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## Magnetic ordering in hydrofullerite $C_{60}H_{24}$

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### Abstract

Hydrofullerites  $C_{60}H_x$  synthesised at hydrogen pressures of 0.6 and 3 GPa were found to possess ferromagnetic properties at room temperature. The magnitude of magnetisation varied from sample to sample and reached 0.001–0.16 Bohr magnetons per  $C_{60}$  molecule at  $H=10$  kOe. The coercivity of all the samples was about 100 Oe. The hydrofullerites had either an *fcc* or *bcc* lattice formed of  $C_{60}H_x$  units. The maximum values of magnetisation were observed for the *fcc* hydrofullerites with  $x \approx 24$ . © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Hydrofullerites; Organic ferromagnets

### 1. Introduction

In contrast to the diamagnetism of pure  $C_{60}$  fullerite [1], a ferromagnetic behaviour at room temperature was recently observed for the  $C_{60}H_{36}$  hydrofullerite [2] synthesised by reduction of  $C_{60}$  in the melt of 9,10-dihydroanthracene at 350°C. The magnetisation,  $\sigma$ , of the  $C_{60}H_{36}$  samples reached  $\sigma_{\max} \approx 0.005 \mu_B/C_{60}$  in the 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. The  $C_{60}H_{36}$  compound therefore behaved as a ferromagnet with the Curie temperature of  $T_c > 300$  K.

Among organic ferromagnets, the tetrakis-dimethylaminoethylene (TDAE)- $C_{60}$  compound was earlier found to have the highest value of  $T_c=16$  K [3,4]. No magnetic ordering was observed previously in the substances composed only of carbon and hydrogen atoms.

However, the magnetisation of the  $C_{60}H_{36}$  samples prepared in Ref. [2] was too small to ensure that it was not due to ferromagnetic impurities. The present paper reports on the synthesis of  $C_{60}H_x$  samples which had much higher values of magnetisation and were certified to have a low total concentration of magnetic impurities so that these

impurities could not give rise to the magnetisation observed.

### 2. Sample preparation and experimental details

The starting material,  $C_{60}$  of 99.99 wt.% purity, was sublimed 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 (1 Torr=133.322 Pa). Each pellet of about 150 mg mass was placed into a copper capsule and covered with a disc of 0.01 mm thick Pd foil as schematically shown in Fig. 1. 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 compressed to 0.6 or 3 GPa in a Toroid-type high-pressure chamber and maintained at a fixed temperature in the range 250–350°C for 24 h. The  $AlH_3$  decomposed above 150–220°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

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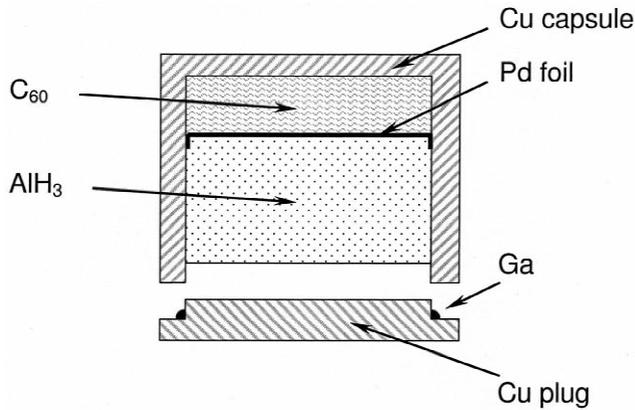


Fig. 1. Schematic diagram of the high-pressure cell using aluminium trihydride as a solid hydrogen source.

a ratio of  $H/C_{60} \approx 90$  therefore hydrogen was always in excess during the experiments.

Twelve  $C_{60}H_x$  powder samples were prepared in this way. The samples were examined at room temperature by X-ray diffraction using a SIEMENS D-500 diffractometer and monochromated Cu  $K\alpha$  radiation. About 15 to 40 mg of each sample were packed into a nylon sample holder and studied with a vibrating sample magnetometer EG&G PARC M-4500 at temperatures from 80 to 300 K. A few milligrams of the sample with the maximum magnetisation were used for the atomic-emission analysis for metal impurities.

Our previous measurements showed [5–7] that hydrofullerites quenched to 80 K 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  $x \approx 24$  to  $x \approx 32$  for the pressures of 0.6 to 3 GPa. No hydrogen losses from the samples with  $x \approx 24$  were observed at ambient conditions during a few months.

### 3. Results and discussion

#### 3.1. Magnetisation measurement

The  $\sigma(H)$  curves were measured at fixed temperatures from 80 to 300 K with the magnetic 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 literature [1]. Every  $C_{60}H_x$  sample showed a  $\sigma(H)$  dependence characteristic of a ferromagnet, with a well-resolved hysteresis loop.

Within the experimental errors of 10 and 5%, respectively, neither the coercivity nor the magnetisation of the  $C_{60}H_x$  samples decreased with temperature increasing from 80 to 300 K. This is indicative of the Curie temperatures

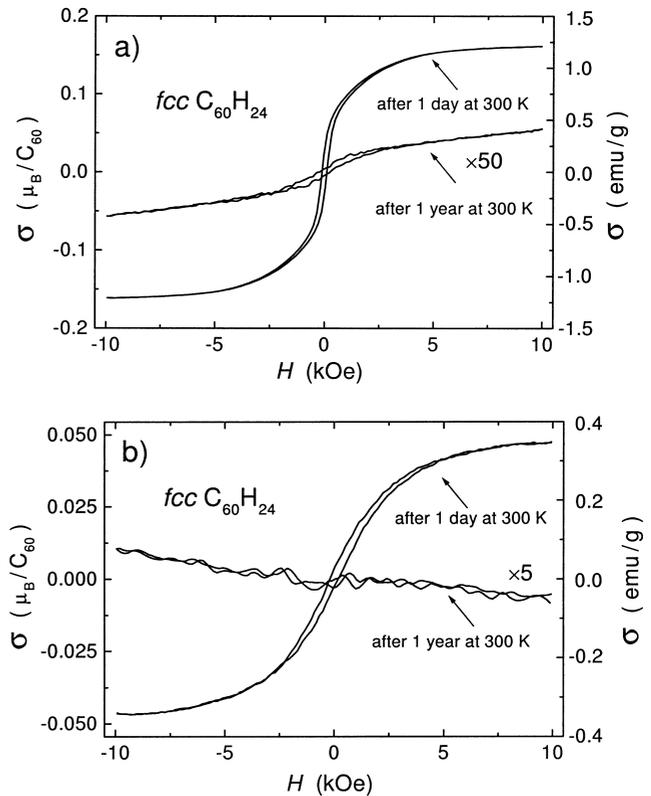


Fig. 2. Magnetisation  $\sigma$  as a function of magnetic field  $H$  at room temperature for two samples of  $C_{60}H_{24}$  synthesised at  $P_{H_2} = 0.6$  GPa and  $T = 350^\circ\text{C}$  and exposed to ambient conditions for 1 day and for 1 year.

much exceeding 300 K. The coercivity was about 100 Oe for all the  $C_{60}H_x$  samples. At the same time, the magnetisation magnitude strongly varied from sample to sample. Most hydrofullerites had  $\sigma_{\max} \approx 0.001\text{--}0.003 \mu_B/C_{60}$  at  $H = 10$  kOe that was even less than the value found in Ref. [2]. Nevertheless, two samples had  $\sigma_{\max} = 0.046$  and  $0.054 \mu_B/C_{60}$ , and one sample had  $\sigma_{\max} = 0.16 \mu_B/C_{60}$ .

All three samples with the largest values of magnetisation were synthesised under a hydrogen pressure of 0.6 GPa at  $350^\circ\text{C}$  and their compositions were close to  $C_{60}H_{24}$ . The room temperature  $\sigma(H)$  dependences for two of those  $C_{60}H_{24}$  samples are shown in Fig. 2. The concentrations of metal impurities in the sample with the maximum magnetisation value are given in Table 1.

The relatively large value of  $\sigma_{\max} = 0.16 \mu_B/C_{60}$  of the  $C_{60}H_{24}$  sample together with the results of its chemical

Table 1

The impurity content of the  $C_{60}H_{24}$  sample with  $\sigma_{\max} = 0.16 \mu_B/C_{60}$  determined by atomic-emission analysis

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

The detection threshold was 0.001 wt.%.

analysis 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 not magnetically ordered and their presence in the sample could not give rise to the hysteresis in the  $\sigma(H)$  dependence or significantly contribute to the magnetisation. In addition, copper, the main impurity in the sample, is diamagnetic therefore its presence resulted in a decrease in  $\sigma_{\max}$ . The concentrations of all ferromagnetic impurities, Fe, Co and Ni, that could contaminate the sample and show a magnetic hysteresis were obviously too small to be responsible for the observed value of  $\sigma_{\max} = 0.16 \mu_B/C_{60}$ . For example, the sample would have this value of  $\sigma_{\max}$  if it contained either 0.5 wt.% Fe with the saturated magnetisation  $\sigma_s = 2.2 \mu_B/\text{atom}$  or 0.7 wt.% Co with  $\sigma_s = 1.7 \mu_B/\text{atom}$  or 1.7 wt.% Ni with  $\sigma_s = 0.6 \mu_B/\text{atom}$ . Furthermore, even these limiting concentrations that exceed the experimental ones by orders of magnitude may be significantly underestimated as the estimation implies that the impurities were in the form of particles sufficiently large to be magnetically ordered.

Fig. 2 also shows another interesting feature of the studied hydrofullerites. A long storage of the samples with high  $\sigma_{\max}$  values at ambient conditions in air resulted in a drastic decrease in  $\sigma_{\max}$  to values of the order of  $0.001 \mu_B/C_{60}$  (Fig. 2a) and further to a diamagnetic behaviour of the magnetisation (Fig. 2b). For any positive  $\sigma_{\max}$  value down to the smallest detectable, this value remained independent of temperature from 80 to 300 K and the  $\sigma(H)$  dependences demonstrated the same coercivity about 100 Oe.

The observed decrease in the magnetisation due to the ageing, in the first place, corroborates the conclusion that the ferromagnetism of the studied samples is a property of the hydrofullerites themselves and cannot be attributed to ferromagnetic metal impurities because such impurities could not leave the samples during the ageing at room temperature.

The invariance of the  $\sigma(H)$  curves over the wide temperature range 80 to 300 K confirms that the  $C_{60}H_{24}$  samples with vanishing magnetisation still had  $T_c > 300$  K. This combination of magnetic properties is very improbable in the case of a bulk collinear ferromagnet whose magnitudes of  $\sigma$  and  $T_c$  are strongly interrelated. The samples could have small  $\sigma$  and high  $T_c$  in the case of 'weak' ferromagnetism resulting from spin canting or just from defects in the otherwise antiferromagnetic structure with a high ordering temperature. However, the occurrence of weak ferromagnetism in  $C_{60}H_{24}$  is inconsistent with the observed diamagnetism of the samples after their long storage under ambient conditions because the samples should have remained antiferromagnets after the disappearance of the spin misalignment.

Another possible explanation is that the  $C_{60}H_{24}$  samples were not single-phase and consisted of a mixture of a diamagnetic phase and a ferromagnetic phase with a

relatively large magnitude of magnetisation, and that the magnetisation of the samples decreased upon ageing at room temperature due to the decreasing content of the ferromagnetic phase. The bad reproducibility of the  $\sigma_{\max}$  values for the samples synthesised under the same conditions then could be attributed to the different content of the ferromagnetic phase formed at some intermediate stage of hydrogenation.

### 3.2. X-Ray diffraction

Pristine fullerite at room temperature has an *fcc* lattice of  $C_{60}$  units [8]. Hydrofullerites studied so far had either an *fcc* or *bcc* lattice of  $C_{60}H_x$  units. In particular, the ferromagnetic  $C_{60}H_{36}$  hydrofullerites from Ref. [2] had the *fcc* lattice and the high-pressure  $C_{60}H_{24}$  hydrofullerite from Ref. [3] had the *bcc* one.

The X-ray examination of the  $C_{60}H_x$  samples prepared in the present work showed that about half of them had an *fcc* lattice whereas the other half had a *bcc* lattice, without regard for the synthesis conditions. The representative X-ray diffraction patterns are given in Fig. 3. The *fcc* and *bcc* samples synthesised under the same hydrogen pressure had approximately the same composition and similar values of volume per  $C_{60}H_x$  unit varying from  $V_a \approx 800 \text{ \AA}^3/C_{60}$  for  $C_{60}H_{24}$  to  $V_a \approx 840 \text{ \AA}^3/C_{60}$  for  $C_{60}H_{32}$ . Presumably, the *fcc* and *bcc* modifications of hydrofullerites had close values of free energy in the studied  $T$ - $P$  region and their formation therefore depended on minor differences in the hydrogenation process.

All three  $C_{60}H_{24}$  samples with the maximum values of

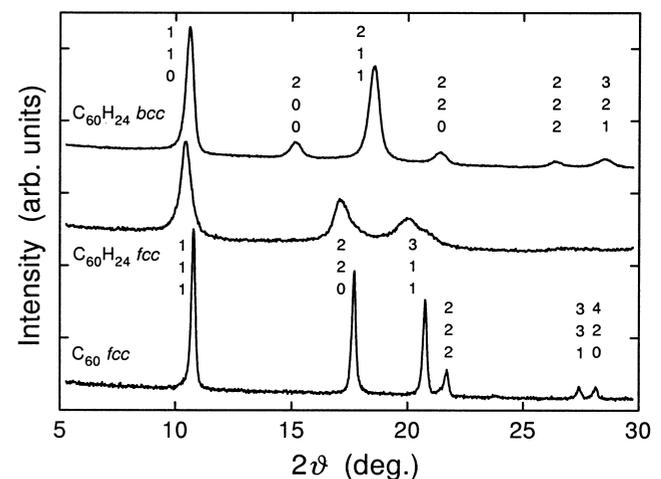


Fig. 3. X-Ray powder diffraction patterns for diamagnetic *fcc* pristine  $C_{60}$  with  $a = 14.17 \text{ \AA}$ ,  $V_a = 711 \text{ \AA}^3/C_{60}$ ; for ferromagnetic *fcc* hydrofullerite  $C_{60}H_{24}$  with  $a = 14.71 \text{ \AA}$ ,  $V_a = 796 \text{ \AA}^3/C_{60}$ ,  $\sigma_{\max} = 0.046 \mu_B/C_{60}$  (the magnetisation curves are presented in Fig. 2b) and for *bcc* hydrofullerite  $C_{60}H_{24}$  with  $a = 11.72 \text{ \AA}$ ,  $V_a = 805 \text{ \AA}^3/C_{60}$ ,  $\sigma_{\max} = 0.002 \mu_B/C_{60}$ . Both hydrofullerites were synthesised at  $P_{H_2} = 0.6 \text{ GPa}$  and  $T = 350^\circ\text{C}$  and exposed to ambient conditions for 1 day.  $V_a = a^3/4$  and  $a^3/2$  for the *fcc* and *bcc* structures, respectively. Monochromated  $\text{Cu K}\alpha$  radiation, room temperature.

magnetisation had the *fcc* lattice and their X-ray patterns showed no traces of any other phase. Moreover, neither the lattice parameter of the *fcc* lattice nor the line widths of the diffraction pattern changed after a 1-year exposure of the sample to room temperature that destroyed its ferromagnetism. We infer therefore that the crystal structure of the ferromagnetic  $C_{60}H_{24}$  phase could be considered as *fcc* within the experimental accuracy. Further investigations are necessary, however, to decide whether the studied ferromagnetic  $C_{60}H_{24}$  samples were single-phase or they consisted of a mixture of diamagnetic and ferromagnetic *fcc* phases with similar values of the lattice parameter.

#### 4. Conclusions

Hydrofullerite  $C_{60}H_{24}$  with the *fcc* packing of  $C_{60}H_{24}$  units has a ferromagnetic modification with the Curie temperature exceeding 300 K and the magnetisation no less than  $0.16 \mu_B/C_{60}$  in the magnetic field of 10 kOe. This is the first example of a ferromagnet composed only of carbon and hydrogen and the first example of an organic ferromagnet with the Curie temperature exceeding 16 K.

The specific ferromagnetic structure of the hydrofullerite is presumably formed at some intermediate stage of hydrogenation of  $C_{60}$  under a high hydrogen pressure. The magnetisation values are not well reproduced at the sample synthesis and gradually decrease when the sample is stored at ambient conditions. A 1-year storage brings most samples to a diamagnetic state without noticeable changes in their composition and lattice parameter.

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