Superconductivity for CaC\(_6\) to 32 GPa hydrostatic pressure

M. Debessai, J. J. Hamlin, and J. S. Schilling

Department of Physics, Washington University, CB 1105, One Brookings Dr., Saint Louis, Missouri 63130, USA

D. Rosenmann, D. G. Hinks, and H. Claus

Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

(Received 21 April 2009; revised manuscript received 2 August 2010; published 4 October 2010)

The dependence of the superconducting transition temperature \(T_c\) of CaC\(_6\) has been determined as a function of hydrostatic pressure in both helium-loaded gas and diamond-anvil cells to 0.6 GPa and 32 GPa, respectively. Following an initial increase at the rate +0.39(1) K/GPa, \(T_c\) drops abruptly from 15 to 4 K at \(\sim 10\) GPa. Between 18 and 32 GPa, no superconducting transition is observed above 2 K.

DOI: 10.1103/PhysRevB.82.132502 PACS number: 74.62.Fj, 74.70.Ad, 74.62.Bf, 61.05.cp

I. INTRODUCTION

The s,p-electron metal CaC\(_6\) possesses with \(T_c\) \(\approx 11.5\) K the highest superconducting transition temperature of all known graphite-related compounds.\(^1^2\) Magnetic susceptibility measurements by two separate groups have shown that \(T_c\) increases under pressure at the rate \(\sim +0.50(5)\) K/GPa (to 1.2 GPa) (Ref. 3) or +0.42 to +0.48 K/GPa (to 1.6 GPa),\(^4\) where the pressure medium used was, respectively, kerosene or silicone oil. This relatively large positive value of the initial slope \(dT_c/dP\) stands in contrast to the negative dependence normally found in those s,p-electron metals which superconduct at ambient pressure.\(^5\) An electrical resistivity study on CaC\(_6\) to 16 GPa using Fluorinert pressure medium reported that \(T_c\) initially increases under pressure at the rate \(\sim +0.5\) K/GPa, reaching a maximum value of 15.1 K before dropping abruptly at 8 GPa to \(\sim 5\) K, apparently due to a first-order structural phase transition.\(^6\) Recent room-temperature synchrotron x-ray diffraction studies to 13 GPa using helium or argon pressure media report the onset of reversible peak broadening above 9 GPa which is interpreted as giving evidence for an unusual order-disorder phase transformation with no change in space-group symmetry from \(R\bar{3}m\) rhombohedral.\(^7\) Further \(T_c(P)\) studies to higher more nearly hydrostatic pressures would clearly be useful to establish whether or not the abrupt drop in \(T_c\) near 8 GPa is an intrinsic effect or possibly induced through shear stresses from the solid pressure medium. Dense He is the most nearly hydrostatic pressure medium available in experiments at low temperatures.

In the present work, the pressure dependence of \(T_c\) for CaC\(_6\) is studied in ac susceptibility measurements both in a He-gas pressure system to 0.6 GPa and in a diamond-anvil cell (DAC) to 32 GPa utilizing dense He pressure medium. Following an initial increase under pressure to 15 K at the rate +0.39(1) K/GPa, a sharp drop in \(T_c\) from 15 to \(\sim 4\) K is observed at 10 GPa.

II. EXPERIMENTAL

CaC\(_6\) samples are prepared using the alloy method described by Emery et al.\(^2\) A stainless steel tube is cleaned, baked at 900 °C in vacuum, and loaded with lithium and calcium in the atomic ratio 3:1. Natural Madagascar graphite flakes or highly oriented pyrolitic graphite (HOPG) pieces (GE ZYA grade) are added to the Li-Ca alloy. The tube is mechanically sealed in an argon atmosphere and placed inside a one-zone furnace which is evacuated to \(2 \times 10^{-7}\) Torr and subsequently filled with argon gas. The furnace is then heated to 350 °C and the reaction takes place for 10 days. After this time, the furnace is turned off allowing the sample to slowly cool down to room temperature. The tube is opened inside an argon-filled glove box and the samples, exhibiting a golden appearance, removed by dissolving the alloy in ethylenediamine (Sigma Aldrich >99%).

Figure 1 shows the x-ray diffraction data for a typical CaC\(_6\) flake sample with the (00l) diffraction peaks obtained using a Rigaku x-ray diffractometer with Cu \(K\alpha\) radiation and taken in a Bragg-Brentano geometry.\(^8\) The pattern is consistent with the rhombohedral structure model for CaC\(_6\) of Emery et al.\(^2\) No lines corresponding to hexagonal graphite are visible within our detection limits, showing the bulk nature of the sample. From the diffraction data, we find the lattice parameters \(a=4.33\) Å and \(c=13.57\) Å, yielding a mass density of 2.53 g/cm\(^3\).

For hydrostatic pressures to 0.6 GPa, a He-gas compressor system from Harwood Engineering was used in combi-
nation with a CuBe pressure cell from Unipress with a 7 mm diameter bore. Using a primary/secondary compensated coil system immediately surrounding the sample in the cell bore, ac susceptibility measurements at 0.1 Oe rms and 1023 Hz can be carried out under pressure to the same high accuracy as measurements at ambient pressure. A two-stage Balzers closed-cycle refrigerator was used to cool the pressure cell to below the superconducting transition temperature of CaC₆; all measurements were carried out upon warming up slowly through the transition at the rate 0.06 K/min. All susceptibility measurements were repeated at least once to verify that the transition temperature at a given pressure was reproducible to within 20 mK.

The membrane-driven DAC (Ref. 9) in this experiment employed 1/6-carat type Ia diamond anvils with 0.5 mm cu-llets and a 3 mm girdle. After the nonsuperconducting, nonmagnetic NiMo-alloy gasket was preindented from 380 μm to 80 μm, a 235 μm hole was spark-cut through the center. Tiny ruby spheres¹⁰ are placed on or near the sample to allow the pressure determination at a temperature near 20 K using the revised ruby calibration of Chijioke et al.¹¹ The ac susceptibility in the DAC is measured using two compensated primary/secondary coil systems with an applied field of 3 Oe at 1023 Hz. Further details of the DAC (Refs. 9 and 12) and He-gas compressor¹³ techniques are given elsewhere.

III. RESULTS AND DISCUSSION

In Figs. 2(a) and 2(b), the diamagnetic transition to superconductivity for both CaC₆ samples is seen to shift to higher temperatures with increasing hydrostatic pressure. The size of the superconducting shielding is more than twice as large for the HOPG-graphite sample as for the natural graphite sample. In Fig. 3, the superconducting transition temperature $T_c$ is plotted versus pressure for both samples.¹⁴ The measured $T_c(P)$ dependence is seen to be reversible and not depend on the temperature at which the pressure is changed. Within experimental error, the rate of increase, $dT_c/dP \approx 0.40(1) \text{ K/GPa}$, is the same for both samples but 5–10% less than that reported previously in experiments where less hydrostatic pressure media were used.³,⁴,⁶

The results of the present ac susceptibility experiments on the HOPG graphite CaC₆ sample in a DAC are shown in Fig. 4. Following the initial pressurization to ~5 GPa at 2 K, the pressure was changed in the temperature range 100–150 K. The transition is seen to shift to higher temperatures with pressure to 9.5 GPa, but then to suddenly fall to 8 K at

![FIG. 2.](image-url)  
**FIG. 2.** (Color online) Real part of the ac susceptibility versus temperature at different pressures to ~0.6 GPa in the He-gas cell for CaC₆ made from (a) natural graphite or (b) HOPG graphite.

![FIG. 3.](image-url)  
**FIG. 3.** (Color online) Superconducting transition temperature versus pressure to ~0.6 GPa for CaC₆ using data from Figs. 2(a) and 2(b). $T_c$ is determined from the transition midpoint (see Ref. 14). Numbers give order of measurement. Pressure is changed at room temperature for solid symbols, at 50 K for open symbols.

![FIG. 4.](image-url)  
**FIG. 4.** Real part of the ac susceptibility signal at different pressures in the DAC to 18.3 GPa for CaC₆ made from HOPG graphite. Data taken with increasing pressure.
FIG. 5. Superconducting transition temperature versus pressure to 32 GPa for CaC$_6$ using data from Fig. 4. $T_c$ is determined from the transition midpoint. Solid line is guide to eyes; dashed line reproduces data from Ref. 6. Above 20 GPa, $T_c$ lies below 2 K. Error bars give 20–80 % transition width.

10.7 GPa and broaden. At 11.8 GPa $T_c$ lies near 4 K and decreases moderately at higher pressures to 18.3 GPa. At higher pressures the transition shifted to temperatures below our temperature window and did not reappear to 32 GPa.

In Fig. 5, this dependence of $T_c$ on pressure is shown explicitly and compared to the previous results of Gauzzi et al.$^6$ to 18 GPa. In both measurements, $T_c$ is seen to plummet downward rapidly at a pressure near 10 GPa, indicating a possible first-order phase transition. This possibility is supported by the sudden marked broadening of the transition at 10.7 GPa. The initial slope $dT_c/dP=+0.39(1)$ K/GPa to 9.5 GPa agrees well with the results of our He-gas studies to 0.6 GPa in Fig. 3.

In summary, the dependence of the superconducting transition temperature of CaC$_6$ on nearly hydrostatic pressure has been studied to 32 GPa. Following an increase from 11 to 15 K under 9.5 GPa pressure, $T_c$ abruptly drops to 4 K at 11.8 GPa. For pressures between 18 and 32 GPa, no superconducting transition is observed above 2 K. The present results are in reasonable agreement with the less hydrostatic studies of Gauzzi et al.$^6$ to 18 GPa where the drop in $T_c$ occurs at a slightly lower pressure. The $T_c(P)$ dependence for CaC$_6$ given in Fig. 5 is thus intrinsic and not the result of shear stress effects.

ACKNOWLEDGMENTS

Thanks are due to V. G. Tissen for supplying the NiMo-alloy gaskets used in the DAC experiments. The authors at Washington University gratefully acknowledge research support by the National Science Foundation through Grant No. DMR-0703896.

$^*$Present address: Institute for Shock Physics, Washington State University, Pullman, Washington 99164, USA.

$^1$Present address: Department of Physics, University of California, San Diego, La Jolla, California 92093, USA.

$^2$Present address: Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, USA.


$^{14}$At ambient pressure (pt. 1 in Fig. 3) $T_c$ is defined from the midpoint of the superconducting transition. $T_c$ at high pressure is most accurately determined from the shift of the entire transition curve relative to that at ambient pressure.