

# Studies of Superconductivity and Structure for CaC<sub>6</sub> to Pressures above 15 GPa

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## Abstract

The dependence of the superconducting transition temperature  $T_c$  of CaC<sub>6</sub> has been determined as a function of hydrostatic pressure in both helium-loaded gas and diamond-anvil cells to 0.6 and 32 GPa, respectively. Following an initial increase at the rate +0.39(1) K/GPa,  $T_c$  drops abruptly from 15 K to 4 K at  $\sim 10$  GPa. Synchrotron x-ray measurements to 15 GPa point to a structural transition near 10 GPa from a rhombohedral to a higher symmetry phase.

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# 1 Introduction

The  $s, p$ -electron metal  $\text{CaC}_6$  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) [3] or  $+0.42$  to  $+0.48$  K/GPa (to 1.6 GPa) [4], where the pressure medium used was, respectively, kerosene or silicon oil. This relatively large positive value of the initial slope  $dT_c/dP$  stands in contrast to the negative dependence normally found in  $s, p$ -electron metals which superconduct at ambient pressure [5]. An electrical resistivity study on  $\text{CaC}_6$  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 9 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 9 GPa is an intrinsic effect and to more fully characterize possible structural transitions in this pressure region. 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  $\text{CaC}_6$  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 K to  $\sim 4$  K is observed at 10 GPa. Parallel room temperature synchrotron x-ray studies to 15 GPa suggest a structural transition near 10 GPa from rhombohedral to a higher symmetry structure rather than the order-disorder transition suggested by Gauzzi *et al.* [7].

## 2 Experimental

$\text{CaC}_6$  samples are prepared using the alloy method described by Emery *et al.* [2]. A stainless steel tube is cleaned, baked at  $900^\circ\text{C}$  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  $2 \times 10^{-7}$  Torr and subsequently filled with argon gas. The furnace is then heated to  $350^\circ\text{C}$  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%).

Fig. 1 shows the x-ray diffraction data for a typical  $\text{CaC}_6$  flake sample with the (001) diffraction peaks obtained using a Rigaku x-ray diffractometer with  $\text{Cu-K}\alpha$  radiation and taken in a Bragg-Brentano geometry [8]. The pattern is consistent with the rhombohedra structure model for  $\text{CaC}_6$  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  $a = 4.33 \text{ \AA}$  and  $c = 13.57 \text{ \AA}$ , yielding a mass density of  $2.53 \text{ g/cm}^3$ .

For hydrostatic pressures to 0.6 GPa a He-gas compressor system from Harwood Engineering was used in combination 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  $\text{CaC}_6$ ; all measurements were carried out upon warming up slowly through the transition at the rate  $\sim 0.06 \text{ K/min}$ . 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 diamond-anvil cell (DAC) [9] in this experiment employed 1/6-carat type Ia diamond anvils with 0.5 mm culets and a 3 mm girdle. After the non-superconducting, non-magnetic NiMo-alloy gasket was preindented from  $380 \mu\text{m}$  to  $80 \mu\text{m}$ , a  $235 \mu\text{m}$  hole was spark-cut through the center. Tiny ruby spheres [10] 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 [9, 12] and He-gas compressor [13] techniques are given elsewhere.

Structural properties of  $\text{CaC}_6$  as function of pressure up to 15 GPa were studied in a DAC using angle-dispersive synchrotron x-ray diffraction techniques at beamline 16ID-B of the High Pressure Collaborative Access Team (HPCAT), Advanced Photon Source (APS). X-ray diffraction measurements were carried out with a focused 33.714 keV monochromatic beam ( $10 \times 10 \mu\text{m}$ ) and a MAR345 image plate detector to record the diffracted x-rays. The diffraction images were integrated using the software FIT2D [14]. Silicon oil was used as pressure medium. Pressures were determined by the ruby fluorescence method.

## 3 Results of Experiment and Discussion

### 3.1 AC Susceptibility Measurements

#### 3.1.1 He-Gas Compressor System

In Figs. 2(a) and 2(b) the diamagnetic transition to superconductivity for both  $\text{CaC}_6$  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 [15]. 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].

#### 3.1.2 Diamond Anvil Cell

The results of the present ac susceptibility experiments on the HOPG graphite  $\text{CaC}_6$  sample in a DAC are shown in Fig. 4. Following the initial pressurization to  $\sim 5$  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 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.

### 3.2 Synchrotron X-Ray Diffraction Studies

The x-ray diffraction patterns for  $\text{CaC}_6$  (HOPG graphite) for increasing pressure are shown in Fig. 6 and are indexed based on 9 to 12 diffraction lines of an hexagonal unit cell consistent with the known rhombohedral structure model of  $\text{CaC}_6$  [2]. The unit cell volume  $V$  and lattice parameters of this phase as a function of pressure are shown in Figs. 7(a) and 7(b). The  $P - V$  data are fit to a third-order Birch-Murnaghan equation of state

$$P = \frac{3}{2} \left[ \left( \frac{V_o}{V} \right)^{7/3} - \left( \frac{V_o}{V} \right)^{5/3} \right] \left\{ 1 - \frac{3}{4} (4 - K'_o) \left[ \left( \frac{V_o}{V} \right)^{2/3} - 1 \right] \right\}, \quad (1)$$

where  $V_o$  and  $K_o$  are the volume and isothermal bulk moduli, respectively, at 1 bar, and  $K'_o$  is the pressure derivative of  $K_o$ . By fixing  $K'_o = 4$ , a least-squares fit yields  $K_o = 119(3)$  GPa, and  $V_o = 220.5(3)$ . As expected for most layered structures, the compression of the low-pressure  $\text{CaC}_6$  phase is anisotropic where the  $c$  axis is more than 10 times more compressible than the  $a$  axis, with the result that the  $c/a$  ratio decreases appreciably with pressure (see inset in Fig. 7(b)). From the data in Fig. 7(b) we find  $\varkappa_a \equiv -a^{-1}da/dP \simeq 0.00039$  GPa $^{-1}$  and  $\varkappa_c \equiv -c^{-1}dc/dP \simeq 0.0069$  GPa $^{-1}$ .

The low-pressure superconducting  $\text{CaC}_6$  phase is stable to 9.0 GPa (Figs. 6 and 8). Between 9 and 10.5 GPa the x-ray diffraction pattern displays evident changes, including the disappearance of some of the diffraction lines of the low-pressure  $\text{CaC}_6$  phase and a significant intensity decrease in the region of the previous (113) diffraction line, the strongest of the low-pressure  $\text{CaC}_6$  structure, as well as the appearance of new diffraction lines. These observations suggest a structural phase transformation, likely to a higher symmetry phase.

In summary, the dependence of the superconducting transition temperature of  $\text{CaC}_6$  on nearly hydrostatic pressure has been studied to 32 GPa. Following an increase from 11 K to 15 K under 9.5 GPa pressure,  $T_c$  abruptly drops to 4 K at 11.8 GPa. Parallel synchrotron x-ray studies reveal that this sudden drop in  $T_c$  results from a structural phase transition from rhombohedral to a phase of higher symmetry.

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- [15] 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.

# Figure Captions

**Fig. 1.** X-ray (Cu  $K\alpha$ ) diffraction pattern for  $\text{CaC}_6$  sample prepared from natural graphite.

**Fig. 2.** (color online) Real part of the ac susceptibility versus temperature at different pressures to  $\sim 0.6$  GPa in the He-gas cell for  $\text{CaC}_6$  made from (a) natural graphite or (b) HOPG graphite.

**Fig. 3.** (color online) Superconducting transition temperature versus pressure to  $\sim 0.6$  GPa for  $\text{CaC}_6$  using data from Figs. 2(a) and 2(b).  $T_c$  is determined from the transition midpoint (see Ref. [15]). Numbers give order of measurement. Pressure is changed at room temperature for solid symbols, at 50 K for open symbols.

**Fig. 4.** Real part of the ac susceptibility signal at different pressures in the DAC to 18.3 GPa for  $\text{CaC}_6$  made from HOPG graphite. Data taken with increasing pressure.

**Fig. 5.** Superconducting transition temperature versus pressure to 32 GPa for  $\text{CaC}_6$  using data from Fig. 4.  $T_c$  is determined from the transition midpoint. Solid line is guide to eye; dashed line reproduces data from Ref. [6]. Above 20 GPa  $T_c$  lies below 2 K. Error bars give 20% - 80% transition width.

**Fig. 6.** Synchrotron x-ray patterns for HOPG  $\text{CaC}_6$  under pressure to 15 GPa. A structural phase transition appears to occur for pressures above 9 GPa. Diffraction peaks in the 2-theta angle from 5 to 7 degrees are not used for unit cell calculations due to the overlap of large single crystal spots in this region.

**Fig. 7.** Unit cell volume and normalized hexagonal lattice parameters  $a$  and  $c$  as a function of pressure to 9 GPa. Inset shows the  $c/a$  ratio versus pressure.

**Fig. 8.**  $d$ -space versus pressure for  $\text{CaC}_6$  to 15 GPa.

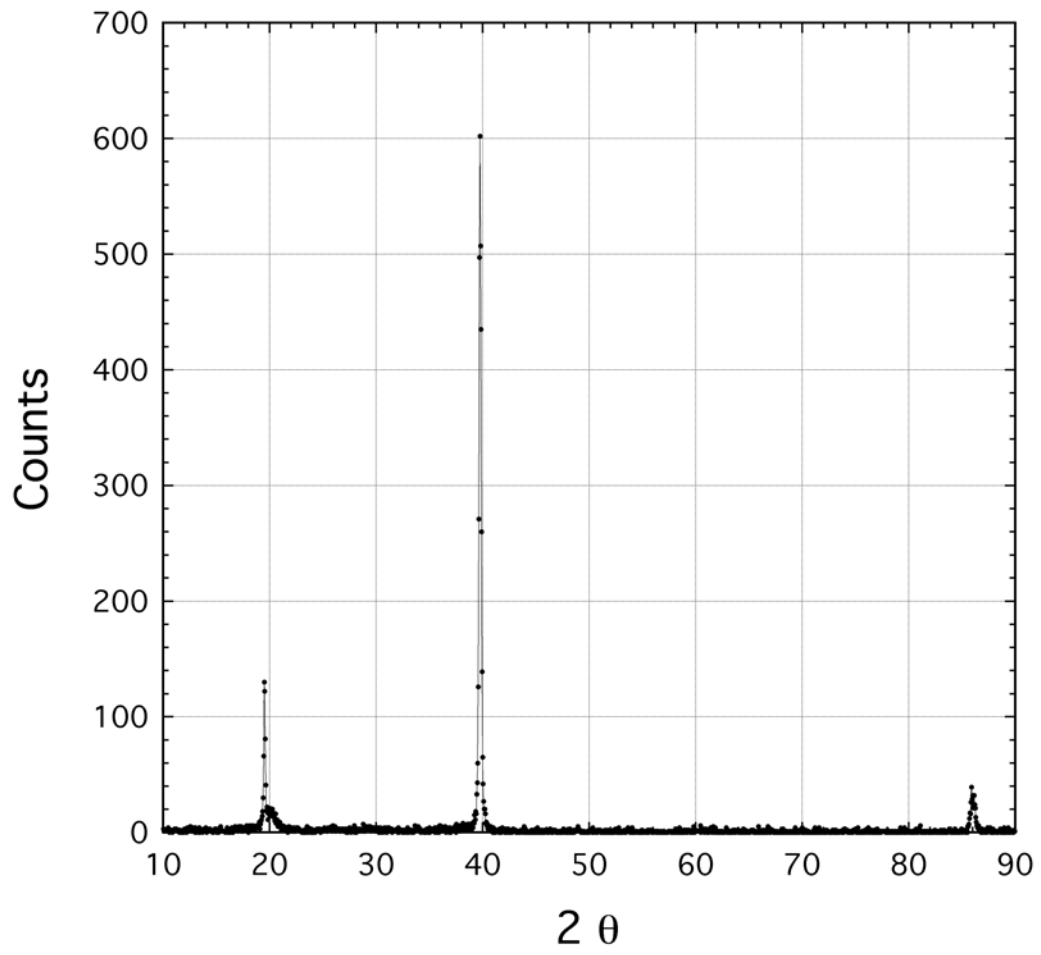


Figure 1

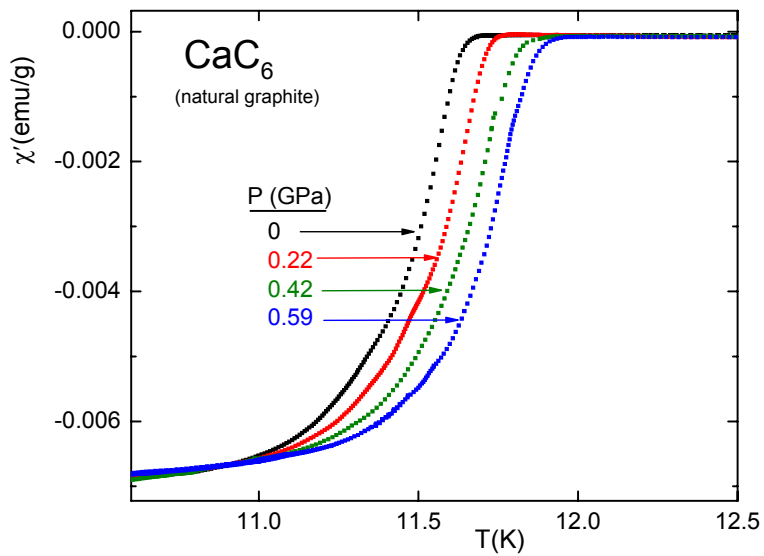


Figure 2(a)

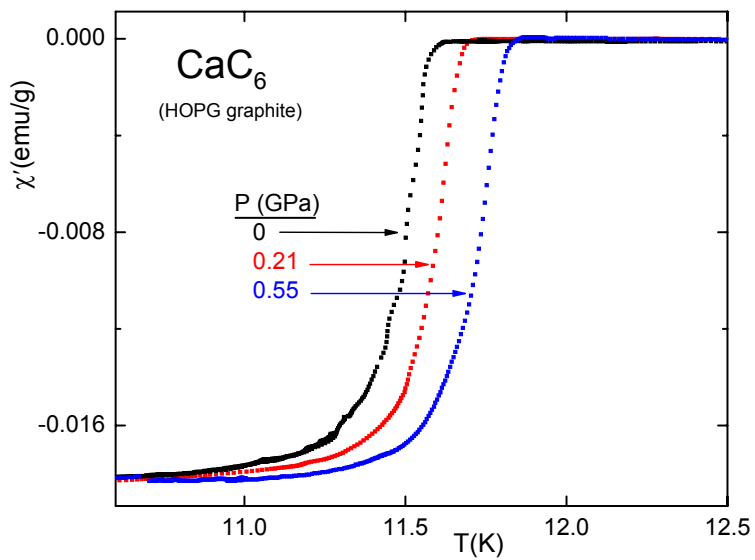


Figure 2(b)

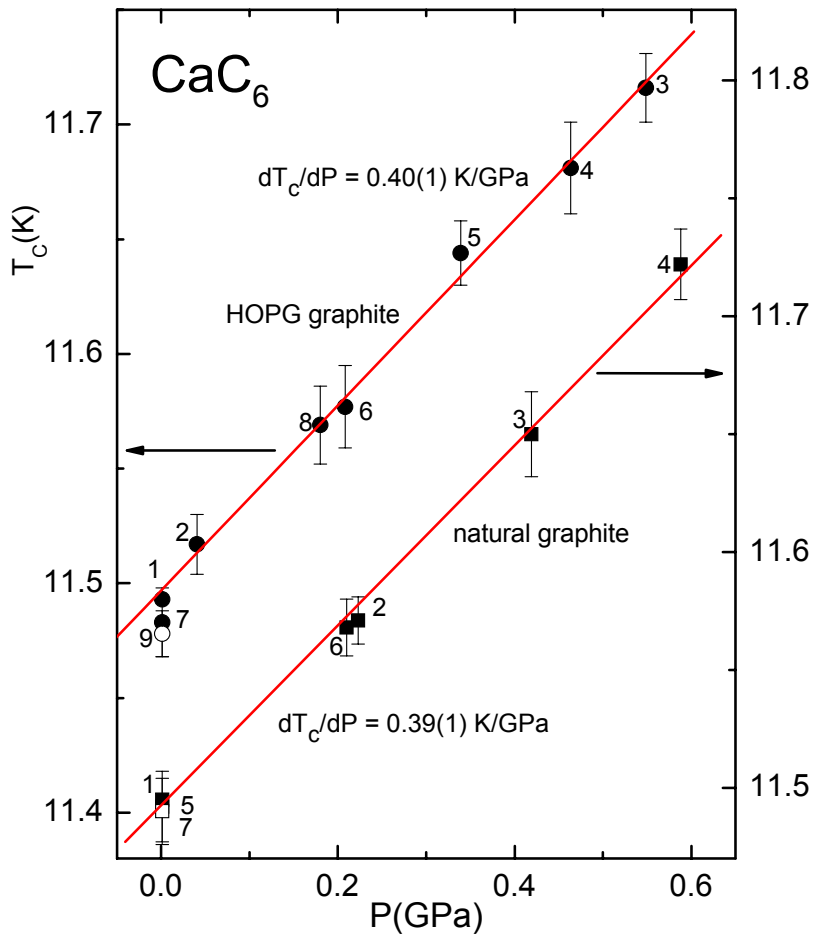


Figure 3

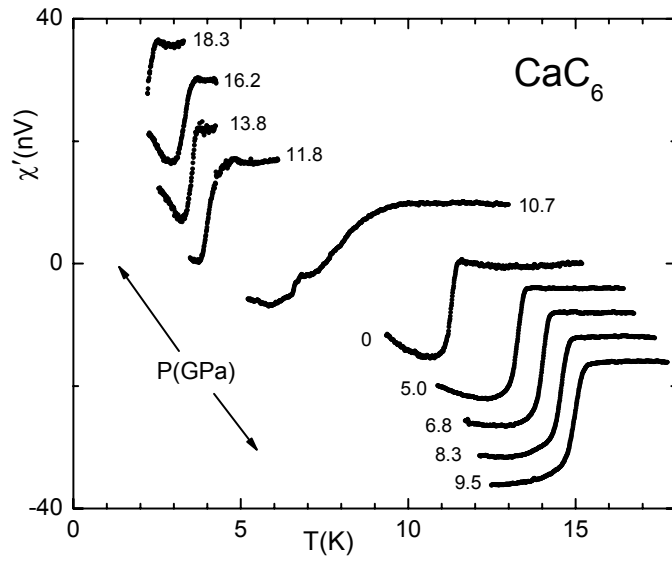


Figure 4

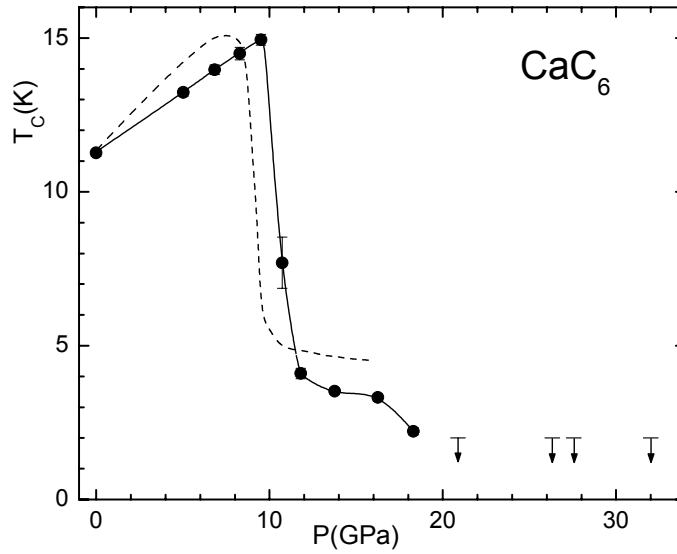


Figure 5

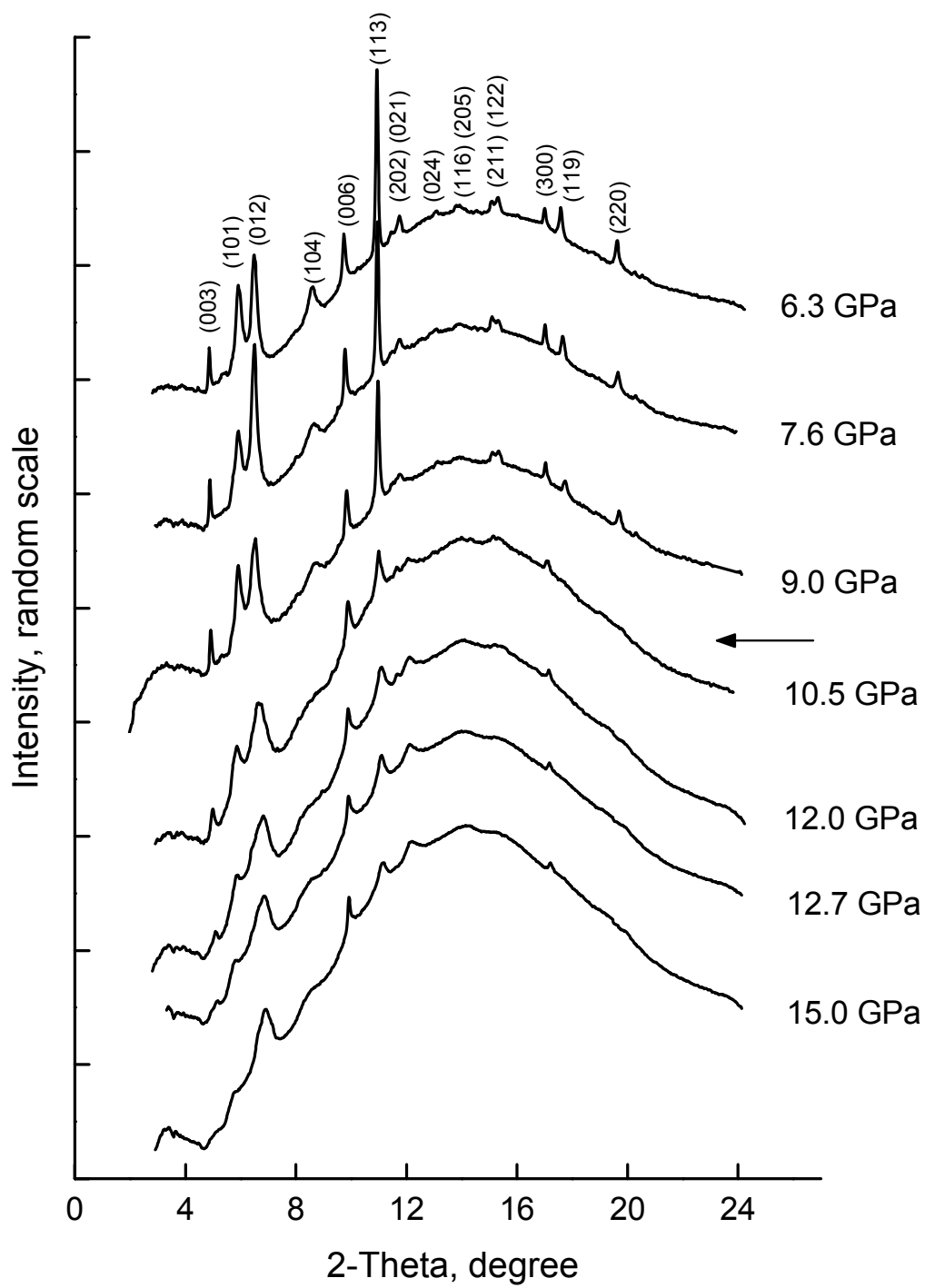


Figure 6

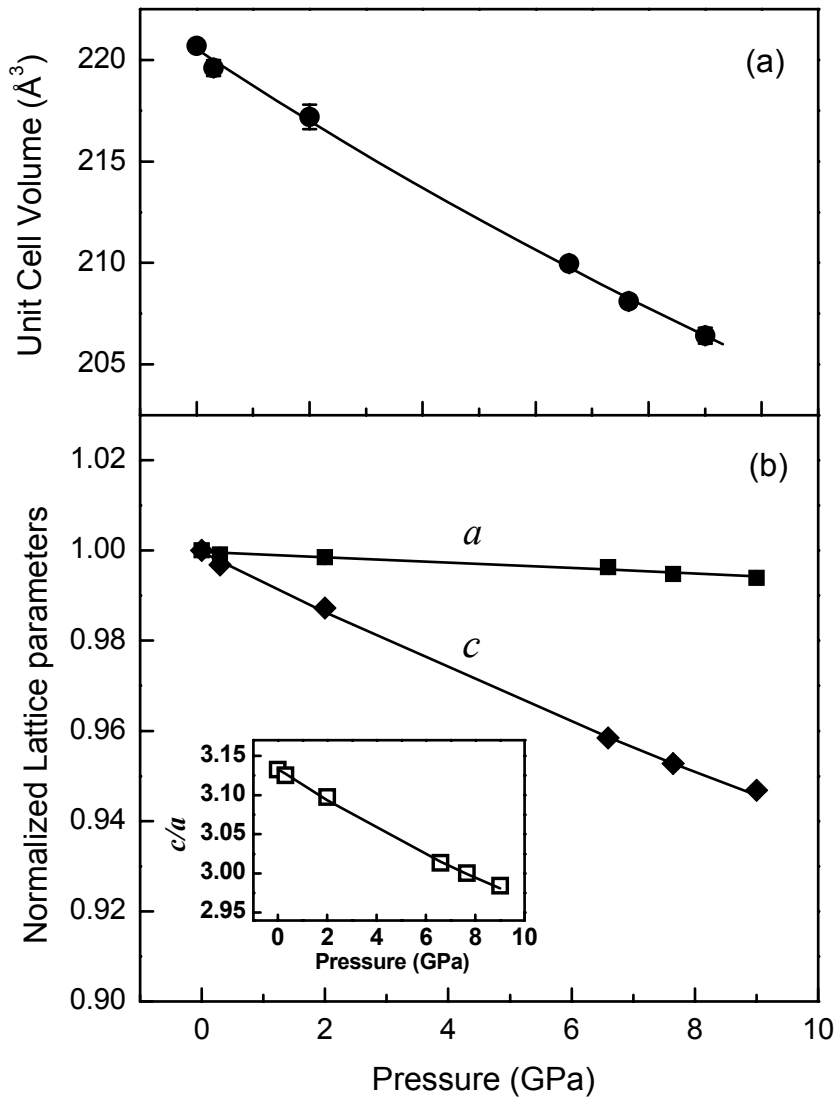


Figure 7

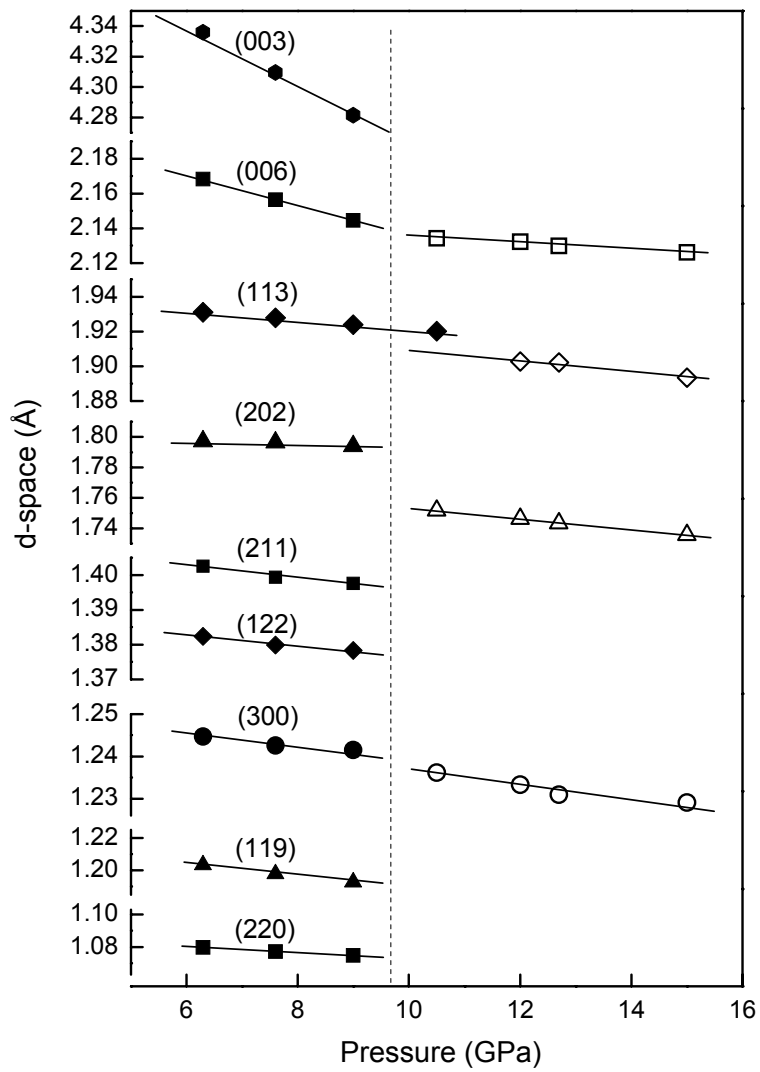


Figure 8