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Superconducting high pressure $CaSi_2$ phase with T_c up to 14 K

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We have studied the occurrence of superconductivity under pressure in the $CaSi_2$ family of compounds, namely the semimetallic trigonal phase and the α-$ThSi_2$-type tetragonal one. Although only the latter is superconducting ($T_c = 1.56$ K) at ambient pressure, starting from the trigonal phase and applying high pressure (>12 GPa) we have found a new superconducting phase with $T_c^{\text{onset}} \sim 14$ K, among the highest ever found in silicon based materials.

Silicon and Si-based compounds are in general extensively studied as they are at the base of electronics and microdevices. Although intriguing and of practical interest, the appearance of superconductivity in these materials has not been so exhaustively explored. Yet the different bonding possibilities of silicon give rise to slightly different structural phases that can differ very much in their physical behavior. In 1985, the sp^2 simple hexagonal phase of pure Si was predicted and then found to be superconducting with transition temperature $T_c = 8.2$ K under high pressure (15 GPa) by Chang and co-workers.[1] Similarly to C_{60} fullerenes, the Si_{20} fullerenes can be doped by alkali-metal atoms, when linked together through their dangling sp^3 bonds to form the structure of the clathrate $(Na, Ba)_xSi_{46}$, a superconductor with $T_c = 4$ K.[2] Some silicides ($NbSi_2$, $TaSi_2$) are also known to be superconductors[3] with typical T_c's of the order of 1 K, with the exception of the A-15 compounds, such as V_3Si ($T_c = 17$ K), where the linear chain bands of vanadium are at the origin of superconductivity.[4] More recently, the high-pressure $EuGe_2$-type phase [Fig. 1(c), named as $h1$ in the following] of $BaSi_2$, built by planes of boat-formed sp^3 silicon hexagons held together by hexagonal planes of calcium atoms, was found to be superconducting with $T_c^{\text{onset}} = 6$ K.[5] Pressure can indeed be a very useful variable allowing a gradual change of the lattice parameter of a particular silicide and forcing it to change to new configurations more favorable for superconductivity. As shown by the experiments on elementary silicon, *in situ* measurements using pressures in the range of 10 GPa may be adequate to scan a succession of interesting phases. Plausible candidates are large volume per unit formula silicides such as $CaSi_2$. At ambient pressure $CaSi_2$ has a trigonal structure [also labeled TR6 in the following][6] [Fig. 1(a)]. In this form it is a semimetal[7] with an electrical resistivity that follows the conventional Bloch-Grüneisen temperature dependence and it is not superconducting down to 30 mK.[8] A high-pressure phase[9] with α-$ThSi_2$ type tetragonal structure [Fig. 1(c)] formed by interconnected sp^2 silicon atoms that rotate alternatively in the c-axis direction has been found to be superconducting with $T_c = 1.58$ K.[10] In this report we describe the effects of high pressures ($\leqslant 22$ GPa) on the behavior of the resistivity of these two $CaSi_2$ phases. We show that under pressure this system undergoes a series of phase transitions which finally develop superconductivity with one of the highest transition temperatures known for a silicon based compound, i.e., $T_c = 14$ K.

The electrical resistivity measurements were performed in a sintered diamond Bridgman anvil apparatus using a pyrophyllite gasket and two steatite disks as the pressure me-

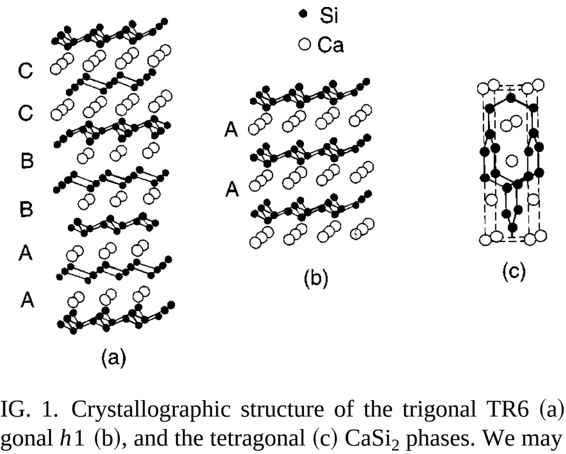

FIG. 1. Crystallographic structure of the trigonal TR6 (a), the hexagonal $h1$ (b), and the tetragonal (c) $CaSi_2$ phases. We may note in the trigonal TR6 phase the silicon sp^3 planes are separated by Ca planes in an *AABBCC* stacking sequence (a), while in the hexagonal $h1$ phase they stack in a simple *AA* sequence (b). Notice also the interconnected sp^2 silicon lattice in the tetragonal phase (c).

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dium. The Cu-Be device that locked the anvils can be cycled between 1.2 and 300 K in a sealed dewar. Pressure was calibrated against the various phase transitions of Bi under pressure at room temperature and by a superconducting Pb manometer at low temperature. The overall uncertainty in the quasihydrostatic pressure is estimated to be $\pm 15\%$. The pressure spread across the sintered diamond anvils was previously determined on Pb manometers to be of about 1.5–2 GPa depending on the applied pressure. The temperature was determined using a calibrated carbon-glass thermometer with a maximum uncertainty (due mainly to temperature gradients across the Cu-Be clamp) of 0.5 K. Four-probe electrical resistivity ac measurements were made using a Stanford Research 830 digital lock-in amplifier and by using platinum wires to make contact on the sample. dc measurements, used mainly to determine current/voltage characteristics, were also carried out using a Keithley 182 nanovoltmeter combined with a Keithley 238 current source.

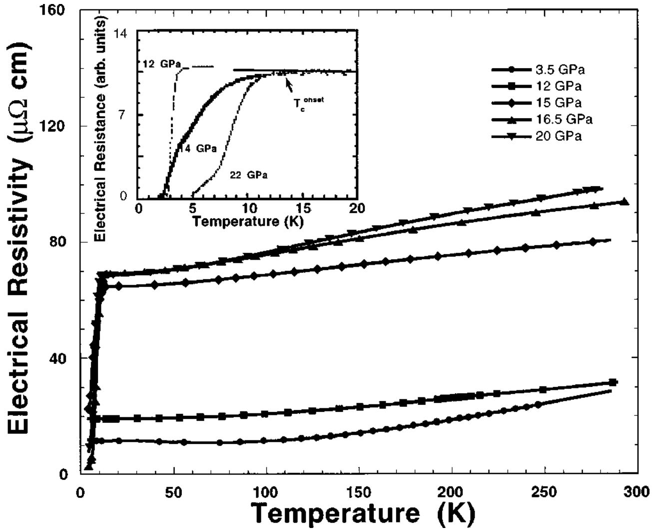

FIG. 2. Electrical resistivity of the starting trigonal $CaSi_2$ under pressure (sample A). We see the large increase of resistivity above 15 GPa where superconductivity is observed. Inset: superconductive transitions measured in sample C.

Polycrystalline trigonal-$CaSi_2$ samples were prepared by melting high-purity Ca and Si in stoichiometric proportions in a tantalum crucible closed by arc welding under inert gas atmosphere. Samples were annealed for 7 days at 900 °C in order to obtain a homogeneous single phase intermetallic compound. X-ray diffraction and micrographic analysis were used to check the sample obtained. By this procedure it was found that the samples were pure phase of trigonal structure (space group D_{3d}^5-$R\bar{3}m$) with lattice parameters $a = 10.4$ Å and $\alpha = 21°30'$. To obtain the tetragonal $CaSi_2$ phase we followed the procedure described by Evers:[9] starting from the trigonal TR6 compound, a treatment at 800 °C and 8 GPa using a belt-type apparatus was applied. After this treatment $CaSi_2$ transforms into the tetragonal phase (the α-$ThSi_2$-type structure, space group $D_{4h}^{19}I4_1/amd$). ac susceptibility measurements performed on this sample showed a sharp superconducting transition at 1.51 K, in agreement with what was previously reported.[10] Samples were then cut and polished down to the size necessary for measurements under pressure, namely $0.05 \times 0.05 \times 0.3\,\mathrm{mm}^3$.

The temperature dependence of the resistivity (ρ vs T) was measured on three $CaSi_2$ samples (named A, B, and C in the following) of the starting trigonal TR6 phase. The ρ-vs-T behavior, in particularly superconductivity, was reproducibly found in the three experiments. Figure 2 shows the electrical resistivity ρ curves of the starting trigonal TR6 phase (sample A) as a function of temperature T for different applied pressures. The parameters of the conventional Bloch-Grüneisen behavior measured at ambient pressure[8] are modified even for the smallest applied pressure. Analysis of the ρ-vs-T data shows that the Debye temperature, which is 456 K at ambient pressure,[8] decreases to about 300 K for $P > 12\,\mathrm{GPa}$.

By applying a pressure between 10 to 14 GPa, depending on the sample, the room-temperature resistivity abruptly increases as shown in Fig. 2. In this range of pressure a superconducting transition with an onset of T_c around 3–4 K was detectable on samples B and C for which measurements down to 1.2 K were performed. Above ~14 GPa, higher superconducting transitions were measured. On the three measured samples the onset of T_c—determined as shown in the inset of Fig. 2—steeply increases, reaching 14 K for $P = 15\,\mathrm{GPa}$, then slightly decreases for increasing applied pressure. $T_c \sim 14\,\mathrm{K}$ is the highest superconducting transition temperature reported so far for a disilicide, almost one order of magnitude higher than those found in other silicides, and comparable to the T_c's of the A-15 compounds. It is worth reminding that elementary Si and Ca exhibit superconductivity with T_c's of 8.2 K at 15 GPa (Ref. 1) and ~2 K at 85 GPa (Ca is not superconducting at lower pressure),[11] respectively. The width of the superconducting transition was in general broad, yet zero resistance was always attained. On the other hand, V-I characteristics were measured at 4 K and critical currents in the range of 1000–10000 A/cm^2 have been estimated, indicating the bulk nature of superconductivity in our samples. In sample C and for $P > 12\,\mathrm{GPa}$, we observe a two-step transition which evidences the presence of two superconducting phases (inset Fig. 2). It is worth reminding that the resistivity of $CaSi_2$ is essentially temperature independent below ~30 K at ambient pressure being dominated by the residual value,[7] and that such a broad superconducting transition is likely to be due both to inhomogeneity of the sample and to an inevitable gradient of pressure, rather than to thermal fluctuations. In the case of resistive measurements under high pressure, the onset of T_c is generally considered to be due to the portion of the sample at the optimum accessible pressure for superconductivity and hence to be a genuine indicator of the sample's superconductivity. The dependence of the superconducting transition T_c on applied pressure is reported in Fig. 4 for all samples. The differences in the apparent transition pressures for different samples are due to a slow transformation kinetics, that made results sensible to the time (not the same for the different experiments) that the samples spent at each pressure.

The abrupt appearance of superconductivity at $P = 10\,\mathrm{GPa}$ suggests that a structural phase transition is taking place at this pressure. If we extrapolate the line boundary of the phase diagram reported by Evers[9] we may guess that the phase transition between the starting trigonal phase to the metastable, high-pressure, tetragonal phase may occur in this range of pressure at room temperature. We then measured

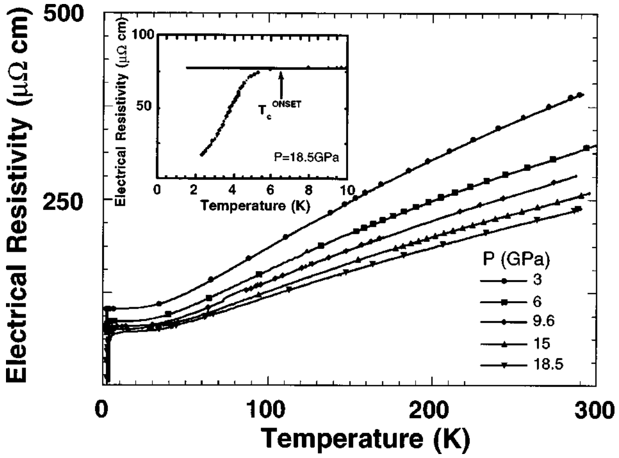

FIG. 3. Electrical resistivity of the starting tetragonal $CaSi_2$ under pressure. The resistivity monotonically decreases with pressure. Inset: superconducting transition at low temperature.

the resistivity at low temperature of two samples of the tetragonal phase under pressure, in order to check whether the 14 K superconductivity could be ascribed to it. Both tetragonal samples exhibit a metallic behavior of the resistivity with a well pronounced downwards curvature of the ρ-vs-T dependence. The onset of the superconducting transition increases from 1.51 K at ambient pressure up to 6.5 K for $P=9$ GPa. For increasing applied pressure, the T_c^{onset} slightly decreases and the resistive transition seldom attains a vanishing value, suggesting that only a small fraction of the sample actually contributes to superconductivity in this case. We reckon that the T_c's of the trigonal samples for pressures between 10 and 12 GPa are 30 to 50% lower than those measured on the tetragonal samples (see Fig. 3). Furthermore, above ∼12–14 GPa depending on the sample, the observed T_c's are sharply different (see Fig. 4) and the behavior observed on C clearly shows the coexistence of two superconducting phases. This leads us to conclude that the structural changes induced on the starting trigonal $CaSi_2$ phase by the applied pressure go beyond a simple transformation onto the tetragonal phase.

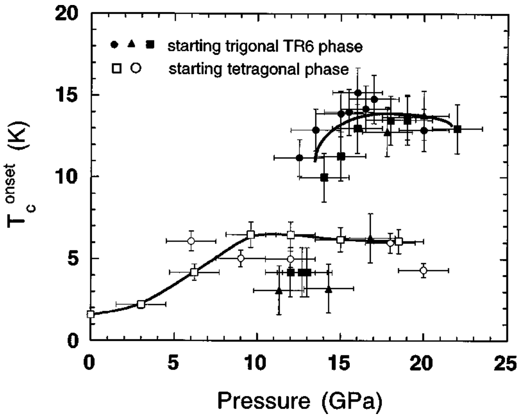

FIG. 4. Pressure dependence of the superconducting transition temperature T_c, for three samples of the trigonal phase (filled symbols) and two samples of the tetragonal $CaSi_2$ phase (empty symbols). The horizontal error bars represent the error in the estimation of the pressure and the pressure gradient. The vertical error bars correspond to the T_c determination.

In order to try to identify this putative new phase, we performed a separate experiment, in which all the volume of the diamond cell was occupied by a sample of the trigonal $CaSi_2$ phase that was then compressed at 16 GPa for 6 days at room temperature and subsequently quenched back to ambient pressure. The main peaks of the x-ray diffraction pattern of the recovered sample were indexed as the hexagonal $h1$ ($EuGe_2$-type) structure [Fig. 1(b)]. This quenched sample was not superconducting down to 4.2 K. From these data we can speculate that starting with a nonsuperconducting trigonal TR6 sample, pressure first induces a transition to a superconducting phase ($2\,\mathrm{K}<T_c<4\,\mathrm{K}$), that may not necessarily be the tetragonal α-$ThSi_2$ phase, as the latter shows a higher T_c in this pressure range ($5\,\mathrm{K}<T_c<6.5\,\mathrm{K}$). At higher pressures a new superconducting ($10\,\mathrm{K}<T_c<15\,\mathrm{K}$) phase seems to be stabilized. Interestingly, as pressure is released, the sample does not go back to the trigonal TR6 structure, but to the $h1$ structure, i.e., the starting *AABBCC* stacking sequence is changed to the simpler *AA* one. We note that the structure that is stable for low volume per unit-cell disilicides, i.e., those formed by the rare-earth metals with smallest ionic radius (Lu, Tm, Er, and Yb),[12] is the AlB_2-type crystal lattice. That is similar to the $h1$ structure but with hexagonal sp^2 (graphitelike) planes instead of sp^3 (diamondlike) planes. This suggests that the high-pressure $CaSi_2$ phase could be the AlB_2-type small-volume-per-unit-formula structure, and explains the recovery of the $h1$ on pressure quenching. Preliminary structural measurements under pressure performed at the European Synchrotron Radiation Facility have actually confirmed that the high-pressure phase observed above 15 GPa has the AlB_2 structure.[13]

Fahy and Hamann[7] found that the stacking sequence of the Si and Ca layers mainly influences the electronlike bands at the Fermi level of $CaSi_2$. One may then expect an enhancement of the density of electronic states (DOS) at the Fermi level changing from the sp^3 to the sp^2 Si bonds in analogy to what Chang and Cohen proposed for the hexagonal superconducting phase of Si.[1] The case of $CaSi_2$ seems, however, to be more complicated since band-structure calculations and photoemission studies on trigonal $CaSi_2$ (Ref. 14) have shown that all the Ca s-p-d states are involved in the Ca-Si bond and, in particular, d states of Ca are present at the Fermi level, despite the fact that free Ca has no d electrons. Furthermore, in general, a peak of the density of metal nonbonding d states was found to move from above the Fermi level for $CaSi_2$ to below E_F as one moves towards heavier d metals in disilicides.[15] It turns out that the DOS of TR6 $CaSi_2$ is rather low and this feature also seems to be maintained for the tetragonal $CaSi_2$ phase, for which the Fermi level was found to be just below a peak of the density of electronic Ca d states.[16] The electronic band calculations for the TR6 and $h1$ structures do not present a peak of the DOS at E_F, which may account for the $T_c \sim 14\,\mathrm{K}$.[7]

There is a further important factor that may favor a high T_c in the high-pressure phase: soft modes of phonons arising from the proximity of several metastable phases associated with the modification of sp^3 bonds into sp^2 bonds. Indeed, the case of $CaSi_2$ is an example in which several slightly different atomic orders may be achieved with little cost of energy. From an electronic point of view, Fahy and

Hamann[7] found that the total energies of the TR6 and $h1$ phases are all within $\sim$0.01 eV, suggesting that transformation between different structures can easily occur as it was also largely discussed by Evers[9] from a thermodynamic point of view. Moreover, we have found a drastic decrease of the Debye temperature (from $\Theta_D = 456\,\mathrm{K}$ at ambient pressure to about 300 K for $P > 10\,\mathrm{GPa}$). Although this determination can be affected by sample inhomogeneity, it is suggestive that soft phonon modes can appear when high pressure is applied. As concerns the Si atoms and their bonding, the main difference among these structures is the sp^3 bond which holds the tetrahedrally coordinated Si in the TR6 and $h1$ structures, while an sp^2 bond can be expected in the α-$ThSi_2$-type tetragonal or the AlB_2-type structure. We remind that the charge conduction is ensured by Ca orbitals that interact with the covalent lattice formed by the sp^3 or sp^2 covalent silicon bands. So as it was shown by Cohen and Anderson,[17] the conjunction of soft modes and covalent bonds between the Si atoms could give rise to local-field effects which should enhance electron-electron attraction and then favor superconductivity. We actually notice that a high T_c is also observed in another silicide $BaSi_2$, which is close to a structural instability.

In conclusion, we have found that the application of pressure on the layered semimetallic $CaSi_2$ induces unexpected 14 K superconductivity, among the highest T_c's found in silicides and in Si-based compounds. We discussed these results in terms of the possible appearance of soft phonon modes associated with the character of the Si bonding in different atomic arrangements. These results show that the search of superconductivity in other alkali earth silicides close to a structural transformation by means of pressure studies may lead to the discovery of additional Si-based superconductors.

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