Superconductivity in High-Pressure Metallic Phases of Si

K. J. Chang, Michel M. Dacorogna, and Marvin L. Cohen
Department of Physics, University of California, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

and

J. M. Mignot
Centre de Recherches sur les Très Basses Températures–Centre National de Recherche Scientifique, F-38042 Grenoble Cedex, France

and

G. Chouteau and G. Martinez
Service National des Champs Intenses–Centre National de Recherche Scientifique, Laboratoire associé à l'Université Scientifique et Médicale de Grenoble, F-38042 Grenoble Cedex, France
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Superconductivity in the simple hexagonal phase of silicon is predicted on the basis of an electron-phonon–coupling calculation and measured experimentally up to a pressure of 25 GPa in a Bridgman-type opposed-anvil device. The highest measured superconducting transition temperature is 8.2 K at 15 GPa for the simple hexagonal phase.

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This Letter reports on the theoretical prediction and subsequent experimental confirmation of superconductivity in highly condensed Si in the simple hexagonal (sh) structure. The calculation gives an estimate of the electron-phonon coupling and the superconducting transition temperature; the experimental study examines the superconductivity of Si in two high-pressure phases at low temperatures as a function of pressure.

Superconductivity in sh Si was suggested earlier by Chang and Cohen[1] on the basis of structural, vibrational, and electronic calculations which show that this material should have a soft transverse acoustic mode and covalent bonds between the Si atoms which could give rise to local-field effects which should enhance electron-electron attractions.[2] Needs and Martin[3] also studied the structural properties of sh Si and mentioned the possibility of superconductivity in this phase.

In the present study a detailed calculation is done, and the electron-electron interactions are evaluated to determine whether superconductivity is possible. The electron-phonon coupling parameter λ is computed explicitly for different phonon modes for two metallic phases of Si (β-Sn and sh) and in both cases a superconducting solution is found. A preliminary description of this calculation is given in by Dacorogna, Chang, and Cohen.[4] Experimentally, the superconducting transition temperature is measured for pressures from 12 to 25 GPa. We find that T_c goes through a maximum of 8.2 K at 15.2 GPa. These pressures are in the range of the sh phase according to recent measurements by two experimental groups.[5,6] This critical temperature is among the highest found for nontransition elemental metals.[7] For the β-Sn phase of Si, T_c is 6.3 K at 12 GPa. This value is somewhat lower than the 6.7 K reported by Wittig[8] on powdered Si or 7 K by Il'ina and Itskevich[9] on p- and n-type monocrystals.

The effect of pressure on the electron-phonon interaction is studied by varying the size of the unit cell and then relating it to the pressure via Murnaghan's equation of state.[10] We find that, within the accuracy of the calculation, λ does not vary with pressure for the β-Sn phase. In sh Si, λ first decreases up to the measured pressures and then increases as a result of the soft transverse-acoustic mode which brings the sh structure into the hexagonal close-packed (hcp) phase.[1,4,11]

The measurements for T_c were performed on p-type Si with an acceptor concentration of about 10^{16} cm^{-3}. A single crystal was polished in the [100] direction down to a thickness of 25 μm. Small slabs of length 0.8 mm and width 0.08 mm were used. Pressures as high as 25 GPa were generated in a Bridgman-type opposed-anvil device with sintered diamond elements. The samples were embedded in a soft solid medium (steatite) to ensure quasihydrostatic conditions. The pressure was deduced from the superconducting critical temperature of a lead sample located very close to the Si specimen. The homogeneity of the pressure was always better than 1 GPa, as indicated by the width of the lead resistive transition. Both samples were connected in series and measured by a conventional four-terminal ac method with a resolution of 0.5 nV for a measuring current of 100 μA. The pressure was increased by steps at room temperature and then the temperature was lowered by successive cycles down to

1.2 K to determine the corresponding critical temperatures. The error in T_c due to thermal gradients and calibration inside the high-pressure assembly was less than 30 mK.

Results for two samples are shown in Fig. 1. The horizontal bars represent the total width of the resistive transitions of lead (0.15–0.25 K). This corresponds to a pressure gradient smaller than 1 GPa. We attribute the width of the Si transitions to this pressure gradient (vertical bars). It is always smaller than 0.2 K. The β-Sn structure is metallic and superconducting with $T_c \sim 6.3$ K at 12 GPa.

Above 14 GPa, the structural transition to the sh phase is evidenced by an abrupt decrease of the resistivity at room temperature. We observe that in the low-pressure range of the sh phase T_c reaches a maximum of 8.2 K at 15.2 GPa after showing a discontinuity at the β-Sn to sh transition around 13.5 GPa. A discontinuity is also reported by Il'ina and Itskevich.[9] At higher pressures, T_c decreases to 3.6 K at 25 GPa. The T_c vs P diagram shows a slight positive curvature above 21 GPa.

To calculate the electron-phonon parameter λ, both the electronic and the vibrational properties of the solid are needed.[12] This is achieved by using an *ab initio* pseudopotential–total-energy scheme[13] where only the atomic number and mass are used as input to calculate the structural[1,14] and lattice-vibrational properties.[11] The method to calculate λ for a given lattice distortion is described elsewhere.[15] The basic result[15] for λ as a function of phonon wave vector $\mathbf{q}$ is

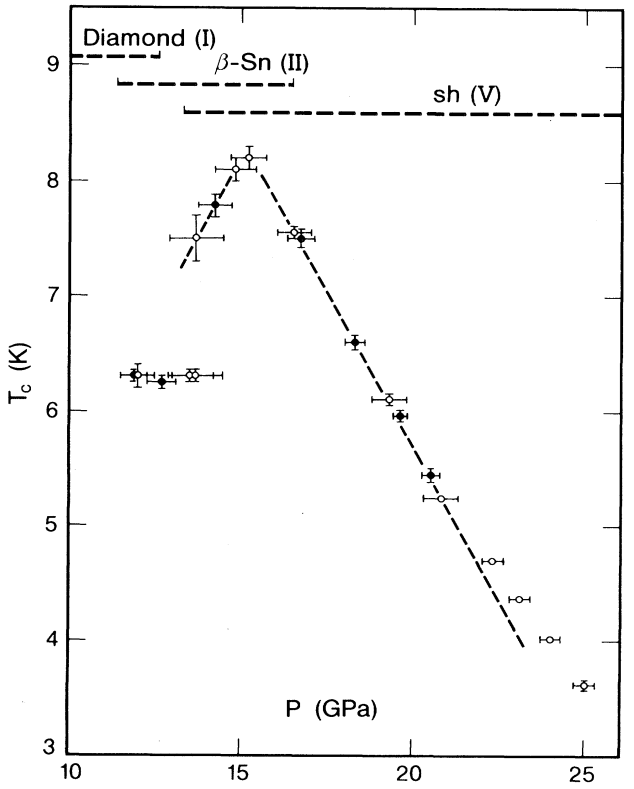

FIG. 1. T_c as a function of pressure. The points represent the measured values with experimental error bars; the two types of points denote two samples. The transition pressures marked are taken from Ref. 6. The dashed line is used as a guide.

$$\lambda(\mathbf{q}) = \sum_\nu \lambda(\mathbf{q}\nu) = \sum_\nu 2N(E_F) \langle\langle |g(n\mathbf{k},\ n'\mathbf{k}',\ \mathbf{q}\nu)|^2 \rangle\rangle / \hbar\omega_{\mathbf{q}\nu} \quad (1)$$

where $N(E_F)$ is the density of states (DOS) per atom and per spin at the Fermi level E_F, $\omega_{\mathbf{q}\nu}$ is the phonon frequency for wave vector $\mathbf{q}$ and branch ν, and the last term is a Fermi-surface average of the square of the standard electron-phonon matrix element.[16]

These matrix elements are calculated for each $\mathbf{q}$ with use of the self-consistent change in the potential associated with a specific frozen phonon of the same $\mathbf{q}$. The average over the Fermi surface is performed by a Gaussian broadening method to ensure good convergence of the results with respect to $\mathbf{k}$-point sampling. Here we used 45 $\mathbf{k}$ points in the irreducible Brillouin zone (BZ) of the supercell for the β-Sn structure and 75 for sh. The McMillan parameter λ [17] is then

$$\lambda = \Omega_{BZ}^{-1} \int \lambda(\mathbf{q}) d^3\mathbf{q}, \quad (2)$$

where Ω_{BZ} is the volume of the BZ.

For the sh structure at a pressure of 12.7 GPa, we have studied different phonon modes along the [001] direction: $\mathbf{q} = \alpha[00q_{max}]$ where $\alpha = \frac{1}{3}, \frac{1}{2}, \frac{2}{3}$, and 1. The results, including phonon frequencies, are given in Table I. We found that the longitudinal mode at the zone boundary is soft, but its softness is reduced under compression. In view of the small number of phonon wave vectors calculated here, an accurate value for λ in Eq. (2) cannot be obtained. However, a spherical approximation of Eq. (2) can be used and it gives $\lambda \sim 0.4$.

McMillan's equation[17] may be used to estimate a transition temperature. We note, however, that numerical factors (his calculation is most appropriate to Nb) and exponential dependence on λ and μ^* make an accurate T_c calculation difficult. We estimate $\mu^* = 0.06$ by scaling Bennemann and Garland's empirical formula[18] using our density of states at E_F. Use of this value of μ^*, a cutoff of the phonon spectrum at the highest calculated longitudinal frequency (623 K), and our calculated λ in the McMillan equation[17] gives a T_c of 5 K. If we use other forms of the T_c equation, we can obtain a range of values which are usually higher by 50%–100%. Because of the uncertainties in averaging λ we did not attempt a more detailed estimate of T_c and are satisfied with the comparison with the ex-

TABLE I. Calculated electron-phonon coupling $\lambda(\mathbf{q})$ at $\mathbf{q}=\alpha[00q_{max}]$ at a pressure of 12.7 GPa for the sh phase. Frequency and DOS are in units of 10^{13} rad/sec and states/Ry per atom per spin, respectively. $\lambda(\mathbf{q}\nu)$ denotes $\lambda(\mathbf{q})$ for the mode ν [see Eq. (1)]. LA denotes the longitudinal-acoustic mode, and TA denotes the transverse-acoustic mode.

$N(E_F)$	α	ν	$\omega_{q\nu}$	$\lambda(\mathbf{q}\nu)$	$\lambda(\mathbf{q})$
2.52	$\frac{1}{3}$	LA	4.8	0.23	
		TA	1.7	0.31	0.85
	$\frac{1}{2}$	LA	6.9	0.16	
		TA	2.1	0.14	0.44
	$\frac{2}{3}$	LA	8.2	0.15	
		TA	2.4	0.09	0.33
	1	LA	7.0	0.23	
		TA	2.5	0.05	0.33

perimental values.

To study the pressure dependence of λ we concentrated on the phonons at the BZ boundary $\mathbf{q}_{max}=[00q_{max}]$ for both the β-Sn and sh phases. Our choice of $\mathbf{q}_{max}$ was governed by the role played by this distortion in the sh phase and by the q^2 weight in the spherical approximation of Eq. (2). These distortions are related to the structural transition into the hcp phase.[1,11] Table II contains the results of the calculation of the DOS[19] at E_F, the phonon frequencies $\lambda(\mathbf{q}\nu)$ and $\lambda(\mathbf{q})$ as a function of pressure. For both the β-Sn and sh phases, the frequencies increase with pressure except for the transverse acoustic mode. The DOS at E_F also decreases with pressure, showing no sign that it crosses a peak. Since the changes of the frequency and DOS for the β-Sn phase are small, significant variation of λ with pressure for this phase is not found within the calculation accuracy. For the sh phase, the longitudinal- and transverse-acoustic modes are found to have different behavior. The electron-phonon coupling gets weaker under compression for the longitudinal mode while the transverse-mode contribution increases. If we assume that in the pressure range considered here the longitudinal mode dominates the behavior of λ, it gives an overall decrease of $\lambda(\mathbf{q})$ consistent with the experimental decrease in T_c.

It should be noted here that the calculated pressures in Table II must be shifted by 1.5 GPa since the transition pressure[1,11] from β-Sn to sh is lower by this amount compared to the measured values.[5,6] Scaling the calculated $\lambda(\mathbf{q})$ for $\mathbf{q}_{max}$ at 12.7 GPa to fit the experimental data and using the McMillan equation, we get a pressure coefficient of $T_c \sim -400$ mK/GPa above 15.5 GPa which is close to the measured value of -520 mK/GPa. At higher pressure above 25 GPa, the transverse mode becomes softer and starts to increase $\lambda(\mathbf{q})$. Therefore, one can expect a further increase in T_c above this pressure and a high T_c near the transition into the hcp structure. Detailed calculations are in progress for these pressures, including the hcp phase.[4]

TABLE II. Calculated electron-phonon coupling $\lambda(\mathbf{q})$ at $\mathbf{q}=[00q_{max}]$ as a function of pressure for β-Sn and sh phases. LOA denotes the longitudinal-optic and -acoustic modes. Pressures are in gigapascals.

Pressure	$N(E_F)$	ν	$\omega_{q\nu}$	$\lambda(\mathbf{q}\nu)$	$\lambda(\mathbf{q})$
		β-Sn phase			
11.0	2.42	LOA	3.0	0.06	
		TA	2.6	0.04	
		TO	8.0	0.09	0.38
12.0	2.41	LOA	3.1	0.06	
		TA	2.6	0.04	
		TO	8.2	0.09	0.38
		sh phase			
14.0	2.51	LA	7.2	0.22	
		TA	2.4	0.05	0.32
18.0	2.49	LA	7.9	0.19	
		TA	2.4	0.06	0.31
21.0	2.48	LA	8.5	0.16	
		TA	2.4	0.06	0.28

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