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SUPERCONDUCTIVITY, SOFT MODES, AND PHASE TRANSITIONS

IN COMPRESSED Si TO 45 GPa

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ABSTRACT

A diamond anvil cell is used to measure the pressure dependence of the superconducting transition temperatures T_c in both primitive hexagonal and hexagonal close-packed (HCP) Si up to 45 GPa. The experimental results verify the prediction of superconductivity in HCP Si and the measured T_c versus pressure curve is found to be in good qualitative agreement with theory. A study of the role of soft phonon modes in enhancing T_c near structural phase transitions is presented along with calculations of the electron-phonon interactions.

Recently there has been considerable interest in the
superconducting properties of Si under pressure. Chang et al.[1]
(hereafter referred to as I) reported a first principle
calculation of the electron-phonon interaction parameter λ in
primitive hexagonal (PH) Si and predicted that PH Si is
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 using a Bridgeman-type opposed-anvil
device. Subsequent calculation of λ in Si at higher pressures
predicted that T_c in PH Si will reach a minimum around 30
GPa, then rise sharply to over 10 K between 35 - 41 GPa and
finally transform into a superconducting hexagonal close-packed
(HCP) phase around 41 GPa.[2] The reason proposed for this unusual
dependence of T_c on P was that before the PH to HCP transition
the transverse acoustic (TA) phonon in the [001] direction of the
Brillouin zone became soft and made a large contribution to the
electron-phonon interaction.

After the theoretical predictions several groups tried to
extend the T_c measurements in Si to higher pressures. Lin et
al.[3] recently reported T_c in 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. However their results also differ
significantly from those of I at pressures below 25 GPa; for
example their value of (dT_c/dP) is smaller by one order of
magnitude. To resolve these differences between theory and
experiment and between experiments, we have developed a new

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technique for introducing copper wires into a diamond anvil cell (DAC) so that we can make low temperature four-probe electrical measurements at pressures exceeding 40 GPa. Using this technique we have measured the pressure dependence of T_c in _single crystalline_ Si for the first time at pressures[2] up to 45 GPa. We find good qualitative agreement with theory in that T_c reaches a minimum around 37 GPa and then increases sharply to 4.9 K before the PH to HCP transition around 40 GPa. This supports the suggestion that, before the structural phase transition, a soft phonon mode with a strong coupling to the electrons causes the increase in T_c. Furthermore we verify the predictions that HCP Si is superconducting and that T_c has a very small pressure coefficient in this phase. The measured value of T_c is 3.5 K for HCP Si. However the value of T_c before the PH to HCP transition is not above 10 K as predicted by theory. This discrepancy between theory and experiment has been resolved by a more complete calculation of the pressure-dependent electron-phonon interaction in PH Si.

Our experiments were performed with a DAC designed for use at cryogenic temperatures.[4] The cell is pressurized at room temperature with a hydraulic press and the pressure locked in with a retainer ring. This DAC allows pressures > 40 GPa to be achieved in a volume small enough to be inserted into an optical dewar, and the discovery of superconductivity in HCP Si presented here demonstrates the usefulness of DAC's in transport measurements at low temperatures and high pressures. The cell is used in a gasketed configuration with the single crystalline Si sample (doped with 3×10^{14} cm^{-3} of phosphorus and approximately

$25 \times 25 \times 75$ μm^3 in size) placed in a 250 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 (Plaster of Paris) surrounds the sample to provide a quasi-hydrostatic 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 A/GPa both at low temperatures and at room temperature. 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 measuring the ac voltage across the sample when excited by an ac current of 0.5 mA. The superconducting transition is always recorded both for increasing and decreasing temperatures. The rate of cooling or heating is kept low enough such 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. The width of this drop depends on pressure and this variation is related to changes in dT_c/dP with pressure rather than to changes in the pressure inhomogeneity.

To extract $T_c(P)$ from the experimental R versus T curves in a consistent and systematic way, we have developed the following

method. First we utilize the fact that, from I, T_c varies almost linearly with P between 20 to 25 GPa. This knowledge enables us to deduce from the R versus T curves at low 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 with pressure. The $T_c(P)$ curve above 25 GPa is then obtained by fitting the experimental R versus T curves. For each curve the mean pressure is determined from the fluorescence of ruby chips around the sample measured while at cryogenic temperature. (This happens to be nearly equal to the pressure of the ruby chip closest to the center of the sample.) The $T_c(P)$ curve obtained in this way is shown in Fig. 2 as the solid circles.

In Fig. 1 some of the computed R versus T curves based on this T_c vs P curve and the $\Delta P(x)$ distribution shown in the inset are compared with the measured curves in Fig. 1. The agreement between the computed curves and the measured curves is fairly good and supports the validity of this procedure. The error bars in Fig. 2 represents the spread in pressure inside the cell as determined from ruby chips around the sample. The fact that this spread remains more or less independent of pressure is consistent with our assumption that the pressure distribution over the sample remains unchanged as the pressure is increased. On releasing the pressure we found good reproducibility in the P dependence of T_c as long as P is above 15 GPa.

Our results for the pressure dependence of T_c for P less than 30 GPa are in good agreement with the results of I and in disagreement with the result of Lin et al.[3] 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 can be attributed to the different methods in determining the pressure.[6] In the P > 30 GPa region we found that T_c reached a well-defined minimum of 3.3 K at 37 GPa in good agreement with earlier theoretical work. However, while this theory predicted that T_c would increase sharply between 35 and 41 GPa, 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. This appears to be the origin of the difference between theory and experiment. In this paper we report new calculations for λ in other high symmetry directions.[7] As shown in Fig. 2, the electron-phonon interaction for q∥[011] behaves differently compared to q∥[001]. A large enhancement of λ for 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[8,9] and its frequency goes to zero at the corresponding transition. So the spherical approximation based on λ for phonons with 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 q∥[010] varies little and has a minimum at P around 33 GPa. The weighted average of these three different contributions to λ reaches a minimum at 33 GPa in agreement with experiment to

within 10 % except for the region close to the β-Sn to the PH phase transition. Close to this phase transition we find that, as in the case of the PH to HCP transition, the electron-phonon interaction is strongly influenced by the soft mode. This point will be elaborated further below. Here we point out that the "measured" electron-phonon coupling constants are derived from the measured T_c using the McMillan equation[10] with the longitudinal acoustic phonon frequency for q∥[001] as a cutoff in the phonon spectrum and assuming a Coulomb interaction μ^* of 0.08.[11] The calculated T_c's are compared with the measured values in Fig.2 and the agreement is reasonably good.

The role of soft phonon modes in enhancing T_c can be explained by examining the volume (V) dependence of λ. From the expression[7,12] for λ, the volume dependence of λ can be expressed as:

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

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 may expect λ to be enhanced when the phonon becomes soft. We find that this is responsible for the high T_c in PH Si near the structural transitions into both the β-Sn and the HCP phases. Although in case of the PH to the 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 et al.[13] have found the transition to the HCP phase occurs. 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 $dT_c/dP = 0.03$ K/GPa.

An additional phase transition into a new and unidentified intermediate phase has been observed by Olijnyk et al.[13] in Si between 36 and 40 GPa and has been labelled by these authors as Si VI. However, this claim has been disputed by Spain and coworker.[14] If we assume that a transition exists, the x-ray diffraction pattern attributed to Si VI can be explained quite satisfactorily by a double hexagonal (DH) crystal structure.[15] A total energy calculation performed for DH Si shows that the DH phase is 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 intermediate phase is also superconducting and that T_c has a large positive coefficient in this phase.

In conclusion we have developed a DAC capable of performing electrical measurements at cryogenic temperatures up to 45 GPa and we have used this cell to measure the pressure dependence of T_c in Si. We find good agreement between experiment and present

a more complete theoretical calculation of the electron-phonon coupling constant in PH Si. We demonstrate that by studying the pressure dependence of T_c it is possible to explore the role of soft phonon modes in enhancing superconducting transition temperatures. Since compressed Si behaves like a typical BCS superconductor, we expect the relationship between soft phonon modes, structural phase transitions and superconductivity discussed here to be applicable to other systems.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Fig. 1   Comparison between the experimental and computed R

versus temperature curves for Si   at   several

pressures. The computed curves are based on the

the pressure distribution shown in the lower inset,

where X is the fractional length along the sample, and

the T_c vs P curve shown in Fig. 2.   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   Pressure dependence of (a) T_c, (b) averaged λ and

(c) contributions to λ from phonons propagating along

three directions.   In (a), the solid circles represent

experimental points and the open circles theoretical

points.   In (a), (b) and (c) the curves have been drawn

as a guide to the eyes with the broken lines representing

the theoretical values and the solid curves experimental

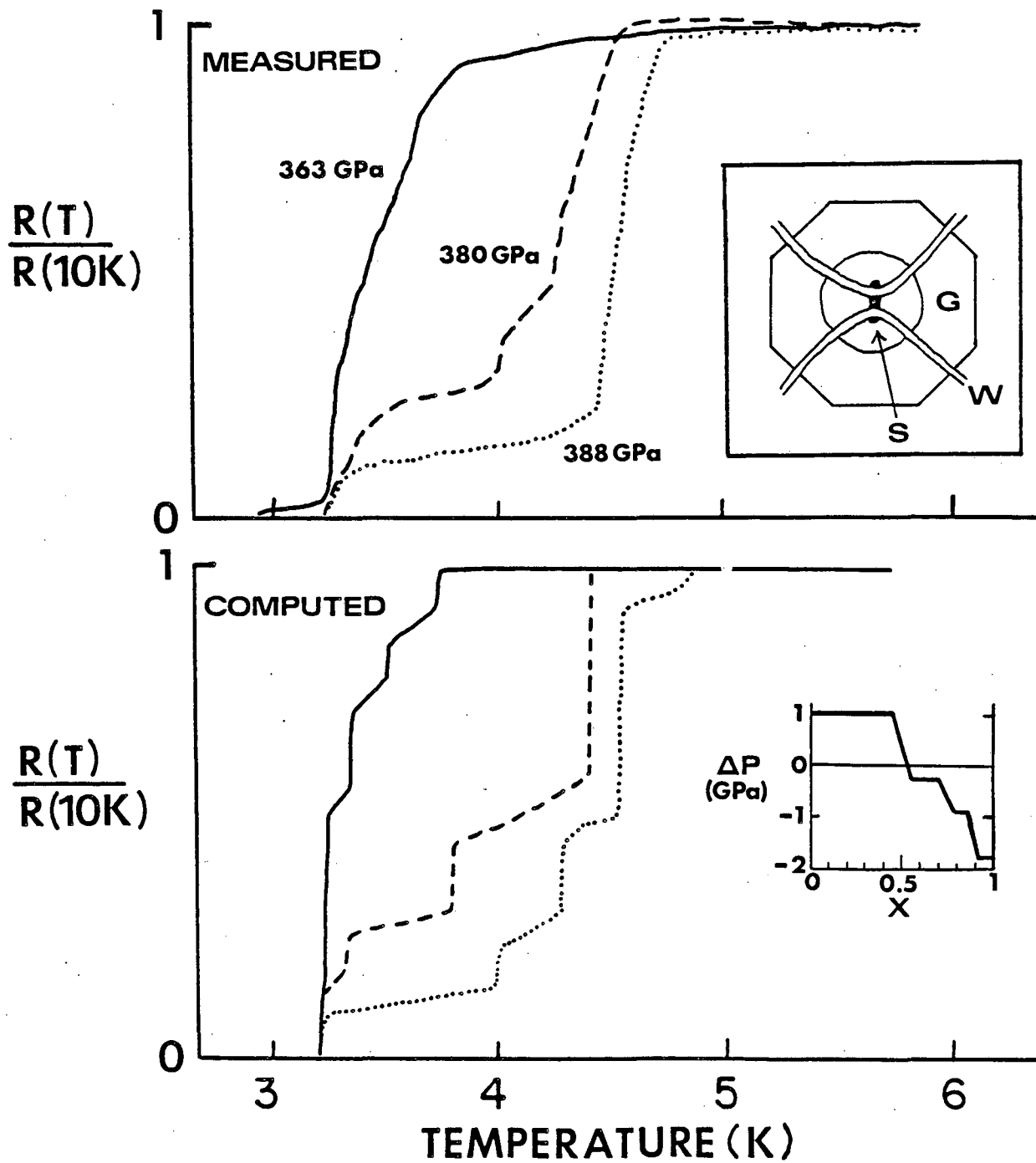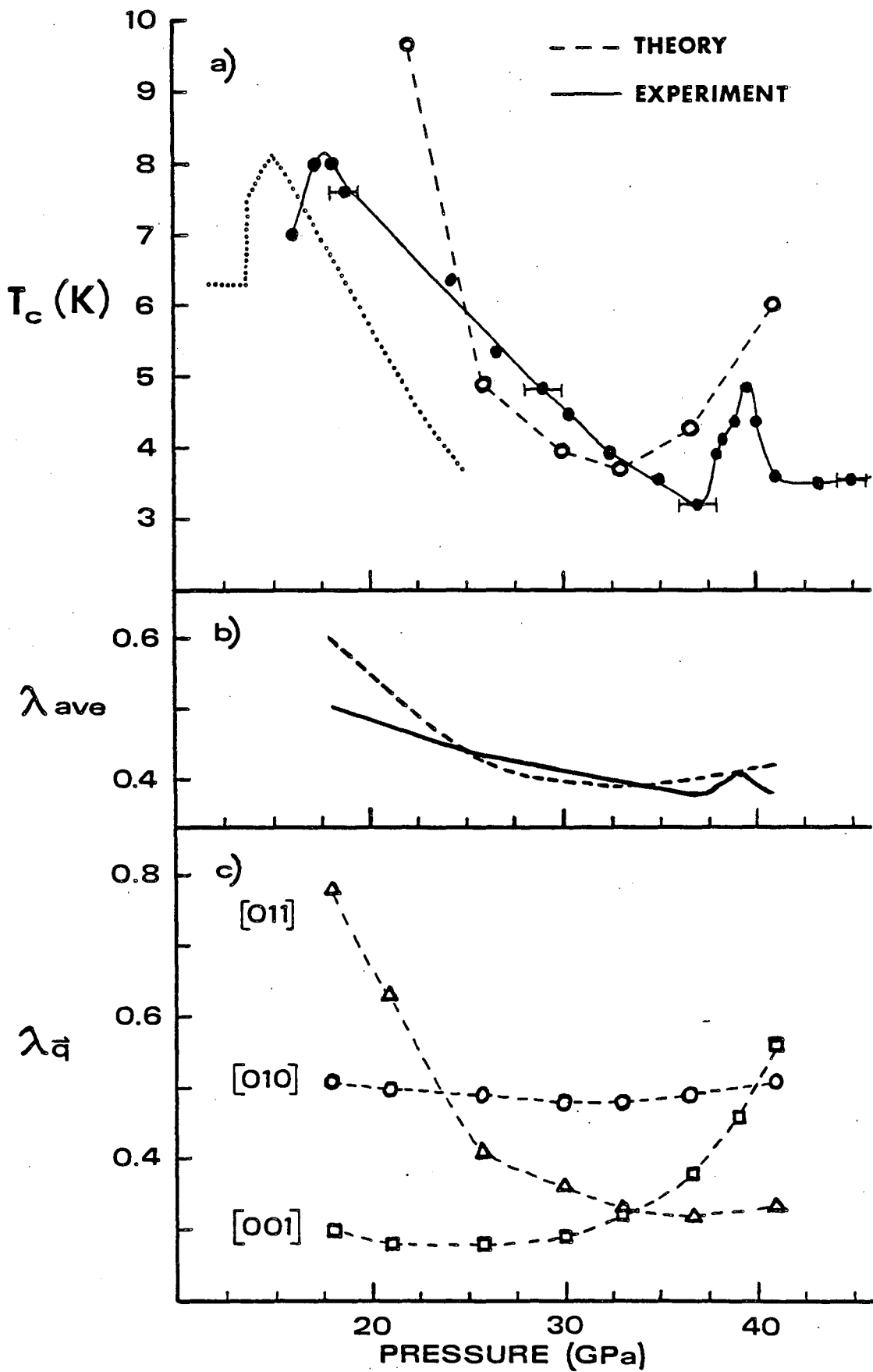values.   The dotted curve is the result of I.

FIG. 1

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FIG. 2

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