

measured with the present apparatus, being less than  $5 \times 10^{-7}$  cm<sup>2</sup>/sec, while  $T_2$  decreased to  $0.34 \pm 0.02$  sec and  $T_1$  decreased to be of the same order as  $T_2$ . At  $0.033^\circ\text{K}$  the susceptibility was a factor of 2 larger at 29.5 atm than at 28.9 atm and displayed a considerably different temperature dependence at the higher pressures from that of the liquid below  $P_{\min}$ . No difference in  $T_2$ ,  $T_1$ , or  $D$  could be observed either upon further increasing the pressure or by heating the He<sup>3</sup> to temperatures where the solid phase should exist.

A portion of the susceptibility data is shown in Fig. 1. It should be noted that in addition to the change in behavior of the susceptibility between 28.9 and 29.5 atm, the susceptibility obeyed Curie's law much better at pressures of 32.9 atm and above than at lower pressures. It is interesting to note that in the region between 29.5 atm and 31.8 atm the susceptibility seems to break away from Curie's law near the temperatures where the melting curve of Edwards *et al.*<sup>5</sup> would predict the solid-liquid phase boundary to occur if the pressure of the sample were that at which the plug was formed.

In view of the measurements of specific heat, sound velocity, susceptibility,  $T_1$ ,  $T_2$ , and  $D$ , it

appears that the nature of He<sup>3</sup> in the region of the phase diagram of pressures greater than  $P_{\min}$  and temperature less than about  $0.1^\circ\text{K}$  is not understood. It is possible that a new phase of solid, rather than liquid, exists in this region, although further experimentation will be necessary to establish such a fact.

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## BEHAVIOR OF STRONGLY SHOCKED CARBON\*

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This Letter gives evidence for the conversion of graphite to the diamond phase when it is subjected to strong, explosively generated shocks. Furthermore, the data lend support to a further conversion at still higher pressures to a new, higher density phase of carbon, presumably the close-packed metallic liquid.

The initial material was, in the majority of the experiments, natural graphite from Ceylon of very high purity which was pressed into suitable uniform-density pellets of about 95% of theoretical density. Some work was done with commercial graphite, which has a density of 75% of theoretical.

The samples were mounted on an aluminum plate, and by optical means<sup>1</sup> both the shock and free surface velocity of carbon and aluminum were determined. The measurements on the aluminum standard could then be used to determine the pressure-volume point of carbon from its

measured shock velocity. This is a more reliable procedure than the use of the free surface velocity when the material does not have a simple behavior. The data are presented in Fig. 1, where the specific volume has been used to avoid artificial corrections due to varying initial densities. However, a correction to the pressure or volume still needs to be made for the increased energy content resulting from a greater change in volume of an initially low-density sample. This correction is insignificant except for samples of  $\frac{3}{4}$  theoretical density.

The shock data at low pressures agree with the x-ray determination of crystal densities under pressure<sup>2</sup> as shown by the triangles in Fig. 1. At somewhat higher pressures the static data of Bridgman<sup>3</sup> are indicated by squares in Fig. 1. Again the agreement is good if those data are corrected for the alleged error in the pressure

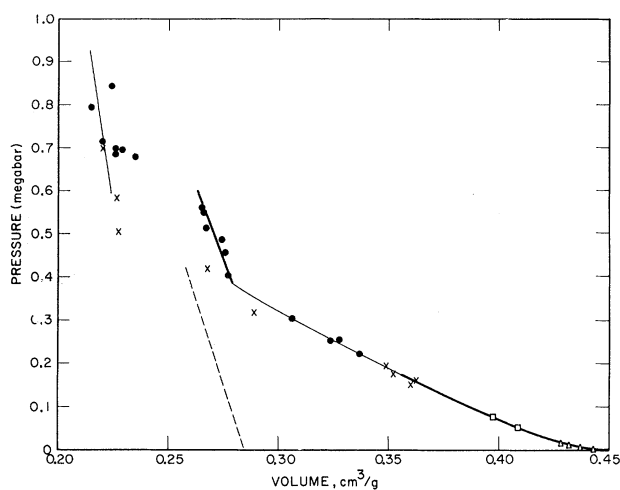


FIG. 1. The Hugoniot equation of state of graphite.  $\Delta$ —x-ray determination of crystal densities under pressure<sup>2</sup>;  $\square$ —static data of Bridgman<sup>3</sup>;  $\times$ —results for sample of low initial density;  $\bullet$ —results for samples with initially higher density; dashed line—extrapolated static compressibility curve of diamond.

scale.<sup>4</sup> Furthermore, there are eight additional shock experiments available below 0.3 megabar,<sup>5</sup> which are not shown on the graph. These unpublished data are in excellent agreement with the present work.

The Hugoniot below about 0.18 megabar is well behaved in that the rarefaction velocity, calculated as the difference between the measured free surface velocity of the carbon sample and the particle velocity obtained from the matching conditions at the aluminum-carbon interface, indicates that the graphite sample rarefies to the theoretical density of graphite. Above that pressure, however, the free surface velocity is such that the final density is greater than that of crystalline graphite. Furthermore, in the region between 0.18 megabar and 0.4 megabar the free surface velocity is dependent on the thickness of the sample. This phenomenon is a characteristic of a relaxation process of duration comparable to shock transit times. The interpretation of the free surface data is thus consistent with partial conversion of graphite to diamond; the larger graphite samples have more time to convert and the rarefaction leads to a density intermediate between graphite and diamond. The thickness variation of the free surface velocity in the 0.3-megabar experiments is such that an infinitely thin sample would rarefy to crystalline graphite and a  $\frac{1}{4}$ -inch

sample is about 40% converted. The curve between 0.18 and 0.4 megabar has thus been drawn lightly to indicate that the Hugoniot obtained might depend on the initial conditions such as density, temperature, and thickness of sample. It can be noted that the low-initial-density sample (indicated by crosses) at slightly above 0.3 megabar has a higher final density consistent with a higher fraction of conversion because of a larger energy content (temperature) than the samples with initially higher density (indicated by circles), although the uncertainties in the measurements from low-density samples are larger. At 0.2 megabar where the fraction converted is small, the low- and high-density samples give the same results.

The temperature at 0.18 megabar can be estimated as only 500°K by taking account of adiabatic and of irreversible heating. The temperature estimates given here are very rough due to uncertainties in the thermodynamic data<sup>6</sup> and temperature-dependent heat capacities. Although static data indicate that under these conditions diamond is the stable phase,<sup>7</sup> the reaction time would be expected to be extremely long if indeed it were at all possible to affect the direct conversion by the mechanisms considered statically.<sup>8</sup> As with other transitions observed under shock, particularly in the various forms of phosphorus,<sup>9</sup> the rapidity of reaction under shock seems to be connected with the extremely large shear forces in the shock front. When the pressure is released, on the other hand, by an adiabatic rarefaction, the temperatures are so low that a reconversion is not expected from statically determined reaction rates. It is thus not surprising that recovery of shocked graphite has shown diamond to be present.<sup>10-12</sup>

A definite break in the Hugoniot curve can be observed at 0.4 megabar when the graphite has been shocked to a density exceeding that of pure diamond under normal conditions. The presumption then is that conditions have been achieved where the reaction rate is such that less than a microsecond is required for nearly complete conversion to diamond. The slope and position of the curve between 0.4 and 0.6 megabar supports this view since it is in reasonable agreement with the extrapolated static compressibility curve of diamond (dashed line). The static curve actually lies at about 5% higher densities, but this could be due to many causes such as corrections for change of compressibility with pressure, uncertainties in the static compressibility<sup>13</sup> itself, temperature corrections, and incomplete con-

version; all of these tend to give corrections in the proper direction. The temperature at 0.4 megabar is estimated to be 800°K if to the previously mentioned energy contributions the further uncertain heat of conversion is added as obtained by a large extrapolation of static data.<sup>6</sup> The temperature at 0.6 megabar is then estimated to be 1300°K. It is unfortunate that due to the high shock velocity in diamond the free surface velocity measurements in the geometry utilized were not interpretable so that it is not possible to determine the density upon rarefaction, but it is expected to be diamond densities.

At 0.6 megabar the shock velocity in the graphite becomes insensitive to pressure. This is characteristic of the two-shock structure associated with a phase change in which only the leading shock is recorded. The data at yet higher pressure give an indication of the Hugoniot of the new phase. The data show a relatively large scatter since the pressure is near the upper limit of the presently used technique; hence the line is drawn lightly. The data points at 0.7 megabar scatter since they are still in the double shock region.

The volume change (15%) associated with the transition is quite large. It is similar to the transition which has been observed in isomorphous germanium both statically<sup>14</sup> and dynamically.<sup>15</sup> Dynamically it was found that the volume change is comparable, and statically that it was associated with the breakdown of the loosely packed diamond lattice into a metallic, close-packed liquid. Since the volume change is comparable in germanium and carbon and since the entropy change upon melting involving similar structural changes can also be expected to be comparable, it is possible to use the experimental melting temperature dependence with pressure for germanium (corrected for the change in static pressure scale) to determine the melting point for diamond at low pressures—namely about

4000°K. This is in agreement with static expectations. Again the initially low-density samples should transform at lower pressures as the data confirm. The two crossed points in the 0.5- to 0.6-megabar region lie approximately on the extension of the top section of the Hugoniot. These low-density points are, however, approximate as the cross slightly above 0.4 megabar indicates, since in that region the results should not strongly depend on temperature.

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