

Review

Peculiar Magnetic Features and Superconductivity in Sulfur Doped Amorphous Carbon

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Abstract: We report on magnetic studies of inhomogeneous commercial and synthesized amorphous carbon (a-C) and a-C doped with sulfur (a-CS) powders which exhibit (i) peculiar magnetic behavior and (ii) traces of two superconducting (SC) phase $\sim T_c=33$ and at 65 K. (i) The temperature dependence of zero-field-cooled (ZFC) curves measured up to room temperature show a well distinguish elusive peaks around 50-80 K, their origin is not yet known. These peaks are totally washed-out in the second ZFC sweeps and in the FC branches as well. As a result, in the vicinity of the peaks, the FC curves lie below the ZFC peaks (FC<ZFC), a phenomenon which is rarely observed. These magnetic anomalies are intrinsic properties of a-C and a-CS materials (ii) SC was observed in three different a-C sources: (a) The commercial a-C powder contains 0.21% of sulfur and it is suggested that two different a-CS phases (at 33 and 65 K) are the origin of the two SC states observed. The compositions of these two phases are not yet unknown. The small SC volume fractions of the 33 K phase can be enhanced by a solid reaction with additional sulfur at 250 °C. (b) The synthesized a-C powder (obtained from decomposition of sucrose) is not SC. However, when mixed with sulfur and heated at 400 °C under a protective atmosphere, the a-CS powder obtained also show traces of a SC phase at $T_c=42$ K. (c) The same occurs in a-C thin films. The as-grown films are not SC but a SC phase at $T_c = 34$ K emerges after the films were reacted with sulfur at elevated temperatures. It is concluded therefore, that all SC phases observed are due to different unknown a-CS phases. Since the a-C and a-CS powders possess SC and magnetic states, we believe that these powders resemble the high TC curates and Fe-As based systems in which the SC and the magnetic states are closed related to each other.

Keywords: amorphous carbon; sulfur; superconductivity; peculiar magnetic behavior

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1. Introduction

Interest in magnetic nano-sized particles has increased in the last few years by virtue of their potential for applications. These materials with dimensions intermediate between molecules and bulk solids are intriguing due to their novel electronic features which depend on the particle size, topology, surface conditions etc. Amorphous carbon (a-C) is a good example for this kind of materials. Its graphitized carbon fragments have a very large surface area and possess both negative and positive curvatures. The most common polymorphs of carbon are: (i) graphite in which sp^2 hybridization (band gap $E_g = 0$) forms planar sheets in a two layer hexagonal stacking and (ii) diamond in which sp^3 carbons (band gap $E_g=5.4$ eV) form a three-dimensional lattice of cubic symmetry. Changing the sp^2/sp^3 ratio tunes the a-C band gap between that of diamond and semimetal graphite.

Ferromagnetism (FM) is typically the property of transition and/or rare-earth metals, alloys and inter-metallic compounds, with unpaired electrons in unfilled atomic shells. On the other hand, carbon atoms show a very strong tendency to pair up their outer-shell electrons in covalent bonds. Nevertheless, various forms of carbon systems have recently been found to exhibit a FM or a FM-

like behavior. Because of the features mentioned above a-C is also a promising candidate for searching for new superconducting (SC) materials (SC). [1-2]

The magnetic properties of two a-C sources have been extensively studied and reported in Ref. 3: (a) An inhomogeneous commercial Fisher (C190-N) powder dated from 1935 and (b) fabricated a-C powder obtained by multi-stage melting of ultra-pure sucrose ($C_{12}H_{22}O_{11}$). Energy dispersive spectroscopy (EDS) study proved that the Fisher product contains: tiny amounts of sulfur (~0.21 at%), ~ 360 ppm of ferri-magnetic magnetite (Fe_3O_4 $T_M = 853$ K) and also other paramagnetic (PM) ions such as Ni and Mn. Due to its inhomogeneity, the extensive zero-field-cooled (ZFC) and field-cooled (FC) magnetic studies of this powder exhibit scatter results. (i) Most of the samples presented the ferri-magnetic behavior of magnetite and at low temperatures the PM ions contribution. (ii) A few samples exhibited well-observed peaks (at 50-80 K) in their first ZFC curves and (iii) the rest showed traces of two SC phases with T_c around 33 and 65 K. Heating these powders with sulfur (a-CS) at elevated temperatures did-not change much their sulfur concentration but increased the amplitude of the ZFC peaks and the SC volume fraction of the lower SC phase. The fabricated a-C virgin powder does not contain sulfur and is essentially diamagnetic. The same three magnetic phenomena have been observed when this powder was doped with sulfur at elevated temperatures.

Superconductivity: The search for SC in carbon-based materials (CBM) triggered a large number of studies in recent years. Most of the research was done on intercalated graphite compounds in which foreign atoms were inserted between the two-dimensional hexagonal sheets of graphite. For example: KC_8 ($T_c = 0.15$ K) [4], and CaC_6 ($T_c = 11.5$ K). [5]. Much higher T_c values were obtained in alkali doped fullerenes Cs_3C_60 ($T_c = 38$ K) [6] and in inter-halogen-doped fullerenes ($T_c > 60$ K) [7]. Inhomogeneous SC at 35 K was obtained at the surface of sulfur-graphite composites.[8-9] Since graphite and fullerene (C_60) are not superconducting, it was suggested, that the transfer of charges from the alkali metals to the graphite (or fullerenes) plays an important role in the appearance of the SC state. However, the simple models existing until now are insufficient to predict the appearance and the magnitude of T_c in these alkali-intercalated materials.

As mentioned above, traces of SC two SC phases (up to 65 K) were detected in two different a-C powders. SC at ($T_c = 34$ K) was also observed in a-C thin films prepared by Electron-Beam Induced Deposition (EBID) after they were synthesized with sulfur at 250 °C. Since in all three cases, SC in a-C was observed only when the powders were exposed to sulfur, it is believed sulfur is essential to the existence of the SC state in all a-C materials. Due to the fact that the SC states already observed are not bulk properties, the exact composition of these phases are as yet not known. All those experiments agree well with theoretical expectations, which predict that intercalated sulfur and structural disorder can locally induce extra carriers into graphite/graphene sheets and therefore induce or enhance the SC state.[10]

The most exciting recent observations in high temperature superconductivity (HTSC) are the new experimental and theoretical results of H_2S samples measured under high pressures. [11-12] SC at $T_c = 203$ K was directly proven by resistivity measurements followed by a Meissner effect study. It is clearly evidenced that under high pressure H_2S decomposed to H_3S which is supposed to be the SC phase. The isotope effect in H_3S provided a direct evidence for the conventional phonon mediated pairing. Thus the common denominator in both a-C ($T_c \sim 67$ K at ambient pressure) and H_3S ($T_c = 203$ K under ~ 200 GPa) systems, is *sulfur* which may serve as the basic crucial ingredient in these new HTSC classes. This similarity will be further discussed in the last section.

Peculiar magnetic behavior: The magnetic features of any amorphous systems are mainly controlled by the disorder state, which affects the temperature dependence of their ZFC and FC branches. Microscopically, disorder may change the extent of the wave function and as a result the change from extended wave function to localized states. On the other hand, impurities, structural disorder and/or topological defects may tune the amorphous disordered nature to slightly ordered states.[13] Indeed, a FM state in CBM was achieved by proton irradiation, [14] or by adsorbed foreign atoms such as hydrogen [15] and/or oxygen [16]. Ferromagnetism was also observed in graphitic sheets with positive or negative curvatures, [17] in fullerene-related carbon, [18] in carbon nano-spheres encapsulating silver nanoparticles, [19] and in carbon nano-foam (CNF). The CNF powder has a high surface area and display peak in the ZFC branches only immediately after their synthesis. They disappear a very short time later. [20-22] Despite the accumulated growing evidences of FM or a FM-like states in CBM, the crucial factors that stabilize them are still unclear.

The a-C powders, also possesses high surface area and low density and are very similar to CNF. Unexpectedly in several a-CS samples, **two** intrinsic anomalies were observed. First, peaks are observed in the ZFC branches and around their positions, the ZFC curves are much higher than the FC ones (ZFC>FC). Second, these peaks are elusive and disappear in the second ZFC as well as in the FC runs. The two anomalies are connected to each other and a qualitative model to explain them is given in the discussion section.

In this paper, we review the most prominent magnetic measurements performed on selected a-C and a-CS samples which exhibit traces of SC and/or unusual magnetic behavior. In addition to the already published data [3] we present here new unpublished results. This manuscript is divided into two major parts. Following the experimental details section, we present first the SC states observed in commercial and synthesized a-C powders, as well as in sulfur doped a-C thin films. Next, we describe the unusual magnetic features of several a-C and a-CS materials and mention similar observations in two other unrelated systems.

2. Experimental Details

Two *commercial* a-C powders are described here: (1) a-C fabricated by Fisher (C190-N) in 1935 and (2) a-C powder manufactured by Prolabo (9009) as charbon R.P. One a-C (Fisher) sample was heated to 800 °C (assigned as a-C800) and then cooled to ambient temperature. Two other a-C sources were obtained by a multi-stage pyrolytic thermal treatment (up to 650 °C) of pure sucrose (C₁₂H₂₂O₁₁),[23] and by growing granular a-C thin films by using the EBID technique. [24] Mixtures of all a-C materials with sulfur (Aldrich Chemical Company, Inc.) in a weight ratio of 2:1 (for commercial or films) and 10:3 (for pyrolytic) were pressed and heated for 20-24 hours at 250 °C (or 400 °C) in evacuated quartz tube (assigned as a-CS).

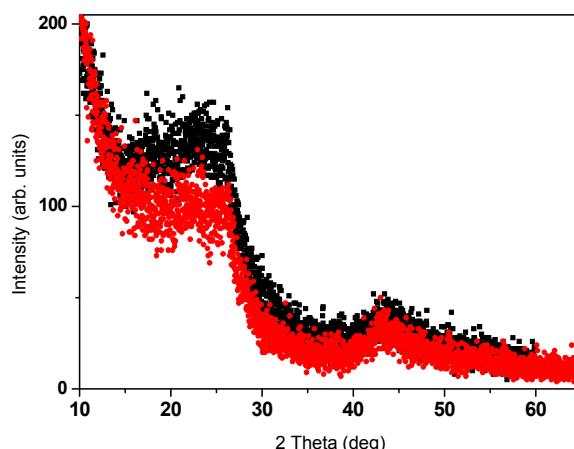


Fig. 1. XRD patterns of commercial (Fisher) a-C (black) and a-C800 (red) powders.

The a-C powders, were structurally and chemically characterized by x-ray diffraction (XRD), SEM, energy dispersive spectroscopy (EDS) JOEL JSM-7700 SEM. Trace elements analysis was performed by inductively coupled plasma (ICP) mass spectrometer (Perkin-Elmer ICP-OES model 3300) of acid extracts. The amorphous nature of the commercial a-C (Fisher) and a-C800 powders is shown in Fig. 1. SEM images taken of both a-C sources exhibit small non-crystalline grains with an average particles size of 9-10 nm.[3] EDS chemical analysis of commercial a-C (Fisher) powder yields: Na (0.30(1) at%), sulfur (0.21 at%) and oxygen (2.44(1) at%) as extra elements. ICP analysis shows the presence of the non-magnetic ions: V=2.0, Zn=7.1, Cu=11.1, Al=212.7 and Na=4625 ppm (similar to EDS), and of magnetic ions: Ni=2.8, Mn=133 and Fe=360 ppm. RT ^{57}Fe Mössbauer spectroscopy exhibit two magnetic sub-spectra attributed to ferrimagnetic Fe_3O_4 and confirm the presence of $\sim 300\pm 50$ ppm of Fe (not shown). As for the pyrolytic materials, although the initial Fe content was < 3 ppm, ICP measurements on a-CS reveal the trace element concentrations: Zn=2.7, Al=3.2, Ni=4.3 and Fe 28 ppm. Due to the evaporation of carbon, the Fe amount increases by an order of magnitude but it is still lower than that of the a-C (Fisher) powder. EDS study on this a-CS showed that the average concentrations of carbon, oxygen and sulfur are: 84% 15% and 1% respectively.

Magnetization measurements under applied dc magnetic fields (H) in the temperature range 5 K $< T < 300$ K, were obtained by a SQUID (Quantum Design) magnetometer. Each ZFC curve was recorded after adjusting the magnetometer to be in a "real" $H = 0$ state. The FC branches were recorded either via heating (FC) or cooling (FCC) processes.

3. Experimental Results

Extensive magnetic measurements on 21 pristine commercial (Fisher) samples were performed by taking 15- 20 mg powders directly from their glass container in which they were stored for 75 years. For the sake of clarity, the scattered results obtained are divided into three different groups.

(i) Fourteen samples, exhibited the magnetic features of Fe_3O_4 and the paramagnetic (PM) impurities, as shown (for sample No. 13) in Fig. 2. The temperature dependence of the ZFC and FC plots measured at 50 Oe merge around 120 K (due to magnetite) and the increase at low temperatures is related to the PM impurities. After the FC process, H was switched off and the second ZFC plot was tracked. In contrast to the phenomena shown hereafter, the two ZFC curves are reproducible and overlap. (ii) Three a-C samples have shown SC traces around 33 K and/or 65-67 K. (iii) Four samples have exhibited at low H well-distinguished peaks at 50-85 K. The a-C Prolabo a-C powders exhibited similar magnetic features as obtained for groups (i) and (iii) (Fig. 2 inset), but no SC traces have been observed. We start describing the SC states observed in two pristine commercial a-C (Fisher) powders.

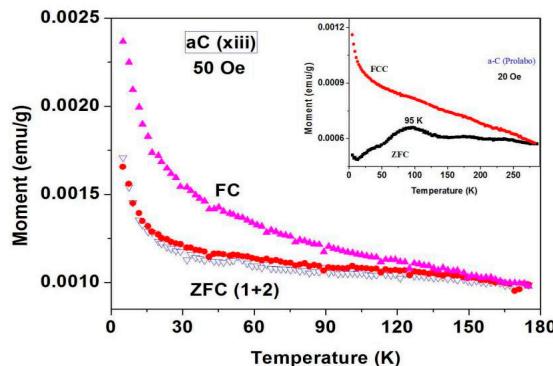


Fig. 2. The temperature dependence ZFC and FC plots measured at 50 Oe of commercial a-C (No. 13) sample. Note the reproducibility of ZFC process. The inset shows the data obtained for "Prolabo" a-C powder.

(A) Superconductivity:

(1) *a-C commercial powder*. Fig. 3 (left) shows two ZFC plots (normalized at 70 K) of the pristine a-C powder (sample No. 1) measured at H=15 and 30 Oe. The 15 Oe curve shows two drops attributed as SC transitions, at $T_c = 33(1)$ K and $T_c = 64$ K(1). The estimated shielding fraction (SF) below 30 K is $\sim 0.03\%$. No corrections for the PM impurity contributions were made. Due to the inhomogeneous a-C powder, this SF value provides the upper limit for the SC volume fraction. Since the a-C powder contains 0.21 atm% of sulfur we tend to believe that the two SC phases are due to two different a-CS phases. Due to their lower SF fractions, all attempts to isolate these phases and/or to determine their compositions were unsuccessful. The signature at $T_c = 64$ K is washed out for H= 30 Oe, which is probably higher than the critical fields of this SC phase. The lower T_c transition shifts with H (up to 1.5 kOe) to lower temperatures as expected as shown in Fig. 3 (right inset). For $H > 1.5$ kOe the PM impurities as well as the presence of magnetite obscure the SC transition. The $T_c(H)$ is proportional to the conventional BCS relation: $\sim [1 - (T/T_c)^2]$ where $T_c = 31$ K is free parameter obtained. Since the SC transition is not visible at higher fields, any determination of $H_{C2}(0)$ is misleading. Due to the contribution Fe_3O_4 and the PM ions further characteristic parameters of the SC states were not evaluated. The amorphous nature of the nano-size a-C particles, does not permit compact the powder into pellets therefore no resistivity studies could be performed.

Fig. 3 (left panel inset) also shows the isothermal magnetization $M(H)$ curve at 5 K in which a linear increase up to ~ 50 Oe and instabilities at higher fields are observed. Due to the presence of ~ 350 ppm of Fe_3O_4 we believe that the linear part is a superposition of the negative Meissner contribution of the SC phases and the positive linear $M(H)$ shape of magnetite. Therefore these instabilities presumably express the magnetic flux line penetration above $H_{C1} \sim 50$ Oe of the SC phases. A similar curve at 10 K yields H_{C1} of 40 Oe.

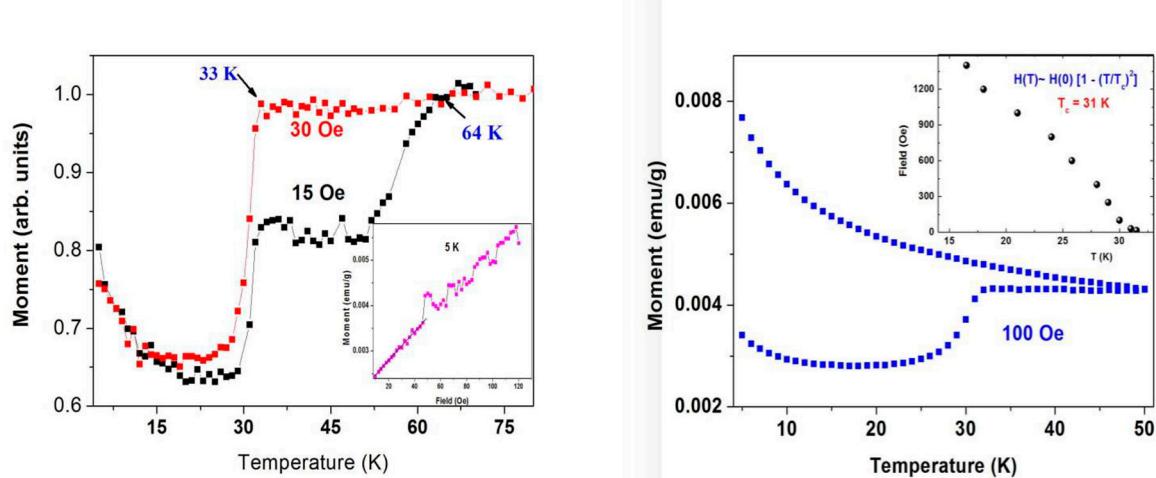


Fig. 3. ZFC curves of commercial (Fisher) a-C powder (sample No. 1) measured at 15 and 30 Oe (left). The ZFC and FC plots measured at 100 Oe are shown in the right panel. The insets show the low field isothermal magnetization at 5 K (left) and the variation of T_c with field (right).

Fig. 3 also shows the ZFC and FC branches for sample 1 measured at 100 Oe. The SC transition around 33 K is observed in the ZFC branch only. At low temperatures, both branches decrease with temperature and adhere closely to the PM Curie-Weiss (CW) law: $\chi(T) = \chi_0 + C/(T - \theta)$, where χ_0 is the independent part of the susceptibility, C is the Curie constant, and θ is the CW temperature. The PM parameters deduced from the FC are: $\chi_0 = 4 \times 10^{-5}$ emu/g Oe, $C = 4.3 \times 10^{-4}$ emu K/g Oe and $\theta = -5.8(2)$ K.

The two SC phases at $T_c = 34(1)$ K and $T_c = 64$ K(1) were also observed separately in other a-C systems. The SC phase with $T_c = 34$ K was obtained in a-C thin films and presented later in Fig. 8. Whereas, the highest $T_c = 64$ K phase was observed in another a-C commercial sample (No. 18), where the ZFC and FC plots (measured at 40 Oe) show distinct SC transitions at $T_c = 67$ K and 64 K respectively (Fig. 4). The SF=0.07% is twice as much as that of the previous sample, but still too low to determine its composition. This T_c is highest achieved for all a-C powders reported here. In order to reduce the magnetic contributions of magnetite and the PM impurities we show in (Fig. 4 inset) the ZFC-FC plot which becomes almost zero around 65 K. The low temperature FC branch PM behavior can be fitted with the same CW law (Eq. (i)) with almost similar parameters as listed above.

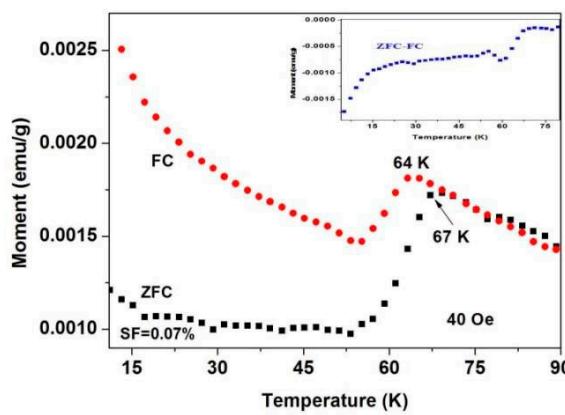


Fig. 4 ZFC and FC curves of another commercial a-C powder (No. 18) measured at 40 Oe, with $T_c = 67(1)$ K. This is the highest T_c achieved among all a-C materials. The ZFC-FC plot is shown in the inset. (Taken from Ref. 3)

Commercial a-C reacted with sulfur at 250°C (a-CS). EDS studies showed that the pristine a-C material contains ~ 0.21 at% of sulfur. Bearing in mind that the SC phase originates from a-CS phases, an attempt to increase the sulfur content by mixing different commercial a-C powders with sulfur (ratio 2:1) and heating the mixtures at 250°C have been made. It appears that also the synthesized a-CS products are inhomogeneous. That means that parts taken from the same synthesized batch may exhibit different magnetic behavior. Two a-CS samples (out of many) have shown SC signatures as follows.

The first a-CS sample (see Ref. 2) shows a clear SC transitions in both ZFC and FC branches at $T_c = 38(1)$ K. EDS measurements on this a-CS sample indicate that only the sulfur content increased to ~10.3 at%, whereas practically no change was detected for all other extra element concentrations. The data obtained for this sample are presented in Figs. 5. In addition to the ZFC and FC plots we also show in Fig. 5 the remnant magnetization (M_{rem}) plot which was recorded after tracing the FC (via cooling) down to 5 K, and switching off H to zero. The pronounced step-like features in both ZFC

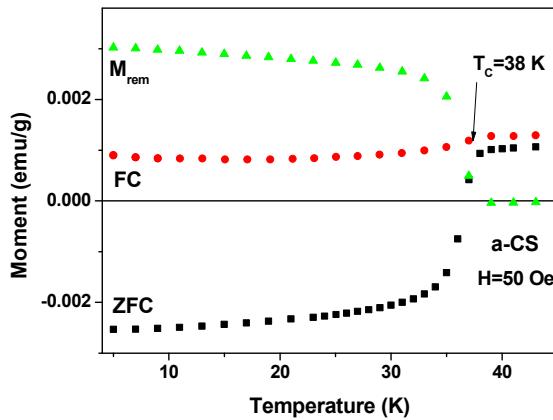


Fig. 5. ZFC, FC and the remnant magnetization (M_{rem}) of a-CS measured at 50 Oe. The magnetization due to Fe_3O_4 is subtracted from all three branches.

and M_{rem} definitely prove the existence of a type II SC state below $T_c = 38 \pm 1$ K. The estimated SF=0.15% is higher than that obtained for pristine a-C, therefore the diamagnetic nature of the ZFC is clearly observed. This expresses the enhancement of the SF triggered by sulfur. Due to the higher SF, a drop at T_c (the Meissner effect) though smaller in magnitude, is well observed in the FC branch. This drop serves as the typical fingerprint for bulk SC in a-CS.

The second a-CS sample (prepared separately at 250°C), shows a sharp peak at $T_c = 65$ (1) K. (Fig.6). In that sense, this T_c value agrees well with the highest T_c SC phase exhibited in Fig. 3. It may be speculated that this peak is attributed to the peculiar magnetic features observed in a-C and a-CS materials as described below, however, the isothermal $M(H)$ plots of this sample (Fig. 6 inset) definitely oppose this assumption. The linear diamagnetic signal of the normalized isothermal $M(H)$

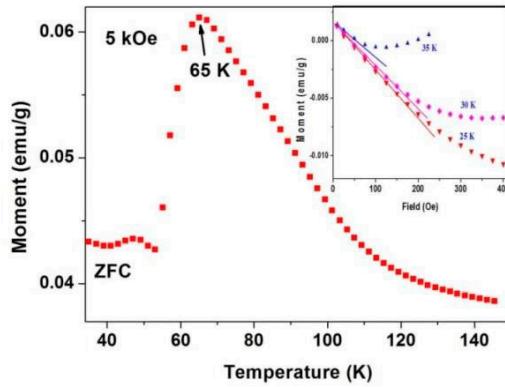


Fig. 6. ZFC plot measured at 5 kOe of a second a-CS sample. The inset shows the typical SC isothermal $M(H)$ curves measured at 25, 30 and 35 K.

plots up to H_{C1} and the deviations from linearity for $H > H_{C1}$ (which decreases with temperature) prove undoubtedly the Meissner state of this SC phase. In the PM range the M/H values are fitted by the CW law with: $\chi_0 = 7.1 \times 10^{-6}$ emu/g Oe, $C = 3 \times 10^{-5}$ emu K/g Oe and $\theta = 86$ (1) K. Thus, Figs. 5-6 definitely prove that the two SC phases of a-C (Fig. 3) are reproducible and also observed in a-CS.

(2) *Pyrolytic a-C powder.* In contrast to the commercial a-C powder, this a-C powder was fabricated by heat treatment of sucrose up to 650 °C. Here again, XRD pattern and SEM images confirmed the amorphous nature of this a-CS powder. The two ZFC and FC plots of the fabricated blank a-C powder (prior to the synthesis with sulfur), are depicted in Fig. 7 (inset). This powder is diamagnetic and the low temperatures PM behavior is induced by tiny amount of impurities. The PM parameters values deduced (for the ZFC branch) are: $\chi_0 = -4.4 \times 10^{-7}$ emu/g Oe, $C = 8.32 \times 10^{-6}$ emu K/g Oe and $\theta = 0.16$ K.

The a-CS materials were obtained by mixing this fabricated a-C powder with sulfur and heated the mixture at 250 °C and/or 380-400°C under a protective atmosphere. Extensive magnetic measurements have been performed on many pyrolytic a-CS powders. It appears that all these a-CS materials are not homogeneous and exhibits scattered results. Similar to the commercial powders, the a-CS examples may be divided into three groups. (i) Most of the samples have shown the similar magnetic behavior as presented in Fig. 2. (ii) One a-CS sample (obtained at 250 °C) showed a sign of a SC phase at $T_c = 17$ K (not shown). (iii) The rest exhibited pronounced peaks at 50-60 K in their *first* ZFC curves as described later. A second stage of heating at 380 °C for 3 hours, yields a SC phase at $T_c = 42$ K its SF is around 0.02% (Fig. 7). The lower positive PM moments are caused by PM impurities. As a result, the so called-Verwey transition of Fe₃O₄ at 120 K is readily observed where the two branches merge. This Verwey transition is attributed to electron hopping between the octahedral sites of Fe²⁺ and Fe³⁺ ions in Fe₃O₄. The peaks at 53 K in both ZFC and FC branches (Fig. 7) are related to the spontaneous magnetic order of solid oxygen which apparently has been detected by the EDS studies. It is important to note that the presence of oxygen appears as peaks in **both** ZFC and FC branches. [25]

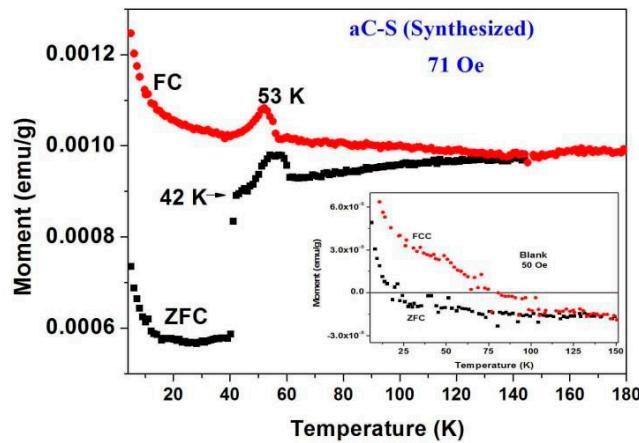


Fig. 7. ZFC and FC curves measured at 71 Oe of a pyrolytic a-CS powder obtained after heating at 380 °C. The inset shows the almost diamagnetic behavior of the pyrolytic blank a-C material.

(3) *Superconductivity in a-C thin films:* As a third example we present here the magnetic data collected on a-CS thin films. Six a-C thin films were grown by the EBID method (blank) and show a positive constant magnetization. This clean system is a result of an absence of PM and/or iron impurities. These films were treated with sulfur and two them exhibit SC traces.[24] One a-SC film (heated with sulfur at 250 °C), exhibits a clear SC at $T_c = 34.4(0.5)$ K (Fig. 8), where the presented ZFC and FC plots were obtained after subtracting the blank magnetization. It is readily observed that below T_c , both the ZFC and FC

magnetization curves are diamagnetic (as expected) and the FC curve exhibit the typical expulsion of the field lines (the Meissner effect). T_c shifts with H (up to 2 kOe) to lower temperatures with a rate of $dH/dt = 0.45$ kOe/K (not shown). The blank films contain W inclusions embedded in the a-C matrix. These inclusions are not responsible to the SC state, since SC appears only after the sulfur treatment. They only enhance the phase coherences by Josephson coupling of nearby localized SC regions. Fig. 8 (inset) shows two typical isothermal hysteresis loops. Below H_{c1} at ~ 600 and ~ 400 Oe for $T = 5$ and 10 K, respectively the M(H) curves are linear. The non-percolative small SF does not permit resistivity or STM studies.

Thus, in addition to the *commercial* a-C and a-CS samples (Figs 3-6), The SC state observed in the *pyrolytic* a-CS powders and in a-CS thin films were induced by sulfur. This definitely prove our claim that the various a-CS phases are the origin of SC in all a-C materials studied.

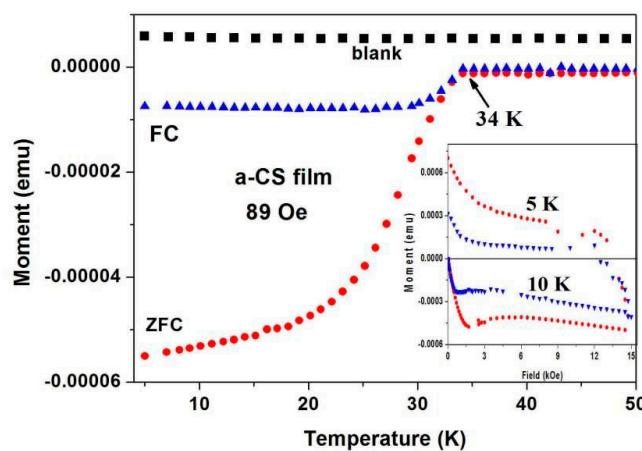


Fig.8. ZFC and FC branches of a-CS thin film without any PM and Fe impurities. The M(T) plot of the blank a-C film (black) is also shown. The Inset exhibits two typical isothermal M(H) plots at 5 and 10 K, confirming conclusively the SC state in this film. (Taken from Ref. 3)

(B) Unusual Magnetic properties:

Thermal irreversibility in dc magnetic measurements at constant dc field (H) is a well-known common phenomenon. It is readily found in FM, antiferromagnetic (AFM), spin-glass systems and in SC materials as well. In all standard cases the FC curves lie *above* the ZFC curves (FC>ZFC) up to a typical characteristic transition temperatures attributed to the various physical states.

The unusual magnetic behavior where the FC branches cross the ZFC curves (ZFC>FC) has been recently observed in two unrelated materials: in (i) inhomogeneous commercial and fabricated a-C and a-CS [2] and (ii) in a chiral-based magnetic memory device its structure and electrical properties are reported in Ref. [26]. Unexpectedly, in a-C and a-CS, two anomalies are observed. (1) Pronounced peaks at 50-80 K are observed in the ZFC branches only. Around the peaks position, (in contrast to the usual behavior) the ZFC branches lie above the FC curves (ZFC>FC). (puzzle 1) (2) This unusual behavior is irreproducible and disappears in the second ZFC run (puzzle 2). These two phenomena are intrinsic properties of the a-CS materials and are connected to each other. They are not ascribed neither to conventional FM nor to any magnetic impurities such as magnetite and/or oxygen. We present here the most unexpected magnetic results appeared in both commercial and fabricated a-C and a-CS materials, starting with the commercial a-C800.

(i) *Magnetic studies of commercial a-C samples:* Around 200 mg of the commercial a-C were heated at 800°C under ambient condition (a-C800). At that temperature the amorphous carbon particles were completely evaporated and the residue contained inorganic impurities only. The ZFC and FC plots for a-C800 measured at 100 Oe are shown in Figure 9. It is observed, that this material is composed of two magnetic phases: (i) The FM-like feature with a sharp transition at 123(1) K in both branches (the Verwey transition) which are related to the presence of ferri-magnetically Fe_3O_4 as deduced from both ICP and Mössbauer spectroscopy studies discussed above. The Verwey transition is attributed to electron hopping between the octahedral sites of Fe^{2+} and Fe^{3+} ions in Fe_3O_4 . The bifurcation of the ZFC and FC curves at RT is caused by Fe_3O_4 its magnetic transition is at 853 K. The narrow hysteresis loop measured at 10 K (Fig. 9 inset) confirms this interpretation. (ii) At low temperatures, the ZFC branch exhibits the typical PM shape and by using the CW law we obtain: $\chi_0 = 1.7 \times 10^{-6}$ emu/g Oe, $C = 3.24 \times 10^{-5}$ emu K/g Oe and $\theta = -0.5$ K. Extrapolation of these values to high temperatures yields the curve assigned as PM in Fig. 9, which is well below both ZFC and FC curves. This PM curve serves as a background to all other a-C materials shown below.

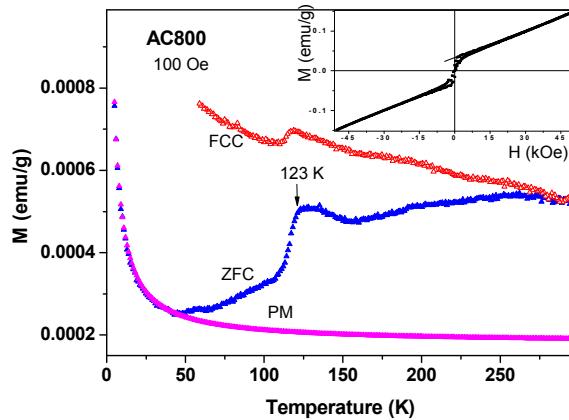


Fig. 9. ZFC, FC and PM branches for a-C powder heated to 800 °C measured at 100 Oe and the hysteresis loop at 10 K (inset).

Four pristine commercial a-C samples have exhibited pronounced peaks at 65-85 K in their ZFC branches and a typical behavior (sample No. 6) is shown in Fig. 10. The ZFC plot demonstrates a pronounced peak at 80 K and the FC branch lies above ZFC one in the entire temperature range. The peak position is field dependent and shifts with H to higher temperatures (Fig. 10 inset). The bifurcation of the two curves at RT is due to Fe_3O_4 .

Peaks at $T \sim 50$ -60 K may originate from adsorbed oxygen.[18] Indeed, solidified of oxygen traces are already observed (see Fig. 7) but the peaks in Fig. 10 cannot be attributed to oxygen because (i) they appear at much higher temperatures. (ii) Solidification of oxygen appears in **both** ZFC and FC curves (Fig. 7) and the related peaks are small and negligible as compared to the major magnetization peak. Therefore these peaks are believed to be intrinsic to all a-C materials which contain another magnetically unpaired localized spins active phases. As a result, the magnetic behavior of

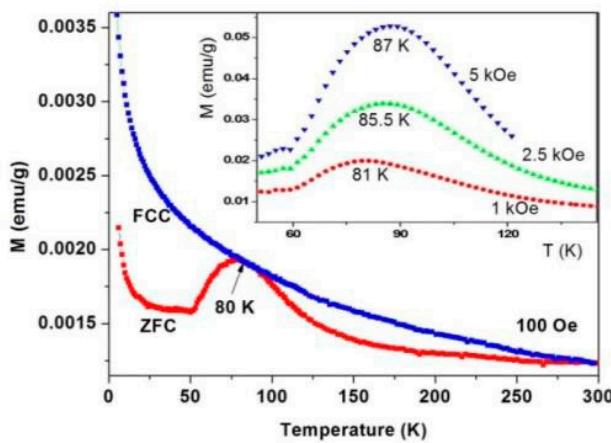


Fig. 10. ZFC and FC curves for a-C powder (No.6). The ZFC curve lies below the FC one. The field dependence peak position is exhibited in the inset.

pristine a-C sample is composed of three sources: Fe_3O_4 (as discussed above), the PM impurities which are responsible to the low temperature rise and an unknown additional intrinsic magnetic phase which does not exist in crystalline carbon as discussed later. The peak amplitude in Fig. 10 is higher than that of a-C800 (Fig. 9). Therefore the Verwey transition around 120 K is not visible. Another a-C sample (No.5) shows that in a certain range of temperatures the ZFC curve lies above the FC one (Fig. 11). This is a rare phenomenon which is more pronounced in the a-CS materials synthesized at 400 °C, as presented below.

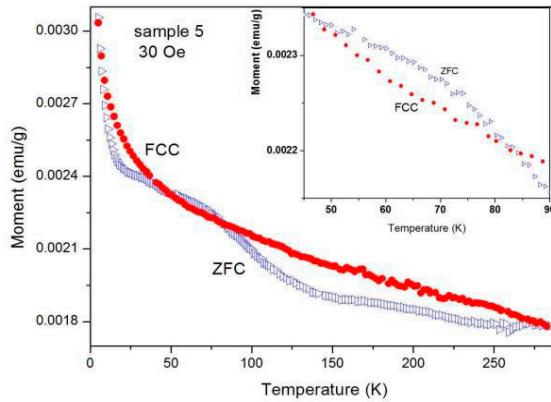


Fig.11. ZFC and FC branches of commercial a-C powder (No.5) measured at 30 Oe. The ZFC curve lies above the FC one. The inset extends the temperature range in which this phenomenon occurs.

Magnetic studies of a-CS samples synthesized at 400 °C. The Traces of SC phases in a-C and in a-C synthesized with sulfur (a-CS) at 250°C discussed above motivated us to explore a-CS materials which were synthesized at 400°C. Several a-CS samples were synthesized. Since the a-C powder is not homogeneous, it may be expected that synthesis at elevated temperatures, would produce better homogeneous products. It appears however, that all synthesized samples remain inhomogeneous. In what follows, the magnetic properties of two a-CS parts (part I and III) taken from the **same** batch of sample 1 are described. Part II exhibited similar magnetic behavior to that shown in Fig.2. EDS study of this a-CS sample shows that the sulfur content increases to 0.69 at %, value which is a bit higher than 0.21 at % obtained for pristine a-C powder, but much smaller than that of a-CS sample synthesized at 250 °C.

Sample 1 part I. The ZFC and FC curves measured at $H = 100$ Oe and 1 kOe are presented in Figs. 12-13. The magnetic irreversibility up to RT, and the peak in ZFC(T) at 78 K can easily be seen. Due to the high ZFC peak, the FC branch crosses the ZFC one, (see also Fig. 11) thus in this temperature range (63 - 106 K) we observe unexpectedly that ZFC>FC (puzzle 1). Here again, the ZFC(T) and FC(T) merging at RT is due to Fe_3O_4 . Note the minor peak around 50 K which is attributed to the spontaneous magnetic order of solid oxygen as discussed above. At low temperature the PM plot follows the CW law and the PM parameters deduced are: $\chi_0 = 6.1 \times 10^{-6}$ emu/g Oe, $C = 1.72 \times 10^{-5}$ emu K/g Oe and $\theta = 0.41$, values which are very similar to these obtained for a-C800 (Fig. 9). This C value corresponds to PM effective moment $P_{\text{eff}} = 0.04 \mu_B/C$. Here again, the additional PM curve, which lies below the ZFC and FC plots, is the extrapolation of the low temperature range of ZFC(T) to higher temperatures. The isothermal magnetization $M(H)$ curve measured at 5 K (Fig. 12 inset) first increases linearly up to 20 kOe and then tends to saturate. This curve may be fitted as: (ii) $M(H) = H(-\chi_d + \chi_p)$, where $\chi_d = -2.8 \times 10^{-5}$ and $\chi_p = 2.7 \times 10^{-5}$ emu/g*Oe are the a-C matrix intrinsic diamagnetic and the PM ions contributions, respectively.

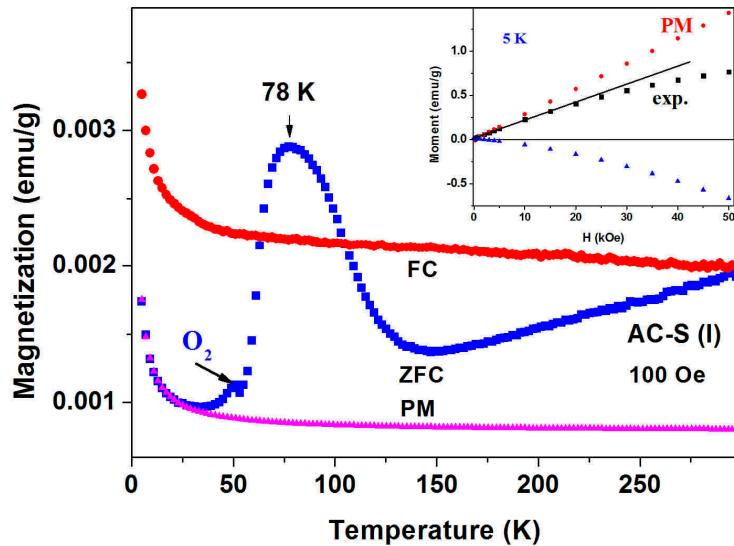


Fig. 12. ZFC, FC and PM branches measured at 100 Oe for a-C-S (sample 1, part I) heated to 400 °C. The black arrow points to the oxygen solidification contribution. The inset shows the experimental isothermal $M(H)$ (in black) and the linear PM contribution (in red) at 5 K.

At 1 kOe the irreversibility observed in Fig. 12 disappears and both ZFC and FC curves coincide in one curve (Fig. 13). The peak position is field dependent and shifts to lower temperatures with H , in contrast to Fig. 10. The peaks are at: 71, 67 and 59 K for $H=1$, 5, and 10 kOe respectively (Fig. 13, inset). At higher applied fields, the PM contribution masks the peaks and they are not visible.

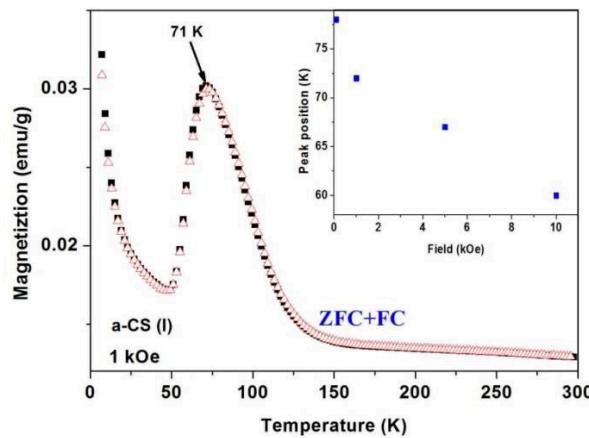


Fig. 13. ZFC and FC branches of a-CS (sample 1, part I) measured at 1 kOe. The field dependence of the peak position is shown in the inset.

The measurements of a-CS sample 1, part III, are exhibited in Fig. 14. The most striking effect is that below 150 K, the entire ZFC curve is **above** the FC one down to 5 K, whereas at higher temperatures (inset) the FC signals exceed the ZFC curves as expected. This indicates that this peculiar behavior does not stem from any experimental failure. The two ZFC>FC phenomena (Figs 12 and 14) have the same origin and the slightly discrepancy may be caused by tiny differences in their inhomogeneous composition.

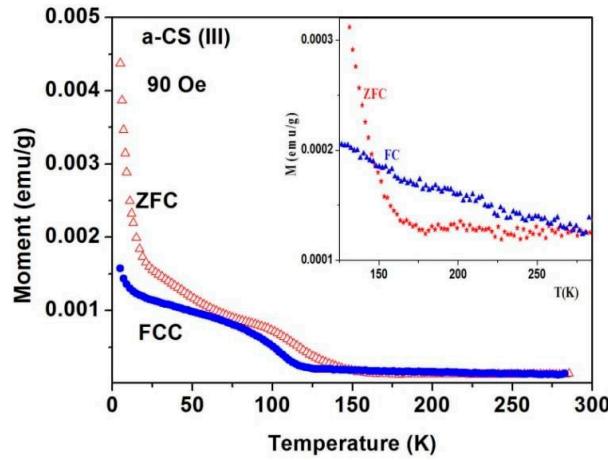


Fig. 14. ZFC and FC branches of a-CS (sample 1, part III) measured at 90 Oe. The inset shows the normal behavior of these plots above 150 K.

Magnetic properties of pyrolytic a-CS samples synthesized at 400 °C. The magnetic behavior of the blank pyrolytic a-C powder was already presented in Fig. 7(inset). Several a-CS samples have been synthesized at 400 °C and the scattered results obtained are very similar to that shown above. In Fig. 15 and 16 we show two examples, out of many, which definitely prove that puzzle 1 is reproducible.

Sample 1. In order to explore the peak nature in the ZFC branch we show in Fig. 15 the measurements at 500 Oe of sample 3 (part III) where two ZFC and FC processes were performed. The protocol of Fig. 15 is as follows. (a) In order to shorten the elapsing time between the two measurements, the SQUID magnetometer was set to 20 K at H=0. Then, the field was turned on to 500 Oe to trace ZFC(I) curve. (b) At 150 K the FCC(I) (via cooling) plot was measured back to 20 K. (c) The field was switched off, the SQUID was heated to RT and *immediately* cooled back to 20

K. (d) The field was switched back on to 500 Oe to record the ZFC(ii) up to 70 K and (e) the FCC(ii) process was completed.

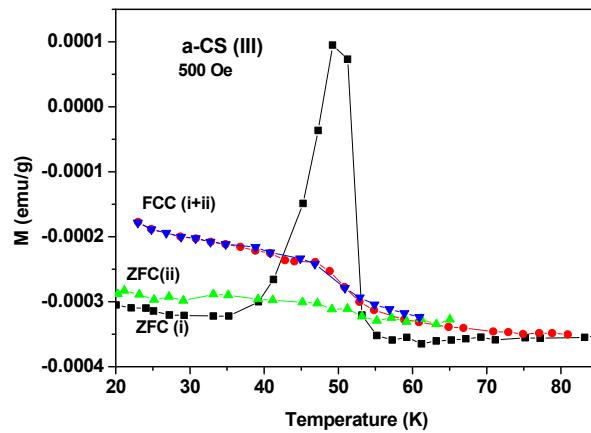


Fig. 15. Two ZFC and FC plots of pyrolytic a-CS (sample 1 part III) measured at 500 Oe. The ZFC(i) (in black) and FCC(i) (in red) curves were measured up to 150 K and ZFC(ii) and FCC (ii) up to 70 K. (Taken from Ref. 3)

Similar to Figs. 11-12 the pronounced peak around 50 K in the ZFC(i) run did not show up in the FCC(i) plot which crosses the ZFC(i) one at 42 and 53 K (ZFC>FC, puzzle 1). Moreover, this peak is totally suppressed in the ZFC(ii) curve which was measured half an hour later (puzzle 2). It is interesting to note that FCC(i) coincide FCC(ii), indicating that the peak in ZFC(i) does not stem from adsorbed oxygen, and is not an experimental artifact. This also proves that the sample was not damaged and that no extra magnetization was gained during these short measurements.

Sample 4(part III). Fig. 16 shows three sequences performed on another pyrolytic a-CS using the same protocol as for Fig. 15. Here again, the two puzzles are present and the two FCC branches overlap. For the sake of clarity FCC(II) is not shown. The $M(H)$ at 5 K of the pyrolytic a-CS sample is shown in Fig16 (inset). Due to small amount of magnetite and PM impurities, $M(H)$ at low fields is positive, saturates at $M_S = 0.0021$ emu/g and then becomes diamagnetic. This M_S value corresponds to 20.3 ppm of Fe_3O_4 ($M_S = 94.5$ emu/g) and fits well to Fe concentration accepted from ICP study reported above. This material was restored under protective conditions and was measured again 18 months later. Surprisingly, the peak in the ZFC(III) run re-appear at 63 K. Although this temperature is lower than 75 K, the fact that the elusive ZFC peak is restored with time is appealing.

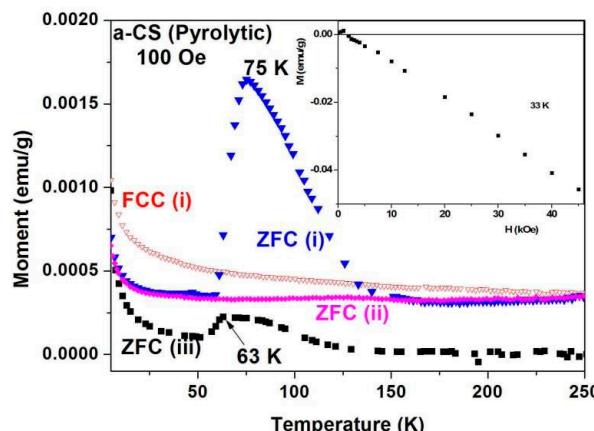


Fig.16. Two ZFC and FC plots of a-CS synthesized from pyrolytic a-C at 400 °C (sample 4 part III) measured at 500 Oe. ZFC(III) was measured 1.5 years after ZFC(I) and ZFC(II). The almost diamagnetic M(H) plot at 5 K is shown in the inset. (Taken from Ref. 3)

(iii) *Magnetic studies of a-C+B and crystalline graphite*. The same two puzzles described above have been observed in a mixture of pristine a-C powder and boron powders (instead of sulfur) which were reacted at 400 °C (a-C+B). Fig. 17 shows two ZFC and one FCC measured similarly to the protocol described previously. All the features described above appear here too. However, since this a-C powder contains sulfur, it is possible that this behavior is related to tiny a-CS fraction imbedded in the a- C+B matrix.

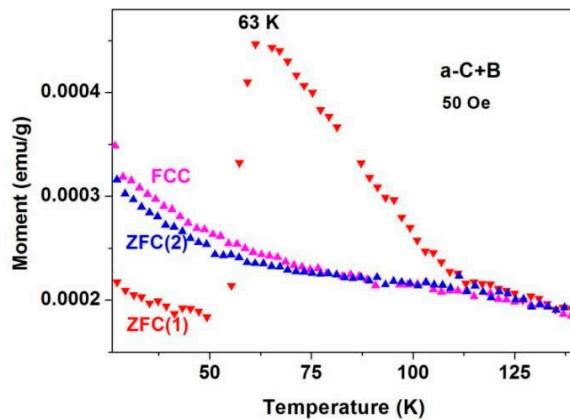


Fig. 17. ZFC and FC curves measured at 50 Oe for commercial a-C powder synthesized with boron at 400 °C. (Taken from Ref. 3)

As a final point of interest, Fig. 18 shows magnetic studies performed on a mixture of crystalline graphite (BDH) and sulfur which was synthesized at 400 °C under the same conditions described above. The magnetic impurities traces (not determined), dictate the plots shape in Fig. 18. None of the two mentioned puzzles are observed here. The results obtained are consistent with resent data published on highly ordered pyrolytic graphite (HOPG). [27]

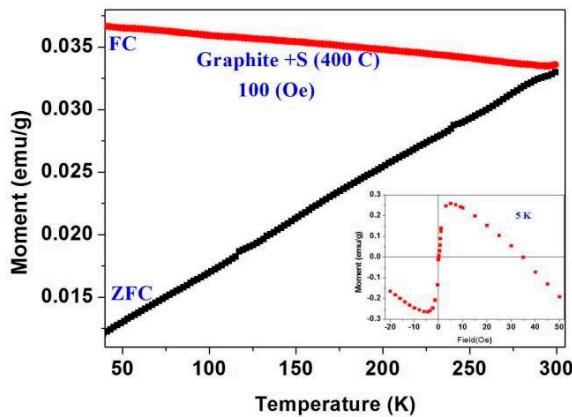


Fig. 18. ZFC and FC curves measured at 100 Oe for crystalline graphite synthesized with sulfur at 400 °C. The isothermal M(H) plot at 5 K is shown in the inset.

The accumulated experimental results of both inhomogeneous commercial and fabricated pyrolytic a-C powders (Figs 9-17) can be summarized as follows: (1) both a-C powders are magnetically inhomogeneous. (2) The materials and their a-CS products contain traces of Fe_3O_4 and PM impurities. (3) At low applied fields, a few a-C powders reveal huge peaks in their ZFC curves at 50-80 K their positions and relative amplitudes are sample and field dependent. (4) In a-CS, the FC curves cross the ZFC ones, (puzzle 1). (5) These peaks are present in the first ZFC(I) runs only and suppressed in the ZFC(II) or FC processes performed very shortly later (puzzle 2). (6) This peak reappears after 18 months (Fig. 16). (7) The two puzzles are also observed in a-C+B but not in crystalline graphite. (9) The two puzzles are intrinsic properties of the a-CS materials. Even if this maximum is related to extra magnetic impurities, the mechanisms that produce such anomalies remain still unclear. (10) This complex inhomogeneity, does not allow neither to measure twice the same material nor to compare results between two samples which were taken from the same batch. Obviously, the two puzzles are inter-related and connected to each other. It is quite obvious that the first puzzle is a direct consequence of the second one. Since these peaks appear only in the ZFC(I) plots, the following ZFC(II) and/or the FC branches, behave "normally" and as shown in Fig. 2. The main problem remains as to the origin of the elusive peaks as discussed hereafter.

4. Discussion

Defect-induced magnetism in CBM may become the "Next Big Thing" in materials science, in particular, the sulfur doped porous carbons materials which have gained a great deal of attention in the last few years. [28] The above results on inhomogeneous commercial and fabricated amorphous carbon powders definitely prove the existence of: (i) traces of type II superconducting phases with T_c up to 65-67 K and (ii) two unusual magnetic phenomena rarely observed in the past. All samples contain small amounts of sulfur and it is believed that both features are due to various intrinsic a-CS phases their structures and compositions are yet unknown. All a-C powders studied contain FM (probably Fe_3O_4) and PM impurities, their presence may obscure parts of the results. However, the plausible consequence is that both SC and/or peculiar magnetism are intrinsic to the a-C carbon matrix and do not arise from these impurities (or from adsorbed oxygen).

Superconductivity. The data presented above reveal clear evidences for **two** type II superconducting states in a-C powders or a-CS, at $T_c \sim 34$ -42 and ~ 65 K, suggesting that these states stem from **two** different a-CS phases. Traces of the two SC phases were observed in **three** independent a-C sources. (i) A 75 year old commercial a-C powder which contains 0.21 at % sulfur (Figs. 3- 4). A reaction of this a-C powder with sulfur at 250 °C increases the sulfur concentration and the SC volume fraction by an order of magnitude although T_c remains 38 K. That enables to deduce the lower and upper critical fields phase diagrams and to confirm the type II SC state. [2] (ii) A diamagnetic fabricated a-C powder (sulfur-free) synthesized from sucrose. [23] However, when powder reacted with sulfur at 250°C and further heated to 400 °C, traces of a SC phase at $T_c = 42$ K was observed. (iii) The most convincing evidence comes a-C thin films grown by EBID which are free from PM and magnetic impurities. The reaction with sulfur at 250 °C induces a sharp SC transition at $T_c=34$ K and the flux expulsion in the FC branch is clearly observed.

The existence of these two SC phases in a-CS should be taken with a grain of salt. (i) The low SF deduced clearly indicates that the SC states observed are not bulk properties (ii) Due to the unavoidable FM and PM impurities not all SC phases exhibit the Meissner effect. (iii) The a-C powder is incompressible and it was impossible to confirm the SC states by transport and/or STM measurements. (iv) The two SC phases compositions are yet unknown. (v) Since only traces of the SC phases have been detected, any attempt to classify their nature (s-type or p-type etc.) would be misleading. However, the accumulate results presented here prove unambiguously that two SC phases with T_c up to 65 K do exist in a-C powders when doped with sulfur. We may assume that these traces support the long-sought after interfacial mechanism proposed by Ginzburg in 1964. [29]

The present observations are consistent with recent results on double-wall carbon nanotubes tube DWCNT bundles, in which SC at $T_c=15$ K was deduced. It is assumed that adsorbed sulfur may induce structural disorder can locally trigger extra carriers (doping effect) into the graphite/graphene walls and to enhance SC [30]. They are also consistent with theoretical approach which claims that structural disorder, topological defects and/or foreign atoms adsorption (S or P), may induce SC in graphite [31]. Note, that in all these experiments only localized (not bulk) SC traces (low SF) were observed and that the SC transitions are significantly scattered among the different samples.

As a final point of interest, we cannot disregard the breakthrough made last year. Although HTSC was discovered in 1986, much of their SC properties nature remains unexplained. The last year discovery that sulfur hydrides under high pressure (200 GPa) becomes SC at $T_c = 203$ K, enlarged the mystery of the HTSC materials. [11-12] SC in H_2S was definitely proven by resistivity measurements followed by the Meissner effect. It was clearly evidenced that under high pressure H_2S decomposed to H_3S which is supposed to be the HTSC phase. The strange thing about SC in H_3S is that (unlike other HTSC) it follows the conventional BCS theory by showing a huge isotope effect. The key for SC in H_3S is the interaction between the electrons and the high frequencies hydrogen vibrations of the light hydrogen atoms. We may add with some confidence that using the same token we may explain the SC state in sulfur doped a-C. The relatively light nonmetallic carbon atoms (next to hydrogen in the periodic table) and their high vibration frequencies as simple harmonic oscillators induce SC even at *ambient pressure* with T_c as high as 67 K. Thus the common denominator in both a-CS and H_3S systems are low mass atoms and sulfur which may be the basic ingredient components in new HTSC. Alternatively, it is possible that the a-C and a-CS powders contain small amount of hydrogen (not detected by EDS) and that the observed SC states are pressed H_2S (H_3S) embedded or adsorbed in the amorphous carbon particles. This scenario implies that a-CS and/or other CBM materials are promising candidates for discovery new high T_c superconductors.

Peculiar magnetic behavior. We have observed an impressive thermal irreversibility in FC and ZFC curves of the inhomogeneous a-C powders which also contain magnetite and PM impurities. The plausible consequence is that this irreversibility does not arise from these impurities or from molecular adsorbed oxygen. In commercial and fabricated a-CS samples (synthesized at 400 °C), two unexpected reproducible magnetic phenomena are observed: (a) pronounced peaks at 50-80 K appear in the virgin ZFC branches, and around the peak positions the FC curves cross the ZFC plots (ZFC>FC, puzzle 1). This unique phenomenon is in contrast to the general trend where FC > ZFC. (b) The peaks appear are elusive and suppressed in the second ZFC and/or FC runs performed short times later (puzzle 2). (c) The suppressed peak reappears after 18 months (Fig. 16). These peculiarities are not observed in crystalline graphite. That means that these two puzzles are not accidental, but are connected to the amorphous appearance of the a-C powders. We do not have any consistent explanation to these three phenomena. Nevertheless, it is quite obvious that the first puzzle is a direct consequence of the second one. The suppression of extra magnetization gained in the first ZFC, directly affects the second ZFC and/or the FC branches which exhibit a normal behavior (FC>ZFC) as shown in Fig. 2. The possibility that experimental errors and/or adsorbed oxygen are the reason for these phenomena have been excluded. Two questions remain unanswered yet: (i) the origin of the peaks and (ii) the reason for their disappearance after the first ZFC run.

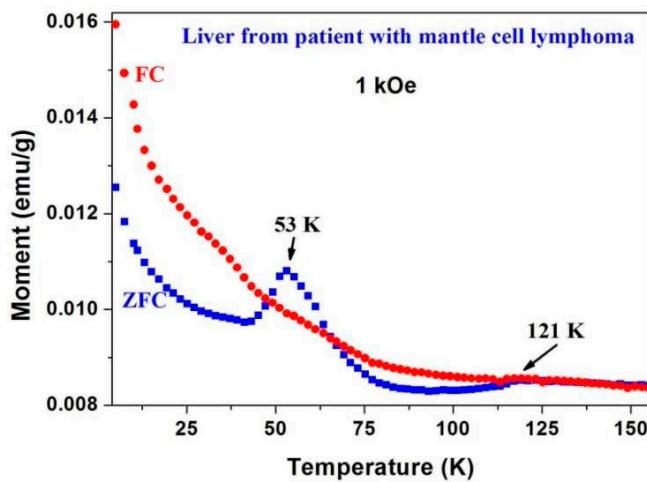


Fig. 19. ZFC and FC curves of human liver taken from a patient with mantle cell lymphoma.

As a hand waving qualitative explanation, we may assume that the a-CS systems are in a double-well potential state with a probability to find the system in one of the two wells. Sulfur in a-CS is distributed in an inhomogeneous manner and may induce several ordered states such as: FM or AFM, spin-glass, etc.). It may occur that in virgin ZFC run the system is trapped in a one magnetic potential well state and shifts to the second state in the following ZFC(II) or FC processes. As more preferable explanation, we may propose that prior to applying the external field the carbon magnetic moments are *randomly distributed* over the entire volume. The low H directs these moments to flip *along* its direction in a parallel FM-like manner. Above the peaks position which are sample dependent (55-80 K), the antiparallel exchange coupling is more favored and the AFM-like behavior is more preferred. As a result, in the following sequences, the net magnetic moment is lower than that of the virgin ZFC one. Note that at high H the irreversibility is absent (Fig.12) and the system behaves "normally".

It should be noted that in addition to a-CS reported here, the magnetic peaks in the ZFC branch as well as the unusual ZFC>FC behavior, was observed in three other unrelated systems: In (i) chiral-based magnetic memory device [26], in (ii) double DWCNT in which the peak is elusive and disappears after the ZFC run, [30] and unexpectedly (iii) in liver taken from a patient with mantle cell lymphoma (Fig 19). The common denominator is that all four samples contain (a) carbon (the major component in the chiral-based magnetic memory device) and (b) a magnetic element such as Fe or Ni. Since the magnetic state is metastable phenomenon, long, systematic experimental research is needed. The current state of experiments does not allow us to suggest any consistent explanation to the peculiar phenomena presented here. They definitely warrant further theoretical and experimental investigations.

The highest SC T_C values (65 K) and the peak position in the first ZFC(I) branches are very close to each other. Therefore we may suggest that the extra magnetization gained in the ZFC process, effectively affects the SC state formation in a way which is similar to the well-known HTSC cuprates. The present work triggers other important questions such as: the composition of the two SC phases in a-CS and the interrelation between the magnetic and SC states. Most urgent is to proceed in a systematic experimental work, aiming to increase the reproducibility and to achieve a bulk SC phases in a-CS.

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References

- [1] Y. Kopelevich, P. Esquinazi, J. H. S. Torres, and S. Moehlecke, *J. Low Temp. Phys.* 119, 691 (2000); R. Audillo, X.Gao, R. Escudero, M. Jose-Yacaman, and J.B. Goodenough, *Phys. Rev. B* 74, 214418 (2006).
- [2] I. Felner and Y. Kopelevich, *Phys. Rev. B* 79, 233409 (2009).
- [3] I. Felner, *Mater. Res. Express* 1, 016001 (2014).
- [4] N. B. Hannay, T. H. Geballe, B. T. Matthias, K. Andres, P. Schmidt, D. Macnair, *Phys. Rev. Lett.* 14, 225 (1965).
- [5] T. E. Weller, M. Ellerby, S. S. Saxena, R. P. Smith, N. T. Skipper, *Nature Physics* 1, 39 (2005).
- [6] A. Y. Ganin, Y. Takabayashi, Y. Z. Khimyak, S. Margadonna, A. Tamai, M. J. Rosseinsky, and K. Prassides, *Nature Mater.* 7, 367 (2008).
- [7] L. W. Song, K. T. Fredette, D. D.D. Chung, and Y. H. Kao, *Solid State Commun.* 87, 387 (1993).
- [8] R. R. da Silva, H. Torres and Y. Kopelevich, *Phys. Rev. Lett.* 87, 147001 (2001).
- [9] Y. Kopelevich, R. R. da Silva, J. H. S. Torres, S. Moehlecke and M. B. Maple, *Physica C* 408,77 (2004).
- [10] A. M. Black-Schaffer and S. Doniach, *Phys. Rev. B* 75, 134512 (2007).
- [11] A.P. Drozdov, M.I. Eremets, I.A. Troyan., V. Ksenofontov and S.I. Shylin, *Nature* 525, 73 (2015). [12] A. Bianconi, and T. Jarlborg, arXiv: (1510.05264).
- [13] L. Kumari and S.V. Subramanyam, *Materials Science and Engin. B* 129, 48 (2006)
- [14] P. Esquinazi, D. Spemann, R. Höhne, A. A. Setzer, K.-H. Han, and T. Butz, *Phys. Rev. Lett.* 91, 227201(2003).
- [15] P. Esquinazi, R. Hohne, K.H. Han, A. Setzer, D. Spemann and T. Butz, *Carbon* 42, 1213 (2004).
- [16] S. Bandow, T. Yamaguchi, and S. Iijima, *Chem. Phys. Lett.* 401, 380 (2005).
- [17] Y. Kopelevich, R. R. da Silva, J. H. S. Torres and A. Penicaud, and T. Kyotani, *Phys. Rev. B* 68, 092408 (2003).
- [18] K.H. Han, D. Spemann, R. Hohne, A. Setzer, T. Makarova, P. Esquinazi and T. Butz, *Carbon* 41, 785 (2003).
- [19] R. Caudillo, X.Gao, R. Escudero, M. Jose-Yacaman, and J.B. Goodenough, *Phys. Rev. B* 74, 214418 (2006).
- [20] A.V. Rode, E.G. Gamaly, A.C. Christy, J.F. Fitz Gerals, S.T. Hyde, R.G. Elliman, B. Luther-Davies, A.I. Veinger, J. Androulakis, and J. Giapintzakis, *Phys. Rev. B* 70, 054407(2004).
- [21] D. Arcon, Z. Jaglicic, A. Zorko, A. V. Rode, A.G. Christy, N.R. Madsen, E.G. Gamaly, and B. Luther-Davies, *Phys. Rev. B* 74, 014438 (2006).
- [22] C. Mathioudakis and P. C. Kelires, *Phys. Rev. B* 87, 195408 (2013).
- [23] I. Felner and E. Prilutskiy, *J. Supercond. Nov. Magn.* 25, 2547(2012).
- [24] I. Felner, O. Wolf and O. Millo, *J. Supercond. Nov. Magn.* 26,514 (2013).
- [25] S. Bandow, T. Yamaguchi, and S. Iijima, *Chem. Phys. Lett.* 401, 380 (2005).
- [26] O. Ben Dor, S. Yochelis, S. P. Mathew, R. Naaman and Y. Paltiel, *Nature Commun.*, 4 2256 (2013).
- [27] Y. Wang, P. Pochet, C. A. Jenkins, E. Arenholz, G. Bukalis, S. Gemming, M. Helm and S. Zhou, *Phys. Rev. B* 90, 214435 (2014).
- [28] W. Kicin'ski, M. Szala and M. Bystrzejewski, *Carbon* 68, 1 (2014).
- [29] V.L. Ginzburg, *JETP* 47, 2318 (1964).
- [30] J. Barzola-Quiquia, P. Esquinazi, M. Lindel, D. Spemann, M. Muallem, and G.D. Nessim, *Carbon* 88, 16 (2015).
- [31] G. Larkin and Y. Vlasov, *Supercon. Sci. Tech.* 24, 092001 (2011).

