Superconductivity and Phase Transitions in Compressed Si to 45 GPa

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A diamond-anvil cell is used to measure the pressure dependence of the superconducting transition temperature T_c in both primitive hexagonal and hexagonal-close-packed Si up to 45 GPa. The experimental results verify the prediction of superconductivity in hcp Si and the measured curve of T_c versus pressure is found to be in good qualitative agreement with theory, in contrast to a recent experiment by Lin *et al.* who claim complete disagreement with theory.

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Recently Chang *et al.*[1] (hereafter referred to as I) reported a first-principles calculation of the electron-phonon interaction parameter λ in primitive hexagonal (ph) Si and predicted that ph Si would be superconducting with a transition temperature T_c in the range of 5–10 K. In I the theoretical prediction of superconductivity and the decrease in T_c with pressure P for $P < 30$ GPa were verified experimentally up to 25 GPa with a Bridgman-type opposed-anvil device. Subsequent calculation of λ in Si at higher pressures predicted that T_c in ph Si would reach a minimum around 30 GPa, then rise sharply to over 10 K between 35 and 41 GPa, and finally ph Si would transform into a superconducting hexagonal-close-packed (hcp) phase around 41 GPa.[2] Shortly after these theoretical predictions, Lin *et al.*[3] (hereafter referred to as II) reported T_c for Si powder at pressures up to 43 GPa using a sintered-diamond-compact anvil device. Contrary to the theoretical predictions these authors observed no minimum in T_c as a function of pressure. Thus the results in II raised considerable doubt about the accuracy of the theoretical predictions. In addition, these results also differ significantly from those of I at pressures below 25 GPa; for example, the value for dT_c/dP reported in II is smaller by 1 order of magnitude.

To resolve these differences between theory and experiment and between experiments, we have developed a new technique for introducing copper wires into a diamond-anvil cell (DAC) which allows low-temperature four-probe electrical measurements at pressures exceeding 40 GPa. Starting with single-crystalline Si we have measured the pressure dependence of T_c in Si up to 45 GPa. In sharp contrast to the result of II, we find good qualitative agreement with theory[2] in that T_c reaches a minimum around 37 GPa and then increases sharply before the ph-to-hcp transition around 40 GPa. Furthermore we verify the prediction that hcp Si is superconducting. The measured value of T_c is 3.5 K for hcp Si and its pressure coefficient is very small and positive. However, the value of T_c before the ph-to-hcp transition is only 4.9 K and not above 10 K as predicted by theory. A more complete calculation of the pressure-dependent electron-phonon interaction at more high-symmetry points in the Brillouin zones of ph Si has now been performed and suggests that this remaining discrepancy between theory and experiment can be resolved.

Our experiments were performed with a DAC designed for use at pressures exceeding 40 GPa and at cryogenic temperatures.[4] The cell, containing a pair of beveled diamond anvils, is pressurized at room temperature with a hydraulic press and the pressure locked in with a retainer ring. This design allows the DAC to be small enough to be inserted into an optical Dewar. The cell is used in a gasketed configuration with the single-crystalline Si sample (doped with 3×10^4 cm^{-3} of phosphorus and approximately $25\times25\times75$ μm^3 in size) placed in a 200-μm hole drilled in the steel gasket. Fine copper wires electrically insulated from the gasket by compressed Al_2O_3 powder are pressed into contact with the Si sample. The arrangement of the wires relative to the sample is shown schematically in the upper inset of Fig. 1. A soft powder, such as plaster of Paris or steatite, surrounds the sample to provide a quasihydrostatic environment. Small chips of ruby are placed adjacent to the sample for pressure measurement. It is assumed that the pressure coefficient of the ruby R_1 fluorescence is 3.65 Å/GPa both at low temperatures and at room temperature.[5] The sample temperature is monitored by a calibrated Si diode in thermal contact with one of the diamond anvils. The sample resistance is determined by measurement of the ac voltage across the sample when excited by an ac current of 0.5 mA. The superconducting transition temperature is recorded both for increasing and decreasing temperatures. The rate of cooling or heating is kept low enough so that the cooling and warming curves show no hysteresis.

Figure 1 shows several resistance-versus-temperature curves of Si for pressures above 30 GPa. Because of pressure gradients across the sample, the drop in resistance (R) to the superconducting state always occurs over a small range of temperature (T). The width of this drop depends on pressure (P) and this dependence is

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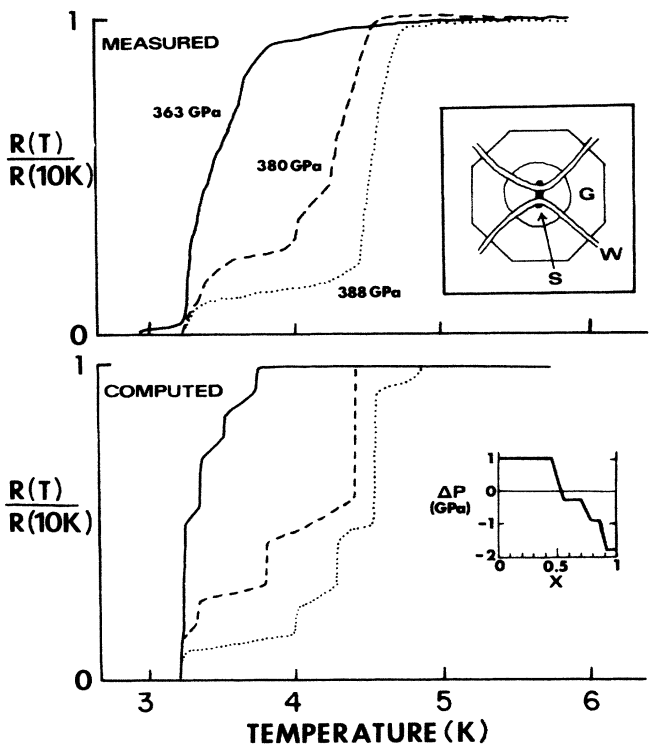

FIG. 1. Comparison between the experimental and computed $R(T)$ curves for Si at several pressures. The computed curves are based on the pressure distribution shown in the lower inset, where x is the fractional length along the sample, and the $T_c(P)$ curve shown in Fig. 2(a) with solid circles. The upper inset shows a schematic arrangement of the copper wires (W) relative to the Si sample (S). G is the steel gasket.

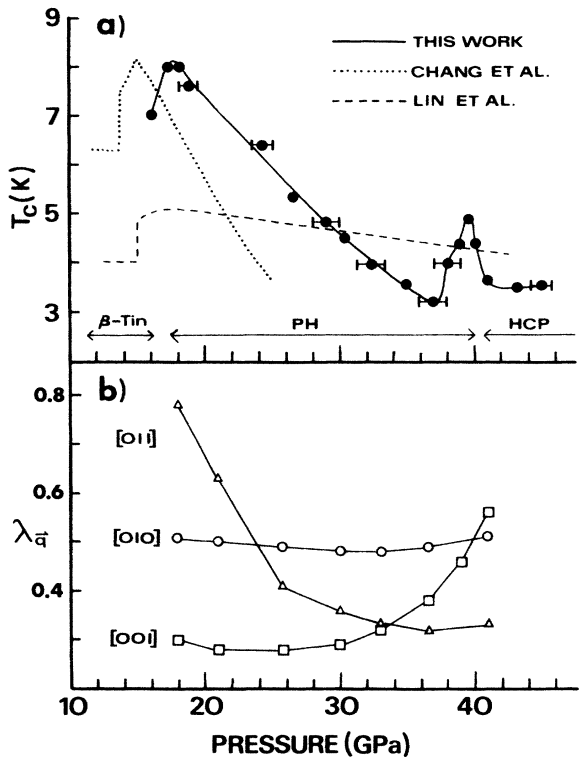

FIG. 2. (a) Pressure dependence T_c in Si determined by three different groups with use of three different types of pressure cells. The horizontal bars indicate the spread in pressure over the sample determined from ruby chips around the sample. Arrows show crystal-structure transition pressures measured by x-ray diffraction (Ref. 6). (b) The pressure dependence of λ computed for phonons propagating along three high-symmetry directions.

related to changes in dT_c/dP with pressure rather than to changes in the pressure inhomogeneity.

We have developed the following method to extract T_c from the experimental R-vs-T curves in a consistent and systematic way. First we utilize the fact that, from I, T_c varies almost linearly with P between 20 and 25 GPa. This knowledge enables us to deduce from the $R(T)$ curves at moderate pressures a pressure distribution function $\Delta P(x)$, where x represents the fractional length of the sample with a given pressure deviation ΔP from the mean pressure. This is shown in the lower inset of Fig. 1. Typically we find that about 40% of the sample is isobaric. This pressure distribution is assumed to remain unchanged for higher pressures. (By using ruby chips scattered throughout the cell and measuring the shift in fluorescence at cryogenic temperatures, we can independently estimate the pressure distribution over the sample and have found it to remain largely unchanged with pressure.) The $T_c(P)$ curve above 25 GPa is then obtained by the fitting of the experimental $R(T)$ curves and is shown in Fig. 2(a) as the solid circles.

In Fig. 1 some of the computed $R(T)$ curves based on this $T_c(P)$ curve and the $\Delta P(x)$ distribution are compared with the measured curves. The agreement between the computed curves and the measured curves is fairly good and supports the validity of this procedure. The horizontal bars in Fig. 2(a) represent the spread in pressures over the sample determined from ruby chips around the sample and show that this spread does not change significantly with pressure. On releasing the pressure we found good reproducibility and almost no hysteresis in $T_c(P)$ for $P > 18$ GPa.

In Fig. 2(a) we compare our T_c-vs-P results with those of I and II. Our results for $T_c(P)$ for $P < 30$ GPa are in good agreement with the results of I and in disagreement with the results of II. The difference in pressure of about 3 GPa between our results (shown as the solid curve) and those of I (shown as the dotted curve) in Fig. 2(a) can be attributed to the different methods of determining the pressure.[7] In the region $P > 30$ GPa we found that T_c reached a well-defined minimum of 3.3 K at 37 GPa, in good agreement with theoretical predic-

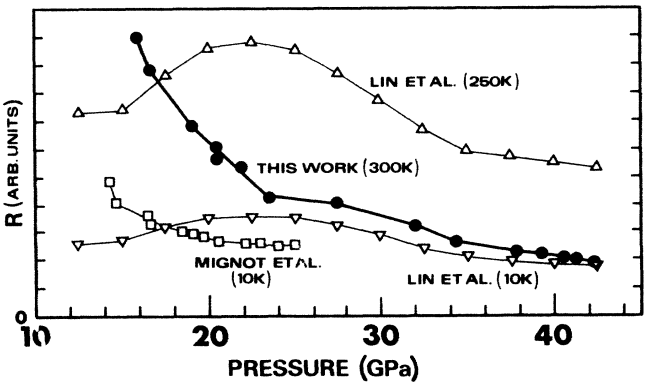

FIG. 3. Normal-state resistance of Si vs pressure measured by three different groups for low and high temperatures. Independently arbitrary units of resistance were used, except that the same unit was used for the 250 and 10 K curves of Lin *et al.*

tions, but not with the results of Lin *et al.*[3] (shown as a dashed curve) who did not observe any minimum value in T_c up to 43 GPa.

In Fig. 3 we show the curve of normal-state resistance versus P for Si that we obtained at room temperature and those reported by II at 250 and 10 K. For comparison we also show the curve at low temperature obtained by Mignot, Chouteau, and Martinez[8] using a Bridgman-type opposed-anvil device. Again we find that our results are quite similar to those reported by Mignot, Chouteau, and Martinez (same group as I) but completely different from those obtained by Lin *et al.* Since our results both for T_c and normal-state R seem to agree much better with those of I and Mignot, Chouteau, and Martinez than with II, one may be tempted to explain the differences in terms of the crystal quality, namely single crystals used in the present experiment and by Mignot, Chouteau, and Martinez versus the crystalline-powder sample used by Lin *et al.* However, at high pressures and after two solid-to-solid phase transitions one may expect crystalline samples to become polycrystalline and not that different from the compressed powder of II. Thus further work is required to resolve the differences between the experimental results for Si.

Although our measured pressure dependence of T_c is in good agreement with the theoretical predictions in general, there remain differences between experiment and theory. In particular the theory predicted that T_c would increase sharply to over 10 K between 35 and 41 GPa, while the measured T_c increased to only 4.9 K. It was recognized in the earlier calculation of $\lambda(P)$ that the use of just the [001] direction for obtaining the average λ is a shortcoming of the calculation. In this paper we report new calculations for λ in other high-symmetry directions.[9] As shown in Fig. 2(b), the electron-phonon interaction for $\mathbf{q}\|[011]$ behaves differently from that for $\mathbf{q}\|[001]$. A large enhancement of λ for $\mathbf{q}\|[011]$ in the region of low pressure results from the soft TA mode in the ph phase. This phonon mode is associated with the ph to β-Sn phase transition[10,11] and its frequency goes to zero at the corresponding transition. So a spherical approximation based only on λ for phonons with $\mathbf{q}\|[001]$ underestimates the value of λ at P below 35 GPa and overestimates it above 35 GPa. In contrast, the electron-phonon interaction for $\mathbf{q}\|[010]$ varies little with pressure and has a minimum at P around 33 GPa.

The role of soft phonon modes in enhancing T_c can be explored by examination of the volume (V) dependence of λ. From the expression for[9,12] λ, the volume dependence of λ can be expressed as

$$\frac{d(\ln\lambda)}{d(\ln V)} = \frac{d(\ln N(E_F))}{d(\ln V)} + \frac{d(\ln\langle\langle M^2\rangle\rangle)}{d(\ln V)} - 2\frac{d(\ln\omega)}{d(\ln V)}, \quad (1)$$

where $N(E_F)$ is the electronic density of states at the Fermi energy. The square of the electron-phonon matrix element $\langle\langle M^2\rangle\rangle$ is averaged over the Fermi surface and ω is the phonon frequency. For $P < 30$ GPa in ph Si we estimated that the terms on the right-hand side of Eq. (1) are approximately 0.34, -2, and 5, respectively. This shows that the volume dependence of λ is dominated by the volume dependence of the phonon frequency. Thus in general one expects λ to be enhanced when the phonon becomes soft. We suppose that this is responsible for the high T_c in ph Si near the structural transitions from the β-Sn phase. For the ph-to-hcp transition, we find that the matrix-element term in Eq. (1) also makes a significant contribution to the enhancement of T_c.

Above 40 GPa the measured T_c drops quickly down to 3.5 K, and for even higher pressures T_c increases only slightly. This drop occurs exactly at the pressure where the x-ray diffraction measurement of Olijnyk, Sikka, and Holzapfel[6] found the transition to the hcp phase to occur. Hence we have attributed the sudden drop in T_c at 40 GPa to a transition to a superconducting hcp phase, and in this phase T_c has a very small positive pressure coefficient of $dT/dP = 0.03$ K/GPa.

An additional phase transition into a new and unidentified intermediate phase has been observed by Olijnyk, Sikka, and Holzapfel[6] in Si between 36 and 40 GPa and has been labeled by these authors as Si VI. However, this claim has been disputed by Spain and Hu.[13] The x-ray diffraction pattern attributed to Si VI is consistent with a double-hexagonal-close-packed (dhcp) crystal structure,[14] but our total-energy calculation for dhcp Si gives this phase as metastable with respect to the hcp phase with an energy difference of 0.03 eV. If further x-ray diffraction studies confirm the existence of an intermediate phase, Si VI, then our experimental results

indicate that this phase is also superconducting with a large positive pressure coefficient for T_c.

In conclusion, we have developed a DAC capable of performing electrical measurements at cryogenic temperatures up to 45 GPa and have used this cell to measure the pressure dependence of T_c in Si. We find good agreement with the experimental results reported by Chang *et al.*[1] and Mignot, Chouteau, and Matinez[8] for $P < 30$ GPa and disagreement with the results of Lin *et al.*[3] over the entire range of measurement. In general our results are in good agreement with theoretical predictions and suggest that first-principles electron-phonon calculations are now precise enough to predict superconducting properties such as transition temperatures.

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