STRUCTURE AND ELECTRONIC PROPERTIES OF NANO-GRAPHITE

T. Enoki, O. E. Andersson, H. Sato, Y. Hishiyama, Y. Kaburagi*, and M. Yoshikawa***
Dept. of Chem., Tokyo Inst. of Tech., 2-12-1 Ookayama, Meguro-ku, Tokyo 152.
**Dept. of Phys., Musashi Inst. of Tech., 1-28-1, Tamazutsumi, Setagaya-ku, Tokyo 158.*
***Dept. of Ctrl. & Syst. Eng., Tokyo Inst. of Tech., 2-12-1 Ookayama, Meguro-ku, Tokyo 152.*

Introduction

When the sample size gets sufficiently small the conduction electron spectrum may no longer be considered to be continuum. The finite number of conduction electrons causes the energy spectrum to be discrete. At low temperatures this will lead to a quantum size effect, QSE, on the electronic properties. The nanoparticles will show very different thermodynamic behavior depending on whether they have odd or even number of electrons [1]. Moreover, recent theoretical works suggest the presence of remarkable edge-shape dependence in the electronic structure of graphite nanoparticles [2]. For these reasons we have investigated the structure and measured the electronic properties of nanosized graphite by means of TEM, X-ray diffraction, Raman scattering, ESR, and Magnetic susceptibility.

Experimental

Nanosized graphite was prepared by heat treatment, in inert Argon atmosphere, of diamond powder (grain size 40 - 60 Å). We prepared samples heat treated at 1600, 1700, 1800, and 2750 °C, where the lowest limit was based on the results of Evans et al.[3].

Results and Discussion

Figure 1 shows the X-ray diffractograms of the 1600, 1700, 1800, and 2750 °C heat treated samples. HTT 1600 °C shows a very broad peak at the graphite (002) position as well as additional sharp peaks corresponding to diamond and impurities. HTT 1700 °C shows the coexistence of a very broad peak and a relatively sharp peak at the graphite (002) position around 26° in addition to a broad peak at 42-44° corresponding to the graphite peaks (100) and (101). At HTT 1800 °C the sharp peak at 26° is more pronounced indicating that the sample size is getting larger in the c-axis direction. This is also shown in the sharper (100) and (101) peaks. For the sample heat treated at 1800 °C we can also see peaks of graphite (004), (110), and (112). Increasing the heat treatment temperature to 2750 °C does not result in any major change of the X-ray diffractogram, except that the peak at 26° now splits into two narrow peaks. On the basis of the X-ray diffractograms we investigate further the sample heat treated at 1700 °C, as a target for QSE since this sample is well graphitized with the features of nanoparticles and there is only a small amount, ~20%, of large sized particles. The intensities of that sample were corrected for the Lorentz-polarization factor, the atomic form factor, and the absorption factor. The (002) peak of graphite was then fitted to two Lorentzian functions, one for the broad peak and one for the narrow peak. In the same way, Lorentzian functions were fitted to the (100) and (101) peaks. With the fitted values using standard corrections and calculations we could estimate the thickness and inplane size of the particles. For the broad peak we find an sample thickness of t = 22 Å and for the narrow peak t = 193 Å. The inplane size is estimated at 80 Å.

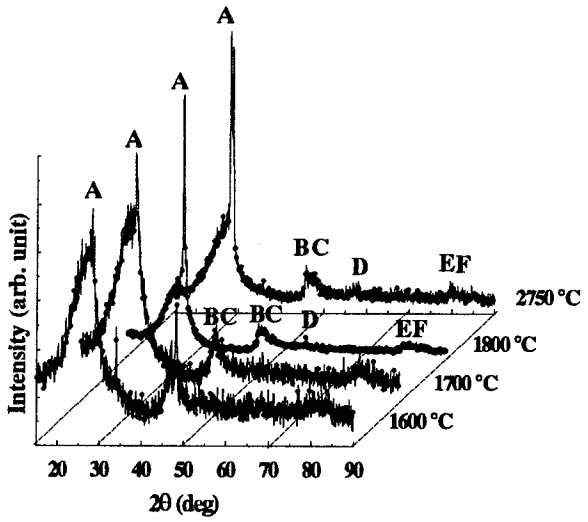

Figure 1. X-ray diffractograms of the samples HTT 1600, 1700, 1800, and 2750 °C. A=(002), B=(100), C=(101), D=(004), E=(110), and F=(112) of graphite.

The Raman scattering shows two broad peaks at around 1570 cm^{-1} and at 1350 cm^{-1} which are assigned to the E_{2g2} and A_{1g} modes of graphite respectively, consistent

with the finite size of the particles. Using the empirical formula $L = 44 \times I_{1570}/I_{1350}$, where I_{1570} and I_{1350} are the intensities of the peaks, we estimated the inplane size at 76 Å, which is consistent with the X-ray analysis. In Figure 2, we show the result of the ESR investigation on the same sample. The ESR spectra reveals two signals. At temperatures above 170 K we have one broad signal with $\Delta H \sim 35$ G at 295 K. Below 170 K a second narrow signal appears with $\Delta H = 4$-5 G. The intensity of the broad signal is essentially independent of the temperature which gives the value of the spin susceptibility $\chi_S = 2.8\times10^{-7}$ emu/g, while the intensity of the narrow signal shows a Curie type temperature dependence. Fitting the data for the narrow signal to the Curie law we get the concentration of the localized spins $N = 3.3\times10^{17}$ spins/g. The line width of the broad peak is decreasing with decreasing temperature.

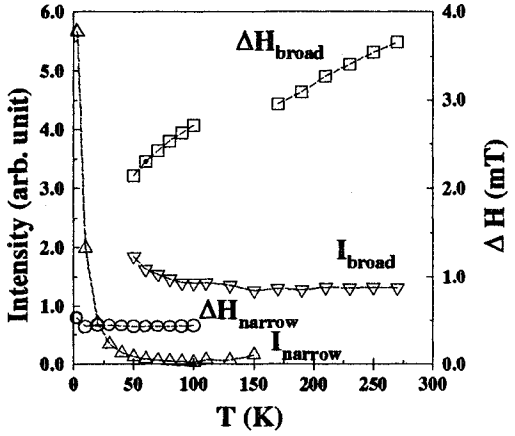

Figure 2. The ESR intensities and line widths of the sample HTT 1700 °C as a function of temperature.

In Figure 3, we show the magnetic susceptibility of the sample HTT 1700 °C. At 295 K the total magnetic susceptibility χ is -2.45×10^{-6} emu/g. The susceptibility decreases monotonically with decreasing temperature. At low temperature the susceptibility shows a Curie like increase. The data has been analysed on the basis that the total susceptibility consists of: $\chi_{Observed} = \chi_{Pascal} + \chi_{Curie} + \chi_{Orbital} + \chi_{Pauli}$, where the Pascal rule gives $\chi_{Pascal} = -0.5\times10^{-6}$ emu/g. The Curie contribution χ_{Curie} gives the estimate of the localized spin concentration $N = 3.5\times10^{17}$ spins/g, in good agreement with the result of the ESR narrow signal. The $\chi_{Orbital}$ is calculated using the Kotosonov equation for disordered graphite [4];

$$\chi_{Orbital} = 1/3\left[-138\times10^{-2}/(T+\Delta T)\,\mathrm{sech}^2\left\{E_F/2k_B(T+\Delta T)\right\}\right]$$

where E_F is the Fermi energy and ΔT is the Dingle temperature respectively. $E_F = 0.08$ eV and $\Delta T = 590$ K are taken as typical values of activated carbon fibers having the same size of micrographite, the latter of which is estimated from the mean free path and the Fermi velocity of graphite [5]. χ_{Pauli} is taken as the remaining susceptibility and corresponds to the broad ESR signal. χ_{Pauli} is strongly enhanced with a value of 2.0×10^{-6} emu/g which should be compared from what we get for bulk graphite by calculating χ_{Pauli} as $0.1\times10^{-6}\cdot E_F$ emu/g $= 8.1\times10^{-9}$ emu/g. This enhancement of χ_{Pauli} is evidence of QSE in the nanographite we prepared. According to the theoretical predictions for nanographite [2], the presence of non-bonding π-orbitals sensitive to the edge-shape gives a strong enhancement in the density of states at E_F, which is expected to be related to the behavior of the spin paramagnetism we observed.

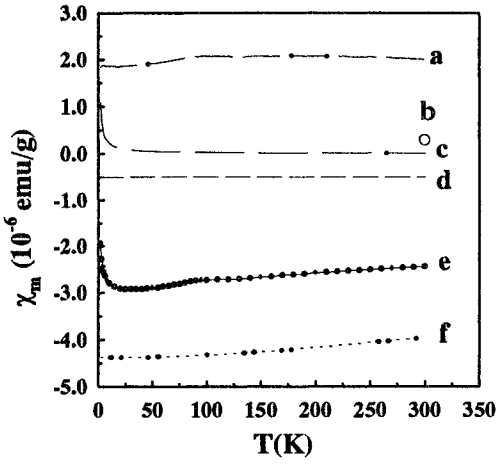

Figure 3. The magnetic susceptibility for sample HTT 1700 °C, (e), and the contributions from (a) Pauli, (b) Pauli contribution obtained from ESR, (c) Curie, (d) Pascal, and (f) Orbital magnetism.

References

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