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Temperature driven structural-memory-effects in carbon nanotubes filled with Fe_3C nano crystals

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Abstract

We report the observation of novel temperature-driven structural-memory-effects in carbon nanotubes (CNTs) filled with Fe_3C nano-crystals. These structural-transitions were measured by means of temperature (T) dependent x-ray diffraction (XRD) in the T-range from 298 K to 12 K. A clear reversible 2θ-shift in the 002-peak of the graphitic-CNTs-walls is found with the decrease of the temperature. As determined by Rietveld refinement, such 2θ-shift translates in a not previously reported decrease in the value of the CNT graphitic *c*-axis with the decrease of the temperature (from 298 K to 12 K). Also, a clear reversible 2θ-shift in the 031 and 131 diffraction-peaks of Fe_3C is observed within the same T-range. Rietveld refinements confirm the existence of such memory-effect and also reveal a gradual decrease of the 010-axis of Fe_3C with the decrease of the temperature. These observations imply that the observed structural-memory-effect is a characteristic of CNTs when Fe_3C is the encapsulated ferromagnet. The generality of such memory-effects was further confirmed by additional measurements performed on other types of CNTs characterized by continuous Fe_3C-filling. XRD measurements in the T-range from 298 K to 673 K revealed also an unusual reversible decrease of the Fe_3C-peak intensities with the increase of the temperature. These observations can have important implications on the magnetic data recording applications of these nanostructures by helping in better understanding the unusual temperature-dependent magnetic instabilities of iron-based nano-crystals which have been recently reported in literature.

1. Introduction

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical-like nano-structure closed at each end with fullerene-like caps. These structures have attracted an important attention for applications in numerous areas of material-science, nanotechnology, physics and aerospace, electronics and semiconducting technology [1–7], nano-medicine [8–11], and many others. Thanks to their important chemical stability CNTs have been considered and used as nano-containers with the aim of protecting chosen materials, molecules and/or crystals of interest from interaction with the external environment (which would otherwise lead to oxidation) [12–20]. In the last decade much attention has been focused on encapsulating magnetic iron-based nano-crystals inside CNTs [12–22]. These systems have been considered suitable for applications in energy storage, magnetic data recording, exchange bias systems and many others [12–14]. In a iron-filled CNTs- device/prototype data densities up to 66 Gigabit/inch^2 have been estimated [12].

These nanostructures are generally grown in the form of vertically aligned films by chemical vapour deposition (CVD) methods involving the use of single or mixed organometallic compounds as synthesis precursors. The obtained CNTs-structures generally exhibit partial filling rates [12–17]. In the attempt to

control and tune the nano-crystal filling-rate and therefore the magnetization characteristics, the addition of (1) Cl-containing precursors [19–21, 23] or (2) local-perturbations has been proposed [18]. It has been shown that the metallocene-pyrolysis leads to the formation of numerous molecular species which include: $Fe + H_2 + CH_4 + C_5H_6 + \ldots$ [17]. The CNTs obtained from these syntheses methods have been reported to encapsulate mixed- or single-iron-based phases. Specifically, the presence of mixed Fe_3C, α-Fe and γ-Fe phases has been reported for experiments involving the pyrolysis of the only ferrocene precursor [12–17]. Instead, when additional Cl-containing precursors are added to ferrocene, the presence of large quantities of Fe_3C has been shown [19–21, 23]. In the attempt to enhance the magnetization properties of these structures, the use of annealing methods has been considered for the conversion of γ-Fe into α-Fe [24–26]. Particularly, it has been shown that annealing of Fe-filled CNTs in vacuum can allow an efficient conversion of γ-Fe into α-Fe at relatively low annealing-temperatures [27].

However, despite the large number of reports on this topic, very little is known about the temperature-dependent structural arrangement of these structures. Indeed previous literature works have mainly focused their attention on the room-temperature structural properties, without analysing the effect of cooling or heating on the structure of these important materials. In this paper we address this missing point and we report the observation of not previously reported temperature-driven structural-memory-effects in CNTs filled with Fe_3C nano-crystals.

Such transitions were measured by the means of temperature dependent x-ray diffraction in the temperature range from 298 K to 12 K. A clear reversible 2θ-shift in the 002 peak of the graphitic CNTs walls is found with the decrease of the temperature. As determined by Rietveld refinement methods, such 2θ-shift translates in a not previously reported decrease in the value of the CNT graphitic *c*-axis with the decrease of the temperature from 298 K to 12 K. Additionally, a clear reversible 2θ-shift in the 031 and 131 peaks of the encapsulated Fe_3C crystals within the XRD patterns is found in the same temperature range. Such memory effect in the encapsulated Fe_3C is further confirmed by Rietveld refinements analyses, which show a clear decrease in the value of the encapsulated Fe_3C-010 crystal-axis with the decrease of the temperature. These observations clearly prove the existence of a not previously observed temperature-dependent structural memory effect in both the encapsulated Fe_3C crystals and the CNTs. The generality of such memory-effects was further confirmed by additional measurements performed on other types of CNTs produced with different synthesis methods and characterized by a continuous Fe_3C filling. These observations imply that the observed structural transition (structural-memory-effect) is a characteristic of both partially-filled and continuously filled CNTs when Fe_3C is the encapsulated ferromagnet.

2. Experimental

The synthesis experiments were carried out by using a CVD system composed of a quartz tube of length 1.5 m, one zone electric furnace and an Ar flow rate of 10–12 ml min^{-1}. The reactor dimensions used for the production of Fe_3C-filled CNTs were as follows: for the partially-filled CNTs a quartz tube with an inner diameter of 44 mm and a wall thickness of 3 mm was used. The temperature of pyrolysis was set to that of 990 °C. The precursors (approximately 1 g of ferrocene and 0.15–0.65 ml of dichlorobenzene) were evaporated with a preheater at a temperature of approximately 200 °C and 70 °C. Instead, for the continuously-filled CNTs, a different type of CVD reactor consisting of a quartz tube of 22 mm outer diameter, wall thickness of 2.5 mm and length of 1.5 m was used together with lower quantities of ferrocene and dichlorobenzene (60 mg of ferrocene and 0.05 ml of dichlorobenzene). In both cases the samples were cooled down until the temperature of 25 °C by removing the furnace along a rail-system.

Variable low-temperature XRD measurements were performed with a Panalytical Empyrean powder x-ray diffractometer (Cu K-α, $\lambda = 0.154$ nm) equipped with a primary Johansson monochromator, an Oxford Cryosystems PhoeniX cryostat operating under vacuum below 10^{-2} Pa, and a X'celerator linear detector. All the high temperature experiments were performed with a Rigaku Smartlab powder x-ray diffractometer (Cu K-α, $\lambda = 0.154$ nm) under vacuum values below 7 Pa in the temperature range from 139 K to 673 K. A 200 kV American FEI Tecnai G2F20 was employed to obtain transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images. XPS measurements were performed with a Escalab 250Xi. Magnetic measurements were performed with a Quantum Design MPMS XL-7.

3. Results and discussion

The morphological properties of the as grown filled CNTs were first revealed by TEM analyses performed in transmission and scanning TEM mode. Typical examples of the as grown CNTs with the two synthesis approaches described above are shown in figures supp. 1, 2,is available online at stacks.iop.org/MRX/5/025010/mmedia

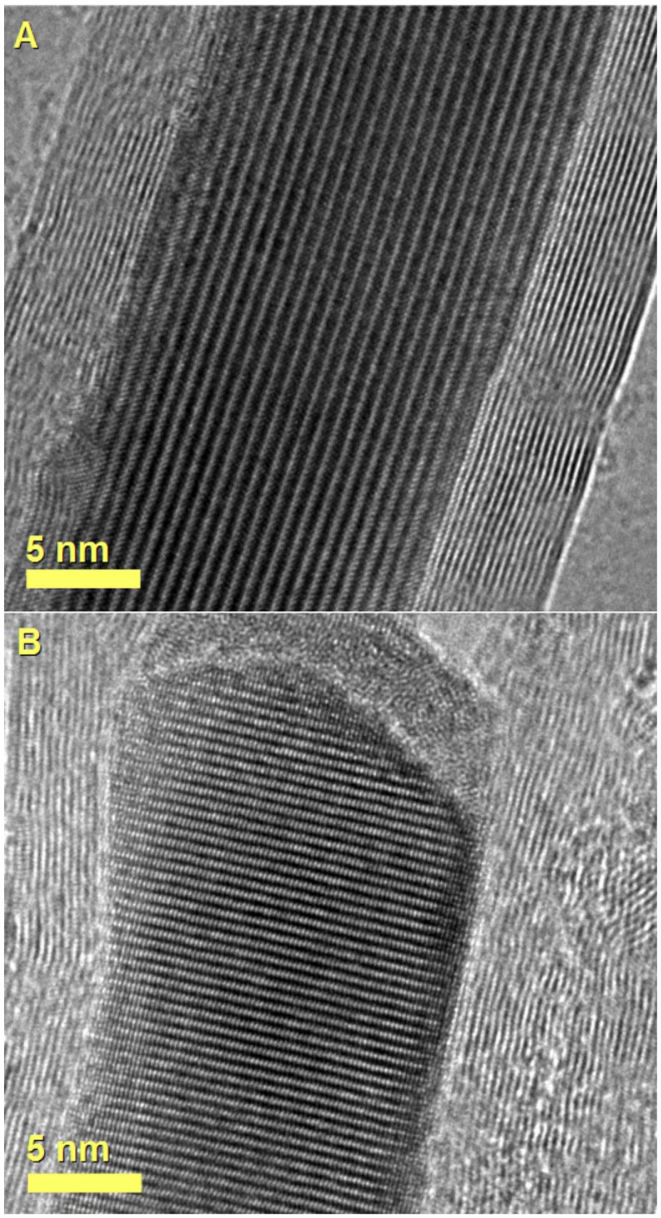

Figure 1. HRTEM micrographs showing the single-crystalline arrangement of the Fe_3C crystals encapsulated inside the CNTs. Note the preferred 010 orientation of the Fe_3C crystal in A and the preferred 100 orientation in B.

while typical HRTEM images are shown in figure 1. The observed lattice spacings characterized by a preferred direction with respect to the CNT-axis (see figure 1) were associated to the 010 and 100 reflections of Fe_3C with space group Pnma (see also figure supp. 13 for XPS analyses).

The evaluation of the temperature-dependent (T-dependent) structural properties of the as grown CNTs was carried out by XRD analysis under vacuum at variable temperatures. As a first step, the attention was focused on the structural properties of CNTs partially filled with Fe_3C in the temperature range from 298 K down to 12 K. The presence of a multi-walled arrangement of the CNTs-walls was revealed by the XRD patterns in the 2θ range from 23 to 30 degrees (see figure 2). A clear peak at approximately 26 degrees 2θ was found and associated to the 002 reflection, which identifies the graphitic arrangement of the CNT-walls. Also, as shown in figure supp. 3, XRD measurements in the 2θ range from 35 to 55 degrees revealed the presence of a large quantity of Fe_3C crystals with space group Pnma (as confirmed by Rietveld refinement in figure supp. 3) and minor quantities of γ-Fe with space group Fm-3m and α-Fe with space group Im-3m phases. Interestingly, as shown in figure 2, the T-dependent measurements revealed the presence of a shift in the position of the 002 peak toward higher values of 2θ degrees with the decrease of the temperature. Such shift could be associated to a decrease in the value of the *c*-axis of the graphitic-unit cell of the CNT with the decrease of the temperature.

Such reversible transition can be observed in figure 3(A), where the variation of the graphitic-CNT-unit-cell *c*-axis is plotted against the temperature. Curiously, as shown in figure 3(B) a decrease in the value of the 010

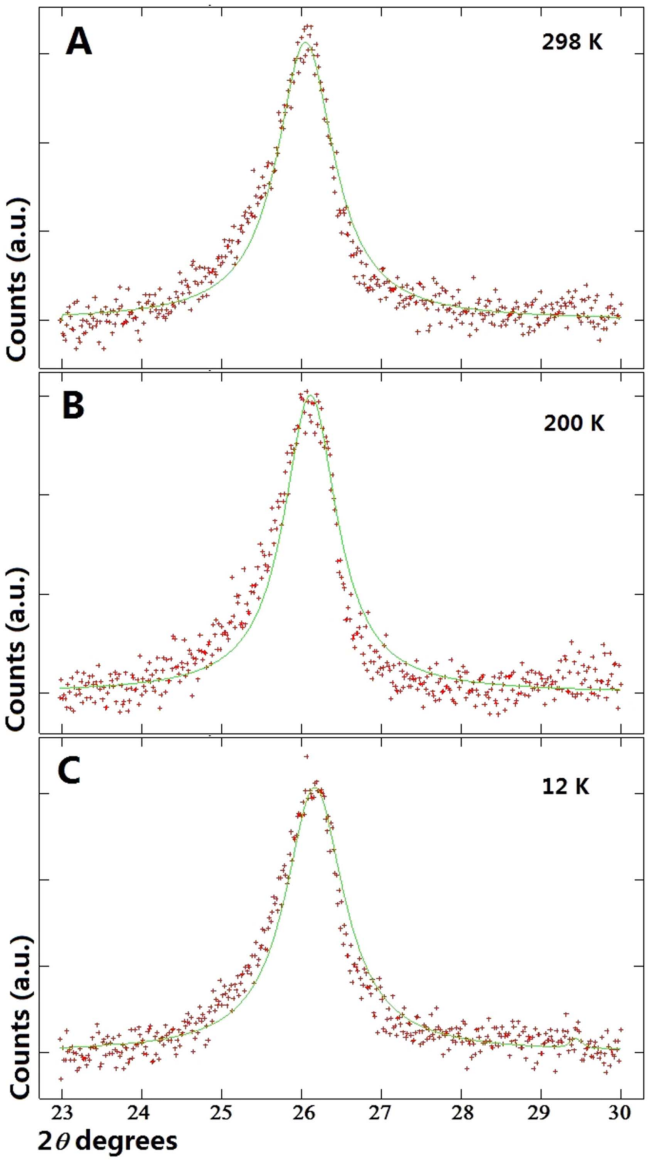

Figure 2. T-dependent experimental XRD patterns (red line) and Rietveld refinement (green line) showing the variation of the graphitic CNT 002 peak-position with the decrease of the temperature. A clear shift toward higher values of 2θ degrees is observed with the decrease of the temperature.

crystal-axis of Fe_3C with the decrease of the temperature was also found (as determined by Rietveld refinement analyses, see figure supp. 3 for examples of XRD measurements performed at 298 K and 12 K and the respective Rietveld refinements); note that each data point in figure 3(B) was extracted by Rietveld refinement analyses of individual XRD diffractograms. Such reversible transition is shown with a higher detail in the XRD patterns in figures 4(A), (B), where a clear reversible shift in the 031 peak-position of the Fe_3C structure is present (see also figures supp. 4(A), (B) for details of 131 peak). Such observation implies that a reversible and cooperative structural transition induced by the decrease of the temperature is present in both the Fe_3C and CNTs systems (see also figures supp. 4(A), (B), note that the diffractograms of figures supp. 3 and 4(A) belong to the same dataset).

In addition, Rietveld refinement of the data (shown in figure supp. 3) provides evidence that the observed shift in the 131 peak-position may be associated to a slight increase of the 100 and 001 axis-values of Fe_3C with the decrease of the temperature (note however that such slight change could not be well quantified due to the accuracy limit of the instrument, as shown in figures supp. 5, 6). These observations imply that Fe_3C-filled CNTs are characterized by unusual structural-memory characteristics as confirmed by the observations in figure 4(B).

In the attempt to verify the generality of this property, further measurements were carried out on a different type of CNTs filled with Fe_3C (CNTs filled with continuous Fe_3C crystals) produced with different synthesis conditions (60 mg of ferrocene, 0.05 ml of dichlorobenzene, see experimental section). As shown in figures supp. 7, 8, also in this case, a similar trend is found. A shift in the position of the 002 graphitic-peak toward

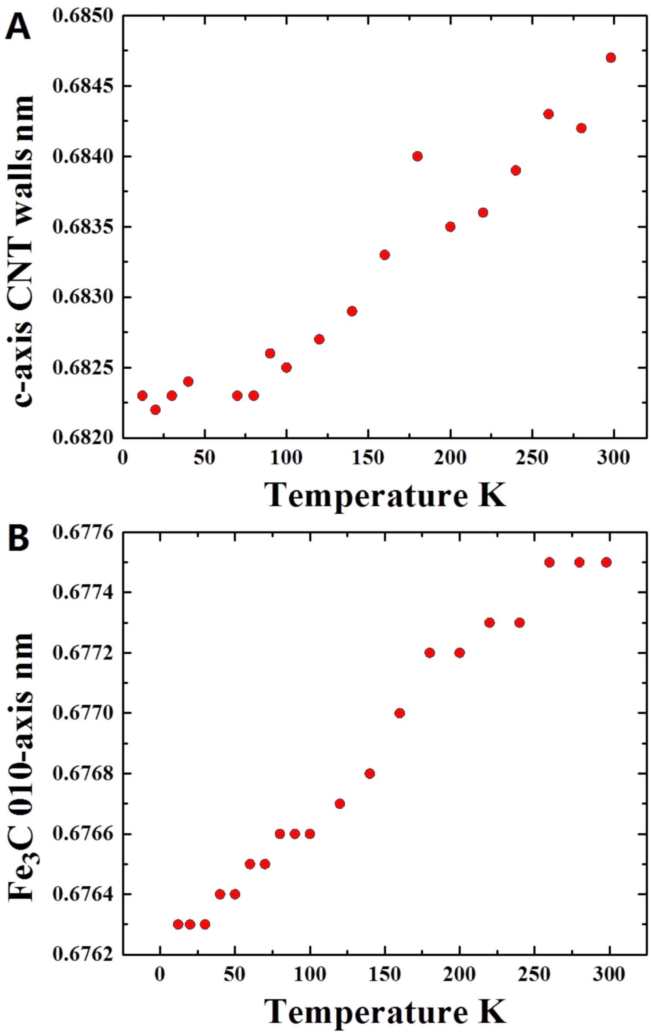

Figure 3. Plots showing the variation of the graphitic CNT *c*-axis (A) and of the Fe_3C 010 axis (B) with temperature. Note that the values plotted in A and B were obtained by Rietveld Refinement (see supplementary information figure 3 for typical examples of the Rietveld refinement analyses).

higher values of 2θ degrees is found with the decrease of the temperature. Furthermore, a similar shift in the 031 peak position is observed also in this type of CNTs.

These findings suggest that the observed structural-memory-effect is a general characteristic of multiwall CNTs filled with Fe_3C crystals (independent from the used synthesis method, see also figures supp. 14, 15 for additional measurements performed in a third type of Fe_3C-filled CNTs). It is important to mention that previous literature works have shown that the magnetic moment of Fe_3C can be strongly influenced by the values of the crystal unit cell axes [30–34]. Therefore our observations may have important implications from a magnetic perspective, by helping in better understanding the unusual magnetic properties of iron-based crystals which have been recently reported in literature by zero field cooled (ZFC) and field cooled (FC) studies of the magnetization [30–34]. Particularly it is interesting to notice that Karmakar *et al* [33] have reported an unusual variation of the magnetization with temperature and applied field in CNTs films containing large quantities of α-Fe and Fe_3C and very small quantities of γ-Fe (below 1%). These observations are in agreement with our magnetization analyses (shown in figures supp. 16 and 17) where ZFC measurements exhibited a similar unusual variation in the magnetization values with temperature and applied field. Therefore a possible influence of the structural-memory effect reported in this work on such unusual variation of the magnetization characteristics cannot be excluded. Future neutron diffraction experiments may be helpful to fully elucidate the origin of such magnetic effects.

In the attempt to further investigate the T-dependent structural properties of Fe_3C filled CNTs, the attention was then turned on possible high temperature structural transitions in the range from approximately 298 K to 673 K. The result of the XRD measurements performed in such temperature range is shown in figures supp. 9–11 and in figure 5. Interestingly a reversible shift of the 002 peak-position toward lower values of 2θ degrees

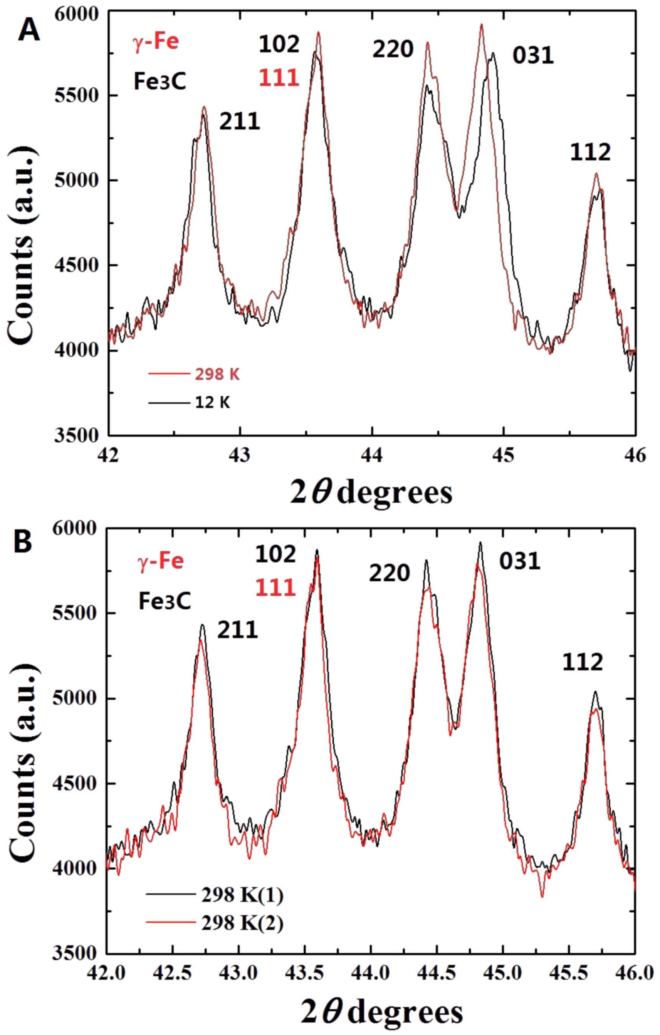

Figure 4. XRD patterns of CNTs partially filled with Fe_3C measured at 298 K and down to 12 K. A clear reversible shift of the 031 peak in (A), (B) (structural-memory-effect) is found, after taking back the sample to 298 K (see also supplementary info).

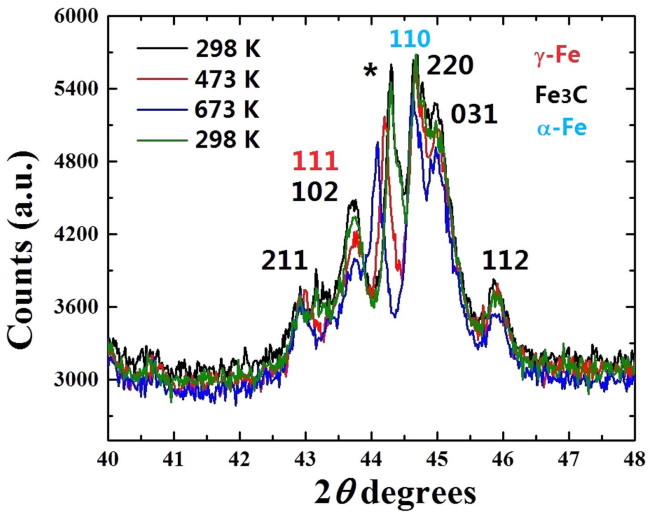

Figure 5. High temperature XRD patterns of CNTs partially filled with Fe_3C showing the structural arrangement of the encapsulated crystals in the temperature range from 298 K to 673 K. The black star refers to the peak associated to the substrate used for the XRD measurements.

was found with the increase of the temperature. Rietveld refinement analyses confirmed (see figure supp. 9), that an increase in the value of the graphitic *c*-axis of the CNT-unit cell (graphitic-unit-cell) is present with the increase of the temperature (figure supp. 10).

This last observation is in agreement with that recently reported in the case of annealing-experiments of CNTs-buckypapers filled with α-Fe/γ-Fe crystals at high temperatures by T-dependent XRD in vacuum [27]. However, the observed shift is different with respect to that reported by F Y Wu *et al* [28] in the case of hollow multiwall CNTs, where significant shifts (in the same high temperature range from 298 K to 673 K) in the 002 peak were observed only after high temperature treatment of as grown CNTs (due to the improved structural arrangement) and not in the as grown samples [28]. A complementary interpretation was also given by the work of Y Maniwa *et al* [29], where the presence of disorder and defects in the graphitic layers of carbon nanotubes was classified in different CNTs structural-arrangements, namely: (1) Russian Doll, (2) Jelly Roll, (3) mixed Russian Doll and Jelly Roll and (4) polyhedral graphite with defects at the ridges [29]. In the specific case of our measurements, it is important to notice that at high temperatures no significant changes in the values of the 031 Fe_3C peak position are found (see supp. figure 11). Such difference with respect to the low-temperature characteristics could be associated to the increase of the thermal agitation which may also affect the structural arrangement of the Fe_3C crystals. Indeed an unusual reversible change in the observed peak-intensities and shape is found with the increase of the temperature and can possibly be associated to such increase in the thermal agitation. Note that the observed diffraction peak-position and intensities were found to come-back to the original position after cooling-down the samples back to room temperature, as shown in figure supp. 12. In this context, future works with additional techniques will be considered to extract deeper information on the origin of such unusual reversible peak-intensities variations.

4. Conclusion

In conclusion we reported the observation of temperature-dependent structural-memory-effects in CNTs filled with Fe_3C nano-crystals. These transitions were measured by the means of temperature dependent XRD in the temperature range from 298 K to 12 K.

A reversible decrease in the values of (1) the graphitic CNTs-*c*-axis and (2) the 010 Fe_3C crystal-axis (with the decrease of the temperature) was extracted by using Rietveld refinement methods. The presence and the generality of such memory-effects were further confirmed by additional XRD measurements performed on other types of CNTs characterized by continuous Fe_3C filling. In addition XRD measurements were also performed at high temperatures in the range from 298 K to 673 K where an unusual reversible decrease of Fe_3C peak intensities was found with the increase of the temperature.

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References

[1] Hata K, Futaba D N, Mizuno K, Namai T, Yumura M and Iijima S 2004 Water-assisted highly efficient synthesis of impurity-free single-walled carbon nanotubes *Science* **306** 1362–4
[2] Iijima S 1991 Helical microtubules of graphite carbon *Nature* **354** 56
[3] Iijima S and Ichihashi T 1993 Single-shell carbon nanotubes of 1 nm diameter *Nature* **363** 603
[4] Radushkevich L V and Lukyanovich V M O 1952 Strukture ugleroda, obrazujucegosja pri termiceskom razlozenii okisi ugleroda na zeleznom kontakte ('about the structure of carbon formed by thermal decomposition of carbon monoxide on iron substrate') *Zurn Fisic Chim.* **26** 88–95
[5] Oberlin A, Endo M and Koyama T 1976 Filamentous growth of carbon through benzene decomposition *J. Cryst. Growth* **32** 335–49
[6] Dresselhaus M S 2004 Nanotubes a step in synthesis *Nat. Mater.* **3** 665–6
[7] Vohrer U, Kolaric I, Haque M H, Roth S and Detlaff-Weglikowska U 2004 Carbon nanotube sheets for the use as artificial muscles *Carbon* **42** 1159–64
[8] Klingeler R and Sim R B (ed) 2011 *Carbon Nanotubes for Biomedical Applications.* (Berlin: Springer)

[9] Lutz M U, Lipert K, Krupskaya Y, Bahr S, Wolter A and El-Gendy A A 2011 Feasibility of magnetically functionalised carbon nanotubes for biological applications: from fundamental properties of individual nanomagnets to nanoscaled heaters and temperature sensors ed R Klingeler and R B Sim *Carbon Nanotubes for Biomedical Applications. Heidelberg* (Berlin: Springer) pp 97–124
[10] Taylor A *et al* 2009 Biocompatibility of iron filled carbon nanotubes *in vitro J. Nanosci. Nanotechnol.* **9** 5709–16
[11] Elhissi M A A, Ahmed W, Hassan I U, Dhanak V R and D'Emanuele A 2012 Carbon nanotubes in cancer therapy and drug delivery *J. Drug Delivery* **2012** 837327
[12] Terrones H *et al* 2006 Magnetism in Fe-based and carbon nanostructures: theory and applications *Solid State Sciences* **8** 303–20
[13] Prados C *et al* 2002 Hysteresis shift in Fe-filled carbon nanotubes due to γ-Fe *Phys. Rev.* B **65** 113405
[14] Marco J F *et al* 2002 Mossbauer study of iron-containing carbon nanotubes *Hyperfine Interact.* **139** 535–42
[15] Hampel S *et al* 2006 Growth and characterization of filled carbon nanotubes with ferromagnetic properties *Carbon* **44** 2316–22
[16] Muller C, Golberg D, Leonhardt A, Hampel S and Buchner B 2006 Growth studies, TEM and XRD investigations of iron-filled carbon nanotubes *Physica Status Solidi* (a) **203** 1064–8
[17] Weissker U, Hampel S, Leonhardt A and Buchner B 2010 Carbon nanotubes filled with ferromagnetic materials *Materials* **3** 4387–427
[18] Boi F S, Mountjoy G and Baxendale M 2013 Boundary layer chemical vapor synthesis of self-organized radial filled-carbon-nanotube structures *Carbon* **64** 516–26
[19] Lv R *et al* 2009 *In situ* synthesis and magnetic anisotropy of ferromagnetic buckypaper *Carbon* **47** 1141
[20] Wang W *et al* 2007 Synthesis of Fe-filled thin-walled carbon nanotubes with high filling ratio by using dichlorobenzene as precursor Letters to the Editor *Carbon* **45** 1105–36
[21] Guo J *et al* 2015 Enhanced saturation magnetization in buckypaper-films of thin walled carbon nanostructures filled with Fe3C, FeCo, FeNi, CoNi, Co and Ni crystals: the key role of Cl *Physical Chemistry Chemical Physics* **17** 18159
[22] Xiang R, Luo G, Qian W, Zhang Q, Wang Y, Wei F, Li Q and Cao A 2007 Encapsulation, compensation, and substitution of catalyst particles during continuous growth of carbon nanotubes *Adv. Mater.* **19** 2360–3
[23] Guo J, He Y, Wang S and Boi F S 2016 Mapping the transition from free-standing vertically-aligned Fe3C filled carbon nanotube films to entangled randomly-oriented carbon nanotube buckypapers in presence of a great excess of ferrocene *Carbon* **102** 372–82
[24] Leonhardt A *et al* 2005 Enhanced magnetism in Fe-filled carbon nanotubes produced by pyrolysis of ferrocene *J. Appl. Phys.* **98** 074315
[25] Gui X *et al* 2008 Improved filling rate and enhanced magnetic properties of Fe-filled carbon nanotubes by annealing and magnetic separation *Mater. Res. Bull.* **43** 3441–6
[26] Peci T and Baxendale M 2015 Length and α-Fe content control of self-organised ferromagnetic nanowires encapsulated by multiwalled carbon nanotubes by low flow-rate CVD *Carbon* **98** 519–25
[27] Boi F S, Hu Y and Wen J 2017 New insights on the dynamics of the γ-Fe/α-Fe phase-transition inside iron-filled carbon nanotubes *RSC Advances* **7** 25025
[28] Wu F Y and Cheng H M 2005 Structure and thermal expansion of multi-walled carbon nanotubes before and after high temperature treatment *J. Phys. D: Appl. Phys.* **38** 4302–7
[29] Maniwa Y *et al* 2001 Multiwalled carbon nanotubes grown in hydrogen atmosphere: an x-ray diffraction study *Phys. Rev.* B **64** 073105
[30] Duman E 2005 Magnetic instabilities in Fe3C cementite particles observed with Fe k-edge x-ray circular dichroism under pressure *Phys. Rev. Lett.* **94** 075502
[31] Hofer L J E and Cohn E M 1958 Saturation magnetization of iron carbides *Journal of American Chemical Society* **81** 1576–82
[32] Kumar R *et al* 2016 Fe3C filled carbon nanotubes: permanent cylindrical nanomagnets possessing exotic magnetic properties *Nanoscale* **8** 4299–310
[33] Karmakar S, Sharma S M, Mukadam M D, Yusuf S M and Sood A K 2005 Magnetic behaviour of iron-filled multiwalled carbon nanotubes *J. Appl. Phys.* **97** 054306
[34] Mühl T, Elefant D, Graff A, Kozhuharova R, Leonhardt A, Mönch I, Ritschel M, Simon P, Groudeva-Zotova S and Schneider C M 2003 Magnetic properties of aligned Fe-filled carbon nanotubes *J. Appl. Phys.* **93** 7894