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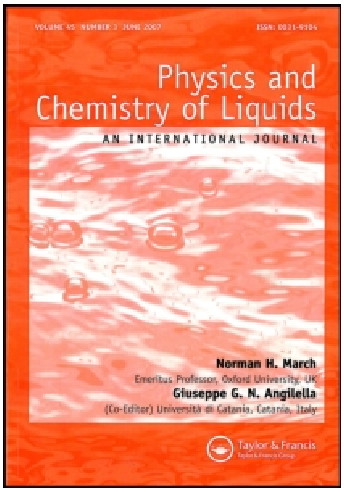

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Liquid Phase Metal-Non Metal Transition In Carbon

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Liquid Phase Metal-Non Metal Transition In Carbon

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It is proposed that the liquid phase metal-non metal transition in carbon takes place between an sp hybridized non-metallic liquid, with coordination number two, and a strongly correlated liquid metal in which directional bonding remains important though the hybridization and coordination number will probably change. Only at higher pressures is a quadrivalent liquid metal carbon to be expected, the formation of which should occur at the known maximum in the melting line of graphite. Motivated by a phenomenological argument, possible experiments to clarify the nature of these different liquid phases are proposed.

I INTRODUCTION

The known features of the phase diagram of carbon are shown in Figure 1. The considerations in this note refer primarily to the region where, above a few hundred bars, graphite melts and the experiments of Bundy,[1] and of Jones,[2] show the existence of a metal-non metal transition wholly within the liquid phase.

By way of background, we note that, on melting, the covalently bonded semiconductors silicon and germanium become good liquid metals, which Hall measurements show to have four conduction electrons per atom. Melting of these materials evidently corresponds to a transition from a semiconducting state characterized by sp^3 covalent bonding to a metallic form in which, though some residuum of directional bonding may perhaps be retained, the main characteristics are in common with the simple liquid metals.

It is also relevant in this connection to mention a third transition to a metallic phase in carbon, namely that induced in diamond at low temperatures by applying a high pressure of around 1 megabar. This transition

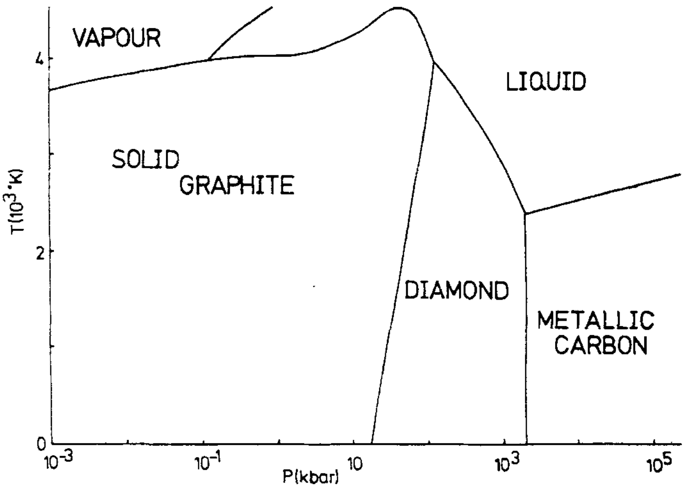

FIGURE 1 *T-p* phase diagram for carbon, as given by Bundy.[1]

from sp^3 hybridization to a good metallic conductor is in common with Si and Ge, where the low temperature transitions occur at substantially lower pressures; related to the smaller energy gaps compared with diamond.

These phase transitions have the common element that the non-metallic phase is characterized by chemical bonding. Since this chemical character, or electron localization in bonds, is a manifestation of electron correlation, it is fair to say that these three metal-non metal transitions involve electron-electron Coulomb repulsions in an essential way. Naturally, however, the two high temperature transitions, involving at least one phase which is liquid, will have to be described by a treatment which includes eventually not only Coulomb correlations but also the liquid disorder.

II NATURE OF NON-METALLIC STATE OF MOLTEN CARBON

There is evidence from quantum-mechanical calculations of Pitzer and Clementi[3] that in the vapour phase of carbon, shown in Figure 1, chains of carbon atoms will form, with sp hybridization. Experimental evidence presently available, though not decisive, appears to be consistent with these theoretical predictions.

The simplest viewpoint therefore of the nature of the liquid insulating phase above a few hundred bars is to assume the existence of a chainlike liquid structure characterized by sp hybridization and therefore a coordination number of 2. Such polymerization may lead to a liquid semiconducting phase with some properties which should be similar to liquid Se and/or liquid Te, which are known to have chainlike structures in the liquid state. A further study of the electrical transport properties beyond the pioneering work of Bundy and of Jones, which established the existence of a metal-non-metal transition wholly within the liquid phase of carbon, would seem called for, to ascertain whether there are similarities with transport in other chainlike structures.

III METAL-NON METAL TRANSITION

At first sight, it might seem that the character of the liquid metal phase involved in the metal-non metal transition, by analogy with Si and Ge, will be a simple liquid metal with 4 conduction electrons per atom. However, this does not seem to be consistent with the known features of the phase diagram of carbon, as discussed below.

Consider the maximum in the melting line of graphite, which can be seen to occur at some tens of kbars. To get the equation of the melting line, we have the Clausius–Clapeyron equation

$$\frac{\Delta S}{\Delta V} = \frac{\partial p}{\partial T} \tag{1}$$

Clearly, to obtain $\partial T/\partial p = 0$, we must have $\Delta V = 0$, and around this point we must change from $\partial T/\partial p$ positive at lower pressure to $\partial T/\partial p$ negative at pressures beyond the maximum. It would seem clear, by analogy with Si and Ge, though of course these melt from the diamond structure, that the quadrivalent liquid metal phase will be denser than graphite, i.e. $V_{\text{metal}} - V_{\text{graphite}} < 0$, whereas the liquid metal will have higher entropy than the solid semimetal. Thus, from Eq. (1), $\partial T/\partial P$ will be negative for a transition to this phase.

Since we expect $S_{\text{metal}} - S_{\text{graphite}}$ to be positive in the pressure range below the maximum in the graphite melting line, it is clear from Eq. (1) that we must have for positive $\partial T/\partial P$ that $V_{\text{metal}} - V_{\text{graphite}} > 0$, and we must expect a low coordination number and open structure in the metal.

It is, of course, well known that solid graphite can be treated as consisting of layers in which sp^2 hybrids lead to covalent bonding, the layers being held together by weak van der Waals forces. Thus, the low coordination liquid metal presumably comes about by disruption of the van der Waals bonding between the graphite planes. It would clearly be of interest to investigate whether there is an additional phase boundary in the liquid metal phase meeting the graphite line at its maximum.

IV PHENOMENOLOGICAL TREATMENT OF METAL-NON METAL TRANSITION

We shall sketch below a tentative phenomenological treatment of the liquid phase metal-non metal transition. It will turn out in this treatment to be necessary to restrict the discussion to the neighbourhood not only of the metal-non metal transition but also to the graphite melting line. The reason for this will become clear after we have discussed the choice of order parameter by which to characterize the metal-non metal first-order phase transition.

Our tentative treatment is based on the notion that one might use the experimental (reduced) band-gap Δ, to be defined precisely below, as the order parameter. Then, provided we accept that even in the presence of liquid disorder we can operationally define a band gap, it follows as a consequence of the first-order transition that Δ, the 'gap' in the density of states of the liquid semiconductor changes discontinuously across the metal-non metal phase boundary.

This situation is to be contrasted with the semimetal phase of solid graphite where the density of states has the form shown in Figure 2(a), from the work of Wallace,[4] Coulson,[5] Lomer[6] and others, since the conduction and valence bands touch at a point at which the quantity Δ defined by

$$\Delta = 1 - \frac{\text{Eval. band max}}{\text{Econd. band min}} \tag{2}$$

becomes zero, as shown in Figure 2(a).

In the corresponding density of states of the non-metallic phase of liquid carbon, there must be a finite discontinuity, since the conduction and valence bands do not overlap. The situation is depicted in Figure 2(b), with Δ greater than zero. On the other hand in the liquid metal phase, the conduction and valence bands obviously overlap with, we assume, two conduction electrons per atom, and thus the density of states has the form shown in Figure 2(c) and $\Delta < 0$.

Hence following Landau,[7] the Gibbs free energy will be expanded using Δ as the order parameter. Then for small values of Δ we can write

$$G(P, T) = G_0 + A(P, T)\Delta + B(P, T)\Delta^2 + C(P, T)\Delta^3 + \cdots \tag{3}$$

where on the melting curve of graphite $A = 0$, $B > 0$ and $C > 0$. Thus in the neighbourhood of the melting line, for a fixed value of temperature, we can write

$$A = a(P^* - P) \tag{4}$$

where P^* is the corresponding transition pressure.

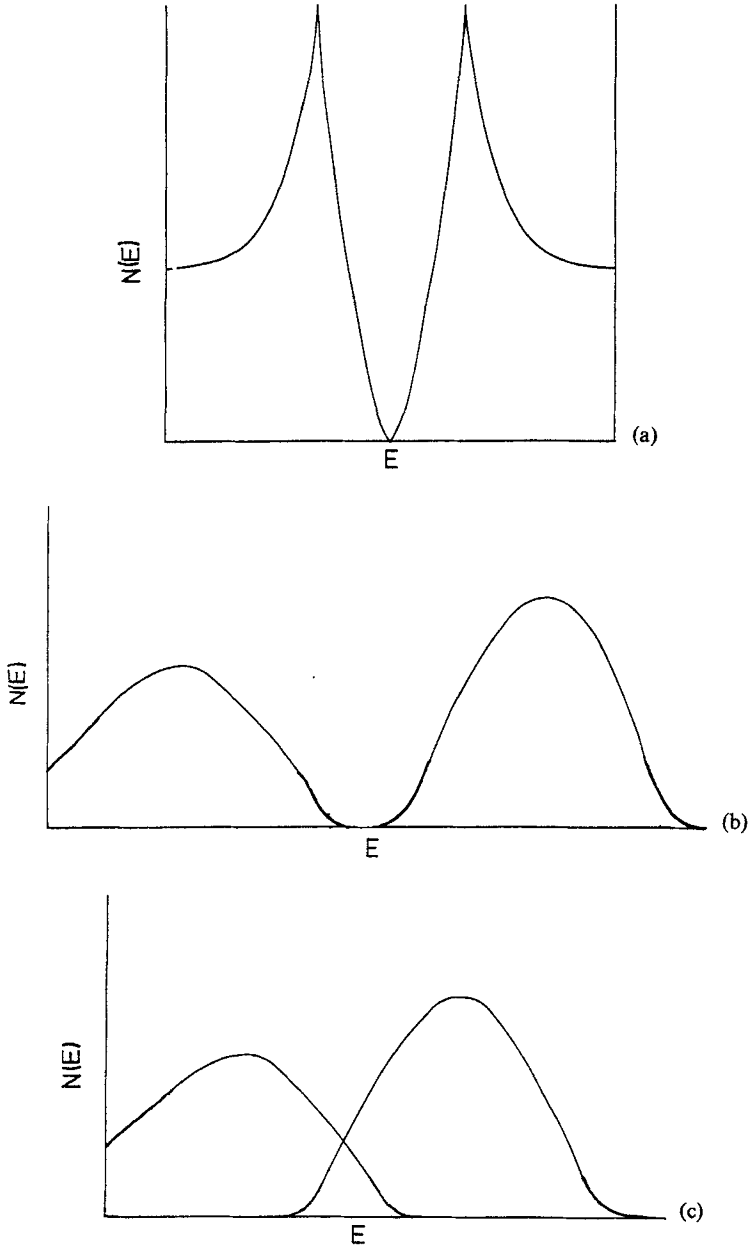

FIGURE 2 (a) Approximate form of density of states of solid graphite, with reduced band gap $\Delta = 0$. (b) Approximate form of density of states of the non-metallic liquid, with $\Delta > 0$. (c) Approximate form of the density of states of the open structure liquid metal phase, with $\Delta < 0$.

The equilibrium condition between any two phases is the equality of the Gibbs free energies, i.e. $G(\Delta) = G_0$ on the transition curve, yielding

$$\Delta(A + B\Delta + C\Delta^2) = 0 \tag{5}$$

where the solution $\Delta = 0$ corresponds to solid graphite.

For any stable state in the liquid phase of carbon, $\partial G(\Delta)/\partial\Delta = 0$ and therefore

$$A + 2B\Delta + 3C\Delta^2 = 0 \tag{6}$$

Hence in the neighbourhood of the liquid phase metal-non metal transition line, determined by the condition $B = 0$, the order parameter Δ has two possible values

$$\Delta \sim \pm\left(\frac{A}{3C}\right)^{1/2} \tag{7}$$

where C is always greater than zero.

In the non-metallic liquid, $\Delta > 0$ $(B < 0)$ since $E_{\text{cond. min}} > E_{\text{val. max}}$ and in the liquid metal $\Delta < 0$ $(B > 0)$ since $E_{\text{cond. min}} < E_{\text{val. max}}$. Thus at the point at which the liquid metal, non-metallic liquid and solid graphite coexist in equilibrium, $A = B = 0$ and $C > 0$. Then the order parameter Δ, which measures the band gap, in the neighbourhood of the triple point, in the non-metallic liquid phase is

$$\Delta \sim (P_t - P)^{1/2}, \tag{8}$$

for a fixed value T_t of the temperature. However we want to re-emphasize that the metal-non metal transition in liquid carbon is of first order. The order parameter Δ changes discontinuously across the equilibrium line and thus relation (8), though valid in the defined region, must break down at the triple point.

It would therefore be of considerable interest to study experimentally the electrical resistivity ρ in the non-metallic phase, as a function of pressure, to see whether the law (8) is validated from the band gap extracted from the resistivity ρ.

V SLOPE OF THE LIQUID PHASE METAL-NON METAL LINE

The slope of the metal-non metal line in the T–P phase diagram is quite generally determined for a first-order transition by the Clausius–Clapeyron Eq. (1) which we write as

$$\frac{dT}{dP} = \frac{V_m - V_n}{S_m - S_n} \tag{9}$$

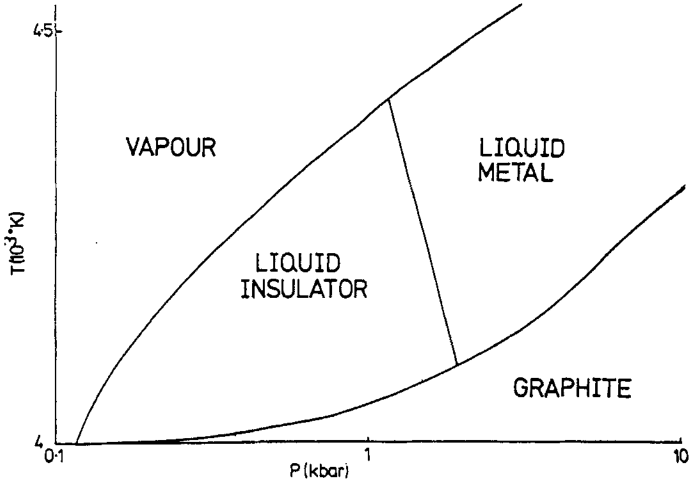

FIGURE 3 Phase transition line separating the non-metallic liquid from the liquid metal with open structure and low coordination number.

where V and S denote volume and entropy as usual, and subscripts m and n refer to metallic and non-metallic phases respectively.

The entropy of the liquid phase of carbon is

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,\Delta} \simeq S_0 - \left(\frac{\partial A}{\partial T}\right)\Delta \tag{10}$$

for small values of Δ in the neighbourhood of the transition line. Hence using Eq. (7) for such small values of the order parameter we find

$$S_m - S_n = 2\left(\frac{\partial A}{\partial T}\right)_P \left(\frac{A}{3C}\right)^{1/2} \tag{11}$$

We expect the open metallic phase to have a smaller volume than the non-metallic phase. Furthermore we expect the entropy of the metallic phase to be higher and hence dT/dP to be negative, as sketched in Figure 3.

VI PREDICTIONS OF MAGNETIC PROPERTIES

As discussed above it seems probable that the metal-non metal transition wholly within the liquid phase of carbon is associated with a change in the low coordination number of ~3 in the open liquid metal phase to a coordination number of ~2 in the non-metallic phase. The polymerization may lead to a semiconducting behaviour and hence the non-metallic liquid may exhibit paramagnetism. However if the non-metallic liquid proves to be a more insulating phase it seems likely that the π-electrons would then be more localized by Coulomb repulsion and thus the liquid may be antiferromagnetic.

It is well known that solid graphite is diamagnetic due to π-electron motion in the hexagonal rings of carbon atoms in the graphite layers. Hence we suppose that the disruption of the van der Waals forces between the graphite plane will not alter the magnetic behaviour, and thus the open structure liquid metal phase may also be diamagnetic.

VII PROPOSED EXPERIMENTS

The proposals made here raise a number of questions which it would seem important to try to answer experimentally. We recognize, of course, that the experiments involve extreme conditions of temperature and pressure and will undoubtedly push experimental techniques to the limit.

First, it would be important if it could be established that there are two liquid metal phases of carbon, one with a low coordination number and open structure with 2 conduction electrons per atom, and the other with 4 conduction electrons per atom with characteristics in common with liquids Si and Ge. Here there appears to be no substitute for electrical transport measurements of resistivity and Hall effect.

Secondly, can the structure of the non-metallic liquid be determined to establish whether it has the low coordination number ~ 2 predicted here? It is hard to see though how this could be done without diffraction experiments and these will be enormously difficult.

Thirdly, can the electrical resistivity be measured in the neighbourhood of the triple point T_t as a function of pressure in order to test the prediction that the reduced band gap Δ will vary according to Eq. (8)? According to Bundy[1] there is a possibility of verifying this by using transient heating and probing techniques on special cells in the appropriate high pressure apparatus.

Fourthly, the magnetic nature of the liquid phase would be of interest. If the π-electrons don't become localized by electron correlation the polymerization may lead to a semiconducting behaviour, and hence the non-metallic liquid may be a paramagnetic state.

VIII SUMMARY

Finally we reiterate that the phase diagram of carbon features three first-order metal-insulator transitions. The first is the low temperature phase transition to a metallic state which occurs when diamond is compressed greatly. This transition is, of course, similar to the phase transition which takes place, at lower pressures, in cold Ge and Si. The second metal-insulator transition is concerned with melting. It is suggested that the liquid phase metal-non metal transition occurs between a chainlike non-metallic liquid to a highly correlated divalent metal. It is also proposed that there may be an additional phase transition between the correlated liquid metal with low coordination number to a quadrivalent liquid metal, which has characteristics in common with both molten Ge and Si as well as molten diamond, which should take place at the known maximum on the melting line of graphite. The three metal-insulator transitions may involve electron correlation in an essential way. Though experiments are difficult, further understanding of chemical bond formation ought to be gained by such studies.

Acknowledgements

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Note added in proof

In addition to the 3 metal-non metal transitions referred to in this paper, one must expect that as one proceeds towards the liquid metal-vapour critical point, the metal stable at the highest temperature will ultimately go over to an insulating fluid, not necessarily by a first-order transition. We wish to thank Professor N. E. Cusack for this and other valuable comments.