

Superconductivity for CaC₆ to 32 GPa hydrostatic pressure

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The dependence of the superconducting transition temperature T_c of CaC₆ 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 ~ 10 GPa. Between 18 and 32 GPa, no superconducting transition is observed above 2 K.

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I. INTRODUCTION

The s,p -electron metal CaC₆ 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 CaC₆ 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 ~ 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 CaC₆ 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 ~ 4 K is observed at 10 GPa.

II. EXPERIMENTAL

CaC₆ 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 pyrolytic 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 2×10^{-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 CaC₆ 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 rhombohedra structure model for CaC₆ 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/cm³.

For hydrostatic pressures to 0.6 GPa, a He-gas compressor system from Harwood Engineering was used in combi-

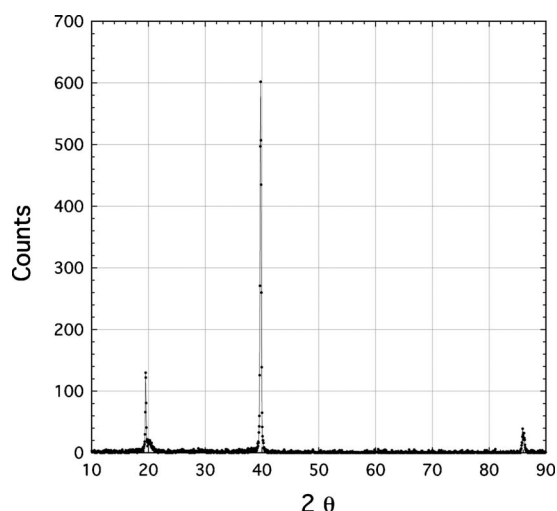


FIG. 1. X-ray (Cu $K\alpha$) diffraction pattern for CaC₆ sample prepared from natural graphite.

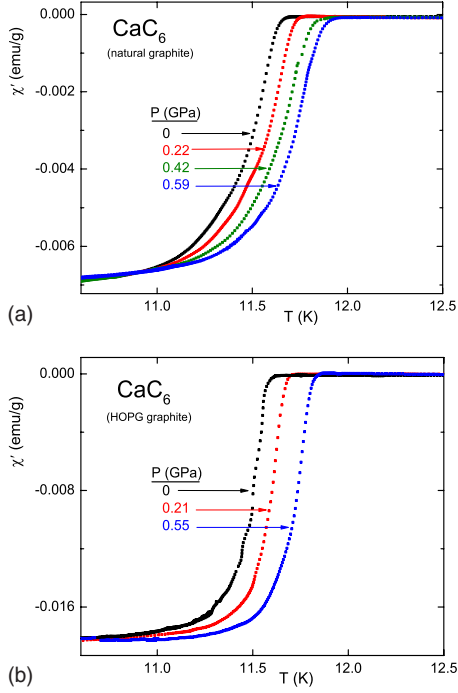


FIG. 2. (Color online) Real part of the ac susceptibility versus temperature at different pressures to ~ 0.6 GPa in the He-gas cell for CaC_6 made from (a) natural graphite or (b) HOPG graphite.

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 CaC_6 ; 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. T_c is determined from the transition midpoint in the ac susceptibility.

The membrane-driven DAC (Ref. 9) in this experiment employed 1/6-carat type Ia diamond anvils with 0.5 mm culets and a 3 mm girdle. After the nonsuperconducting, non-magnetic 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 rms 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 CaC_6 samples is seen to shift to higher temperatures with increasing hydrostatic pressure. The size

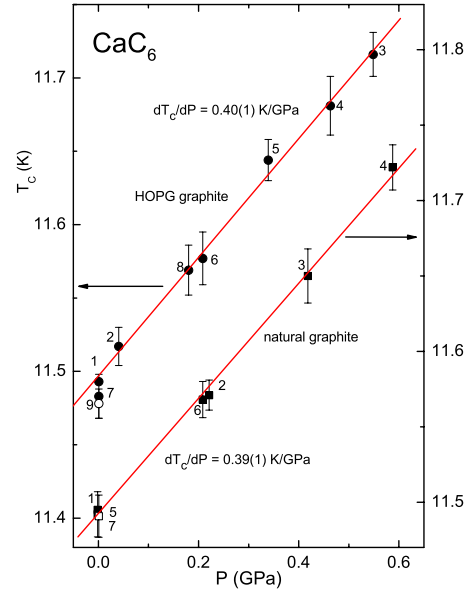


FIG. 3. (Color online) Superconducting transition temperature versus pressure to ~ 0.6 GPa for CaC_6 using data from Figs. 2(a) and 2(b). T_c is determined from the transition midpoint (see Ref. 14). Numbers give order of measurement. Pressure is changed at room temperature for solid symbols, at 50 K for open symbols.

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, $dT_c/dP \approx +0.40(1)$ 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 CaC_6 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

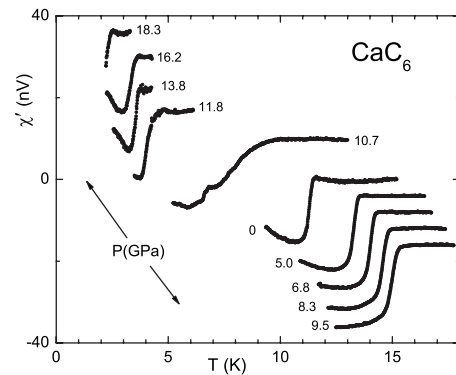


FIG. 4. Real part of the ac susceptibility signal at different pressures in the DAC to 18.3 GPa for CaC_6 made from HOPG graphite. Data taken with increasing pressure.

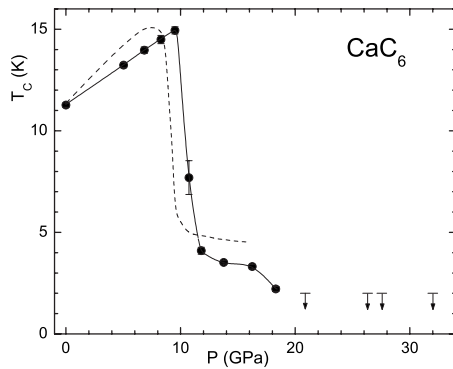


FIG. 5. Superconducting transition temperature versus pressure to 32 GPa for CaC_6 using data from Fig. 4. T_c is determined from the transition midpoint. Solid line is guide to eyes; dashed line reproduces data from Ref. 6. Above 20 GPa, T_c lies below 2 K. Error bars give 20–80 % transition width.

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 $dT_c/dP \approx +0.39(1)$ 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.

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