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Structural and magnetic properties of polymerized C_{60} with Fe

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Abstract. We provide evidence that high-pressure high-temperature (2.5 GPa and 1040 K) treatment of mixtures of iron with fullerene powders leads to the complete transformation of iron into iron carbide Fe_3C. The comparison of the magnetic properties (Curie temperature and magnetic moment) of the here studied samples and those for the ferromagnetic polymer Rh-C_{60} indicates that the main ferromagnetic signal reported in those samples is due to Fe_3C and not related to the ferromagnetism of carbon as originally interpreted. Taking into account the results obtained in this study the original paper on "Magnetic carbon" [Nature **413**, 716 (2001)] was recently retracted.

PACS. 75.50.-y Studies of specific magnetic materials – 75.50.Bb Fe and its alloys – 72.80.Rj Fullerenes and related materials

1 Introduction

The recently re-discovered ferromagnetism in carbon-based compounds is a subject of actual interest in solid state physics [1]. Magnetic order at room temperature and above in a material with nominally only *s*- and *p*-electrons and without metallic ions is of importance for basic research as well as for possible bio-compatible and spin-electronic applications. Reports on the magnetic order observed in pressure-[2–4] and photo-polymerized [5] fullerenes as well as in hydrofullerite $C_{60}H_{24}$ [6] triggered a renaissance of the interest in the magnetic response of carbon structures. The earlier experimental study by [7], who induced magnetic ordering in C_{60}-crystals exposing them to light from a xenon lamp in the presence of oxygen, has been recently confirmed in reference [5]. Remarkable is the fact that the Curie temperature measured by the authors in reference [7] reaches 800 K.

The C_{60} can be polymerized by square ring connections (2+2cycloaddition mechanism) as a result of photo-irradiation, irradiation with an electron beam or high-pressure high-temperature (HPHT) treatment. Variety of one-, two- and three-dimensional structures have been reported for polymerized fullerenes. According to the original reports, polymerization at temperatures and pressures near the C_{60} cage collapse and graphitization of the 2D rhombohedral Rh-C_{60} phase leads to ferromagnetism with $T_C \sim 500$ K [2]. The work of Wood et al. [3] showed a maximum in the magnetization for samples prepared at conditions near the cage collapse, though no clear information on the impurities was provided in their publication. The studies done by Narozhnyi et al. [4] on pressure polymerized fullerenes indicated a Curie temperature higher than 800 K, clearly above that reported in reference [2]. One would speculate that the density of localized spins can vary from sample to sample and therefore, within a mean field theory one might expect different Curie temperatures. However, this difference added to the non negligible impurity concentration [8–10] found in the samples from reference [2] cast some doubts about the intrinsic nature of the ferromagnetic signal. Therefore, the formation of iron-carbon compounds cannot be ruled out.

The aim of this work is to show that HPHT treatment of fullerene powder mixed with iron powder produces iron-carbide (Fe_3C, cementite). In this study we compare the magnetic properties of the so prepared samples with the previously reported ferromagnetism of Rh-polymer of C_{60}. We argue that the formation of Fe_3C during the synthesis of the samples prepared in reference [2] explains not only the 500 K Curie temperature but also the absolute value of the magnetic moment of those samples taking into account the measured Fe concentrations.

2 Experimental

Powders of C_{60} (99.5%, MTR Corporation) and iron (GoodFellow, 99.9995% with nominal particle size ~ 2 μm) in different proportions (three mass percents of Fe in sample 1 and ten mass percents of Fe in sample 2) were gently mixed in the agate mortar. Those powder mixtures were loaded into a platinum capsule with tight lids pressed on mechanically. High-pressure high-temperature treatment was performed using a standard piston-cylinder system

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with a piston of 1/2-inch diameter. An advantage of our piston-cylinder method is the relatively large mass of samples (150–170 mg). The loaded capsule was placed into a standard high pressure assemblage which consists of an alumina sample holder inside a talc-pyrex assembly with resistive heating provided by a graphite tube.

Synthesis of samples was performed at 2.5 GPa and 1040 K with heating time of 1000 s. According to literature data these conditions favor formation of tetragonal polymeric phase of C_{60} [11]. It satisfies also the conditions of ferromagnetism reported in reference [2]: the samples are synthesized just below the boundary of C_{60} collapse. Characterization of samples was performed by X-ray diffraction and Raman spectroscopy. XRD patterns were recorded before and after HPHT treatment using Philips X'Pert and Bruker D8 powder diffractometers $K\alpha_1$-radiation in reflection mode. Silicon was used as an internal standard in some XRD runs. A Renishaw Raman 1000 spectrometer with a 514 nm excitation laser and a resolution of 2 cm^{-1} was used in these experiments.

The magnetic properties of samples 1 and 2 were studied with a SQUID magnetometer from Quantum Design with RSO option. A pristine mixture of 10%Fe in C_{60} powder (without HPHT treatment) was also studied as a reference (sample 3). That powder was taken from the same batch as mixed for the sample 2.

3 Results

3.1 Reaction of iron powder with C_{60}

The XRD data of untreated C_{60} and Fe powders show that no reaction between these two components occurs after gentle grinding them in agate mortar. Peaks from metallic iron were clearly observed in samples 1 and 2 (before treatment) together with peaks from usual fcc C_{60} phase. No peaks from iron oxides were detected confirming the high purity of pristine powder. The XRD data for both samples after HPHT treatment showed that C_{60} powder polymerized into a tetragonal polymeric phase, the same way as it is observed for pure C_{60} at similar conditions. At the same time, the peaks from metallic iron disappeared in HPHT treated samples, see Figure 1. XRD recorded over longer period of time revealed that iron reacted with C_{60} forming iron carbide Fe_3C, as seen in Figure 2 for both samples [12].

Formation of iron carbide is possible only if part of C_{60} molecules collapses due to reaction with iron. The mechanism of reaction is not known in detail, but some interesting observations can be noted. The iron powder used in our experiments was composed by grains with relatively large size (1–2 μm). Nevertheless, it is obvious from XRD data that the iron carbide phase was formed not just on the surface, but whole grains were transformed into Fe_3C. This process requires diffusion of carbon from the surface to the core of iron grains. Formation of other carbon phases was not detected, which means that most of the carbon from the collapsed C_{60} molecules was consumed for the formation of Fe_3C. Formation of Fe_3C is especially likely in the temperature interval where C_{60} molecules start to collapse or just before this point. On one hand the high temperature is required to initiate reaction of Fe with C_{60}, on the other hand reaction with collapsed fullerite (hard carbon phase) which forms above ~1073 K is less likely for several reasons. Unlike C_{60}, graphite is a thermodynamically stable modification of carbon with relatively low chemical activity. Reaction of Fe with graphitic carbon starts at significantly higher temperature (1273 K at 4–8 GPa) [13,14], while complete transformation of iron into Fe_3C (or Fe_7C_3 above 6 GPa) was reported at 1473–1523 K [13,14]. Reactions of carbide forming metals with C_{60} were studied previously only using co-evaporation methods [15,16], but it is likely that other metals like Ti,V,Nb, etc., will also react with C_{60} at the conditions of our experiments. It should be noted that Nb was one of the materials of the

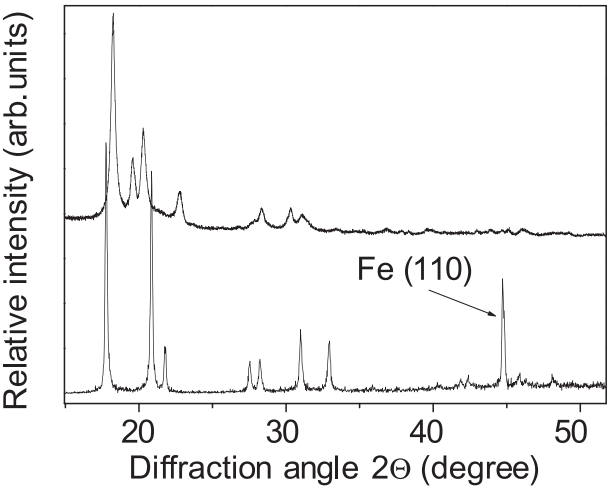

Fig. 1. XRD patterns recorded from the sample 2 (with 10% of iron) before (bottom) and after (top) HPHT treatment.

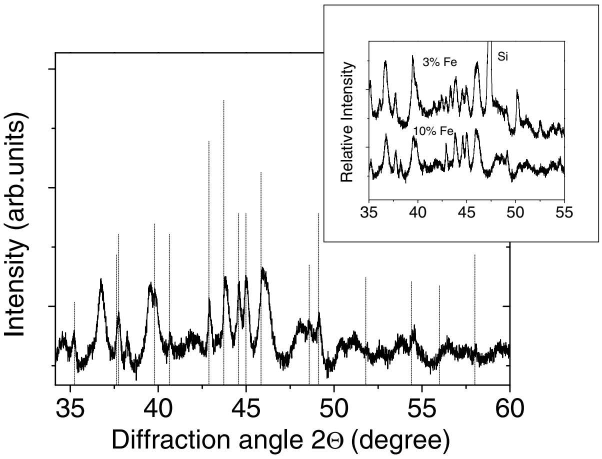

Fig. 2. Fragment of XRD recorded from the sample 2 after HPHT treatment. Peak positions and relative intensity from Fe_3C are marked with lines. Other peaks are from polymeric phases of C_{60}. The inset shows that XRD patterns recorded from both samples 1 and 2 are in good agreement (intensity is scaled for comparison).

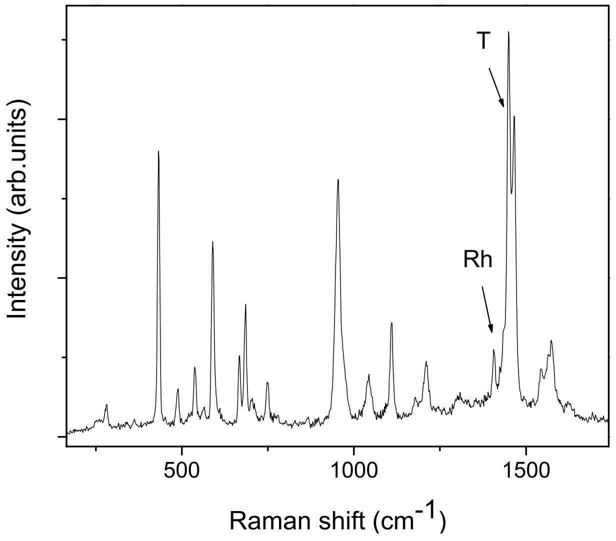

Fig. 3. Raman spectrum of sample 2. Ag(2) mode peaks from Rhombohedral (Rh) and tetragonal (T) polymers are marked.

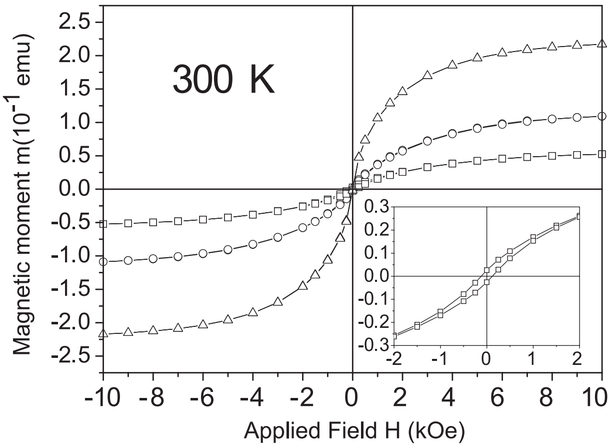

Fig. 4. Hysteresis loops of the magnetic moment measured for samples 1 ((□), mass $\tilde{m} = 13.75$ mg), 2 ((○), $\tilde{m} = 8.39$ mg) and 3 ((△), $\tilde{m} = 10.67$ mg) at room temperature. The inset shows the hysteresis loop for sample 1 in a smaller field region.

sample container in previously reported synthesis experiments [1], which likely resulted in the collapse of the C_{60} at the surface layers of the sample reported in reference [17].

The results obtained by XRD were also confirmed by Raman spectroscopy (see Fig. 3). The Raman spectra recorded in several points of samples 1 and 2 were in good agreement with the spectra of tetragonal polymeric phase of C_{60}. The spectra recorded in several points of the studied samples showed only slight changes in the relative intensity of some peaks. Minor impurity of Rhombohedral polymer was also detected (see Fig. 3, peak at 1407 cm^{-1}). The Fe_3C is difficult to detect by Raman spectroscopy, but iron oxides (hematite and magnetite) would be easy to identify taking into account the relatively large concentration of iron in sample 2. Nevertheless, no traces of iron compounds were found in the Raman spectra for both samples, which is in good agreement with XRD data.

We conclude this section emphasizing our finding that metallic iron reacts with C_{60} at the HPHT conditions of our experiments. Finely dispersed iron particles induce the collapse of some C_{60} molecules with formation of Fe_3C, while the majority of the fullerene molecules transforms into the usual — for these P-T conditions — polymeric phases. It is possible that the reaction described above can be found in mixtures of other metals with fullerenes, therefore it can be proposed as a new method for synthesis of bulk metal carbides in pure form. Formation of Fe_3C was observed in our experiments at significantly lower temperatures compared to reaction of Fe with graphite. It is also relatively easy to remove fullerene from the C_{60}/Fe_3C composite samples. The C_{60} polymers can be depolymerized by annealing at 600 K and dissolved in toluene.

3.2 Magnetic properties

In what follows we present the raw data from the measurements of the magnetic moments of the samples. In principle the total amount of ferromagnetic phase in a sample is not necessarily equal or correlated to its total mass ($\tilde{m}$). Therefore we have chosen to present data using magnetic moment (m) units as it was measured from the samples. In the following discussion we will take into account the different masses of the samples and the expected amount of ferromagnetic material. Figure 4 shows the hysteresis loops at 300 K for the three samples prepared in this study. The inset shows the hysteresis of sample 1 in a restricted field range. Assuming that all iron in the samples 1 and 2 of Figure 4 would transform into Fe_3C after HPHT treatment, we would have a mass $\tilde{m}_{\mathrm{Fe_3C}} \simeq 4.4 \times 10^{-4}$ g and $\simeq 9.0 \times 10^{-4}$ g, respectively. Taking into account the saturation magnetization of Fe_3C at room temperature $M_s \simeq 128$ emu/g [18], the expected magnetic moments at saturation due to Fe_3C are $m_s \simeq 0.056$ emu and $\simeq 0.115$ emu for the two samples, respectively. Both values are in agreement with the measured curves within experimental error. For sample 3 of Figure 4 the mass of Fe is $\tilde{m}_{\mathrm{Fe}} \simeq 0.97$ mg. Taking into account that for pure Fe at room temperature $M_s = 218$ emu/g, the expected magnetic moment at saturation is $m_s \simeq 0.21$ emu, a value similar to the measured one. These agreements also indicate the absence of giant magnetic proximity effect [19,20] between the ferromagnetic particles and the carbon matrix, in agreement with the studies done in reference [21].

3.3 Comparative analysis between C_{60}/Fe_3C composites and magnetic HPHT polymerized fullerene [2]

In this section we demonstrate that the magnetic properties of C_{60}/Fe_3C samples are similar to those previously reported for "magnetic carbon" produced by HPHT polymerization of fullerene [2,8–10]. It was shown in Section 3.1 that all iron introduced into the samples prior (or in the process) of HPHT treatment transforms into Fe_3C. The main question in the comparative analysis can be formulated as follows: was the amount of Fe contamination in previously studied samples of "magnetic carbon" sufficient to explain the observed ferromagnetic signals?

– It should be noted here that the amount of Fe impurity in the original paper on "magnetic carbon" was given only for pristine C_{60} powder [2], while the contamination introduced in process of synthesis was not taken into account. The relatively large amount of Fe impurities in those samples was discovered after the publication of reference [2] and reported in references [8–10]. It can be also noted that the only two other publications that apparently confirmed the existence of ferromagnetism in HPHT C_{60} polymers did not provide any impurity analysis [3,4]. Rigourously speaking they can not be considered as a confirmation for intrinsic ferromagnetism in polymerized fullerenes. It should be also clarified that only two samples of "magnetic carbon" from one set of samples synthesized in 1998 were found to exhibit a Curie temperature $T_c \simeq 500$ K. Below we discuss the Fe contamination levels and the observed ferromagnetic signals for these two samples in more detail.

– Let us estimate the saturation magnetic moment at room temperature expected for the 3.2 mg polymerized fullerene sample studied in reference [2], taking into account the impurity concentration. Particle Induced X-ray Emission (PIXE) measurements indicated that the Fe concentration in similar samples was inhomogeneously distributed within the penetration depth of this method (∼30 μm) [8–10]. In average the magnetic samples had an Fe concentration of the order of 400 μg/g with an uncertainty of a factor of two or larger. If we assume that 400 μg/g iron in carbon would transform into cementite, we expect $\tilde{m}_{\mathrm{Fe_3C}} \simeq 1.37$ μg and a magnetic moment at saturation $m_s(300\ \mathrm{K}, \mathrm{Fe_3C}) \simeq 1.75 \times 10^{-4}$ emu. The measured value [2] was $m_s \simeq 2.5 \times 10^{-4}$ emu. We note that the iron concentration was not determined for that particular sample (named E17 and produced at 6 GPa and 973K) [2]. Similar magnetic fullerene samples, however, showed the same behavior. PIXE measurements of the sample E16 (2.5 GPa, 1123K) reported in references [9,10], before the polishing for MFM measurements, showed the following Fe concentrations (in μg/g): (a) wide-beam measurements: 541, 448 and 340 in three different regions; (b) probed with a microbeam at one of the surfaces: 1.370, 100, 200, 16.000 and 100 (average over the specific surface 482); (c) at other surface: 630, 372, 52, 78 (average 502). The value 175 μg/g Fe written in references [9,10] is the average measured in the polished surface only. The saturation moment measured in this sample of mass 2.2 mg at 300 K was $m_s \simeq 2.0 \times 10^{-4}$ emu [9]. A concentration of 710 μg/g of $\mathrm{Fe_3C}$ would provide this moment.

– Let us discuss now the origin for the 500 K Curie temperature. Figure 5 shows the magnetic moment as a function of temperature for the three samples and the raw data [2,9] for the E17 and E16 samples (right axis). This figure shows clearly that the ferromagnetic transition at ≃500 K observed in those studies agrees with that of cementite, which has a Curie temperature of 483 K (see Ref. [22], p. 366). The differences in the shape and width of the transitions between the samples is mainly related to the difference in grain and stoichiometry distribution; larger applied fields would enhance also the width of the transition. We conclude therefore that the amount of metallic impurities determined by PIXE in the original "magnetic carbon" polymerized samples and the obtained Curie temperatures demonstrate that the magnetic signals observed in these samples should be assigned to contamination.

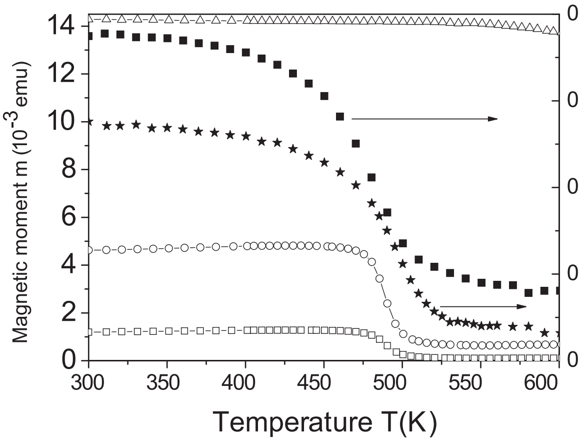

Fig. 5. Magnetic moment as a function of temperature for the three samples studied in this work at an applied field of 500 Oe (the symbols correspond to those in Fig. 4). The sample mass was $\tilde{m} = 2.0$, 2.0, 1.9 mg for samples 1, 2 and 3, respectively. Right axis: raw data (■) for the sample of mass $\tilde{m} = 3.2$ mg from reference [2] and the sample E16 (mass 2.2 mg, ★) from reference [9] at the applied field of 2 kOe.

4 Discussion

The report on intrinsic ferromagnetism of pure carbon in the form of C_{60} polymers produced by HPHT treatment [2] was based on the following arguments:

1) *The contamination level of 22 ppm of the polymerized fullerene samples was too small to account for the observed ferromagnetic moment.* It is clear that only when contamination can be ruled out by a reliable analysis (mainly of the elements Fe, Ni, and Co) the conclusion about an intrinsic nature of the ferromagnetism in some new material can be done. The level of impurities reported in the original paper [2] as well as in a subsequent paper [4] was given only for pristine C_{60} powder. In some other reports about ferromagnetism in C_{60}-based materials [3,17,23] no analysis of the magnetic impurities was presented at all. The contamination of the material during the high pressure experiments was obviously not taken into account. However, a later examination of one of the ferromagnetic samples from reference [2] using PIXE showed a 10 to 20 times larger concentration of ferromagnetic impurities than initially reported [8–10]. It can be noted that the magnetic properties of the samples that exhibited ferromagnetism and a Curie temperature of 500 K were discovered three years after their synthesis

in the year 1998. These samples were actually not intended for studies of ferromagnetism and therefore the required precautions against contamination were not considered at the time of their synthesis [24]. Later studies on cleaner samples have not confirmed the high levels of magnetization. The magnetization found in samples specially synthesized with all possible precautions was on the level 0.004–0.0001 emu/g, which can be explained by less then 10 ppm of Fe contamination, if the Fe particles would have the ferromagnetism as bulk Fe, or correspondingly larger Fe concentrations if it is present as some less ferromagnetic compound [25,23].

2) *An unique Curie temperature of 500 K was assigned to "magnetic carbon".* The Curie temperature of 500 K was observed only for two polymerized samples and can be naturally explained by the formation of Fe_3C as it is shown in the presented study. The Curie temperature was not measured on any other samples of "magnetic carbon". The study reported in reference [4] failed to find T_c within the temperature range of the used equipment (800 K). We may speculate that in those samples some other contamination was involved, for example in the form of magnetite or metallic iron (both with $T_c > 800$ K). The study presented here confirmed that small particles of Fe (~ 2 μm) are completely transformed into Fe_3C at the conditions of HPHT synthesis, but such a transformation could be not complete if the Fe particles are larger. The chemistry in real experiments can depend on many parameters, as for example the particle size, time of the heat treatment and the initial state of iron. For example, it was reported that an amount of 80 μg/g of Fe in C_{60} was found to be in the form of hematite already after the first preliminary part of the high pressure treatment (palletization of powder) [16]. Starting from hematite, the following chain of products could be obtained in the process of HPHT treatment: hematite, magnetite, iron and iron carbide. The final reaction product will strongly depend on the duration of the heat treatment and the initial particle size. As a result, different Curie temperatures can be observed in different HPHT treated samples. The amount of 80 μg/g of hematite reduced to pure iron would give a magnetization of $\simeq 0.018$ emu/g at saturation and in the case of complete transformation to Fe_3C, 0.009 emu/g (similar to the ferromagnetic signals of a tetragonal phase reported in Ref. [17]).

3) *Ferromagnetism was assigned only to special polymeric phases of* C_{60}. In the first publication on the magnetic polymerized fullerene sample, the rhombohedral phase has been attributed to be ferromagnetic. This assignment appeared to be not true. All HPHT polymers of C_{60} are known to depolymerized back to pristine C_{60} if heated above 550–600 K [26]. The ferromagnetism of "magnetic carbon" was preserved after heating up to 640 K for two hours [2] and even after heat treatment at 800 K for several hours [8] which means that the polymeric structure was not anymore present in the samples after the first heating run and therefore responsible for the observed ferromagnetism. We note that some samples of the "magnetic carbon" species of the first publication were studied later and depolymerized as expected below 600 K [27]. Moreover, the same set of samples as in reference [2] was tested in an earlier study and was reported to depolymerize completely at 473 K [28]. Finally, the recently published corrigendum [29] confirmed that one of the two samples which ever showed 500 K Curie temperature was synthesized at 2.5 GPa and 1125 K. The temperature of 1125 K is well above the point of C_{60} collapse. Structural data for this sample were never published explicitly despite very detail characterization of magnetic properties by SQUID and MFM [8–10]. This sample consisted largely of graphite like carbon with small fraction of tetragonal polymer and minor impurity of rhombohedral. Graphite like structure of this sample is evident according to the conductivity measurements performed on the same sample and published prior to the original paper on "magnetic carbon" [28].

4) *Ferromagnetism was reported for samples synthesized only in a "short temperature interval".* According to the original publication [2] only samples prepared in the temperature region of 1025 K to 1050 K were ferromagnetic. This assignment appeared to be wrong as it follows from the published Corrigendum [29]. Ferromagnetic loops shown in reference [2] appeared to be obtained on the sample synthesized at 973 K, which was the lowest temperature in the studied set (970–1170 K), while the second sample was synthesized at 1125 K (above the point of C_{60} collapse). It can also be noted that a contamination with metallic impurities is most likely to occur near the point of C_{60} collapse. A collapse of C_{60} into a more dense graphite-like hard carbon phase is also associated with a significant volume decrease. Due to these reasons some pressure containers were possibly cracked during experiments and contamination from outside could penetrate into the reactive sample volume.

It can be concluded that the existing evidence is not sufficient to support a bulk intrinsic ferromagnetism in fullerene samples obtained by high pressure high temperature treatment. The claim of intrinsic ferromagnetism in carbon samples can be made only when the contamination with magnetic impurities is ruled out, but this is not the case for the polymeric C_{60} at the moment. The study presented here clarifies the last question that remained unanswered, namely how to explain a Curie temperature of 500 K by contamination with magnetic impurities.

5 Conclusion

In summary, we have shown that high-temperature high-pressure treatment of fullerene samples intentionally mixed with iron powder before treatment leads to the transformation of Fe into Fe_3C. The magnetic data obtained in this work compared with that from references [2,9] show strong similarity, which indicates that the *main* magnetic signal and the ferromagnetic transition originally reported as intrinsic magnetism of carbon was likely originated from Fe_3C. Taking into account the results obtained in this study the original paper on "magnetic carbon" [2] was recently retracted [30]. Although

MFM data indicate the existence of magnetic domains in pure regions of some samples produced from C_{60} by HPHT treatment [9,10], it is not possible from those data to estimate their contribution to the total magnetic signal. We note that recent experimental study [25] performed on samples prepared from fullerenes with lower impurity content and after HPHT treatment showed vanishingly small bulk magnetization, indicating that the pressure polymerization of fullerenes is not an appropriate method to produce magnetic carbon.

Our work shows that the reaction of Fe with C_{60} can be proposed as an alternative method for synthesis of pure carbides. The method has certain advantages compared to traditionally used reaction of Fe with graphite: lower synthesis temperatures and relatively easy procedure for removal of the remaining C_{60} from the reaction products.

The results presented in this work do not rule out the possibility of having magnetic order at high temperatures in metal-free carbon compounds. There are recent experimental results, which provide strong evidence [31,32] as well as indications [33] for its existence.

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