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THEORY OF THE CARBON PHASE DIAGRAM AT HIGH PRESSURES AND TEMPERATURES

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Despite the great technological and scientific importance of graphite and diamond, the carbon phase diagram is poorly understood. Here we develop simple theoretical models for the prediction of this diagram at very high pressures. We find that the diamond melting curve has a positive dP/dT slope, and that solid diamond has a very large stability field.

Because of the enormous technological importance of graphite and diamond, there has been a long-standing interest in the carbon phase diagram. This diagram presents a significant challenge for both experiment and theory. Progress of experimental work on the carbon phase diagram has been slow because of the very high temperatures and pressures involved. At present, only the graphite-diamond and graphite-liquid phase boundaries have been measured.[1] The data suggest the existence of a graphite-diamond-liquid triple point near 120 kbar and 4000 K. Although there is now evidence that diamond does melt,[2,3] the melting curve has not been measured to date.

The most significant theoretical work on carbon has been the *ab initio* pseudopotential and Linear Muffin-Tin Orbital (LMTO) band structure calculations which have been performed on various crystal structures in order to obtain their total static lattice energies and to determine the stability range of diamond.[4-6] The most recent calculations suggest that diamond will transform to the BC8 distorted tetrahedral structure at 12 Mbar, and that the next most stable phase is the simple cubic (sc).[4,5] The body-centered cubic (bcc) and close packed (fcc and hcp) phases become stable at still higher pressures.[6] The close agreement between LMTO calculations and experiments[7] on diamond shows that the theory is accurate. It is difficult to extend these calculations to nonzero temperature, so there is not yet a rigorous calculation of the complete carbon phase diagram, including the liquid.

For theoretical calculation of the phase diagram, we need Helmholtz free energy models for all phases. For this purpose we develop simple models which are carefully fitted to experimental data.

For graphite and diamond we approximate the Helmholtz free energy A as the sum of a static lattice energy E_0 and a Debye vibrational free energy A_D:

$$A = E_0 + A_D \qquad (1)$$

For E_0 we use either the Murnaghan (graphite) or the Birch-Murnaghan (diamond) equation,[8] which requires the bulk modulus and its pressure derivative at normal volume V_0. The Debye term requires values of the Debye temperature $\Theta_D(V_0)$ and the Grüneisen parameter $\gamma(V_0)$. The Grüneisen parameter is assumed to vary linearly with volume and to take the value 0.5 at infinite compression. Experimental isothermal compression, shock Hugoniot, 1 bar high temperature volume and entropy data,[9,10] and LMTO calculations[6] are used to determine the parameters in Eq. (1). The static lattice

diamond energy at zero pressure is taken to be the zero of energy. The rather small experimental enthalpy difference[10] H(graphite) - H(diamond) = -1900 J/mol at 300 K and 1 bar is added as a constant to the graphite free energy.

Since the graphite entropy data[10] have been obtained to much higher temperatures than for diamond, we take the graphite value $\Theta_D(V_0)$ = 1500 K computed from these data as fixed, and adjust slightly the diamond value until good agreement with the experimental graphite-diamond phase boundary is obtained. The theoretical and experimental phase boundaries are compared in Fig. 1.

The theory of the liquid phase of carbon is more difficult to work out because few experimental data are available. At low pressures, the liquid is thought to be a mixture of linear C_n molecules, as found in the vapor phase.[11] At high pressures, the liquid probably becomes a denser monatomic phase.[12]

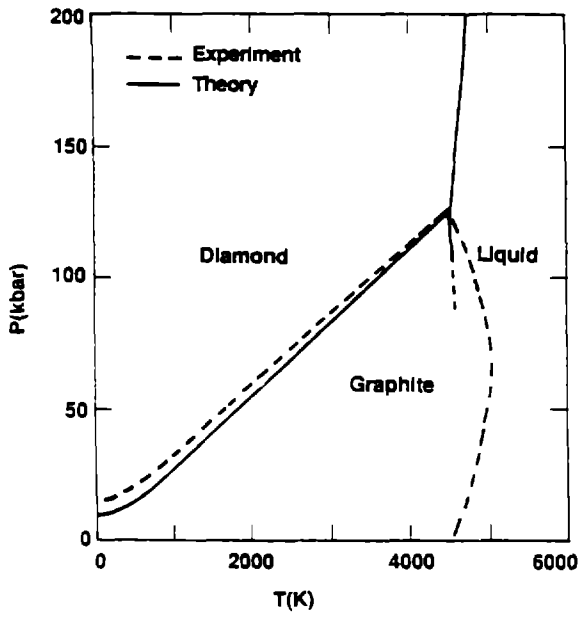

FIGURE 1
The theoretical and experimental low pressure phase diagrams of carbon.

LMTO calculations on sc, bcc, and fcc phases of carbon show that carbon is metallic in these structures.[6] Since the coordination number of monatomic liquids near melting is typically about 10, lying between bcc(8) and fcc(12), we surmise that high pressure liquid carbon is metallic, with valence Z = 4. To describe this phase, we use the simplest model available, namely the nearly free electron pseudopotential model of liquid metals.[13,14] Here the Helmholtz free energy is given by

$$A \leq A_{HS} + A_{12} + E_{eg} + E_M + E_0 + E_{BS}, \qquad (2)$$

where A_{HS} is the hard sphere free energy, A_{12} is the inverse 12th power potential soft-sphere correction to the hard sphere free energy, and E_{eg}, E_M, E_0, and E_{BS} are the electron gas, Madelung, Hartree, and band structure energies, respectively. The total Helmholtz free energy is the minimum value of the right hand side upon variation of the hard sphere diameter σ.

The electron-ion pseudopotential is chosen to be a Heine-Abarenkov square well with two parameters, the core radius r_c and the well depth w_0, which are adjusted to fit the LMTO bcc static lattice pressure. The energy difference between the liquid and diamond is then adjusted to fit the graphite-diamond-liquid triple point estimated to lie at 4500 K and 125 kbar.

There are unfortunately very few data on liquid carbon which could be used to check the theory. However, two multimegabar nuclear impedance matching Hugoniot points have recently been obtained by Livermore.[15] These shock states are so hot that they must be in the liquid, and so they are useful benchmark points for testing the liquid carbon model. The model calculations are in good agreement with experiment, and this lends weight to the validity of the liquid model.

We now use the free energies of the three phases to compute the melting curves of graphite and diamond near the triple point. These curves are shown in Fig. 1. The graphite melting curve is predicted to have a negative slope, as is observed experimentally. The conclusion of most interest is the positive slope of the diamond melting curve. This prediction is in disagreement with the argument by analogy with the negative slopes of elements Si and Ge, but it is consistent with the absence of melting at high shock temperatures found by Shaner et al.[16]

At very high pressures, diamond will transform to denser metallic phases. The phase boundary between diamond and BC8 can be estimated by fitting the parameters in Eq. (1) to the *ab initio* pseudopotential calculations for the BC8 phase.[4] The resulting theoretical very high pressure phase diagram is shown in Fig. 2.

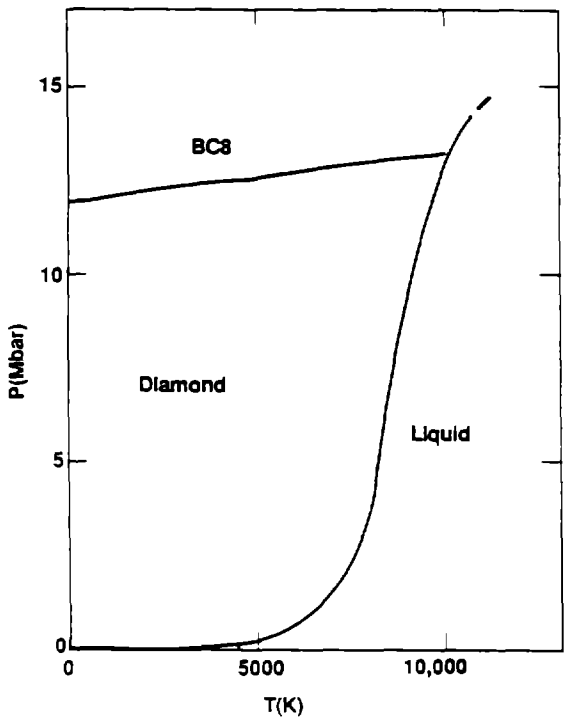

FIGURE 2
The theoretical carbon phase diagram at very high pressure.

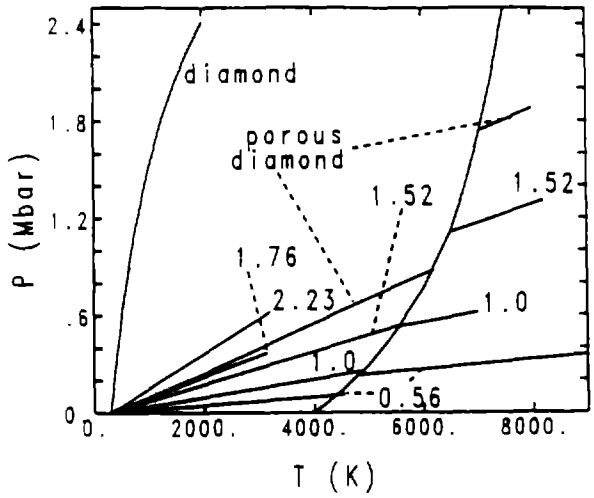

FIGURE 3
Experimental graphite and diamond Hugoniot data superimposed on the carbon phase diagram. The initial solid densities are indicated.

A large number of shock Hugoniots have been measured on graphite[17] and diamond[18] for different initial states. It is useful to compare these data with the theoretical phase diagram in order to determine in which phase the uppermost data points lie. This is done in Fig. 3. From this plot it is evident that only the most porous graphite is likely to be shocked into the liquid. A pressure-volume comparison between experiment and theory for $\rho_0 = 1.0$ is shown in Fig. 4. It is clear that the experimental data scatter is too large to allow a sensitive check of the model predictions.

The large diamond stability field predicted here has several significant implications. First, the pressure-temperature range of applicability of the diamond anvil high pressure device depends on the thermodynamic stability of diamond, and hence is expected to be very wide. Second, carbon present in the interiors of the outer planets Uranus and Neptune is at approximately 7000 K and 6 Mbar.[19] We predict this carbon to be in the solid diamond form. Likewise, any free carbon in the Earth's mantle is predicted to be solid.

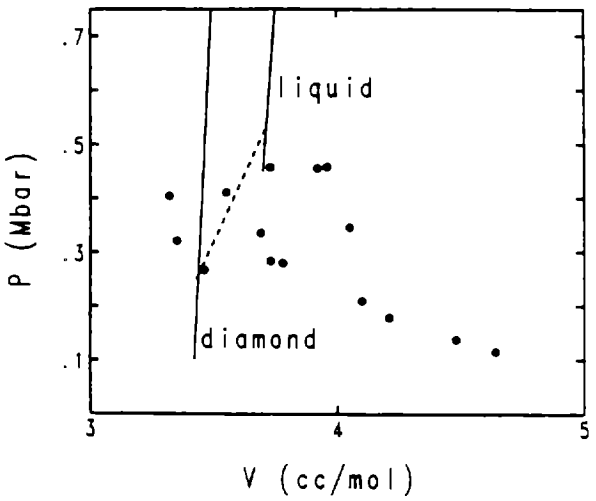

FIGURE 4
Comparison of theoretical diamond and liquid Hugoniot curves and experimental points for shocked graphite with initial density ρ_0 = 1.0.

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REFERENCES

1. F. P. Bundy, J. Geophys. Res. 85 (1980) 6930.

2. R. Grover, J. Chem. Phys. 71, (1979) 3824.

3. J. S. Gold, W. A. Bassett, M. S. Weathers, and J. M. Bird, Science 225, (1984) 921.

4. R. Biswas, R. M. Martin, R. J. Needs, and O. H. Nielsen, Phys. Rev. B 30 (1984) 3210.

5. M. T. Yin, Phys. Rev. B 30, (1984) 1773.

6. A. K. McMahan, Phys. Rev. B 30, (1984) 5835.

7. H. J. McSkimin, and P. J. Andreatch, J. Appl. Phys. 43, (1972) 2944.

8. F. Birch, J. Geophys. Res. 83, (1978) 1257.

9. P. Gustafson, Carbon 24, (1986) 169.

10. R. Hultgren, Selected Values of the Thermodynamic Properties of the Elements (American Society for Metals, Metals Park, Ohio, 1973) pp. 87-98.

11. H. R. Leider, O. H. Krikorian, and D. A. Young, Carbon 11, (1973) 555.

12. A. Ferraz and N. H. March, Phys. Chem. Liq. 8, (1979) 289.

13. M. Shimoji, Liquid Metals (Academic Press, London, 1977).

14. J. A. Moriarty, D. A. Young, and M. Ross, Phys. Rev. B 30, (1984) 578.

15. A. C. Mitchell, and W. J. Nellis, to be published.

16. J. W. Shaner, J. M. Brown, C. A. Swenson, and R. G. McQueen, J. de Physique 45, (C8) (1984) 235.

17. S. P. Marsh, (ed) LASL Shock Hugoniot Data (Univ. Calif. Press, Berkeley, 1980) pp. 28-51.

18. M. N. Pavlovskii, Fiz. Tverd. Tela 213, 893 (1971) [Sov. Phys. Solid State 213, (1971) 741].

19. M. Ross, Nature 292, (1981) 435.