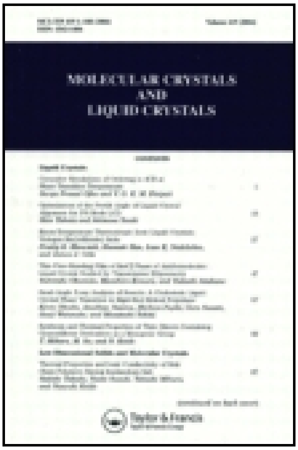

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Peculiar Magnetic Property of Pyrolytic Carbon Prepared From Adamantane

Kazuyoshi Tanaka [a] , Masahiro Kobashi [a] , Hideki Sanekata [a] , Akira Takata [a] , Tokio Yamabe [a] , Shigeyoshi Mizogami [b] , Kazushige Kawabata [b] & Jun Yamauchi [c]

[a] Department of Hydrocarbon Chemistry and Division of Molecular Engineering, Faculty of Engineering, Kyoto University, Kyoto, 606-01, Japan

[b] Central Research Laboratories, Idemitsu Kosan CO., LTD., 1280 Kami-izumi, Sodegaura, Chiba, 299-02, Japan

[c] College of Liberal Arts and Sciences, Kyoto University, Kyoto, 606-01, Japan

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KAZUYOSHI TANAKA, MASAHIRO KOBASHI, HIDEKI SANEKATA, AKIRA TAKATA, AND TOKIO YAMABE
Department of Hydrocarbon Chemistry and Division of Molecular Engineering, Faculty of Engineering, Kyoto University, Kyoto 606-01, Japan

SHIGEYOSHI MIZOGAMI AND KAZUSHIGE KAWABATA
Central Research Laboratories, Idemitsu Kosan CO., LTD., 1280 Kami-izumi, Sodegaura, Chiba 299-02, Japan

JUN YAMAUCHI
College of Liberal Arts and Sciences, Kyoto University, Kyoto 606-01, Japan

Abstract Magnetic-property measurements of pyrolytic carbon prepared by the thermal CVD of adamantane were carried out using the Faraday balance method and the ESR spectroscopy. The content of ferromagnetic metallic oxide as impurity in the samples has been confirmed to be low enough not to influence on the present magnetic-property measurements. Analysis of the measurement results has shown that the sample obtained are basically superparamagnetic and, even, ferromagnetic at low temperatures in a certain sample.

INTRODUCTION

Several numbers of documents have been accumulated with respect to intriguing magnetic property of the materials mainly consisting of carbon network prepared by chemical synthesis, pyrolysis, and so on.[1-4] The present authors' group has recently published preliminary report that a pyrolytic carbon prepared from vaporized adamantane by the thermal CVD method at 1000°C exhibits a clear magnetization hysteresis in its own characteristics based on the VTS SQUID susceptometer measurement.[5,6] It is rather interesting that a pyrolytic carbon can be made from pure hydrocarbon such as adamantane and that it shows a clear ferromagnetic hysteresis. But, as a matter of course, it is of our main concern whether such property of the sample is "stable" and "reproducible" for different batches of the preparation by the thermal CVD process.

In the present study, we attempt to examine those employing two samples prepared under independent batches of the preparation. The magnetization curves and the ESR spectra are measured for these samples and the results obtained are analyzed for understanding of the magnetic nature of the material.

EXPERIMENTAL

The starting material, adamantane, put in a small quartz container was evaporated, pyrolized, and deposited on the inside of the quartz tube at 1000°C under Ar flow. The thermocouple part was completely sheathed with a quartz tube to keep out of metallic impurities. The pyrolytic carbon sample thus obtained by the thermal CVD treatment was easily peeled off from the surface and collected for the successive measurements. In the present work, two kinds of the samples labelled A and B were independently prepared for the check of the batch dependence. The both samples are lustrous black in color, being insoluble and infusible. The electrical conductivities of the samples were almost common, the value of which was 1.2×10^2 S/cm at room temperature.

The magnetization measurement was carried out with an Oxford Instruments Faraday-type balance in the temperature range 2-260 K for the both samples with scanning the magnetic field between ±5 Tesla to check the magnetic hysteresis. The ESR measurement was carried out by a Varian E-112 ESR spectrometer at the X-band for the temperature range 13-298 K.

IMPURITY CHECK

In order to check the ferromagnetic impurities such as transition metallic oxides, an analysis based on the inductively coupled plasma (ICP) emission spectroscopy was performed for the samples with respect to Fe, Co, and Ni resulting in the confirmation of no inclusion of these impurities down to the lowest limit of the detection (25 ppm). Note that 600 ppm of Fe_3O_4 (that is, 430 ppm of Fe; Fe_3O_4 is equal to Fe_2O_3•FeO, magnetite) is required to give the saturation magnetization of $\approx6\times10^{-2}$ emu•G•g^{-1} found out in one of the present samples, for instance (see Table I). Furthermore, our preliminary ESR check of the samples confirmed that there was no background broad peak due to such extrinsic ferromagnetic impurities.

RESULTS AND DISCUSSION

Magnetization Curve

In Figures 1 and 2 the M-H curves at selected temperatures are plotted after the subtraction of the $\chi_0 H$ term by the conventional method equivalent to the Honda-Owen plot. In the sample B the hysteresis loop appeared at low temperature as has been reported in the previous study.[5,6] The data from the magnetization curves are listed in Table I.

The values of M_s differ by one order of magnitude between the samples A and B, showing the preparation-batch dependence. The residual magnetization (M_r) and the magnetic field for saturation (H_s) also showed such dependence. Note that the coercive force (H_c) of the sample B at 4.5 K is extraordinary large, but since the correction to demagnetizing field could not been performed in the present powdery samples, certain reservation should be required to interpret this H_c value. The hysteresis loop of the sample B was actually observed up to the temperature of 200 K and then disappeared as shown in Figure 2(b), probably due to thermal perturbation to the spin alignments. A large differential magnetization value at $H=0$ in Figure 2(b), however, results in an apparent value of M_r. In any case, the blocking temperature of this sample exists at the temperature over 200 K. On the other hand, the sample A showed a clearer superparamagnetic or even spin-glass like behavior with the absense of M_r and H_c at least down to 2 K as seen in Figure 1.

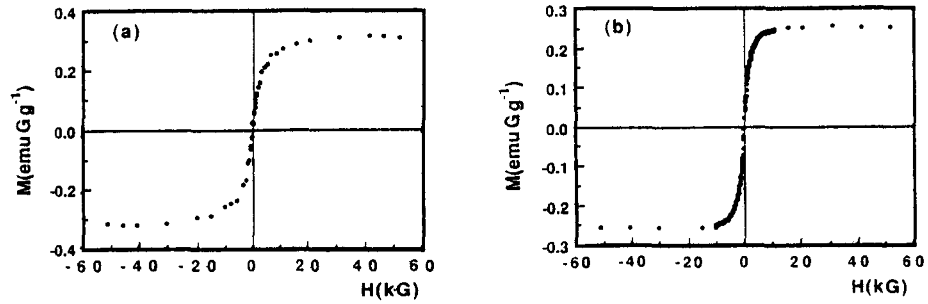

FIGURE 1 Magnetization curves of the sample A with the magnetic field scanning 0→5T→0→-5T→0→5T at (a)2K and (b)260K.

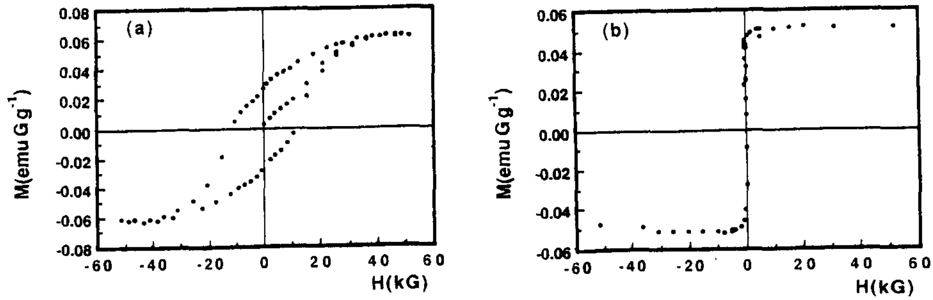

FIGURE 2 Magnetization curve of the sample B at (a)4K and (b)260K. See the caption of Figure 1.

The effective Bohr magneton number n_{eff} and the spin quantum number S were estimated as listed in Table II from the initial M-H curves for the both samples at low temperature in Figures 1(a) and 2(a). The S values suggest that about 14 to 22 spins are correlated in the parallel direction. However, it is noted that these values show the average on the spin alignments without the microscopic information and do not necessarily express the apparent ferromagnetic behavior as understood in the case of sample A.

ESR Spectra

The ESR lineshape of the sample B showed the overlap of two different peaks; a broad (ΔH_{pp}=4.35-7.39 G) and a narrow (ΔH_{pp}=2.28-2.51 G), whereas A only showed a broad one. The broad one becomes sharpened with the decrease in temperature, whereas the narrow one a little broadened. The former suggests the

TABLE I Some selected data of the saturation magnetization (M_s), the magnetic field for saturation (H_s), the residual magnetization (M_r), the coercive force (H_c), and the ordinary magnetic susceptibility (χ_0) of the samples at several measurement temperatures (T).

Sample	T	M_s	H_s	M_r	H_c	χ_0
		[±1.3%][a]	[±0.7%]	[±0.7%]	[±0.9%]	[±0.9%]
	(k)	($\times 10^{-2}$ emu $\cdot$G$\cdot$g^{-1})	($\times 10^4$ G)	($\times 10^{-2}$ emu$\cdot$G$\cdot$g^{-1})	($\times 10^4$ G)	($\times 10^{-7}$ emu$\cdot$G)
A	2	32.07	3.383	0	0	-10.33
	250	25.41	2.054	0	0	-8.477
B	4.5	6.256	4.616	2.698	1.175	-11.39
	250	5.136	1.542	4.541[b]	0	-10.44

[a] The values in the square brackets indicate the relative errors.

[b] Apparent M_r value due to the large differential magnetization value at H=0.

TABLE II. Effective Bohr magneton number (n_{eff}) and the spin quantum number (S) of the samples for the initial magnetization curves at low temperatures.

Sample	n_{eff}	S
A (at 2 K)	23.4	11.2
B (at 4 K)	15.2	7.1

ferromagnetic resonance and the latter the suppression of the motional narrowing by a slight degree at low temperatures. Furthermore, the ESR signal saturation of these two kinds of peaks due to the microwave power indicated that the saturation occurs more slowly in the broad peak, signifying the faster relaxation of microwave power injected among the spins corresponding to this peak. This suggests that the spins giving the broad peak are more apt to correlate in a kind of ferromagnetic fashion and that rather mobile π electrons give the narrow peak. This narrow peak has not been so frequently found in the similarly prepared samples.

It is possible to interpret that this narrow peak comes from the π–type spins occurring in frustrated sp^2-carbon network. On the other hand, it is currently not clear whether the appearance of this narrow peak is directly or indirectly associated with the ferromagnetic behavior. We tentatively assign that the spins responsible for the superparamagnetic or, even more, occasional ferromagnetic behavior and for the broad ESR peak are of sp^3-type (that is σ-type) radicals in the product structure originating from the dangling bonds reflecting the partially remaining adamantane structure.

Furthermore, the ESR lineshape of the sample B has satellite peaks with g=2.2-2.4, whose amplified pictures are shown in Figure 2, which the sample A does not show at all. The peaks may possibly come from the secondary excitation of the "collective motion" of ferromagnetic-type spins, that has never been observed in the 'magnetic' pyropolymers prepared at near 200°C.[4]

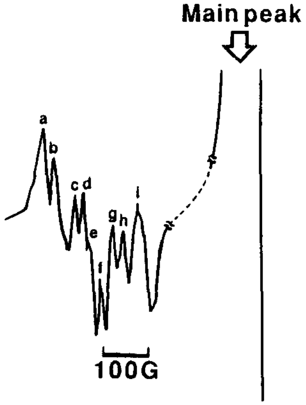

FIGURE 3 Amplified satellite peaks of the main ESR peaks of the sample B at room temperature. The g-values are in the range (a); 2.3987-(i); 2.2085.

CONCLUSION

Two independently prepared pyrolytic carbon samples A and B by the thermal CVD of adamantane at 1000°C confirmed to be impurity-free (less than 25 ppm of Fe) have been examined on the magnetic properties. An obvious batch dependence in these properties has been found out by the analyses of the magnetization and the ESR measurements. However, we believe that these magnetic properties originate from common background, which is probably connected with the existence of spin-rich domains or spin islands, the volume of which is not necessarily the same, distributing in the whole structure.

The sample B suggests a special case of correlated alignments of spins, possibly involving those through the inter-spin island interaction, to manifest ferromagnetic features occasionally found in the present materials.[5,6] The blocking temperature of this sample has been found to exist in the range 200-250 K. In this sense, constant ferromagnetic behavior would be expected even at room temperature if such materials are prepared under more finely controlled thermal CVD process.

ACKNOWLEDGMENT

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