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THE USE OF ELECTRICAL CONDUCTIVITY EXPERIMENTS
TO STUDY THE PHASE DIAGRAM OF CARBON*

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Abstract

Recent theoretical and experimental work on the properties of carbon at very high pressures indicates that the diamond phase may dominate the carbon phase diagram. The work of Yin and Cohen indicates that diamond may be the stable carbon phase to pressures as high as 20 Mbar. Recent work by Shaner et al. is compatible with solid diamond on the Hugoniot at pressures up to 1.4 Mbar. Using previously developed techniques, we have carried out conductivity measurements on shock-compressed graphite to pressures in excess of 600 kbar and temperatures up to 5000 K. No diamond - liquid transition was observed under the experimental conditions achieved.

Keywords: carbon, diamond, shock wave, phase diagram, electrical conductivity.

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Introduction

The phase diagram of carbon has been of continuing interest, particularly since the discovery by the General Electric Company that artificial diamonds could be produced in industrially interesting quantities [1]. In order to achieve this result, it is important to develop a thorough understanding of the diamond-graphite phase line and the metastable conditions encountered. In addition, a knowledge of the melting behavior of graphite is needed to provide limits for its application as a refractory material [2]. Finally, melting behavior also limits the pressure which can be attained in static apparatus [3].

Until recently, the phase diagram for pure carbon was thought to be approximately represented by the diagram shown in Fig. 1 [4]. The low pressure limits on this phase diagram were set by thermodynamic measurements [5] to 1200 K. Details of the graphite-liquid transition and other associated high temperature, low pressure (~ 100 kbar) phenomena have been summarized by Bundy [6]. The high temperature, high pressure portion of the phase line was based on work by Alder and Christian [7] who claimed to have observed a transition to a "metallic close packed liquid". This claim derived from corresponding states arguments, based on the behavior of germanium at high pressure, and some experimental artifacts, which were later shown to be spurious [8,9].

In 1973, van Vechten [10] proposed a metallic solid carbon with a density greater than diamond. Grover [11] subsequently proposed a diamond-metal-liquid triple point at 1.18 Mbar and 3080 K based on the van Vechten model. These ideas are incorporated in Fig. 2, taken from the work of Clarke and Uher [12]. Grover also proposed an improved diagram involving a low density metallic phase in which there

was no direct transition between diamond and liquid. This phase diagram was based in part on the shock wave work of Gust [13]. Grover argued that since the shock compression data for diamond did not extrapolate to the bulk sound speed of diamonds at zero pressure, a diamond-metal transition had been observed at the intersection of the acoustically calculated Hugoniot and the shock Hugoniot. He joined the diamond-metal curve and the metal-liquid curve directly to the graphite phase boundary the interpreted discontinuity of slopes as the diamond to metal transition. This phase diagram is shown in Fig. 3.

In the meantime, static high pressure researchers, notably Mao and Bell [14] and Ruoff and Vanagel [15], proposed that extremely high pressures in diamond anvils could be attained using the indentation technique. Most recently, Goettel, Mao and Bell [16] claimed to have actually achieved a pressure of 2.7 Mbar.

From the theoretical side, Yin and Cohen [17] have recently predicted that all known and hypothesized phases of diamond should transform under pressure to a simple cubic metallic phase and not to the analogous β -tin phase observed in silicon, germanium and tin. This transition pressure was calculated to be 23 Mbar. Even if another phase could exist, their work indicated that it would be impossible for it to be formed at pressures below 10 Mbar. They also showed that corresponding states arguments comparing silicon, germanium and tin to carbon were spurious. Unlike the situation in germanium, the high pressure transformation of diamond is to a simple cubic structure with a lower free energy. As an unexpected discovery, the diamond phase, because of its very compact structure, transforms only at very high pressures (the transition from diamond to the simple cubic metal phase would yield a volume reduction of only six percent). The predictions of Yin and Cohen can be further gener-

alized to argue that, in fact, the diamond phase dominates the phase diagram of carbon.

In an important series of measurements, Shaner et al. [18] showed that the sound velocity in shock-compressed graphite at pressures up to 1.2 Mbar was higher than expected, some 16-17 km/s. This work indicated that carbon may have remained in the diamond phase up to those pressures and temperatures, since the sound velocities measured were well above those predicted for graphite or any postulated liquid.

Present Work

The conductivity experiments described here were designed to provide further evidence that the high sound velocity observed by Shaner et al. [18] is characteristic of a diamond phase. Initially shocked graphite does show graphitic conductivity at the lower pressures, but becomes an insulator at the higher pressures, indicating a transition into the diamond phase. The present experiments were carried out by techniques developed previously [19]. Teflon, which remains an insulator at pressures to about 1 Mbar, was used as the "sandwich" or insulating impedance-matched material. Transverse electrical geometry was used along with a current pulser to provide the voltage drop across the pyrolytic graphite sample. Experiments were carried out at the Los Alamos National Laboratory's gas gun facility.

Resistivity results from three experiments are shown in Figs. 4 and 5. Results from the lowest pressure experiment are shown in Fig. 4a. The initial pressure attained was 360 kbar. The initial conductivity was $4 \times 10^2 \Omega^{-1}\text{cm}^{-1}$. As the shock wave hit the sample, the conductivity "ramped up" to $2 \times 10^3 \Omega^{-1}\text{cm}^{-1}$ and remained at that constant value for the duration of the experiment. In this experiment we

have observed graphite at 300 kbar and 2500 K. No evidence of a transition to diamond or any other phase is observed.

In the second experiment, the graphite was shocked to 630 kbar. The measured resistivity is shown in Fig. 4b. Here, a transition to an insulating phase is observed. Again the "ramp" effect is noticed, corresponding to the passage of the shock wave through the sample. The shock front is the boundary between a conducting graphite phase and insulating diamond phase. The diamond transition is fast, taking 10 ns or less.

The third experiment was carried out in the region where a two-wave structure is observed. Its results are shown in Fig. 5. The wave separation is clearly seen. At a time immediately before the emergence of the first shock wave from the sample, there are three phases present: unshocked graphite, shocked graphite, and diamond associated with the second shock. The observed "ramp" is followed by an electrical conductivity representative of the first wave; however, it must be realized that at the time of arrival of the first wave after transit through the sample, the second wave has already propagated some distance into the sample. It is this second wave that causes the low conductivity associated with the diamond phase.

Our results are summarized in Table I. Two pressures are noted. The first is the initial pressure in the sample as shocked from Teflon. The second is the pressure after ringdown in the Teflon. Initial sample conductivity was $200 \Omega^{-1}\text{cm}^{-1}$.

Conclusion

Although this work is preliminary, several general points are clear; first we must drastically alter our present concept of the carbon phase diagram. Evidence is rapidly accumulating that diamond is indeed the phase that dominates the carbon phase diagram. Second, the kinetics of the graphite-diamond transition are extremely fast ($\tau < 10\text{ns}$) at the higher pressures ($> 400\text{--}500\text{ kbar}$). Third, a question is now raised about the kinetics of the graphite-diamond transition at lower pressures (around $200\text{--}300\text{ kbar}$) which are ostensibly within the equilibrium field of diamond. If graphite is making a transition to diamond in the experiment carried out at 360 kbar , the process is 4-5 orders of magnitude slower than the process taking place in the 630-kbar experiment. Perhaps graphite, which is metastable statically under similar conditions, is still metastable under shock conditions even with the violent rearrangements taking place at the atomic level. Finally, the high sound velocities observed by Shaner et al.[18] can now be associated with an insulating diamond phase indicating a positive slope of the diamond-liquid phase line as shown in Fig. 6. More experiments are being carried out to determine the exact boundary of the diamond-liquid transition.

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Table I. Conductivity Data for Graphite under Shocked Conditions

Shot	P(kbar)		$k(\Omega^{-1}\text{cm}^{-1})$	Remarks
	Peak	Final		
1	360	300	2×10^3	Sample remains in graphite phase.
2	630	580	8×10^0	Rapid transf. to diamond phase.
3	470	380	2×10^0	Conductivity of diamond phase after transf. due to second shock.

Figure Captions

Fig. 1. Phase diagram for carbon.

Fig. 2. P-T phase diagram corresponding to a van Vechten high density metallic phase of carbon. Superimposed are Hugoniot for synthetic (s), Ceylon (c), and pyrolytic (p) graphites (α , γ , β_1 and β_2), designate graphite, diamond, liquid, and solid metallic phases of carbon. The α - β_1 transition path shows a large volume change and a large temperature drop. Experimental graphite-diamond-liquid (γ - α - β) triple point indicated by 0.

Fig. 3. P-T phase diagram corresponding to a Grover low density metallic phase of carbon. Superimposed Hugoniot are calculated from the data of Gust. There is no direct transition path between the diamond and the liquid phase. Two triple points, t_1 and t_2 , are predicted. The inset shows an extrapolation of the dynamic compression data for diamond which does not coincide with the bulk sound speed C_B of diamond. This discrepancy has been interpreted by Grover as direct evidence for the α - β transition.

Fig. 4. (a) Electrical resistivity in Shot 1. Final sample pressure is 300 kbar. (b) Electrical resistivity in Shot 2 with final pressure of 580 kbar.

Fig. 5. (a) Electrical resistivity at slow sweep in Shot 3. Final sample pressure is 380 kbar. Data show two phase region, the first exhibits high conductivity and the second, the low conductivity of the diamond phase. (b) Resistivity at faster sweep to show detail in diamond phase.

Fig. 6. (a) Hugoniot data in shock compressed graphite with phase diagram. (b) Sound velocity on the Hugoniot for shock compressed graphite from Shaner et al. Data shows no transition to liquid phase.