Pressure Dependences of the Melting Temperature of Graphite and the Electrical Resistivity of Liquid Carbon

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The melting line of graphite and the electrical resistivity of liquid carbon are investigated along the melting line by a flash-heating experiment under high pressures. The melting temperature of graphite increased from 4650 K at 1.4 GPa to a maximum of 4790 K at 5.6 GPa, then decreased to 4640 K at 9.4 GPa. The electrical resistivity of liquid carbon along the melting line decreased from 900 to 600 $\mu\Omega$ cm with an increase of pressure of 1.4 to 9.4 GPa. Changes in slopes of the melting line and of the electrical resistivity at about 5.6 GPa suggest a possibility for a first-order phase transition in liquid carbon. [S0031-9007(97)04140-9]

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Since Bundy's work [1] on the carbon phase diagram in 1963, only two experimental studies on the melting line of graphite have been reported to date, namely, by Fateeva and Vereshchagin [2] and by Togaya *et al.* [3]. The common feature among these three experimental data is that the melting temperature increases with pressure to a maximum at ~5–6 GPa and then decreases with an increase in pressure toward the triple point of graphite/diamond/liquid. However, these data predict very different curvature of the melting line. Temperature differences between the maximum and the triple point of graphite/liquid/vapor are 1200 K in the data of Fateeva and Vereshchagin [2], 600 K in the case of Bundy [1], and 200 K in recent data by Togaya [3].

Rapoport [4] proposed a "two-species model" to interpret the maximum melting temperature in the p-T phase diagram in terms of a structural change in the liquid state. In this model the melting can occur either by a continuous change of structure or by a first-order phase transition, depending on the magnitude of the mixing energy of two liquids consisting of different species. Korunskaya *et al.* [5] predicted, from their thermodynamic calculation using the melting data of Bundy [1], that the critical point on the metastable equilibrium line between two kinds of liquid occurs inside the stable p-T region of graphite, and that the liquid-liquid phase transition is not realized, unless the liquid is supercooled. On the other hand, van Thiel and Ree [6] could reproduce Bundy's melting line by a model, which is based on a mixture of graphitic and diamondlike liquids whose parameters are fixed by using recent thermodynamic equation of state data for graphite and diamond. They predicted that constraints on the strain energy of mixing two kinds of liquid clusters can allow a liquid-liquid phase transition. With respect to the structure of liquid carbon, Galli *et al.* [7] indicated, by their first-principle molecular-dynamics simulations using the Car-Parrinello method, that the liquid at low pressure is composed of two-, three-, and fourfold coordinated atoms. Also Morris *et al.* [8] suggested, in their simulation by the "tight-binding molecular-dynamics" method, that low-density liquid is dominated by two- and threefold coordinated atoms and that the coordination changes continuously to high-density liquid with considerable tetrahedral diamondlike bonding with increase in pressure. However, they could not detect a phase transition in the liquid phase at temperatures above 6000 K.

So far there is no direct measurement on the structure of the liquid carbon to experimentally resolve this issue. Namely, it is difficult to verify the presence or absence of the liquid-liquid phase transition from the melting data of graphite obtained by Bundy [1] and Fateeva and Vereshchagin [2], as their data contain large experimental uncertainties. A possible discontinuous change in the electrical resistivity of the liquid is also difficult to detect from the resistance data of Bundy.

It is worthwhile to mention that phase changes in the liquid state have been reported for sulfur [9] and other substances (e.g., Bi, Ga, Se, I_2, etc.) [10–12], without concrete connection to the maximum of the melting line of the corresponding solid phases.

The purpose of this Letter is to report (i) an accurate analysis of the melting line of graphite obtained previously by us [3] and (ii) measurements of the electrical resistivity of liquid carbon along the melting line. These data are next used to test the possibility of a first-order phase transition in liquid carbon.

We used rods of spectroscopic graphite with high purity as specimens and melted them directly using a method of flash heating by discharging current from a bank of capacitors in a 6-8 anvil-type high pressure apparatus. The current was measured across a 10 mΩ shunt and the voltage across the graphite rod was recorded with two channel digital memory. These data were used to calculate the inserted energy (integration of heating power) and the resistance. The experiments were carried out at six points of pressure from 1.4 to 9.4 GPa. Other experimental details are described elsewhere [3].

Figure 1 shows three typical plots of resistance vs inserted energy at 2.5, 5.6, and 9.4 GPa. These data were obtained using the capacitor voltage of 120 V and

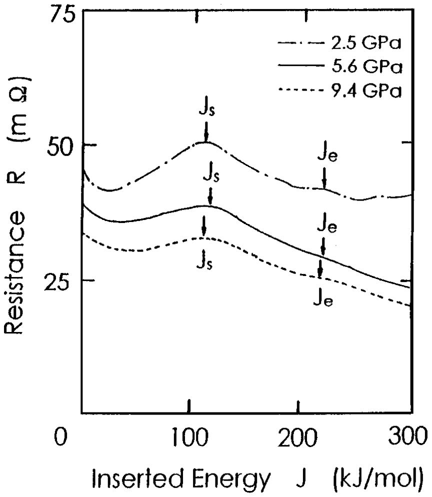

FIG. 1. Resistance vs inserted energy at the pressures of 2.5, 5.6, and 9.4 GPa. The graphite rod starts to melt at J_s, while J_e represents the energy when the entire graphite rod melts. The energy difference $J_e - J_s$ corresponds to the fusion enthalpy of graphite.

the wall material of pyrophyllite. The maximum J_s in the resistance curve signals the start of fusion and the shoulder J_e represents the end of fusion, at which the entire graphite rod completely melted. These assignments were based on the optical microscope observations of texture of samples which were quenched at different inserted energies and recovered at room pressure. The inserted energy J_s at the start of fusion is related to the melting enthalpy and, after correcting for the heat loss, the enthalpy was converted to the temperature by applying the enthalpy vs temperature relation derived by Sheindlin and Senchenko [13] near the melting point at 0.1 GPa. It is assumed that the temperature dependence of enthalpy is insensitive to pressure and that the sample, as it is heated rapidly, is under an isobaric condition without an increase in thermal pressure.

Table I summarizes the melting enthalpy and the melting temperature of graphite obtained in this work. As shown in Fig. 2, the melting temperature tends to increase from 4650 K at 1.4 GPa to a maximum of 4790 K at 5.6 GPa, then decreases to 4640 K at 9.4 GPa. In the strict sense, it is difficult to verify the presence of a discontinuous change in the slope of the melting line around 5.6 GPa, although such a proof will provide an indirect evidence for a first-order phase transition in the liquid carbon. This is so because we cannot continuously measure the melting temperature by increasing the pressure in the present experiments. However, our discrete measurements on the melting temperature at different pressures show that the melting temperature increases with pressure up to 5.6 GPa with a slope of 33.4 K/GPa, then decreases to 9.4 GPa with a slope of −38.7 K/GPa, and that the melting line can be best described if its slope has a discontinuity at about 5.6 GPa.

TABLE I. Melting enthalpy (ΔH_m) and melting temperature (T_m) of graphite vs pressure (P). Conversion of the enthalpy to the melting temperature was made using the enthalpy—temperature relation obtained by Sheindlin and Senchenko [13]. If the data from JANAF were used, the temperatures need to be revised upward by 100 K at 4600 K and 140 K at 4800 K.

P (GPa)	ΔH_m (kJ/mol)	T_m (K)
1.4	110.4 ± 1.1	4651 ± 36
2.5	111.2 ± 1.5	4678 ± 46
4.0	113.4 ± 0.6	4747 ± 20
5.6	114.9 ± 1.4	4786 ± 38
7.4	111.5 ± 0.8	4686 ± 25
9.4	110.0 ± 1.3	4640 ± 39

The difference of inserted energy $J_e - J_s$ between the start and the end of fusion represents the fusion enthalpy (latent heat) of graphite. The fusion enthalpy decreases slowly and linearly with pressure and shows no discontinuous change within experimental uncertainty of ±5 kJ/mol [14]. This is not inconsistent with the possibility of a liquid-liquid phase transition, since the enthalpy difference between two liquid phases is similar to the corresponding difference in the enthalpy of solid phases. The latter is likely very small compared to the fusion enthalpy of graphite.

The volume change in the possible liquid-liquid phase transition is estimated to be about 1.5 cm^3/mol from the above two slopes of the melting line and the fusion enthalpy of about 100 kJ/mol at 5.6 GPa [14]. This value is slightly less than 1.97 cm^3/mol predicted theoretically by van Thiel and Ree [6]. In this regard, one way to obtain a direct evidence of the liquid-liquid transition is to measure the volume change of liquid phase, near the melting line around 5.6 GPa, since the volume change at

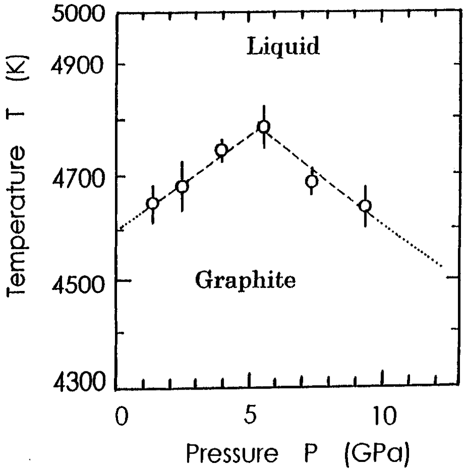

FIG. 2. Melting temperature of graphite vs pressure. The dashed line shows a possible melting line. The melting line is represented by the least squares fit, by a line with a slope of 33.4 K/GPa below 5.6 GPa, and another line with that of −38.7 K/GPa above 5.6 GPa.

the liquid-liquid transition is predicted to be more than 10% of the volume of liquid carbon, and, if so, it would be easily detected.

Figure 3 shows the change in electrical resistivity of liquid carbon with pressure along the melting line of graphite. The resistivity data were obtained from values of resistance at the end of fusion shown in Fig. 1, by assuming a constant ratio of cross-sectional area to length in the sample. The resistivity data are almost the same for three different kinds of wall materials: pyrophyllite, MgO, and *h*-BN. This fact shows that there is little contamination between the wall materials and the molten carbon during the fusion. Although the exact cause of the temperature dependence is still unknown, Fig. 1 shows that the resistance (hence, resistivity) depends very weakly on the inserted energy (hence, temperature). In comparison, there is a much more pronounced dependence of resistivity on pressure as shown in Fig. 3.

The resistivity of liquid carbon decreases with pressure from 900 $\mu\Omega$ cm at 1.4 GPa to 600 $\mu\Omega$ cm at 9.4 GPa, except at 4 and 5.6 GPa, where the resistivity data are approximately equal. This minor irregularity suggests to signal a phase transition between a liquid phase below 4 GPa and another liquid phase with higher resistivity above 5.6 GPa. The irregularity of the resistivity curve may result from a change in the electrical state accompanied by the structural phase transition in the liquid carbon, i.e., a discontinuous slope of the melting line at about 5.6 GPa, as discussed earlier.

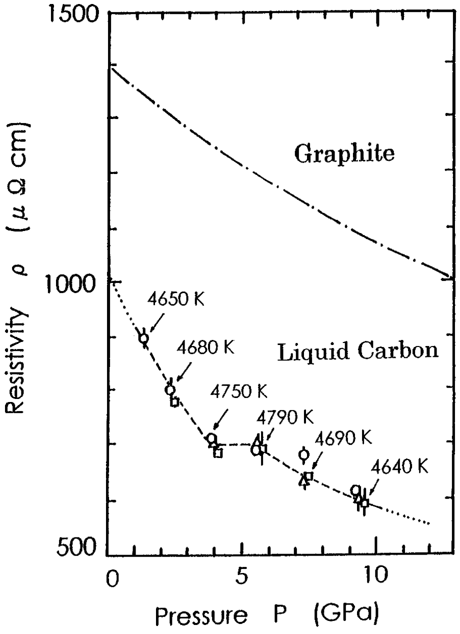

FIG. 3. Changes in the electrical resistivity of liquid carbon with pressure along the melting line of graphite. The wall materials to enclose the graphite rod are pyrophyllite (triangle), *h*-BN (circle), and MgO (square). Dashed line is a guide to the eye. The upper long dash-dotted line shows the pressure dependence of the resistivity of graphite at room temperature. Within the pressure range shown the temperature is nearly constant (about 4800 K) and the observed behavior is qualitatively similar (except for the aforementioned transition region) to that of graphite under isothermal room-temperature conditions shown.

Our resistivity data agree with other experimental data, i.e., 1000 $\mu\Omega$ cm at 0.4 GPa, and 625 $\mu\Omega$ cm at 30 GPa, obtained by Shaner [15] and Reitze *et al.* [16], respectively. The resistivity of liquid carbon is about ten times higher than those of other Column IV liquid metals (e.g., $\sim$80 $\mu\Omega$ cm for Si [17] and $\sim$75 $\mu\Omega$ cm for Ge [18]). Its magnitude is similar to those found in a poorly conducting metal [19]. Liquid carbon may be in a "resistively saturated" state [19] with mean free path comparable to the nearest neighbor atomic distance, as shown by Reitze *et al.* [16]. On the other hand, the resistivity of 150 $\mu\Omega$ cm evaluated by Bundy [1] is much lower than our data, and Heremans's value of 30–70 $\mu\Omega$ cm [20] is too low, although they are consistent with the simulation results by Galli *et al.* [7] and Dharma-wardana and Perrot [21] under the local density approximation. It should be mentioned that the exact origin of the resistivity of liquid carbon will require a further study.

The higher resistivity of liquid carbon may arise from the facts that its structure basically exhibits covalent character such as two-, three-, and fourfold bonding [7] and that three of the four valence electrons of carbon are involved in covalent bonding and the conduction electron tends to be strongly localized [16]. Hence, it is very different from liquid Si and Ge which are quadrivalent metals and have an average coordination number exceeding 6 within the high pressure metallic phases [22]. It suggests that liquids with covalent bond character may be responsible for the liquid-liquid immiscibility.

One can give a qualitative explanation on the resistivity drop with pressure. The use of the "nearly free electron" model and the resistively saturated state provide an expression for the resistivity $\rho \propto a/g^2$ ($a =$ average nearest neighbor distance, $g =$ the ratio of density of state $N(E_f)$ to that of free electron $N(E_f)_{\mathrm{free}}$ at Fermi level, and $g = 1$ for a free electron) [19]. The change of resistivity of liquid carbon with distance a is very small, i.e., about a 3% decrease with the increase of pressure to 4 GPa, based on the compressibility of graphite. Therefore, the resistivity drop of 30% in Fig. 3 is due mainly to an increase of the g factor. This suggests that the pressure affects the resistivity by reducing the electron localization and populating the density of state near Fermi level, namely, the number of free electrons per atom, produced by the breaking of covalent bonding. In this sense the irregularity of resistivity curve around 5.6 GPa may arise from reformation of the covalent bonding by the structural transition.

In summary, we have obtained the melting line of graphite and the electrical resistivity of liquid carbon along the melting line by performing flash-heating experiments of graphite at high pressures. The melting temperature of graphite increased from 4650 K at 1.4 GPa to a maximum of 4790 K at 5.6 GPa, then decreased to 4640 K at 9.4 GPa. The electrical resistivity of liquid carbon along the melting line decreased from 900 $\mu\Omega$ cm at 1.4 GPa to 600 $\mu\Omega$ cm at 9.4 GPa. The slope of the melting line apparently changes discontinuously at about 5.6 GPa, where the electrical resistivity curve also exhibits a small irregular behavior. These results are consistent with a possibility for a first-order phase transition in liquid carbon. In this regard, a more direct experiment to detect the structural change in liquid carbon is difficult to perform, but will be extremely useful.

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