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Pressure increase of the electron-phonon interaction in superconducting hexagonal silicon

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Using an *ab initio* pseudopotential approach, the pressure dependence of the electron-phonon interaction parameter λ and the phonon frequencies for metallic hexagonal phases of silicon is calculated. With changing pressure λ is found to go first through a minimum and then reach its maximum value near the phase transition from simple hexagonal (sh) to hexagonal close packed (hcp). At this point the superconducting transition temperature T_c is expected to be above 10 K. In the hcp phase Si is predicted to be superconducting with T_c in the same range as in the sh phase.

In recent papers[1,2] we have presented theoretical and experimental results on superconductivity in the β-tin and simple hexagonal (sh) phases of silicon. The sh phase was found to be superconducting with a T_c of 8.2 K at pressures in the neighborhood of 15 GPa. At higher pressures, both the theoretical and experimental results gave a decrease of T_c with pressure up to 25 GPa. Using the same theoretical methods we have extended this calculation to pressures beyond 25 GPa and computed the pressure dependence of the phonon frequencies and the electron-phonon interaction constants in the sh structure. We also study these quantities in the hexagonal-close-packed (hcp) structure. With increasing pressure λ in the sh phase is found to go through a minimum at around 25 GPa and then increase again giving rise to a higher T_c close to the sh-to-hcp structural transition.

The approach used allows an *ab initio* calculation of the electronic wave functions, the phonon frequencies[2,3] $\omega_{\mathbf{q}\nu}$, and the contribution to the electron-phonon coupling[2,4] $\lambda(\mathbf{q}\nu)$ of a frozen phonon of wave vector $\mathbf{q}$ and branch ν. Here we present calculations of the density of states (DOS) at the Fermi level, $\omega_{\mathbf{q}\nu}$ and $\lambda(\mathbf{q}\nu)$ along the [001] direction for different pressures. For the sh structure, four points have been chosen along this direction in the following way: $\mathbf{q}=\alpha[00q_{\max}]$, where $\alpha=\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$, and 1, and $\alpha=1$ for the hcp structure. From the results for this direction we obtain λ by using a spherical approximation to the full Brillouin zone (BZ) averaging of the $\lambda(\mathbf{q})$'s,

$$\lambda=\frac{4\pi}{\Omega_{\mathrm{BZ}}}\int_0^{q_{\mathrm{BZ}}} q^2\lambda(q)\,dq \quad , \tag{1}$$

where q_{BZ} is the radius of a sphere with the same volume Ω_{BZ} as the BZ. The $\lambda(\mathbf{q})$'s are given by

$$\lambda(\mathbf{q})=\sum_{\nu}\lambda(\mathbf{q}\nu)$$
$$=\sum_{\nu}2N(E_F)\langle\langle|g(n\mathbf{k},n'\mathbf{k}',\mathbf{q}\nu)|^2\rangle\rangle/\hbar\omega_{\mathbf{q}\nu} \quad , \tag{2}$$

where $N(E_F)$ is the density of states per atom and per spin at the Fermi level[5] E_F. The double brackets represent a Fermi-surface average[4] on $\mathbf{k}$ and $\mathbf{k}'$ of the square of the electron-phonon matrix elements[6] $g(n\mathbf{k},n'\mathbf{k}',\mathbf{q}\nu)$ which are defined as

$$g(n\mathbf{k},n'\mathbf{k}',\mathbf{q}\nu)=\left(\frac{\hbar\Omega_{\mathrm{BZ}}}{2M\omega_{\mathbf{q}\nu}}\right)^{1/2}\delta(\mathbf{k}-\mathbf{k}'-\mathbf{q})$$
$$\times\langle\psi^0_{n\mathbf{k}}|\hat{\epsilon}_{\mathbf{q}\nu}\cdot\nabla v|\psi^0_{n'\mathbf{k}'}\rangle \quad , \tag{3}$$

where M is the atomic mass, $\hat{\epsilon}_{\mathbf{q}\nu}$ is the unit polarization vector of the phonon $\mathbf{q}\nu$, and $\psi^0_{n\mathbf{k}}$ and $\psi^0_{n'\mathbf{k}'}$ are the electron Bloch wave functions for states $\mathbf{k}$ and $\mathbf{k}'$ in bands n and n', respectively, for the undistorted crystal. The quantity ∇v is the total self-consistent change in the crystal potential per unit displacement caused by a phonon distortion. In our calculations this quantity is replaced by the difference[4] between the *self-consistent potentials* (within the local density pseudopotential formalism[7]) of a crystal distorted by a frozen phonon, and an appropriate potential for the undistorted crystal.

In the sh structure, supercells of two, three, four, and six atoms are used for $\alpha=1$, $\frac{2}{3}$, $\frac{1}{2}$, and $\frac{1}{3}$, respectively. The use of identical supercells for *both* distorted and undistorted crystals[4] maps back $\mathbf{k}'+\mathbf{q}$ to $\mathbf{k}$, eliminating the δ function in Eq. (3). However, the limitation of this method is that the phonon wave vector $\mathbf{q}$ must be commensurate with the lattice; that is, $n\mathbf{q}=\mathbf{G}$, where n is an integer number and $\mathbf{G}$ is a reciprocal-lattice vector. The calculation is done with 75 k points in the irreducible BZ (IBZ) for the sh structure and 70 k points in the hcp IBZ. The hcp BZ is approximately half that of the sh. To ensure good convergence of the Fermi-surface average in Eq. (2) we use a Gaussian broadening of the δ functions in the average expression.[4]

The pressure dependence is studied by varying the lattice constant and relating the resulting volume change to the pressure through Murnaghan's equation of state.[8] The crystal structure is determined using the total energy minimization method.[7] The pressure range of the sh phase was calculated[8,9] to be from 12 to 41 GPa. The lower boundary is slightly below the experimental range of 13.2–16.0 GPa given by Hu and Spain[10] and the jump in T_c at 13.5 GPa found by Chang *et al.*[2] Hu and Spain also give an upper boundary of 34.0–42.0 GPa for the sh phase. In addition an unknown Si-VI phase has been reported[10,11] in this pressure range but it is suggested that it might be a mixture of the sh and hcp phases.[3]

The results for DOS, $\omega_{\mathbf{q}\nu}$, and $\lambda(\mathbf{q}\nu)$ at different pressures are given in Table I for the sh structure. In Fig. 1 the spherically averaged λ's using Eq. (1) are plotted as functions of pressure. One can see that the phonon frequencies of the longitudinal modes increase with pressure for all the points considered along the [001] direction. At 12.7 GPa the frequency of the zone-boundary phonon for the longitudinal mode is lower than the value at $\alpha=\frac{2}{3}$. However, as the pressure gets larger the zone-edge frequency increases more rapidly than the $\mathbf{q}=(0,0,2q_{\max}/3)$ phonon. So the overall effect on λ for the pressures 18 and 21 GPa is a decrease, since the longitudinal modes are more important than the transverse at these pressures and the zone-boundary phonon plays a dominant role in the averaging of the $\lambda(\mathbf{q})$'s. This result is consistent with the decreasing behavior of T_c observed by Chang *et al.*[2]

TABLE I. Calculated $\lambda(\mathbf{q}\nu)$ and $\lambda(\mathbf{q})$ at $\mathbf{q}=\alpha\mathbf{q}_{\max}$ as a function of pressure for the sh phase. Pressure (P), $N(0)$, and $\omega(\mathbf{q}\nu)$ are in units of GPa, states/Ry per atom per spin, 10^{13} rad/sec, respectively.

			Longitudinal		Transverse		
P	$N(0)$	α	$\omega(\mathbf{q}\nu)$	$\lambda(\mathbf{q}\nu)$	$\omega(\mathbf{q}\nu)$	$\lambda(\mathbf{q}\nu)$	$\lambda(\mathbf{q})$
12.7	2.52	$\frac{1}{3}$	4.8	0.23	1.7	0.31	0.85
		$\frac{1}{2}$	6.9	0.16	2.1	0.14	0.44
		$\frac{2}{3}$	8.2	0.15	2.4	0.09	0.33
		1	7.0	0.23	2.5	0.05	0.33
18.0	2.49	$\frac{1}{3}$	4.9	0.22	1.6	0.35	0.92
		$\frac{1}{2}$	7.2	0.16	2.1	0.16	0.48
		$\frac{2}{3}$	8.5	0.14	2.4	0.10	0.34
		1	7.9	0.18	2.4	0.06	0.30
21.0	2.48	$\frac{1}{3}$	5.0	0.22	1.6	0.36	0.94
		$\frac{1}{2}$	7.2	0.16	2.1	0.16	0.48
		$\frac{2}{3}$	8.7	0.14	2.4	0.10	0.34
		1	8.5	0.16	2.4	0.06	0.28
36.6	2.42	$\frac{1}{3}$	5.2	0.23	1.6	0.39	1.01
		$\frac{1}{2}$	7.9	0.16	2.1	0.25	0.66
		$\frac{2}{3}$	9.2	0.12	2.3	0.17	0.46
		1	10.4	0.12	2.1	0.13	0.38
40.0	2.42	$\frac{1}{3}$	5.4	0.23	1.6	0.45	1.13
		$\frac{1}{2}$	8.2	0.15	2.1	0.27	0.69
		$\frac{2}{3}$	9.3	0.13	2.3	0.17	0.47
		1	10.5	0.12	1.9	0.18	0.48
41.0	2.42	$\frac{1}{3}$	5.6	0.22	1.6	0.54	1.30
		$\frac{1}{2}$	8.2	0.15	2.1	0.29	0.73
		$\frac{2}{3}$	9.3	0.14	2.2	0.21	0.56
		1	10.9	0.12	1.8	0.22	0.56

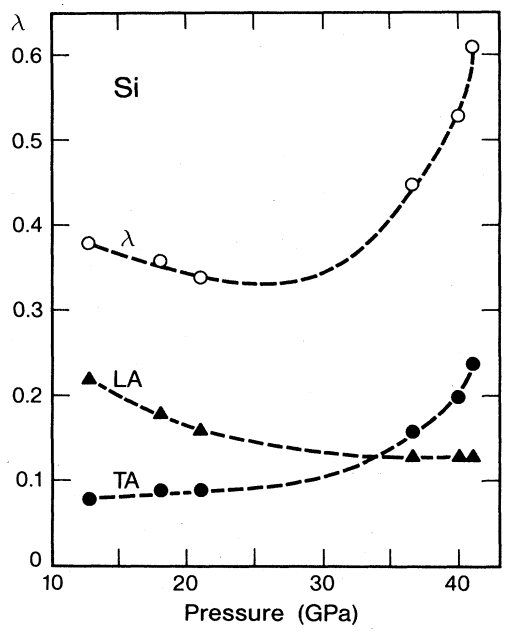

FIG. 1. Pressure dependence of λ for the sh phase.

For this pressure range, the transverse modes yield a small $\lambda(\mathbf{q}\nu)$ and the transverse phonon frequencies are either constant ($\alpha=\frac{1}{3}$ and $\frac{1}{2}$) or decreasing with pressure ($\alpha=\frac{2}{3}$ and 1). In contrast, the corresponding transverse electron-phonon matrix elements continuously increase. So, the net result is a large enhancement of the transverse-mode contribution to λ as the pressure increases. At higher pressures, above 25 GPa, this pressure-sensitive soft mode reverses the overall decreasing trend of λ, which should then have a minimum around 25–26 GPa. Since the density of states at the Fermi level does not show a significant variation with pressure, we do not expect μ^* to change drastically. Thus we predict that T_c should also increase and reach its maximum near the phase transition from sh to hcp. If we use the same value of μ^* and a phonon spectrum cutoff as in Ref. 1 in the McMillan equation,[12] we expect T_c to be above 10 K at around 40 GPa for this phase.

In Table II the results for the hcp structure are given. This phase is described by two atoms per unit cell, so the BZ cell is approximately twice as small as that of sh and we expect the phonon at the zone boundary of the hcp structure to be comparable to the one at $\alpha=\frac{1}{2}$ for the sh structure. Indeed, this is what we find: The longitudinal-mode frequency is 6.9×10^{13} rad/sec in hcp at a pressure of 42 GPa and 8.2×10^{13} for $\alpha=\frac{1}{2}$ in the sh structure at 41 GPa; the transverse-mode frequency is 2.4×10^{13} at 42 GPa for hcp and 2.1×10^{13} at 41 GPa for sh. Moreover, for hcp, $\lambda(\mathbf{q})$ is only slightly lower at the zone boundary than the corresponding one at $\alpha=\frac{1}{2}$ for the sh structure near this pressure (0.54 for hcp and 0.73 for sh at $\alpha=\frac{1}{2}$). Hence we conclude that the electron-phonon couplings for correspond-

TABLE II. Calculated $\lambda(\mathbf{q}\nu)$ and $\lambda_{\mathbf{q}}$ at $\mathbf{q}_{max}$ as a function of pressure for the hcp phase. Units are the same as those in Table I.

P	$N(0)$	ν	$\omega(\mathbf{q}\nu)$	$\lambda(\mathbf{q}\nu)$	$\lambda(\mathbf{q})$
42.0	2.06	LOA	6.9	0.09	
		TOA	2.4	0.09	0.54
46.5	2.02	LOA	7.2	0.09	
		TOA	2.5	0.09	0.54
63.0	2.00	LOA	7.9	0.08	
		TOA	2.9	0.08	0.48

ing modes are not substantially affected by the phase transition from sh to hcp. The DOS at E_F is similar in both structures; so we also expect hcp silicon to be superconducting with a T_c higher than 10 K. We note that, for the points we have calculated, the pressure dependence of λ seems to follow the usual behavior of decreasing due to the hardening of the phonon frequencies. Both the longitudinal and the transverse modes show an increase in frequency with pressure.

In summary, the pressure dependence of the electron-phonon coupling parameter λ in sh structure is governed by two competing effects, the hardening of the [001] longitudinal phonons, which dominate at low pressures, and the softening of the [001] transverse phonons, which, combined with the increase of the electron-phonon matrix elements, become more important as the pressure increases. In the hcp phase our calculations do not show any peculiar behavior of λ with pressure and T_c should decrease with increasing pressure. The superconducting transition temperature at the structural transition should be the highest, and we do not expect the occurrence of a possible mixed phase[11] to reduce T_c below 10 K, since both the sh and the hcp phases are found to have strong electron-phonon couplings.

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