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Temperature dependence of electron spin resonance in amorphous carbon films

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Abstract

Neutron diffraction and electron spin resonance measurements were performed on amorphous carbon prepared by the arc vaporization method in order to investigate the origin of an anomaly in the electrical conductivity at low temperature.

1. Introduction

Amorphous carbon films prepared by various methods have widely different physical properties. The electrical conductivity is particularly sensitive to variations in the atomic and electronic structure. Several facts indicate that a-C materials contain both sp^3 and sp^2 atomic sites. The former configuration corresponds to carbon sites in the diamond structure where each valence electron of carbon is assigned to a tetrahedrally directed sp^3 hybrid orbital forming a strong σ bond with the adjacent atom. In the latter configuration three of the four electrons are assigned to the trigonally oriented sp^2 hybrids forming three σ bonds with adjacent atoms and the fourth one participates in a π bond delocalized over all centers lying in the same plane. The sp^2 type sites are at the origin of the spin paramagnetism of a-C materials and exhibit an electron spin resonance (ESR) signal.

Since the π states are weakly bound their energies are closer to the Fermi level than those of the σ ones. The $sp^2:sp^3$ ratio is one of the most important parameters of a-C. Variations in structure and electronic properties as a function of preparation techniques are mainly determined by this ratio.

Recently, the temperature dependence of the conductivity has been studied in amorphous carbon films [1–4]. An unconventional temperature dependence of the conductivity has been observed in some graphite-vaporized films [4]. Between 30 and 115 K a nearly two orders of magnitude variation of the dc conductivity has been measured [4].

2. Neutron diffraction

Neutron diffraction was performed on such an anomalous sample in order to determine the atomic arrangement and to decide whether the structure changes with temperature [5]. The sample labelled 'anomalous' was prepared by arc evaporation of a graphite rod under a pressure of 10^{-6} atm. The

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diffraction measurement was performed at the hot source of the reactor Orphee at Saclay [6]. In the correlation function the position of the first four main peaks are 1.42, 2.46, 2.83 (third-neighbor cross-ring distance) and 3.73 Å which are very close to the distances in a perfect graphite crystal (1.42, 2.46, 2.84 and 3.64 Å). Beyond 6 Å no atomic order can be found. The first coordination number is about 3, while about 6 atoms belong to the second neighbor shell. This is typical for disordered graphite-like materials. To investigate the variation of the structure two series of measurements in a cryostat were carried out. Neutron diffraction spectra were recorded at 20, 25, 30, 55, 150 K and room temperature. There were small but significant differences of $S(Q)$ at 2 \AA^{-1} for the different temperatures above 30 K. As a control we put another amorphous carbon sample labelled 'normal' prepared under a pressure of 10^{-8} atm into a similar vanadium container and we repeated the neutron diffraction measurement at 25, 150 K and room temperature. There was no remarkable difference between the $S(Q)$ values.

We conclude that in the temperature range from 30 to 150 K the local order of the amorphous structure changes slightly. The effect is small, but reproducible.

3. ESR measurement

As a second step ESR measurements have been carried out in the temperature range of 4.7–293 K using a spectrometer (Bruker 300E). This study yields information about electronic states. The spin susceptibilities of two samples prepared similarly to those in the neutron diffraction study are shown on Fig. 1. The sample labelled 'normal' shows no anomaly in the low temperature conductivity while the sample labelled 'anomalous' has a huge anomaly in the conductivity [4]. The susceptibility of both samples is approximately constant at high temperatures and has a strong increase at low T . This is in sharp contrast with crystalline graphite for which the susceptibility increases with temperature due to an increase in carrier density [7]. In a-C the low T upturn of the susceptibility indicates a gradual localization of the conduction electron states. For the normal sample formally one may separate the 'spin density',

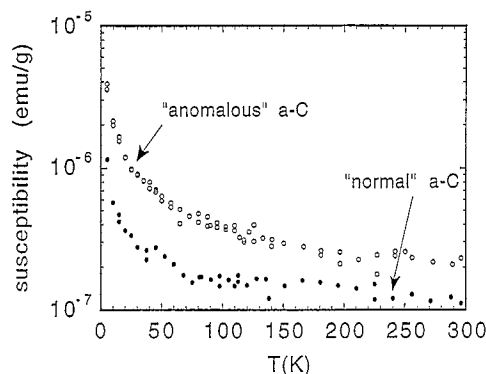


Fig. 1. Spin susceptibilities of a 'normal' and an 'anomalous' sample.

$\rho_s = \chi \times T$, into two parts, a T independent Pauli term and a roughly Curie-like term due to localized electrons:

$$\rho_s = 7.5 \times 10^{18} + C \times T.$$

Localized and itinerant electrons are not independent however — as usual — their overlap results in a single ESR line even if the g factors are slightly different. If metals inhomogeneities are averaged over the spin diffusion length which is usually of the order of a micrometer.

Such a description fails however for the anomalous a-C sample, because at low temperature the increase of χ is not Curie like. This is clearly indicated in Fig. 2 where ρ_s decreases rapidly below 50 K. This decrease may be due to a rearrangement of the electronic structure associated with a reordering of the a C atoms at low T as suggested in Ref. [5].

The linewidth of the anomalous a-C sample at 4

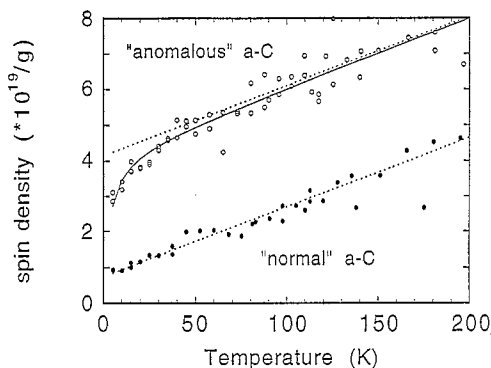


Fig. 2. Measured spin densities as a function of temperature.

K is only 10 G. This is much less than expected for crystalline graphite powder [7] but it is in agreement with other observations on a-C. The g factor anisotropy of crystalline graphite is averaged in a-C because the momentum relaxation rate is very much faster than the spin relaxation rate. The increase of the linewidth from 10 G at 4.7 K to 21 G at room temperature may be at least partly due to the reduction of the spin lattice lifetime. The effect of localization and a change in the spin density may also be an important factor in determining the linewidth.

4. Conclusion

We conclude that there is a small but significant change in the structure of a-C at low temperature. Few atomic sites are involved in this variation of the structure below 50 K. The ESR measurements are also consistent with a rearrangement of the electronic structure at low T .

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