

MAGNETIC PROPERTIES OF HIGH-PRESSURE HYDROGENATED AND POLYMERIC FULLERITES

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Hydrofullerites $C_{60}H_x$ synthesised at high hydrogen pressures were found to possess ferromagnetic properties at 300 K. Their magnetization at $H = 10$ kOe reached up to $\sigma = 1.2$ emu/g, and the $\sigma(H)$ curves exhibited a hysteresis with the coercivity of about 100 Oe. The magnitude of magnetization much exceeded possible contributions from magnetic impurities in the samples.

1. INTRODUCTION

In contrast to diamagnetism of pure C_{60} fullerite [1], a ferromagnetic behaviour of the $\sigma(H)$ dependence at room temperature was recently observed for $C_{60}H_{36}$ hydrofullerite [2] synthesised by reduction of C_{60} in the melt of dihydroanthracene at 300°C. The magnetization of $C_{60}H_{36}$ rose to about 0.04 emu/g $\approx 0.005 \mu_B$ /molecule C_{60} in a magnetic field of $H = 10$ kOe, and the $\sigma(H)$ curves measured at increasing and decreasing field demonstrated a distinct hysteresis with the coercivity of about 100 Oe. Therefore, $C_{60}H_{36}$ behaved as a ferromagnet with the Curie temperature of $T_c > 300$ K.

Among organic magnetics, the TDAE- C_{60} compound [3] was earlier found to have the maximum value of $T_c = 16$ K. No magnetic order was

observed previously in substances composed only of carbon and hydrogen atoms.

However, there was a possibility yet that ferromagnetism of the $C_{60}H_{36}$ samples prepared in [2] was caused by ferromagnetic impurities. For example, the maximum magnetization of $0.005 \mu_B/\text{molecule } C_{60}$ of those samples could be due to the presence of only 0.02 wt.% Fe with the spontaneous magnetization of $\sigma_s = 2.2 \mu_B/\text{atom}$ and $T_c \gg 300 \text{ K}$. The present paper reports on the synthesis of $C_{60}H_x$ samples which had much higher values of magnetization than the samples in Ref. [2] and were certified to have a low total concentration of magnetic impurities so that these impurities could not give rise to the observed magnetization. Both pristine and polymerized C_{60} were used to prepare hydrofullerites in order to test the effect of polymerization on their magnetic properties.

2. SAMPLE PREPARATION

The starting material, C_{60} of 99.99 wt.% purity, was sublimated in a vacuum better than 10^{-5} Torr at 600°C and compacted in a nitrogen dry box into pellets of 12 mm diameter and 1 mm thickness. A few pellets were polymerized by exposing to 2.1 GPa and 350°C as described elsewhere [4]. Each pellet of either pristine or polymerized C_{60} was then placed into a copper capsule and covered with a disc of 0.01 mm thick Pd foil. The space remaining in the capsule was filled with AlH_3 , and the capsule was tightly plugged with a copper lid using gallium as solder. Since both Cu and Ga are largely impermeable to hydrogen, the described encapsulation efficiently prevents hydrogen losses during the subsequent treatment.

The assembled capsules were pressurized to 0.6 or 3 GPa in a Toroid-type high-pressure chamber and maintained at a given temperature between 250 and 350°C for 24 h. The AlH_3 decomposed above 150 to 220°C depending on the pressure, and the evolved hydrogen reacted with the fullerite after permeating through the Pd foil which isolated the fullerite from the chemically active Al. The amount of hydrogen gas inside the capsule corresponded to a ratio of $H/C_{60} \sim 90$ therefore hydrogen was always in excess during the experiments. At the end of the hydrogenation, the high-pressure chamber was quenched to about 80 K and disassembled under liquid nitrogen in order to fix the high-pressure state of the sample. The copper capsule was then opened in a dry box at room temperature. About 15 to 40 mg of the resulting $C_{60}H_x$ powder was packed into a nylon

sample holder for the magnetization measurements. A few milligrams of the sample with the maximum magnetization were used in the atomic-emission analysis for metal impurities.

Our previous measurements showed [5, 6] that hydrofullerites quenched under high hydrogen pressure consist of $C_{60}H_x$ molecules and interstitial molecular hydrogen that leaves the sample on heating to room temperature. The hydrogen content of the $C_{60}H_x$ molecules depends on the synthesis pressure and varies from $x \sim 24$ to $x \sim 32$ for the pressures of 0.6 to 3 GPa. No changes in the composition of the $C_{60}H_x$ molecules at ambient conditions were observed for a period of a few months.

3. RESULTS AND DISCUSSION

The magnetization measurements were carried out at room temperature with a vibrating sample magnetometer EG&G PARC M-4500. The $\sigma(H)$ dependences were measured with the field varying from +10 to -10 kOe and backward at a constant rate of 1.2 kOe/min. A sample of initial C_{60} was found to be diamagnetic and demonstrated a small negative $d\sigma/dH$ in agreement with the literature [1].

Magnetization of hydrofullerites was studied on eleven samples prepared from pristine C_{60} and three samples prepared from polymerized C_{60} . Each sample showed the $\sigma(H)$ dependence characteristic of a ferromagnet, but the values of magnetization strongly varied from sample to sample. The maximum magnetization at $H = 10$ kOe was $\sigma_m \sim 0.01$ to 0.02 emu/g for all hydrofullerites made of polymerized C_{60} and for most hydrofullerites made of pristine C_{60} . This was even less than the value of $\sigma_m \approx 0.04$ emu/g observed in [1]. However, two other samples had $\sigma_m \approx 0.3$ and 0.4 emu/g, and one sample had $\sigma_m = 1.2$ emu/g $\approx 0.16 \mu_B$ /molecule C_{60} . The $\sigma(H)$ dependence of the latter $C_{60}H_{24}$ sample synthesized under a hydrogen pressure of 0.6 GPa at 350°C is shown in Figure 1, the results of its chemical analysis are given in Table I.

TABLE I Concentrations of impurities in a $C_{60}H_{24}$ sample determined by atomic-emission analysis. The detection threshold is 0.001 wt.%.

Metal	Fe	Co	Ni	Pd	Ga	Al	Cu
Wt.%	0.01	—	0.002	0.01	—	0.005	0.1

As can be seen from Figure 1, the $\sigma(H)$ dependence demonstrates a well-resolved hysteresis with the coercivity of about 100 Oe typical of all hydrofullerites studied in the present work and in [2]. The occurrence of a hysteresis is clear evidence of magnetic ordering in the material. The relatively large value of σ_m of the $C_{60}H_{24}$ sample together with the results of its chemical analysis (Table I) unequivocally show that the magnetic ordering is an intrinsic property of hydrofullerites.

In fact, the materials of the high-pressure cell, Pd, Ga, Al and Cu, are non-magnetic and their presence in the sample could not give rise to the hysteresis in the $\sigma(H)$ dependence or significantly contribute to the magnitude of σ_m . In addition, copper, the main impurity in the sample, is diamagnetic and its presence leads to a decrease in σ_m . The concentrations of all ferromagnetic impurities, Fe, Co and Ni, that could contaminate the sample and display a magnetic hysteresis were obviously too small to be responsible for the observed value of $\sigma_m = 0.16 \mu_B/\text{molecule } C_{60}$. For example, the sample would have this value of σ_m if it contained either 0.5 wt.% Fe with $\sigma_s = 2.2 \mu_B/\text{atom}$ or 0.7 wt.% Co with $\sigma_s = 1.7 \mu_B/\text{atom}$ or 1.7 wt.% Ni with $\sigma_s = 0.7 \mu_B/\text{atom}$. Furthermore, even these limiting concentrations that exceed the experimental ones by orders of magnitude may be significantly underestimated as the estimation implied that the impurities were in the form of particles large enough to be magnetically ordered.

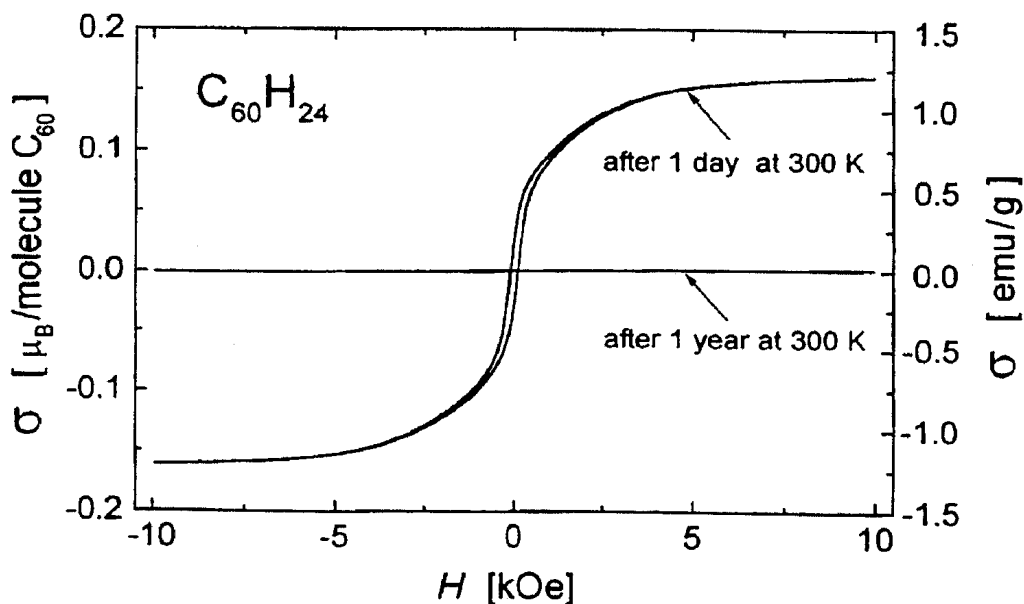


FIGURE 1 Magnetization σ as a function of magnetic field H at room temperature for the sample of $C_{60}H_{24}$ synthesized at $P_{H_2} = 0.6$ GPa and $T = 350^\circ\text{C}$ and exposed to ambient conditions for 1 day and for 1 year.

Figure 1 shows another interesting feature of the studied hydrofullerites. A long storage of the sample with a high value of σ_m at ambient conditions in air resulted in a drastic decrease in σ_m to values of about 0.01 to 0.02 emu/g characteristic of most freshly prepared samples. This observation corroborates the conclusion that ferromagnetism of the studied hydrofullerites was not the property of ferromagnetic metal impurities because such impurities could not have left the samples during the ageing at room temperature. On the other hand, the observed spontaneous decrease in σ_m also indicates that the values of σ_m much exceeding 0.02 emu/g are not the equilibrium property of hydrofullerites. One can suggest therefore that large values of σ_m are characteristic of the specific magnetic structure of hydrofullerites formed at some intermediate stage of hydrogenation. Such a suggestion also agrees with the fact that large values of σ_m were not well reproduced if the samples were synthesized under the same conditions.

4. CONCLUSIONS

Hydrofullerites $C_{60}H_x$ are the first example of a magnetically ordered organic substance composed only of carbon and hydrogen. Compared to other organic magnetics, hydrofullerites have the highest Curie temperature exceeding 300 K. The magnetization of hydrofullerites can reach $\sigma_m = 1.2 \text{ emu/g} \approx 0.16 \mu_B/\text{molecule } C_{60}$ in the field of 10 kOe. The largest σ_m values, however, should be attributed to intermediate stages of hydrogenation of C_{60} . These values are not well reproduced on the sample synthesis and gradually decrease to the values of about $0.02 \text{ emu/g} \approx 0.002 \mu_B/\text{molecule } C_{60}$ typical of most freshly synthesised hydrofullerites when the sample is stored at ambient conditions.

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