

The temperature dependence of the structure of amorphous carbon

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Neutron diffraction measurements were performed on amorphous carbon in order to investigate for the reason the anomalous electrical conduction. A change of the atomic structure at a function of temperature was determined. Using an arc vaporization method 1.0 g pure amorphous C sample was prepared at Gifu University, Japan. The experiment was carried out at the 7C2 spectrometer installed on the hot source of the reactor Orphee at Saclay. The momentum transfer range of 0.5 to 16 Å⁻¹ was covered. The derived S(Q) exhibits a small difference due to the variation of the temperature. The radial distribution functions were also derived from these spectra. Finally, we present a possible explanation of the unexpected variation of d.c. conductivity at low temperature.

1. INTRODUCTION

The ability of carbon atoms to have fourfold, threefold and twofold coordination leads not only to the diamond, graphite and C₆₀ forms, but also to a large number of variations in structure and electronic properties as a function of preparation techniques. The review by Robertson gives an excellent summary about the properties of various types of amorphous carbon [1].

Recently, the temperature dependence of the conductivity has been studied in amorphous carbon films [2-4]. An unconventional temperature dependence of conductivity has been observed in graphite-vaporized films [4]. Between 30 K and 115 K nearly two orders of magnitude variation of the d.c. conductivity has been measured as shown in Fig. 1. The first step towards understanding this unexpected electronic property is to investigate the structure of this type of a-C.

Neutron diffraction was employed in order to (a) determine the short range order of the atomic structure,

(b) identify (if exists) C₆₀ type fragment inside the sample causing superconductivity,

(c) decide whether the structure has a temperature dependence or not.

The structure of sputtered a-C was measured recently by neutron diffraction [5]. The sample had a disordered graphite structure. It's radial

distribution function has no peak at 2.84 Å, the cross-ring distance, indicating a disordering of the ring structure. Another neutron diffraction experiment [6] found that the structure of a-C prepared by plasma-arc deposition is similar to a-Si and a-Ge. The former sample was graphitic-type while the latter had a diamond-type structure. There are two computer simulations of a-C structure obtained by the molecular-dynamics method [7,8].

2. MEASUREMENT

The 1 gram amorphous carbon sample was prepared by arc-evaporation of graphite rod under a pressure of 10⁻⁶ atm. Two 99.99 % pure graphite rods having diameter of 1.9 mm and 5 mm were contacted to each other. Thin film of carbon were prepared on Corning 7059 glass substrate. The deposition rate was about 100 Å/s.

The diffraction measurement were performed at the 7C2 spectrometer installed on the hot source of the reactor Orphee at Saclay. A 640-cell position sensitive detector provides the whole spectrum covering a 128° angle with resolution of 0.2° in a single measurement. In order to minimize the background the amorphous carbon sample was placed in a vanadium container. Using an incident wavelength of $\lambda = 0.7035$ Å, the momentum transfer range of 0.5 to 16 Å⁻¹ was covered [9].

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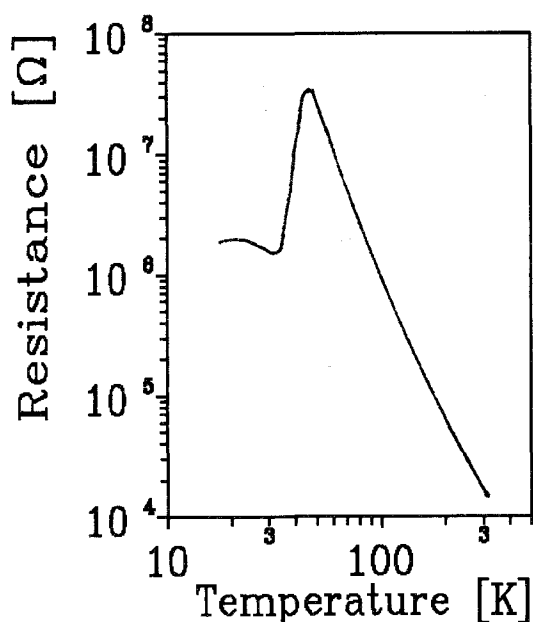


Figure 1. The unexpected temperature dependence of resistance in an a-C sample [3].

About 2 % of hydrogen content was estimated from the neutron scattering data. For the data reduction we used $\rho_0 = 0.1 \text{ at}/\text{\AA}^3$ as the best fitted bulk density which is lower than the density of diamond ($\rho = 0.17 \text{ at}/\text{\AA}^3$) or graphite ($\rho = 0.11 \text{ at}/\text{\AA}^3$).

Figure 2 shows the experimental $S(Q)$ at room temperature. The analysis of the diffraction data shows that the structure factor is similar to the $S(Q)$ of a previous measurement [5]. The only difference seems to be at low Q , which corresponds to differences in the medium range order. A new tight-binding molecular dynamics simulation produces a very similar $S(Q)$ to our measured structure factor [8] even at low Q .

The first four nearest-neighbour distances are 1.42 Å, 2.46 Å, 2.84 Å and 3.64 Å in a perfect graphite crystal. In the measured pair-correlation function (see Figure 3) the position of the first four main peaks are 1.42 Å, 2.46 Å, 2.83 Å (third-neighbour cross-ring distance) and 3.73 Å.

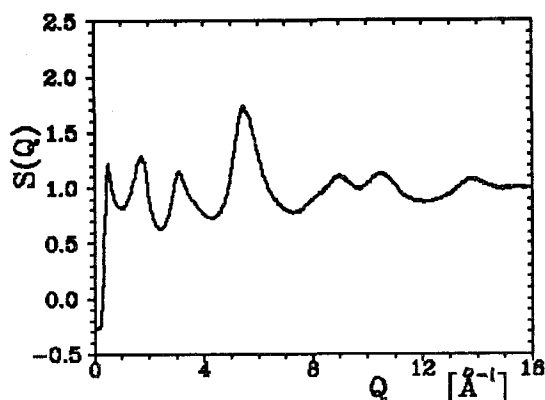


Figure 2. The structure factor of a-C. The $S(Q)$'s measured at different temperatures were nearly identical, so are not shown separately.

It appears that the sample contains a high proportion of threefold coordinated carbon atoms, i.e. it is typically graphite-like material. The nearest neighbour bond length of 1.42 Å is consistent with mainly sp^2 bonding. $g(r)$ has no appreciable medium range order. Beyond 6 Å the absence of atomic structure can be found. There is no typical peak belonging to C_{60} fragments having about a diameter of 7 Å in the measured spectrum. The absence of fullerene clusters means that the reason of unexpected conductivity at low temperature is independent from the well-known superconductivity of C_{60} .

The first coordination number is 2.7, the second neighbour shell around 2.43 Å contains 6.2 atoms, while the third neighbour shell around 2.83 Å has 3.5 atoms. The first coordination number is lower than 3. This number is not so accurate because of the limited Q value at the neutron diffraction measurement but it suggests that the sample should contain twofold coordinated carbon atoms. Similar conclusion was obtained by tight-binding molecular dynamics simulation having very similar $S(Q)$ [8].

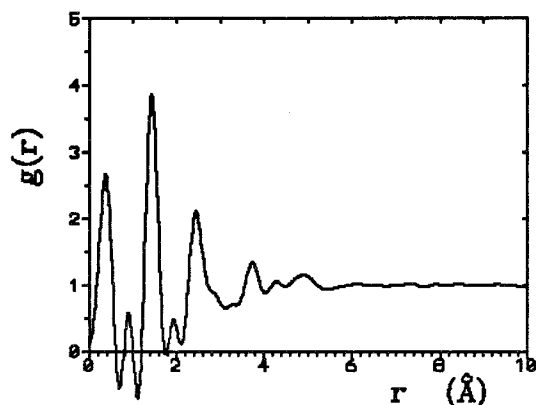


Figure 3. Measured $g(r)$ of a-C obtained by a Fourier transformation procedure of $S(Q)$ measured at room temperature.

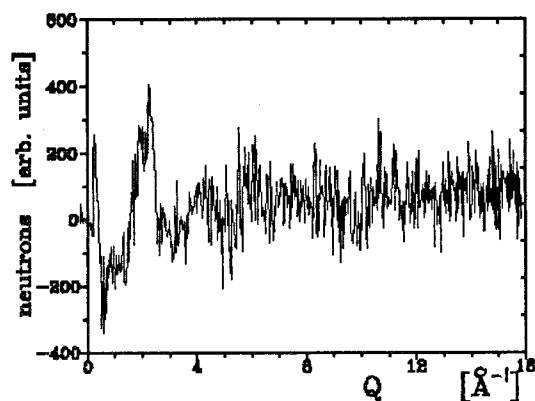


Figure 4. The difference of measured neutron intensities as a function of Q . The measurements were carried out at 30 K and at 55 K temperature.

3. TEMPERATURE DEPENDENCE OF THE STRUCTURE OF a-C

A series of measurements in a cryostat was carried out at different temperatures. The temperature scan permitted neutron diffraction at 55 K, 30 K, 20 K and room temperature.

There were small but significant differences of $S(Q)$ at 2 \AA^{-1} at the different temperatures over 30 K. The spectrum of Fig. 4 displays the difference of neutron intensities as a function of Q measured at 30 K and at 55 K before making any kind of data correction. To decide whether the peak around 2 \AA^{-1} is an artifact due to the given conditions or not, 2 months later we repeated the measurement at 25 K, 150 K and room temperature. In this second case we increased the temperature. The result was the same. The second temperature scan confirmed that there is a small change of the a-C structure on varying the temperature. On increasing the temperature the coordination number of the first neighbour shell became a little larger. Between 20 K and 30 K or 150 K and room temperature we could not find any difference.

Our second control of the result was the following. We put another type of amorphous carbon sample into a similar vanadium container and we repeated the neutron diffraction measurement at 25 K, 150 K and room temperature. The result was very different. There was no remarkable difference among the neutron intensities.

On the basis of these results we conclude that in the temperature range from 30 K to 150 K the local order of amorphous structure should change. The effect is small, significant and repeatable. The reason might be the following. Increasing the temperature few carbon atoms produce $sp^2 \rightarrow sp^3$ or even $sp \rightarrow sp^2$ transitions which cause an increase of average coordination number.

4. ELECTRONIC PROPERTY

We consider that the change of the coordination number is due to breaking up of some carbon-carbon bonds. With decreasing temperature in the range from 30 K to 115 K a transition from low to high conducting states is observed [4].

Let us consider a simple model of conductivity

$$\sigma \sim N(E_F),$$

where σ is the conductivity and $N(E_F)$ is the density of states at the Fermi level. As it was shown previously there are topologically determined electronic states around the Fermi energy and thus they influence considerably the conductivity [10,11]. In the structure of amorphous carbon the existence of atomic sites causing topologically determined electronic states at Fermi energy can be verified very easily if the arrangement of the π -electron network of carbon atoms is known [11,12]. Increasing the coordination number of such an atomic site an electronic state disappears at the Fermi level. It causes a decrease of d.c. conductivity.

5. CONCLUSION

We conclude that there is a small significant difference in the structure of a-C at different temperature. Few atomic sites are involved in this variation of the structure. The average coordination number of the carbon atoms increases proportionally to the temperature. We explain the changing of the d.c. conductivity in the temperature range 30 K–150 K with the help of topologically determined electronic states at the Fermi levels. This might cause the unexpected electronic conductivity.

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