Electrical Property Changes of Liquid Carbon under High Pressures

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Abstract. The homogeneous formation of liquid carbon without the partial melting of carbon specimen is very important to evaluate the physical properties of liquid carbon. The pyrolytic graphite was melted by the direct joule heating with current passed through the specimen along the direction parallel to c-plane. The resistivity of the liquid carbon at the melting point decreases from 630 to 470 $\mu\Omega\text{cm}$ with increase of pressure of 1.4 to 4.0 GPa and then increases 490 to 565 $\mu\Omega\text{cm}$ with increase of 5.6 to 9.4 GPa. The magnitude of resistivity of the liquid carbon at the melting point within this experiment indicates that the liquid carbon is a “poorly conductive metal”. On the other hand the resistivity of liquid carbon tends to change from metal like behaviour (the temperature coefficient of resistivity $d\rho/dT>0$) to non-metal (or semiconductor) like one ($d\rho/dT<0$) at the pressure of around 4 GPa-5.6 GPa. These results are considered to fortify our previous conclusion about the existence of the structural transformation of carbon in the liquid state [1].

1. Introduction
The carbon (mainly graphite) is very important material used under the extreme environments, but the physical properties under high temperatures and high pressures are still remained in the controversial issues, for example, on the melting line of graphite, two triple points temperatures-pressures of graphite/vapor/liquid and graphite/diamond/liquid, the latent heat of graphite in fusion, the electrical resistivity and the temperature coefficient of resistivity in the liquid carbon and so on. The discrepancies among the experimental results are due to the difficulties of the experimental techniques in the extremely high temperature region under high pressures as well as the difference of experimental conditions, such as the kinds of carbon specimen used, the methods and the rates of heating [2].

For the electrical property of liquid carbon, it has been reported that the electrical resistance of liquid is lower than that of graphite, indicating a metallic liquid, over the pressure range of 0.9 to 12 GPa [3] and also by contrast that the liquid carbon is non-metal (insulator?) in the range of 10 to 30 MPa [4], because of vast increase of resistance on the melting. In order to confirm the metal and non-metal characters, however, it is necessary to investigate (1) the magnitude of resistivity and (2) the temperature dependence of resistivity for the homogeneous liquid carbon formed.

The large variation of the magnitude of resistivity with the kinds of graphite from pyrolytic grade to polycrystalline one is due to the anisotropic electrical property of graphite that the resistivity along the direction vertical to c-plane ($\rho_c$) is above 1000 times (up to about 4000 times) as high as that
parallel to c-plane ($\alpha$). The resistivity of graphite with lower resistivity (ex. pyrolytic graphite in //c-plane) increases by the melting. In the case of graphite with higher resistivity (ex. polycrystalline graphite, glassy carbon and pyrolytic graphite vertical to c-plane) the resistivity decreases by the melting [5]. In this experiment of melting using the direct current heating of specimen, the homogeneous melting with no partial superheating of liquid carbon is easy to be realized in the specimen of pyrolytic graphite with lower resistivity ($\alpha$, //c-plane) than that of liquid carbon, because the current tend easily to pass through the c-plane of the graphite with lower resistivity, the supplied joule energy promotes effectively to transform the solid graphite to the liquid with higher resistivity. The homogenous liquid formed like this is expected to enable the precise evaluation of resistivity of liquid carbon.

The purpose of this paper is to investigate the changes of electrical property of liquid carbon with pressure and discuss the experimental results in connection with the structural changes in the liquid phase.

2. Experimental
The graphite was melted by using the flash-heating technique under high pressures (from 1.4 GPa to 9.4 GPa) generated using the Kawai-type high pressure apparatus. The specimen used in this experiment is a pyrolytic graphite (Pyroid from Pfizer Co. Ltd., density: 2.22g/cm$^3$, impurities: ash<10ppm and metal <5ppm). The specimen is shaped in a rectangular solid with 0.545 x 0.545 x 4.863 mm (long axis //c-plane). The heating current was passed through the basal plane (//c-plane) of pyrolytic graphite by discharging the bank of capacitor ($C=96mF$, $V=110V$). The resistivity $\rho$ (or resistance $R$) and the supplied energy $J$ were obtained from the voltage drop $V$ measured by four probe method and the circuit current $I$. The experimental details and the sample assemblages are described elsewhere [6].

3. Results and Discussions

3.1. Curves of resistivity vs. supplied energy at high pressures
Figure 1 shows the curves of resistivity vs. supplied energy at pressures of 1.4GPa to 9.4GPa. The resistivity is obtained assuming that the ratio of cross sectional area to the length between two voltage probes at room temperature and pressure is kept constant under high temperatures and high pressures. As shown in Fig. 1, first the resistivity of graphite ($\rho_a$) increases with increase of supplied energy (in relation to increase of temperature) and the graphite reaches the melting point at $J_s$. Second the melting starts showing an irregular behavior on the resistivity curve and the resistivity further increases with growing the molten region. Third the heating energy equivalent to the fusion enthalpy of graphite is supplied and the melting of graphite is accomplished at $J_e$. Within this experimental pressure region the resistivity of liquid carbon ($\rho_l$) is always larger than that of graphite along the direction //c-plane ($\rho_a$). The resistivity curves of liquid carbon, after the end of melting at $J_e$, show the different behaviors depending on the pressures. Above 5.6GPa the resistivity decreases clearly with increase of supplied energy and the decreasing rate of resistivity becomes large with increase of pressure. This result suggests that the temperature coefficient of resistivity (TCR) tends to be negative ($d\rho_l/dT<0$) and the liquid carbon has a non-metal like character in contrast to the graphite $\alpha$-plane with a metallic character showing the positive TCR ($d\rho_a/dT>0$). On the other hand at 4.0GPa the decrease of resistivity of liquid carbon is very small and at 2.5GPa the resistivity increases after an interval showing nearly the constant resistivity. In the case of 1.4GPa the resistivity of liquid carbon indicates large increase following the increase by the transformation process of graphite to liquid carbon. Therefore the point of the end of melting on the curve of resistivity is not clear so much. In contrast to the behavior of resistivity above 5.6GPa, it is said that rather below 2.5GPa the resistivity tends to increase with increase of supplied energy and the curve for 4.0GPa showing a slight decrease is in an intermediate state.
3.2. Pressure dependence of the resistivity of liquid carbon at the melting point and the change of resistivity after the melting

Figure 2 shows the pressure dependence of the resistivity of liquid carbon at each melting point (shown open square □). The resistivity decreases with increase of pressure up to 4.0GPa, but above 5.6GPa the change of resistivity falls into the increase.

On first viewing these pressure dependence of resistivity might be considered to reflect the temperature dependence on the melting line [1], in which the melting temperature increases up to 5.6GPa and then decreases with increase of pressure, if it is assumed that the liquid carbon has a semiconducting property and the electrical property is unchanged with pressure. However, this point of view has to be rejected, because the TCR of liquid carbon behaves in the different manner at the pressures of above and below 5.6GPa, as shown in Fig. 1. In order to describe the features of electrical property of liquid carbon in Fig. 2, the resistivity at the supplied energy of $J = 300\text{kJ/mol}$, which is much larger than $J_c$ at each pressure, is shown by two kinds of open circles (○, ○). In the cases above 5.6GPa the resistivity of liquid carbon decreases with the addition of supplied energy to 300kJ/mol after the end of melting ($J_e$) and shows remarkably the property of negative TCR. On the other hand at the pressure of 4.0GPa and 2.5GPa the resistivity of liquid carbon at 300kJ/mol is almost the same as that at the melting point, though the TCR is very small negative and positive sign respectively. At 1.4GPa the resistivity of liquid carbon increase largely with increase of supplied energy and shows the large positive TCR. These drastic changes in the pressure and temperature dependence of resistivity of the liquid carbon suggest strongly the possibility of the structural transformation in the liquid state at
about 5.6GPa, in the same manner as the drastic change of melting line which yields the primary evidence for the proposal of existence of liquid-liquid phase transformation (LLPT) in our previous work.

![Graph showing pressure dependence of the resistivity of liquid carbon](image)

**Figure 2.** Pressure dependence of the resistivity of liquid carbon at the supplied energy \( J = J_e \) for the end of melting and the resistivity at the supplied energy of \( J = 300 \text{kJ/mol} \) \((J_e < 300\text{kJ/mol})\).

3.3. On the metal and non-metal like behaviors of liquid carbon

3.3.1. Magnitude of resistivity of liquid carbon

In this experiment the resistivity of liquid carbon exists roughly in between 470 and 630 \( \mu\Omega \text{cm} \) in the pressure region of 1.4GPa to 9.4GPa, as shown in Fig.2. These magnitude of resistivity of liquid carbon are consistent with those magnitudes of resistivity obtained from the recent many experiments, for example, 625\( \mu\Omega \text{cm} \) at 30GPa [7], 700-730\( \mu\Omega \text{cm} \) at 1-2GPa [8]. On the other hand the value of 150\( \mu\Omega \text{cm} \) at 10GPa, obtained by Bundy [9], is much lower than the resistivity of above recent experiments. The resistivity of 30\( \mu\Omega \text{cm} \) by Heremans [10] is too much low. The former has a problem in the estimation of lead resistance which is necessary to be corrected in the electrical resistance measurement by two probe method. The latter has to be investigated about a possibility of creeping discharge under the high voltage discharging pulse heating method. The magnitudes of resistivity of liquid metal are of about 20 ~ 30 \( \mu\Omega \text{cm} \) for alkali metals, Cu and Al [11]. The resistivity of liquid transition metals such as Fe, Ni, Co show the value of 80 to 140 \( \mu\Omega \text{cm} \) [12]. On the other hand the liquids of divalent metals such as Eu and Ba yield the values of resistivity of 250\( \mu\Omega \text{cm} \) and 320\( \mu\Omega \text{cm} \) respectively [13]. The resistivity of liquid carbon is much higher than those of the liquid metals mentioned above and it would be said that the liquid carbon is a “poorly conductive metal”.

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3.3.2. Temperature coefficient of resistivity of liquid carbon

Usually the metal or non-metal like electrical property has been discriminated by the sign of (TCR, \(d\rho/dT\)). As shown in Fig.1, in the pressure region below 2.5GPa the resistivity of liquid carbon (after the point of \(J_e\)) increases with increase of supplied energy (temperature), namely \(d\rho/dT>0\), and at pressure of above 5.6GPa the liquid carbon shows remarkably the negative TCR (\(d\rho/dT<0\)). The former is called as a metal like liquid in the analogy to the normal liquid metals with the positive TCR and the latter is called as a non-metal like liquid.

On the other hand many liquid metals and alloys exhibit a constant (Mg, Ca and Cd etc.) or negative TCR (Ba, Eu and Yb etc.) [13] over a wide range of temperature in contrast to the positive TCR of normal metals. The temperature dependence of resistivity of liquid metals is related to that of the structure factor \(a(K)\) and a positive, null and negative TCR is predicted according the position of the Fermi energy with respect to the first peak of \(a(K)\) [14, 15]. Therefore the TCR of liquid carbon changes with pressure from positive value to negative one and this change suggests that it is possible to be associated with the structural transformation of liquid carbon at the pressure region around 4.0GPa – 5.6GPa.

4. Summary

These experimental results are summarized as follows:

(1) The resistivity of the liquid carbon at the melting point decreases from 630 to 470 \(\mu\Omega\)cm with increase of pressure of 1.4GPa to 4.0GPa and then increases from 490 to 560 \(\mu\Omega\)cm with increase of pressure of 5.6GPa to 9.4GPa.

(2) The liquid carbon at the melting point yielded the value of resistivity of 470 \(\mu\Omega\)cm to 630 \(\mu\Omega\)cm within this experimental pressure region. The magnitude of resistivity is larger than those of metals with large resistivity (Ba, Eu etc.) and is a “poorly conductive metal”.

(3) The resistivity of liquid carbon tends to change from metal like behaviour (the temperature coefficient of resistivity, TCR, \(d\rho/dT>0\)) to non-metal (or semiconductor) like one (\(d\rho/dT<0\)) at the pressure of around 4GPa-5.6GPa. This is an important result, because the temperature dependence of resistivity is related to that of the structure factor \(a(K)\) of liquid.

(4) Above results in the pressure and temperature dependences of resistivity of liquid carbon fortifies the existence of a structural transformation in the liquid carbon, namely LLPT, which was concluded from the analysis of the melting curve of graphite.

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