonded superconductor. Furthermore the predicted U-shaped behavior of T_c with pressure was in reasonable agreement with experiment.[7]

TABLE I. Transition pressures for Si and Ge in GPa. The table is based on the compilation of Refs. 3 and 4.

	Diamond β-Sn	β-Sn ph	ph hcp or dhcp
		Si	
Theory	9.3	12.0	41.0
Experiment	8.8–12.5	13.2–16.4	35–42
		Ge	
Theory	9.5	84	105
Experiment	9.8–10.6	75	102

In the present case we have calculated the electron-phonon interaction parameter λ for primitive hexagonal Ge as a function of pressure and, using an estimate of μ^*, the Coulomb interaction parameter, and the McMillan empirical equation,[8] we estimate that T_c is in the range of 2–7 K with a most probable value of 4 K. The contributions of different phonon modes to λ and their dependence on the phonon frequency, electron-phonon matrix elements, and Fermi-surface nesting are discussed. We find that the contributions from different phonons can vary by an order of magnitude, and that superconductivity is enhanced by phonons with low frequency and large electron-phonon matrix elements.

THEORY

The electronic properties of primitive hexagonal Ge are calculated with the *ab initio* pseudopotential-local-density formalism with a plane-wave basis set.[9] For a fixed crystal structure, we calculate the total energy $E(\mathbf{R}^i)$ as a function of the atomic positions $\mathbf{R}^i$, the self-consistent potential $v_{sc}(\mathbf{r},\mathbf{R}^i)$, and the one-particle wave function $\psi_{m\mathbf{k}}(\mathbf{r})$ and eigenvalue $\varepsilon_{m\mathbf{k}}$ for wave vector $\mathbf{k}$ and band index m. By studying the total energy as a function of atomic positions (the Born-Oppenheimer surface), we are able to calculate the frequency $\omega_{\mathbf{q}\nu}$ and polarization vector $\mathbf{e}_{\mathbf{q}\nu}$ of a phonon with wave vector $\mathbf{q}$ and mode ν, using the frozen phonon approach. The same frozen phonon approach is then used to calculate the electron-phonon matrix elements.[10]

The electron-phonon matrix element $g(m\mathbf{k},m'\mathbf{k}',\mathbf{q}\nu)$ for the scattering of an electron from the state $m\mathbf{k}$ to the state $m'\mathbf{k}'$ by a phonon $\mathbf{q}\nu$ is, for the case of a single atom per unit cell of mass M (the case for primitive hexagonal Ge),[10-12]

$$g(m\mathbf{k},m'\mathbf{k}',\mathbf{q}\nu) = -\left[\frac{\hbar}{2NM\omega_{\mathbf{q}\nu}}\right]^{1/2}\delta_{\mathbf{q}+\mathbf{k}-\mathbf{k}',\mathbf{G}}I(m\mathbf{k},m'\mathbf{k}',\mathbf{q}\nu)\;, \tag{1a}$$

$$I(m\mathbf{k},m'\mathbf{k}',\mathbf{q}\nu) = N\int \psi^*_{m'\mathbf{k}'}(\mathbf{r})\mathbf{e}_{\mathbf{q}\nu}\cdot\nabla_{\mathbf{R}^0}v_{\mathrm{sc}}(\mathbf{r},\mathbf{R}^0)\psi_{m\mathbf{k}}(\mathbf{r})d^3r\;, \tag{1b}$$

where N is the number of unit cells in the crystal, and $\mathbf{G}$ is a reciprocal-lattice vector. The integral is taken over the whole crystal, the wave functions are normalized to unity in the crystal volume, and the gradient of v_{sc} is taken with respect to the displacement of the atom belonging to the unit cell at the origin $\mathbf{R}^0$. The gradient of v_{sc} is calculated numerically within the frozen phonon technique,[10] hence the rigid-ion approximation is not used.

From the lowest-order contribution to the electron self-energy by the electron-phonon interaction we can determine the single dimensionless parameter[10-12]

$$\lambda = 2D(\varepsilon_F)\sum_{\mathbf{q},\nu}\frac{1}{\hbar\omega_{\mathbf{q}\nu}}\langle\langle\,|g(m\mathbf{k},m'\mathbf{k}',\mathbf{q}\nu)|^2\rangle\rangle_{\mathrm{FS}}\;, \tag{2}$$

where $D(\varepsilon_F)$ is the density of states per spin at the Fermi level ε_F, and

$$\langle\langle X\rangle\rangle_{\mathrm{FS}} = \frac{\sum_{m,\mathbf{k}}\sum_{m',\mathbf{k}'}X\delta(\varepsilon_{m\mathbf{k}}-\varepsilon_F)\delta(\varepsilon_{m'\mathbf{k}'}-\varepsilon_F)}{\left[\sum_{m,\mathbf{k}}\delta(\varepsilon_{m\mathbf{k}}-\varepsilon_F)\right]^2}$$

defines the appropriate double average over the Fermi surface (FS).

The electron-phonon interaction parameter λ is usually expressed as an average over the phonon frequencies ω of $\alpha^2F(\omega)$, the dimensionless Eliashberg function,[11,12]

$$\lambda = 2\int_0^\infty \frac{\alpha^2F(\omega)}{\omega}d\omega\;.$$

However, for our discussion, we would like to evaluate the wave-vector dependence and separate the contribution of individual phonon modes to λ. Using Eq. (2) it is possible[10] to express λ as an average over the Brillouin zone of the dimensionless function $\lambda_{\mathbf{q}\nu}$,

$$\lambda = \frac{1}{3n_{\mathrm{at}}}\sum_{\nu=1}^{3n_{\mathrm{at}}}\frac{1}{N}\sum_{\mathbf{q}}\lambda_{\mathbf{q}\nu}\;, \tag{3}$$

where $3n_{\mathrm{at}}$ is the number of phonon modes (three times the number of atoms per unit cell, i.e., $3n_{\mathrm{at}}=3$ in our case).[13] We notice that $\lambda_{\mathbf{q}\nu}$ is proportional[10,11] to the experimentally accessible electron-phonon contribution to the phonon linewidth $\gamma_{\mathbf{q}\nu}$,

$$\lambda_{\mathbf{q}\nu} = \frac{3n_{\mathrm{at}}N\gamma_{\mathbf{q}\nu}}{\pi D(E_F)\hbar\omega^2_{\mathbf{q}\nu}}\;.$$

It is useful for our subsequent discussion to consider four different contributions to $\lambda_{\mathbf{q}\nu}$. (i) The phonon force constant $K^{\mathrm{ph}}_{\mathbf{q}\nu}=M\omega^2_{\mathbf{q}\nu}$ is the second derivative of the total energy with respect to the atomic displacements and is therefore independent of the atomic mass M; its typical value is $M\omega_D^2$, where ω_D is the Debye frequency for the material being considered. (ii) The degree of nesting of the Fermi surface, given by the dimensionless quantity $\langle\langle N\delta_{\mathbf{q}+\mathbf{k}-\mathbf{k}',\mathbf{G}}\rangle\rangle_{\mathrm{FS}}$, which is proportional to $1/\mathbf{q}$ for a spherical Fermi surface. The divergence for $\mathbf{q}=0$ is integrable in three-dimensional space. The nesting depends on the geometry of the Fermi surface and its value is of order unity. (iii) The density of states per spin per unit cell $D(\varepsilon_F)/N$, which is the same for all phonons. (iv) The average value of the square of the electron-phonon matrix element,

$$\bar{I}^{\,2}_{\mathbf{q}\nu} = \frac{\langle\langle\,|I(m\mathbf{k},m'\mathbf{k}',\mathbf{q}\nu)|^2N\delta_{\mathbf{q}+\mathbf{k}-\mathbf{k}',\mathbf{G}}\rangle\rangle_{\mathrm{FS}}}{\langle\langle N\delta_{\mathbf{q}+\mathbf{k}-\mathbf{k}',\mathbf{G}}\rangle\rangle_{\mathrm{FS}}}\;, \tag{4}$$

takes into account the detailed interactions between the phonons and the electrons near the Fermi surface. For the case of atoms with different masses in the unit cell a small dependence of this term on the atomic mass is introduced through the phonon polarization vector. The final expression for the contribution of a specific phonon to the electron-phonon parameter is

$$\lambda_{\mathbf{q}\nu} = \frac{1}{M\omega^2_{\mathbf{q}\nu}}3n_{\mathrm{at}}\frac{D(\varepsilon_F)}{N}\langle\langle N\delta_{\mathbf{q}+\mathbf{k}-\mathbf{k}',\mathbf{G}}\rangle\rangle_{\mathrm{FS}}\bar{I}^{\,2}_{\mathbf{q}\nu} = \frac{K^e_{\mathbf{q}\nu}}{K^{\mathrm{ph}}_{\mathbf{q}\nu}}\langle\langle N\delta_{\mathbf{q}+\mathbf{k}-\mathbf{k}',\mathbf{G}}\rangle\rangle_{\mathrm{FS}}\;, \tag{5}$$

where we have defined a new quantity,

$$K^e_{\mathbf{q}\nu} = 3n_{\mathrm{at}}\frac{D(\varepsilon_F)}{N}\bar{I}^{\,2}_{\mathbf{q}\nu}\;,$$

which can be classified as an "electronic" force constant. Since the electron-phonon coupling constant[11] $g\sim(\hbar\omega_D\varepsilon_F)^{1/2}$, then the electronic force constant is also of the order of $M\omega_D^2$, and the electron phonon parameter $\lambda_{\mathbf{q}\nu}$ is a dimensionless quantity of the order of unity.

The parameter λ can be used to estimate the superconducting transition temperature T_c, through the McMillan equation,[8]

$$T_c = \frac{\Theta_D}{1.45}\exp\left[\frac{-1.04(1+\lambda)}{\lambda-\mu^*-0.62\lambda\mu^*}\right]\;, \tag{6}$$

where Θ_D is the Debye temperature, and the repulsive Coulomb interaction parameter[8] μ^* has a typical value of ~ 0.1. This equation usually gives a good approximation to the solution of the Eliashberg equations for values of $\lambda \lesssim 0.7$, which will be the case in our calculations.

RESULTS

The value of the interaction parameter λ obtained from averaging the contributions of the phonon modes shown in Table II is $\lambda=0.5$ and the average value of the phonon frequency is $\langle\omega\rangle=41$ THz, corresponding to a Debye

TABLE II. The electron-phonon parameter $\lambda_{\mathbf{q}\nu}$, the phonon frequency $\omega_{\mathbf{q}\nu}$, the phonon and electronic force constants, and the Fermi-surface nesting parameter (defined in the text) are shown for several phonons. The phonon polarization is indicated by L for longitudinal, T for transverse, and X,Y,Z for the three directions in space. These results were calculated for a lattice constant of 2.41 Å and a c/a ratio of 0.945.

$\mathbf{q}\nu$	$\lambda_{\mathbf{q}\nu}$	$\omega_{\mathbf{q}\nu}$ (THz)	$K^{\mathrm{ph}}_{\mathbf{q}\nu}$ (Ry/a.u.^{2})	$K^{e}_{\mathbf{q}\nu}$ (Ry/a.u.^{2})	$\langle\langle N\delta\rangle\rangle_{\mathrm{FS}}$
$(0,0,\frac{1}{2})L$	0.29	79	0.98	0.49	0.57
$(0,0,\frac{1}{2})T$	0.09	13	0.025	0.004	0.57
$(\frac{1}{2},0,0)L$	0.23	76	0.90	0.33	0.62
$(\frac{1}{2},0,0)T_Y$	0.30	33	0.17	0.084	0.62
$(\frac{1}{2},0,0)T_Z$	0.30	13	0.028	0.013	0.62
$(\frac{1}{2},0,\frac{1}{2})X$	0.45	65	0.65	0.43	0.68
$(\frac{1}{2},0,\frac{1}{2})Y$	2.77	19	0.053	0.22	0.68
$(\frac{1}{2},0,\frac{1}{2})Z$	0.43	69	0.73	0.47	0.68
$(\frac{2}{3},0,0)L$	0.26	67	0.69	0.22	0.80
$(\frac{2}{3},0,0)T_Y$	0.43	29	0.13	0.070	0.80
$(\frac{2}{3},0,0)T_Z$	0.33	15	0.032	0.013	0.80

temperature of $\Theta_D=420$ K (for comparison the Debye temperature of Ge at zero temperature and pressure is 374 K). Combining these two values with a typical value of the Coulomb parameter for s-p bonded metals of $\mu^*=0.1$, we obtain from the McMillan equation [Eq. (6)] a superconducting transition temperature of $T_c=4.2$ K. According to this equation, T_c depends linearly on Θ_D but exponentially on λ and μ^*. Hence T_c depends very sensitively on the variations in these two parameters. The μ^* parameter enters Eq. (6) mainly through the difference $\lambda-\mu^*$, therefore a study of the effects of changes in λ is sufficient to estimate the sensitivity of T_c to the determination of the various parameters. For a value $\lambda=0.6$ we find $T_c=7.9$ K, and for $\lambda=0.4$ we find $T_c=1.5$ K. These two limits can be used as an estimation of the uncertainty in our calculation of T_c.

The number of wave vectors included in the averaging of λ is very small, because the use of a larger number of points is computationally expensive in the frozen phonon approach.[10] Since the contributions from the phonon modes shown in Table II can vary by as much as an order of magnitude, it is necessary to examine the contributions from various parts of the wave-vector set. If we disregard the large contribution to λ from the $(\frac{1}{2},0,\frac{1}{2})$ phonon polarized in the y direction, and for balance the small contribution of the $(\frac{1}{2},0,0)$ transverse phonons, we obtain a value of $\lambda=0.34$, and a corresponding $T_c=0.5$ K. A single phonon mode is sufficient to increase T_c by almost an order of magnitude in our sampling. This phonon mode is at a high-symmetry point in the Brillouin zone, and is nondegenerate, therefore the gradient with respect to $\mathbf{q}$ of both the phonon frequency $\omega_{\mathbf{q}\nu}$ and the coupling constant $\lambda_{\mathbf{q}\nu}$ is zero. Hence there is significant weighting of these phonons. The other points included in Table II also have high symmetries. They are associated with singularities in the phonon density of states with the exception of the $(\frac{2}{3},0,0)$ wave vector, which was included because it is in the center of the $\frac{1}{6}$ wedge of the Brillouin zone which can be considered as an "average" wave vector.

We have analyzed the different contributions to $\lambda_{\mathbf{q}\nu}$ and determined the origin of the large variations in its value. Inspection of Table II shows that this variation is not due to the Fermi-surface nesting, which is roughly constant, or to the density of states at the Fermi level $D(\varepsilon_F)/N=0.12$ eV^{-1} which does not depend on the choice of phonon mode (for comparison the free-electron value is 0.17 eV^{-1}). The important quantity for understanding the values of $\lambda_{\mathbf{q}\nu}$ is the ratio between the phonon and the electronic force constants. The electronic force constant $K^{e}_{\mathbf{q}\nu}$ is an average [Eqs. (4) and (6)] of the square of the electron-phonon matrix elements [Eq. (1b)] over the Fermi surface and is always positive. The phonon force constant $K^{\mathrm{ph}}_{\mathbf{q}\nu}$ has two contributions, one from the Madelung term in the total energy used to define the "bare" phonon frequencies, and another from the electronic screening of the bare phonons. Each of them can have either a positive or a negative sign, but their sum must be positive in a stable crystal. If a phonon mode stresses a nearest-neighbor interatomic bond, i.e., the interatomic distance is linear in the phonon amplitude, we expect large contributions to the electronic force constant, to the bare phonon frequency, and to its screening. If the phonon mode shears the bond, i.e., if the interatomic distance is quadratic in the phonon amplitude, then we expect only small contributions from that particular bond. The electronic force constant being positive definite will reflect the number and strength of the stressed bonds while the phonon force constant could be accidentally small through the cancellation of large contributions with opposite signs.

There are four phonon modes with low frequencies (less than 20 THz) in Table II. The transverse $(0,0,\frac{1}{2})$ mode and the $(q,0,0)$ transverse phonon modes polarized in the z direction do not stress bonds and therefore they have also small electronic force constants. Their contribution to λ varies from small to average. The y-polarized $(\frac{1}{2},0,\frac{1}{2})$ phonon mode, on the other hand, stresses the bonds in the xy plane and has a large electronic force constant. The small value of $K_{\mathbf{q}\nu}^{\mathrm{ph}}$ for this mode is due to a large electronic screening of the bare phonon frequency. The contribution of this mode to λ is very large. The other phonon modes in Table II stress some bonds, have large electronic and phonon force constants, and give an average contribution to λ.

Two of the low-frequency phonons are related to the structural phase transitions of Ge with pressure. The atomic displacements transforming the primitive hexagonal phase into the β-Sn phase correspond to the displacements of the y-polarized $(\frac{1}{2},0,\frac{1}{2})$ phonon of the primitive hexagonal phase, and the displacements transforming the primitive hexagonal phase into the hcp phase correspond to the transverse $(0,0,\frac{1}{2})$ phonon. The low frequency of these two modes reflects the incipient instability of the primitive hexagonal phase with respect to the β-Sn and hcp structural phases, as was discussed previously.[3,4]

Our calculations of λ and ω as a function of pressure show that we should expect a decrease of T_c of the order of 30% when the pressure is increased from 85 to 105 GPa. This is a consequence of a calculated 10% reduction of λ and a 5% increase of Θ_D. Our results show that this decrease should be essentially linear with pressure. The main reason for the decrease of λ is the increase in frequency of the y-polarized $(\frac{1}{2},0,\frac{1}{2})$ soft phonon.

Comparison with the calculations for Si shows similar values for λ, which is not very surprising since λ is independent of the atomic mass and these atoms have similar electronic properties. Hence the difference in T_c between the two crystals will depend only on their respective Debye temperatures. As was mentioned before, the pressure range where primitive hexagonal Si is stable is different from the range for Ge. The large decrease in T_c for Si with pressure followed by an increase is due to the hardening of the $(\frac{1}{2},0,\frac{1}{2})$ phonon as the pressure increases from its value near the β-Sn structural transition followed by the softening of the transverse $(0,0,\frac{1}{2})$ phonon as the pressure of the hcp structural transition is approached. In the case of Ge near the hcp transition the softening of the transverse $(0,0,\frac{1}{2})$ phonon does not affect λ noticeably and the hardening of the $(\frac{1}{2},0,\frac{1}{2})$ phonon is small, thus T_c as a function of pressure for primitive hexagonal Ge will not have a U-shaped curve but only a gentle linear decrease.

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[13] Notice that we use a slightly different definition of $\lambda_{\mathbf{q}\nu}$ with respect to Ref. 10, as we define the total λ as an average over the phonon modes and not as a sum over the phonon modes. The validity of Eq. (3) is limited to theories where the spectral weight of the bare phonons is a delta function on the real axis, i.e., they have infinite lifetime and a well-defined frequency dispersion relation $\omega_{\mathbf{q}\nu}$, which is our case.