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Temperature driven structural-memory-effects in carbon nanotubes filled with Fe₃C nano crystals

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Abstract

We report the observation of novel temperature-driven structural-memory-effects in carbon nanotubes (CNTs) filled with Fe₃C 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 Fe₃C 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 Fe₃C with the decrease of the temperature. These observations imply that the observed structural-memory-effect is a characteristic of CNTs when Fe₃C 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 Fe₃C-filling. XRD measurements in the T-range from 298 K to 673 K revealed also an unusual reversible decrease of the Fe₃C-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

Keywords

Carbon Nanotubes, Fe₃C, structural-memory effect, magnetic instability

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 [12-21]. 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/inch² 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 + H₂ + CH₄ + C₅H₆ + ... [17]. The CNTs obtained from these syntheses methods have been reported to encapsulate mixed- or single-iron-based phases. Specifically, the presence of mixed Fe₃C, 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 Fe₃C 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 Fe₃C 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 2 θ -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 2 θ -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 2 θ -shift in the 031 and 131 peaks of the encapsulated Fe₃C crystals within the XRD patterns is found in the same temperature range. Such memory effect in the encapsulated Fe₃C is further confirmed by Rietveld refinements analyses, which show a clear decrease in the value of the encapsulated Fe₃C-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 Fe₃C 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 Fe₃C filling. These observations imply that the observed structural transition (structural-memory-effect) is a characteristic of both partially-filled and continuously filled CNTs when Fe₃C 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. The reactor dimensions used for the production of Fe₃C-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 1g 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 Figs. Supp. 1-2, while typical HRTEM images are shown in Fig.1. The observed lattice spacings characterized by a preferred direction with respect to the CNT-axis (see Fig.1) were associated to the 010 and 100 reflections of Fe₃C with space group Pnma (see also Fig. 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 Fe₃C 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 Fig.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 Fig.Supp.3, XRD measurements in the 2θ range from 35 to 55 degrees revealed the presence of a large quantity of Fe₃C crystals with space group Pnma (as confirmed by Rietveld refinement in Fig.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 Fig.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 Fig.3A, where the variation of the graphitic-CNT-unit-cell c-axis is plotted against the temperature. Curiously, as shown in Fig.3B a decrease in the value of the 010 crystal-axis of Fe₃C with the decrease of the temperature was also found (as determined by Rietveld refinement analyses, see Fig. 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 Fig.3B was extracted by Rietveld refinement analyses of individual XRD diffractograms. Such reversible

transition is shown with a higher detail in the XRD patterns in Fig.4A-B, where a clear reversible shift in the 031 peak-position of the Fe_3C structure is present (see also Fig. Supp. 4A-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 Fig. Supp.4A-B, note that the diffractograms of Fig.Supp 3 and Fig. Supp. 4A belong to the same dataset).

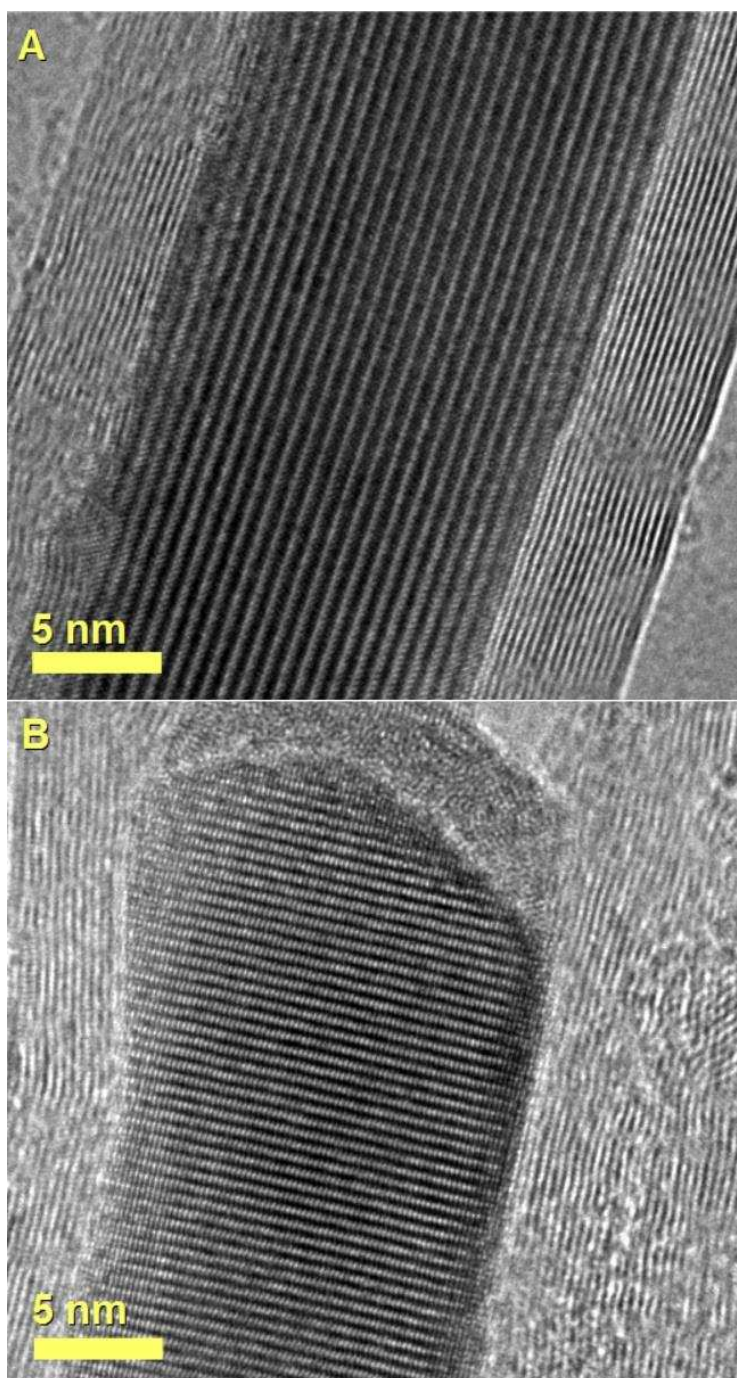


Figure 1: HRTEM micrographs showing the single-crystalline arrangement of the Fe_3C crystals encapsulated inside the CNTs. Note the preferred 010 orientation of the

Fe₃C crystal in A and the preferred 100 orientation in B.

In addition, Rietveld refinement of the data (shown in Fig. 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 Fe₃C 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 Figs.Supp.5-6). These observations imply that Fe₃C-filled CNTs are characterized by unusual structural-memory characteristics as confirmed by the observations in Fig.4B.

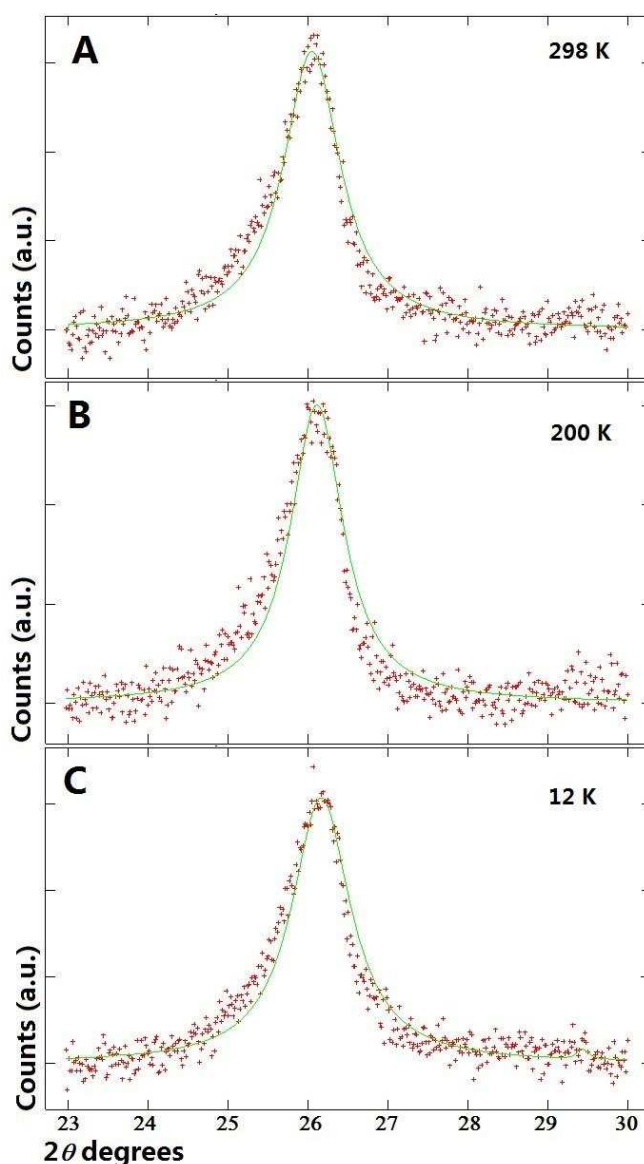


Figure 2: T-dependent experimental XRD patterns (red line) and Rietveld refinement (green line) showing the variation of the graphitic CNT 002 peak-position with the decrease of the temperature. A clear shift toward higher values of 2θ degrees is observed with the decrease of the temperature.

In the attempt to verify the generality of this property, further measurements were carried out on a different type of CNTs filled with Fe₃C (CNTs filled with continuous Fe₃C crystals) produced with different synthesis conditions (60 mg of ferrocene, 0.05 ml of dichlorobenzene, see experimental section). As shown in Figs.Supp.7-8, also in this case, a similar trend is found. A shift in the position of the 002 graphitic-peak toward 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 Fe₃C crystals (independent from the used synthesis method, see also Figs.Supp.14,15 for additional measurements performed in a third type of Fe₃C-filled CNTs). It is important to mention that previous literature works have shown that the magnetic moment of Fe₃C 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 Fe₃C and very small quantities of γ-Fe (below 1%). These observations are in agreement with our magnetization analyses (shown in Figs.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 Fe₃C 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 Fig.Supp.9-11 and in Fig.5. Interestingly a reversible shift of the 002 peak-position toward lower values of 2θ degrees was found with the increase of the temperature. Rietveld refinement analyses confirmed (see Fig.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 (Fig.Supp.10).

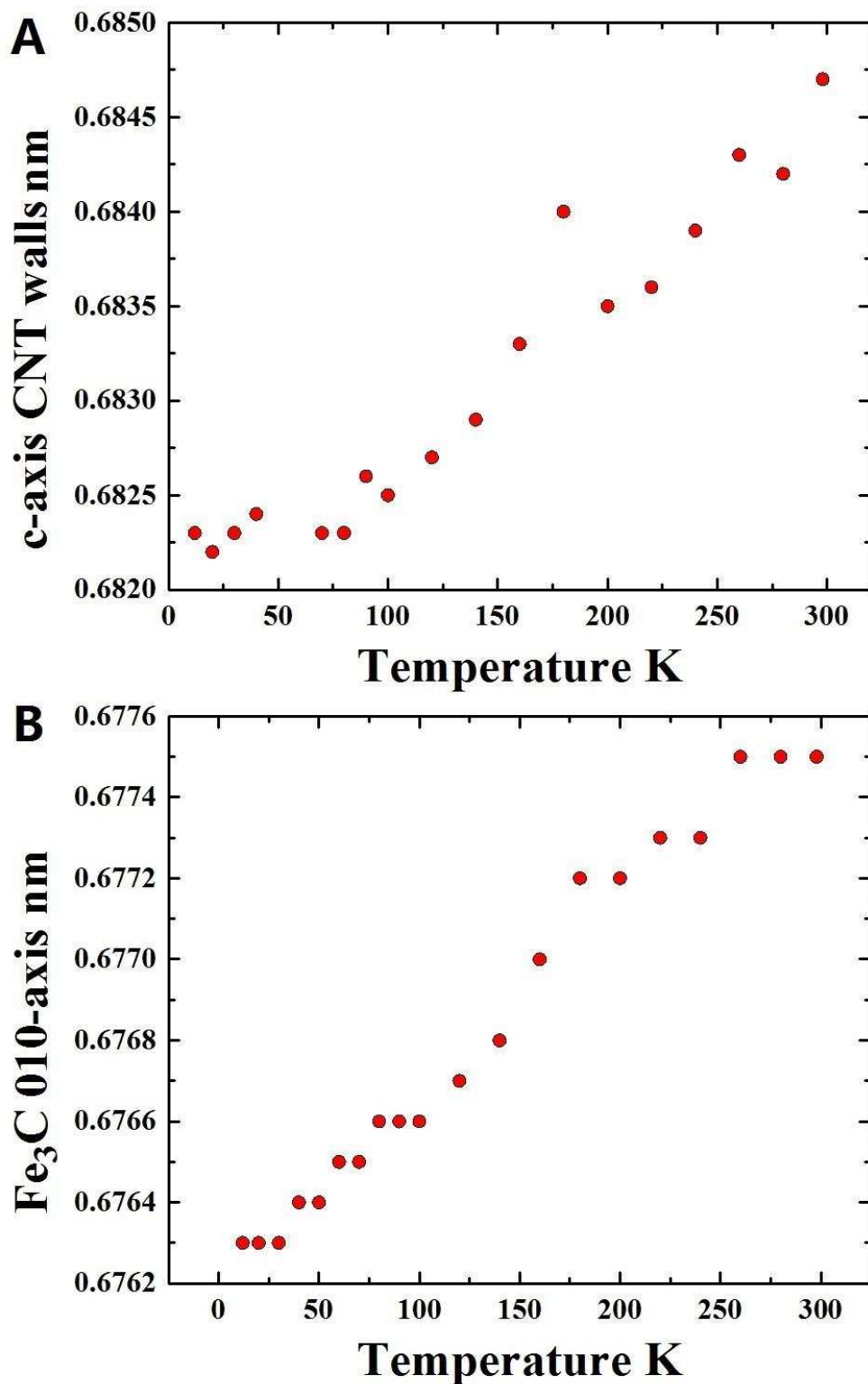


Figure 3: Plots showing the variation of the graphitic CNT c-axis (A) and of the Fe₃C 010 axis (B) with temperature. Note that the values plotted in A and B were obtained by Rietveld Refinement (see supplementary information Fig.3 for typical examples of the Rietveld refinement analyses)

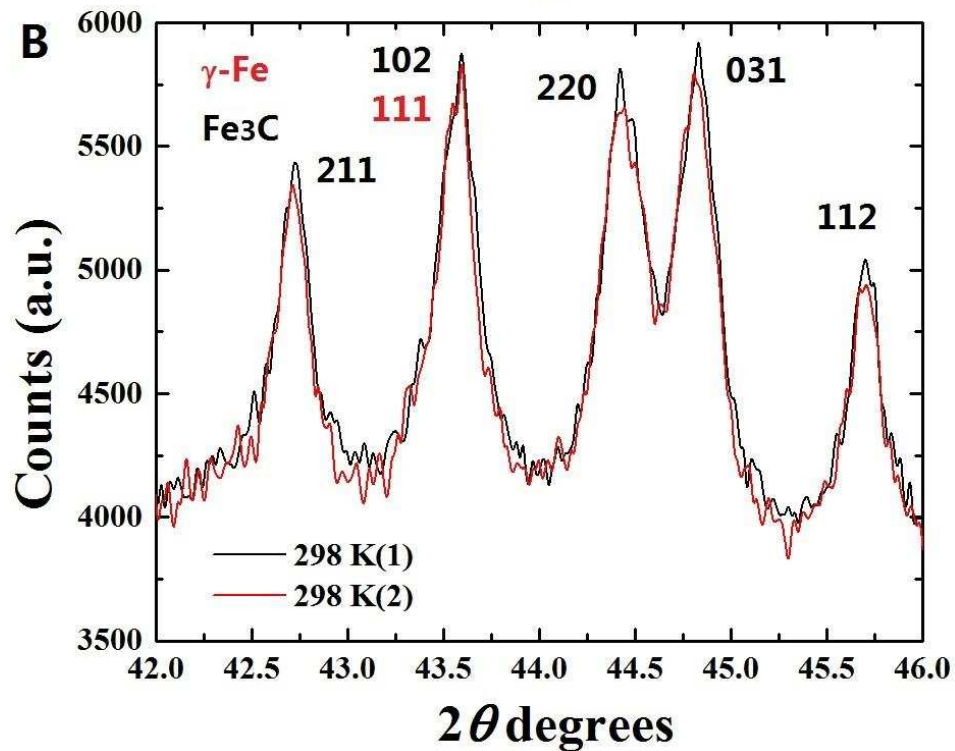
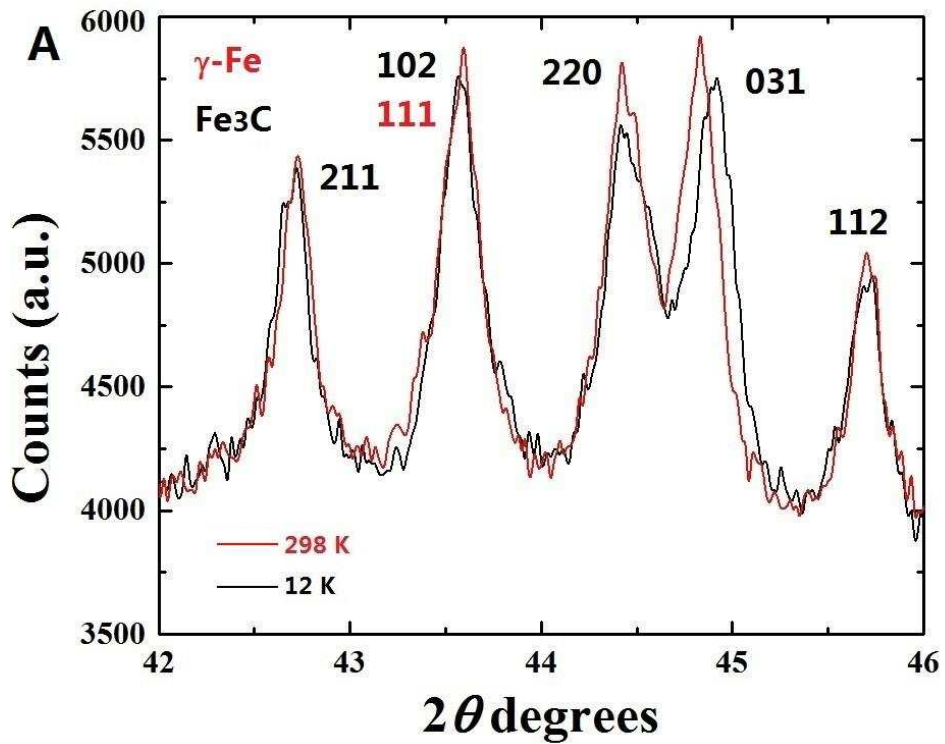


Figure 4: XRD patterns of CNTs partially filled with Fe₃C measured at 298 K and down to 12 K. A clear reversible shift of the 031 peak in A-B (structural-memory-effect) is found, after taking back the sample to 298 K (see also supplementary info).

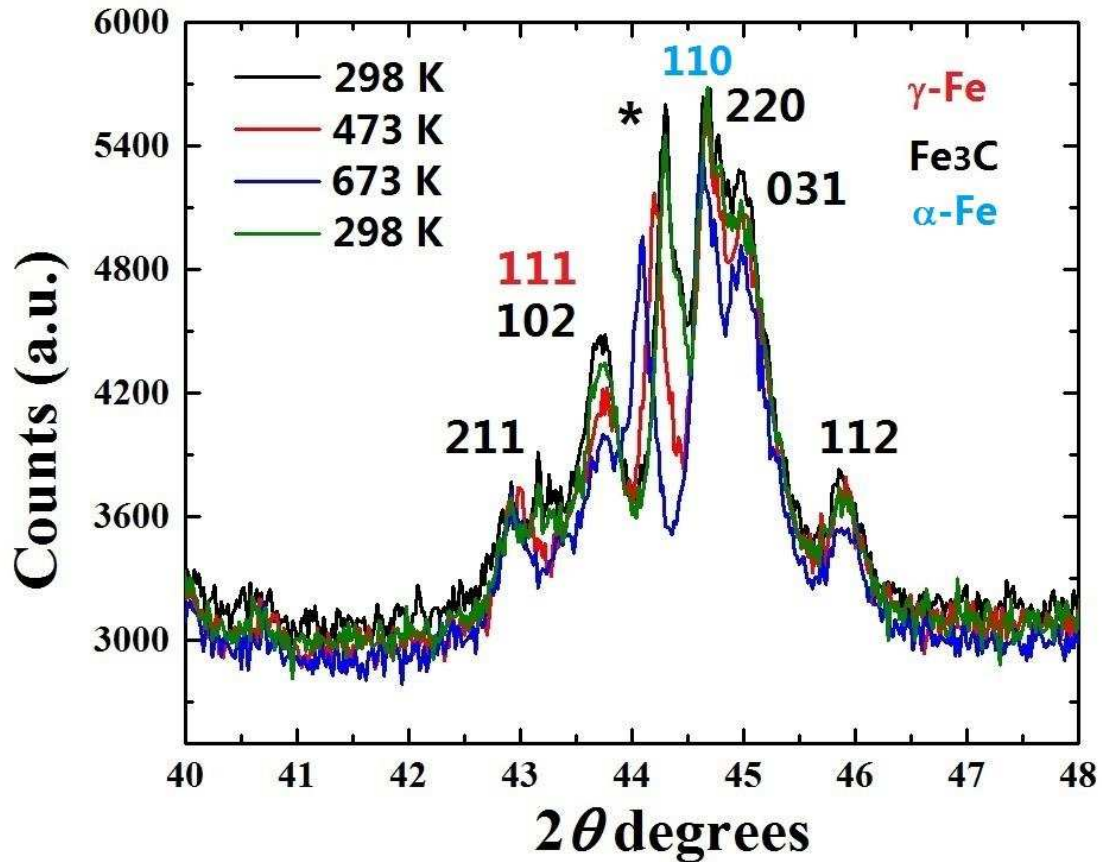


Figure 5: High temperature XRD patterns of CNTs partially filled with Fe_3C showing the structural arrangement of the encapsulated crystals in the temperature range from 298 K to 673 K. The black star refers to the peak associated to the substrate used for the XRD measurements.

This last observation is in agreement with that recently reported in the case of annealing-experiments of CNTs-buckypapers filled with $\alpha\text{-Fe}/\gamma\text{-Fe}$ 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 Fe₃C peak position are found (see Supp. Fig. 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 Fe₃C 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 Fig.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 Fe₃C 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 Fe₃C 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 Fe₃C 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 Fe₃C peak intensities was found with the increase of the temperature.

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Electronic Supplementary Material:

Additional TEM micrographs, XPS analyses, XRD patterns, Rietveld refinements and Magnetic measurements supporting the findings in the manuscript can be found in the supplementary material section.

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Supplementary Materials

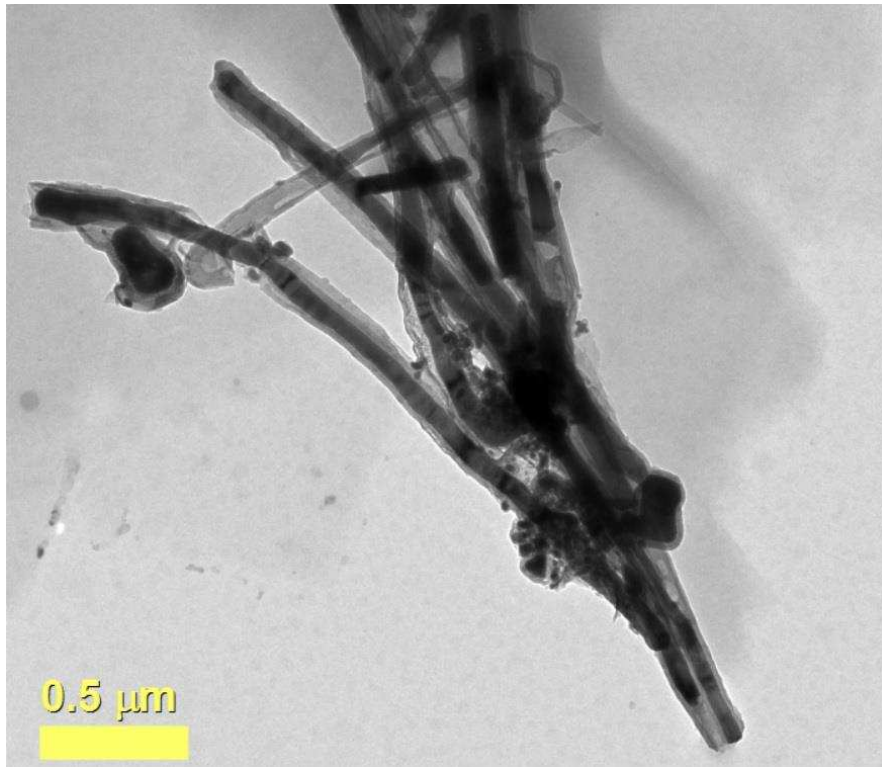


Figure Supp. 1: TEM micrograph showing the cross-sectional morphology of as grown CNTs filled with continuous Fe₃C crystals. See experimental section for method of fabrication.

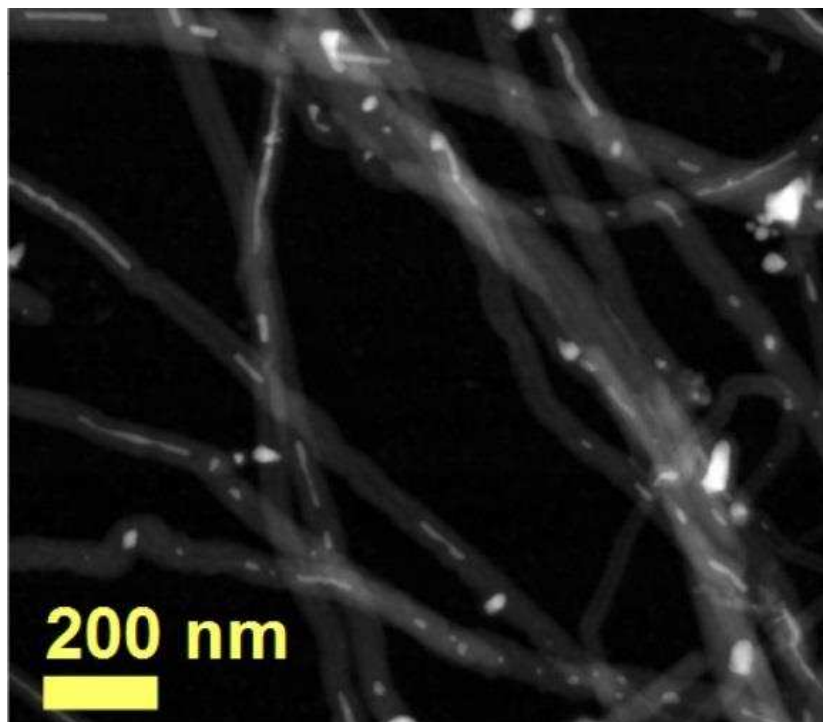


Figure Supp. 2: TEM micrograph showing the cross-sectional morphology of as grown CNTs partially filled with short Fe₃C crystals. See experimental section for method of fabrication.

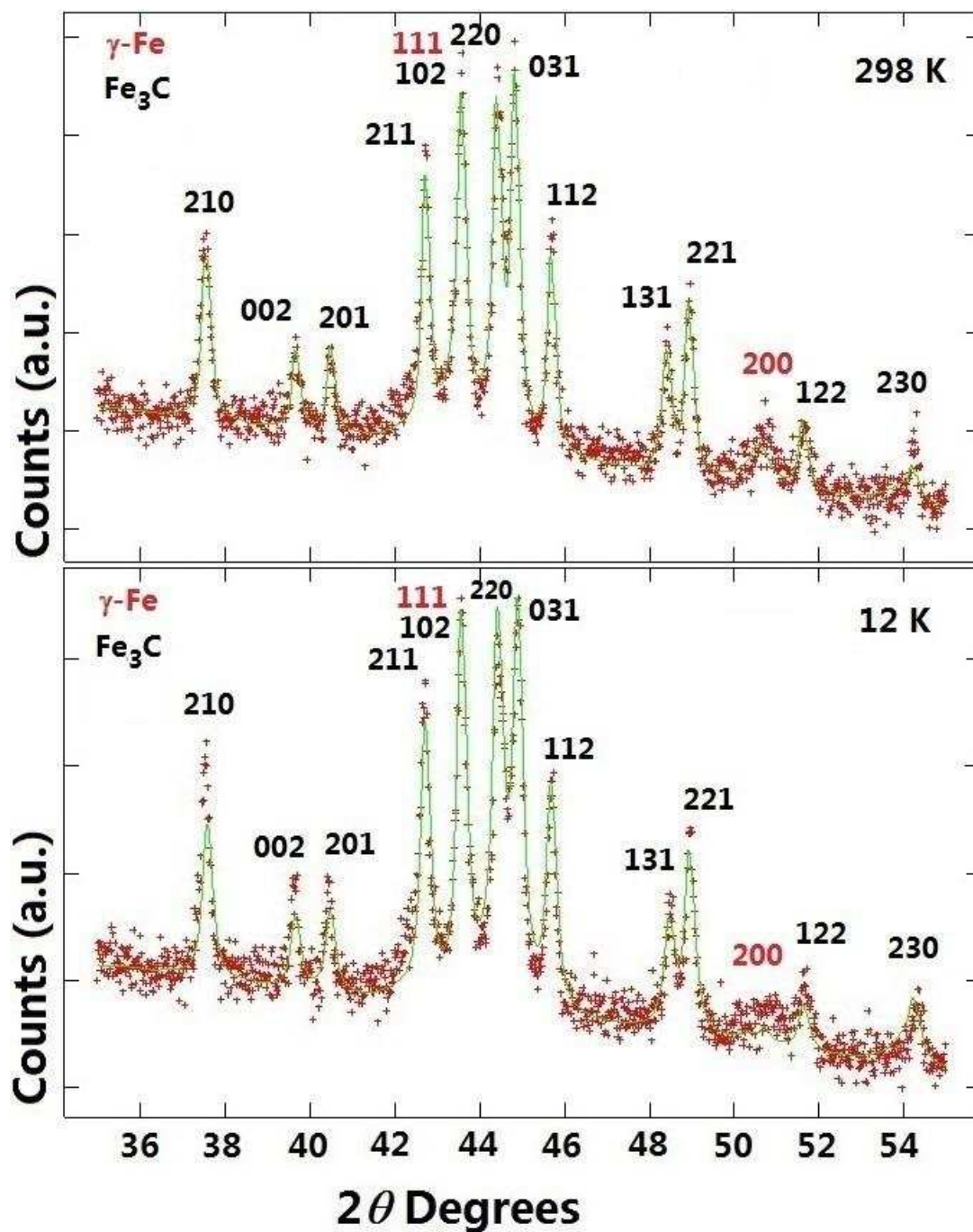


Figure Supp. 3: T-dependent experimental XRD pattern (red line) and Rietveld refinement (green line) of as grown CNTs partially filled with Fe_3C crystals measured at 298 K and 12 K. The following phase abundances could be determined: 23.7% Fe_3C , 3.2% γ -Fe, 0.6% α -Fe, 72.5% graphitic carbon (CNT-walls).

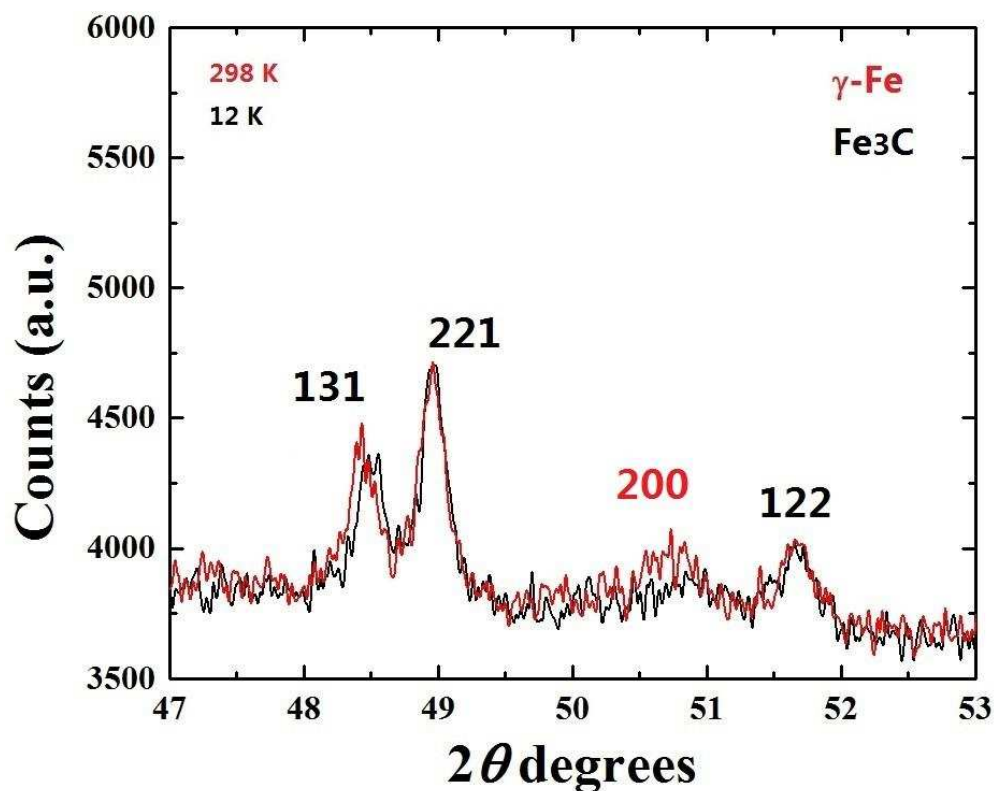


Figure Supp. 4A: Experimental XRD patterns of CNTs partially filled with Fe₃C measured at 298 K and 12 K. Note the shift of the 131 peak.

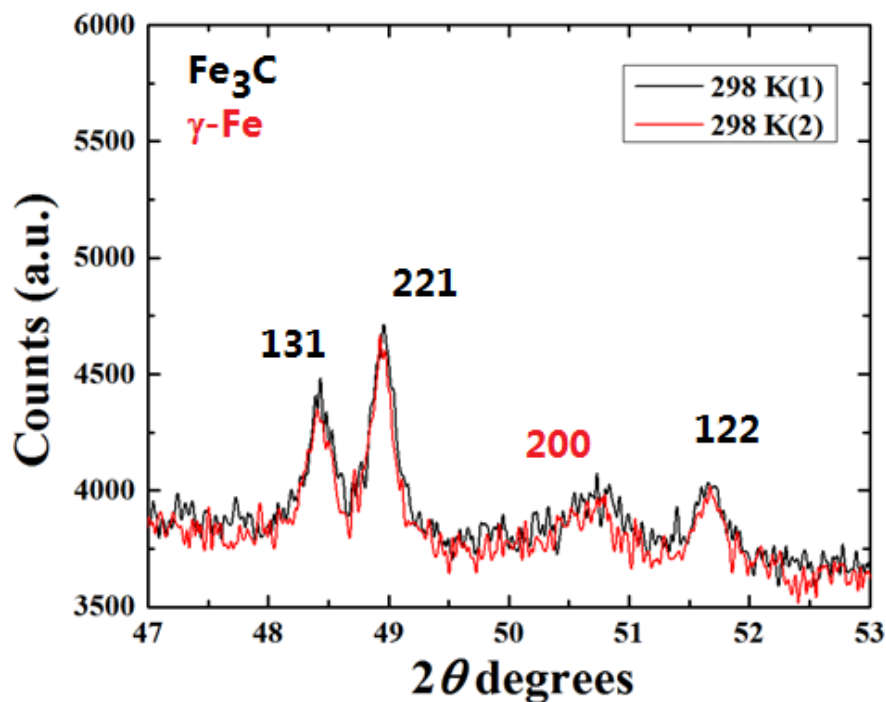


Figure Supp. 4B: XRD pattern of CNTs partially filled with Fe₃C measured at 298 K before cooling down the sample to 12 K, and after taking it back to 298 K. A clear reversible shift (structural-memory-effect) is found. In this case note the reversible shift of the 131 Fe₃C peak.

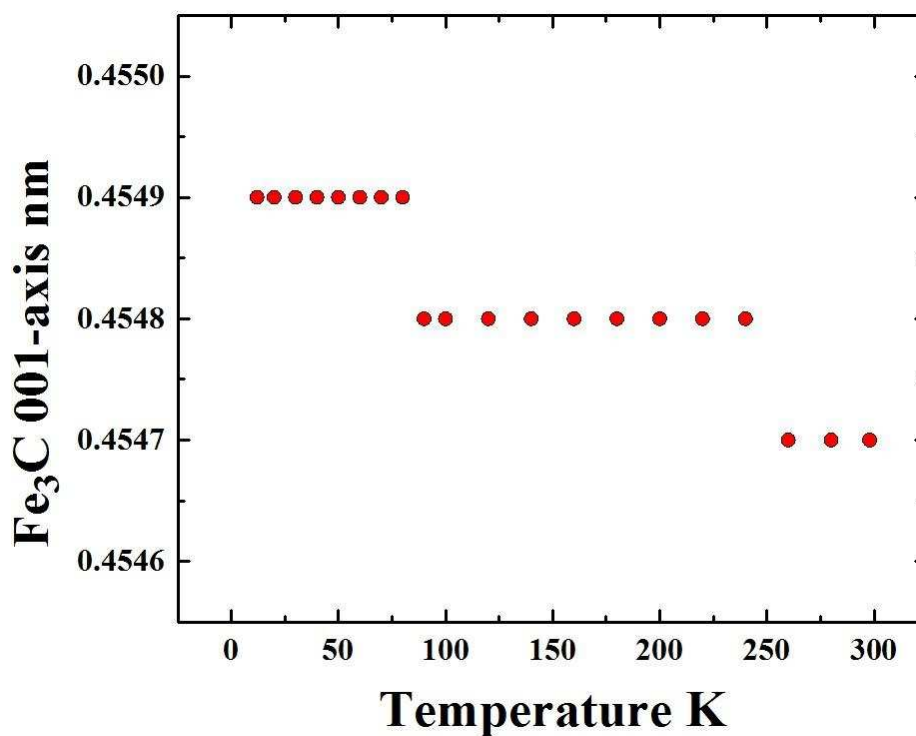


Figure Supp. 5: Plot showing the variation of the Fe₃C 001 axis with temperature. Note that the values plotted in graph were determined by Rietveld Refinement from Fig.Supp.3.

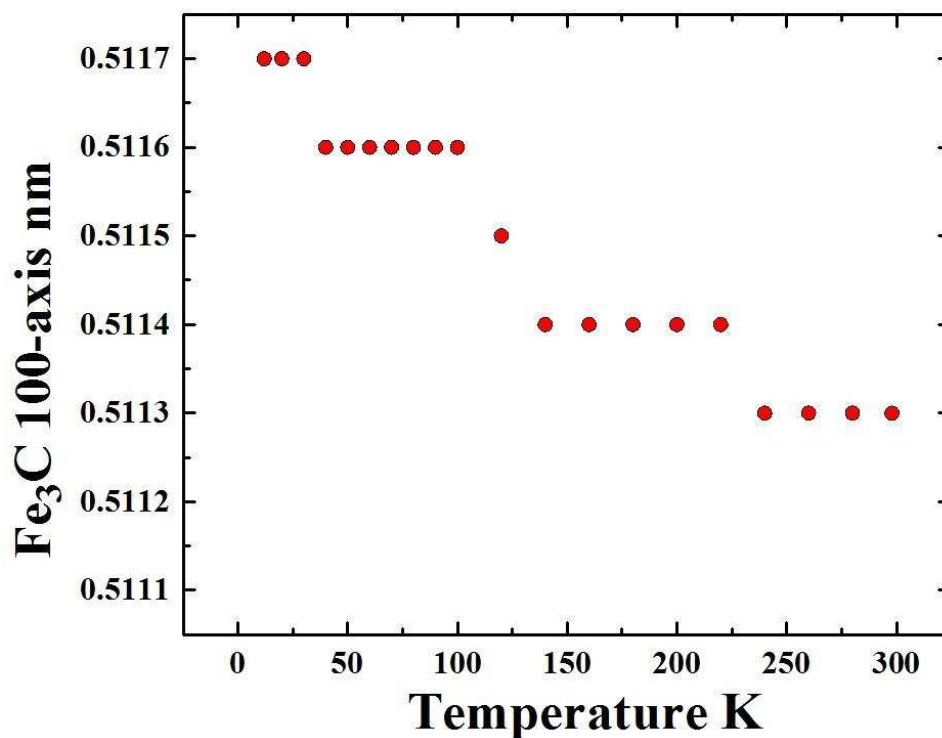


Figure Supp. 6: Plot showing the variation of the Fe₃C 100 axis with temperature. Note that the values plotted in graph were determined by Rietveld Refinement from Fig.Supp.3.

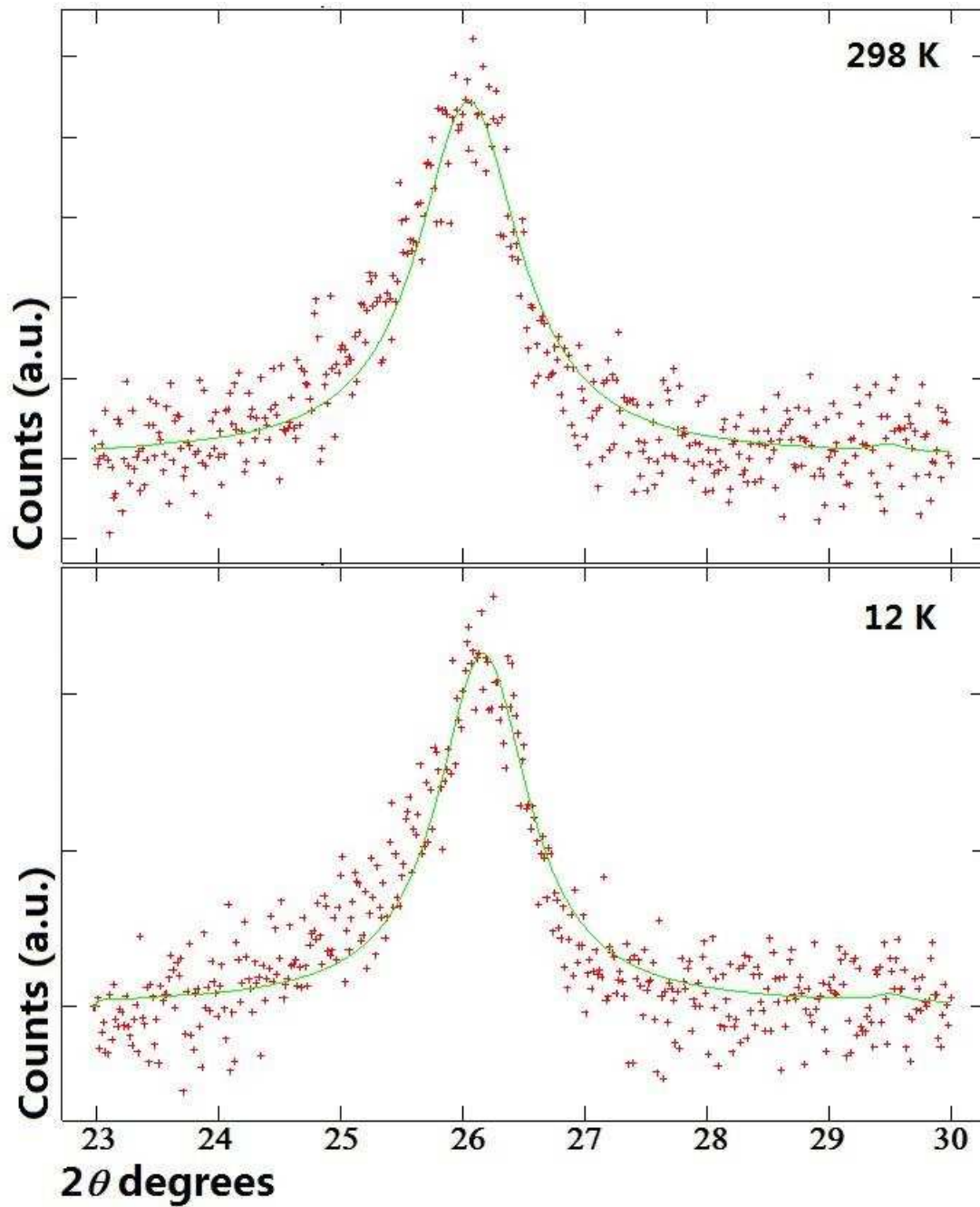


Figure Supp. 7: T-dependent experimental XRD patterns (red line) and Rietveld refinement (green line) showing the variation of the graphitic CNT 002 peak-position with the decrease of the temperature in the case of CNTs filled with continuous Fe_3C crystals. A clear shift toward higher values of degrees 2θ is observed with the decrease of the temperature.

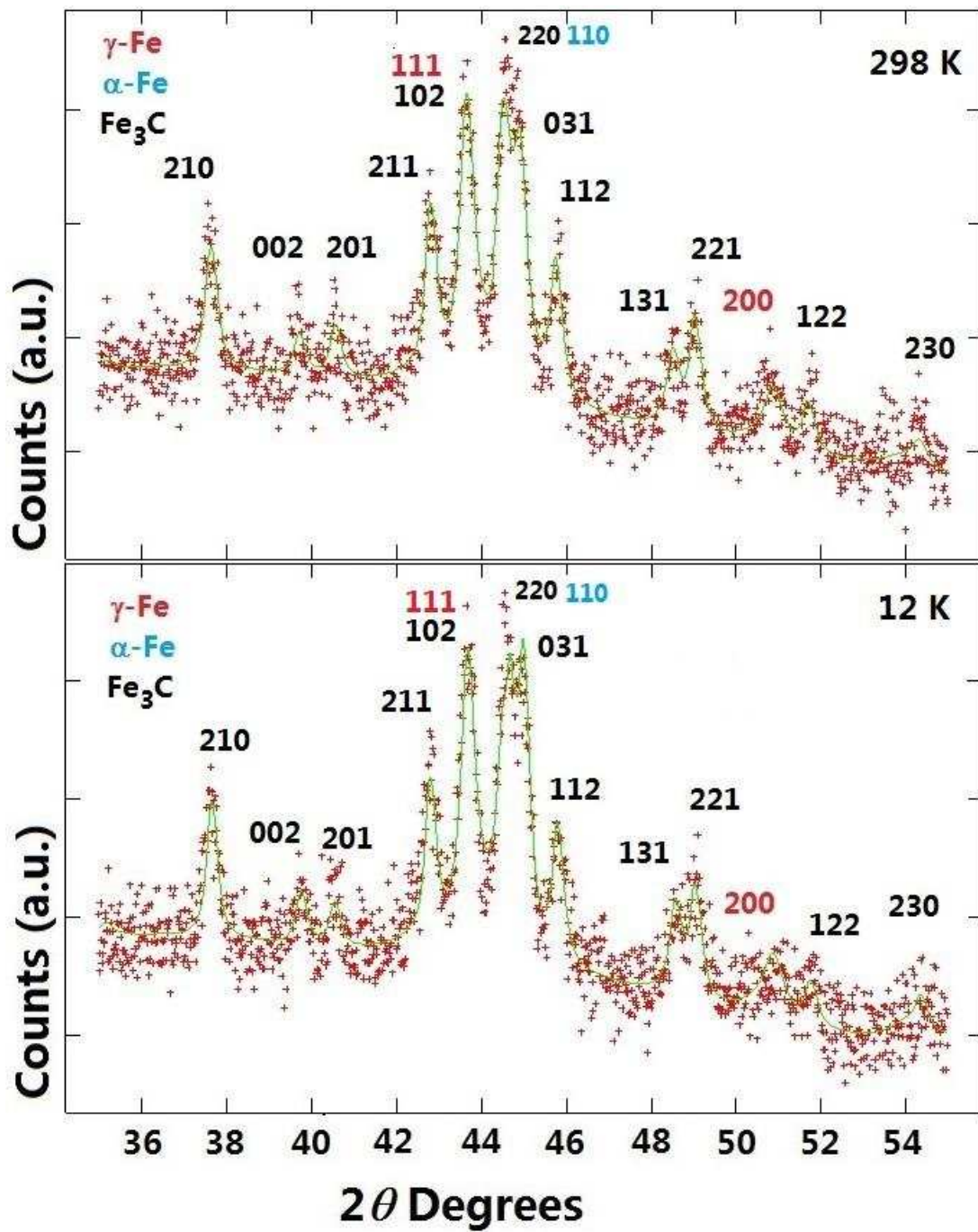


Figure Supp. 8: T-dependent experimental XRD patterns (red line) and Rietveld refinement (green line) of as grown CNTs filled with continuous Fe_3C crystals measured at 298 K and 12 K. Also in this case a shift in the 031 and 131 peaks is found.

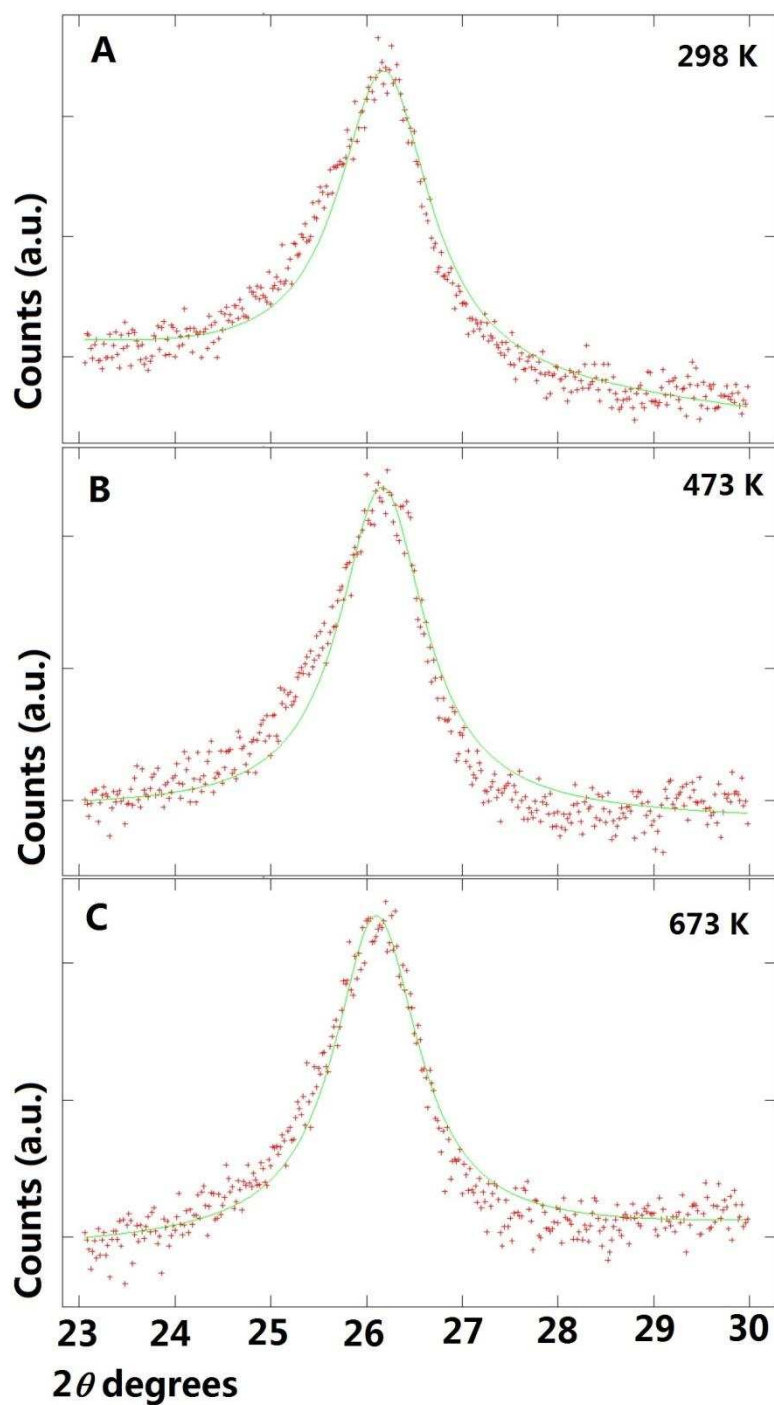


Figure Supp. 9: T-dependent XRD patterns showing the variation of the graphitic CNT 002 peak-position with the increase of the temperature in the case of CNTs partially filled with Fe_3C crystals produced with another synthesis method (0.65 ml of dichlorobenzene and 1g of ferrocene). A clear shift toward lower values of degrees 2θ is observed with the increase of the temperature.

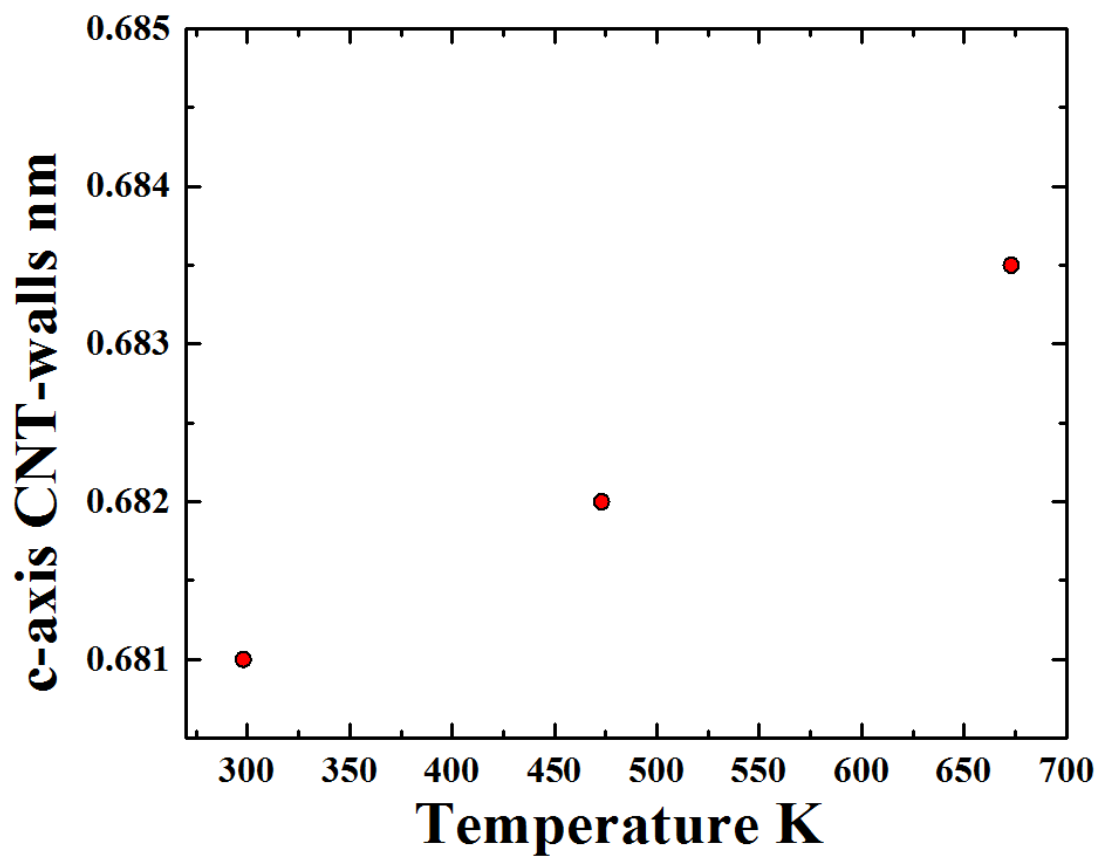


Figure Supp. 10: Plot showing the variation of the graphitic CNT c-axis with temperature. Note that the values plotted in the graph were determined by the Rietveld Refinement in Fig. Supp. 9.

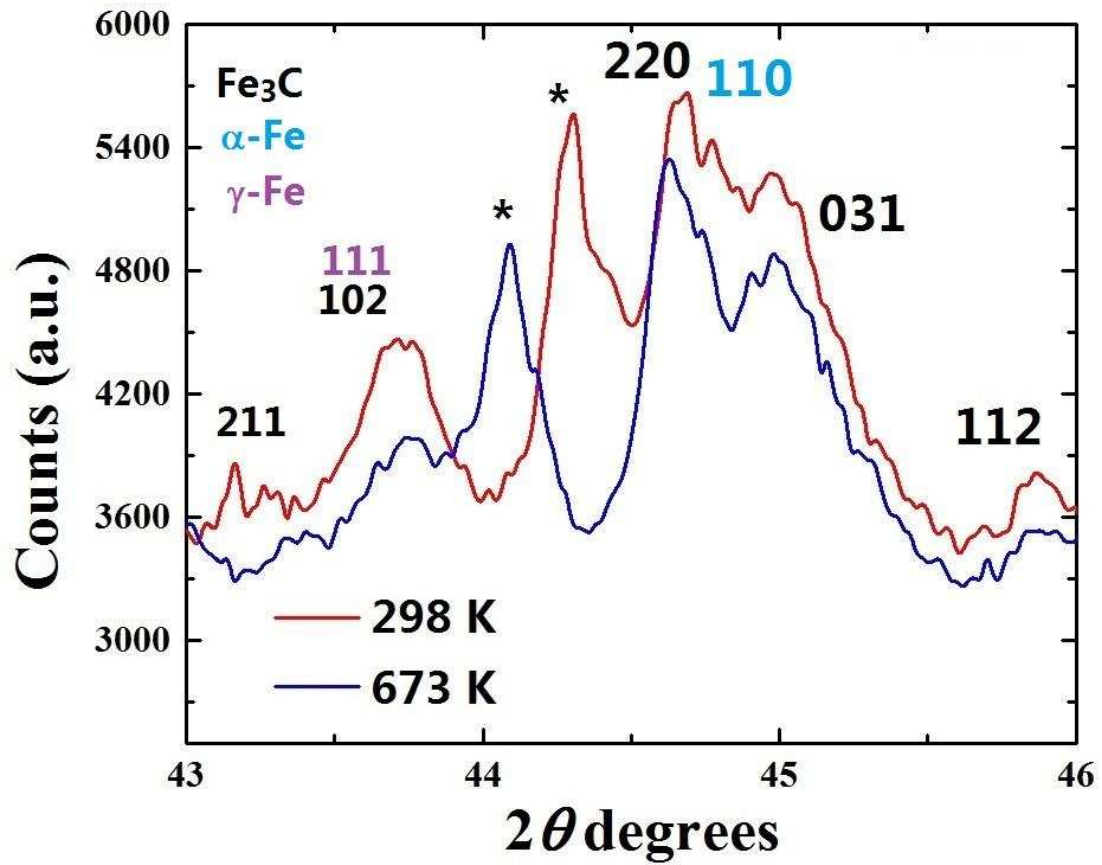


Figure Supp. 11: experimental XRD patterns of CNTs partially filled with Fe₃C (produced by pyrolysis of 1g of ferrocene and 0.65 ml of dichlorobenzene) measured at 298 K and 673 K. In this case an unusual decrease in the intensities of the Fe₃C peaks is found. The black star indicates the peak associated to the substrate used for the XRD experiment.

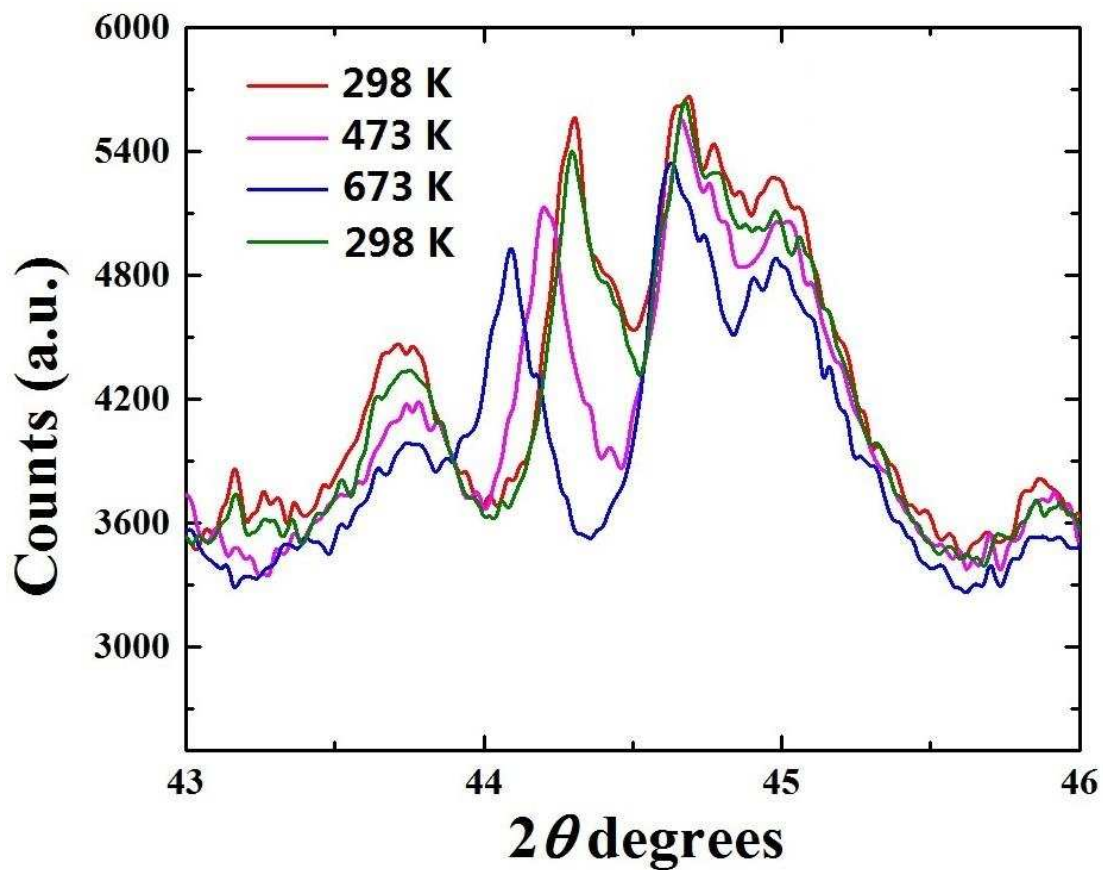


Figure Supp. 12: experimental XRD patterns of CNTs partially filled with Fe_3C (produced by pyrolysis of 1g of ferrocene and 0.65 ml of dichlorobenzene) measured at 298 K, 473 K, 673 K and again at 298 K after cooling. A reversible variation in the intensities of the Fe_3C peaks is found. See Fig.Supp.11 for peak indexing.

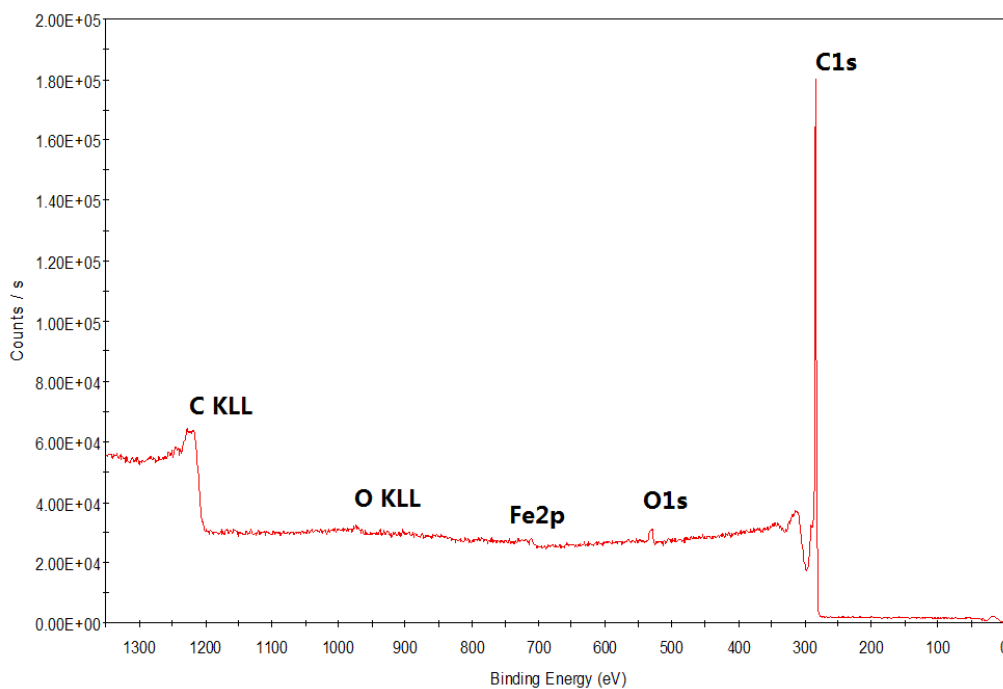


Figure Supp. 13: Typical XPS spectrum of Fe_3C filled carbon nanotubes. The presence of a small peak of oxygen can be associated to small quantities of oxygen chemisorbed in the walls of the CNTs. This is in agreement with the XRD analyses above where no iron oxide peak was found.

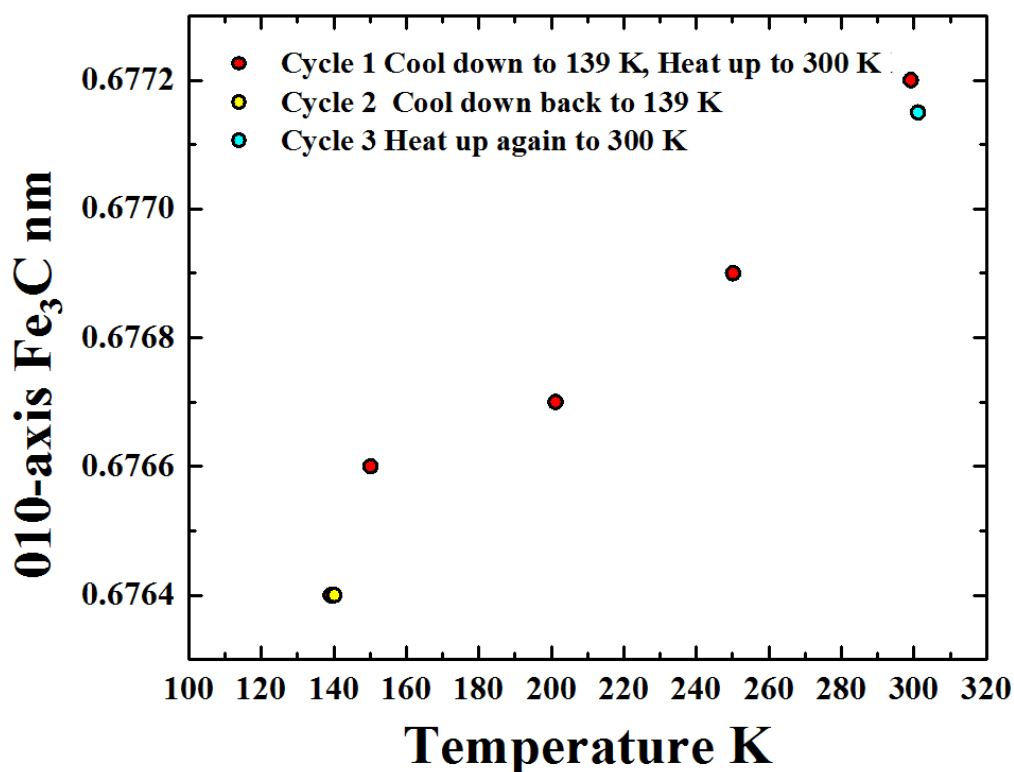


Figure Supp. 14: Plots showing the variation of the Fe_3C 010 axis with temperature in the T-interval from 140 K to 300 K. These measurements were performed in an additional Fe_3C -CNT sample prepared with synthesis conditions similar to those used for the partially-filled CNTs analysed above (i.e. in this case a higher quantity of ferrocene of 1.5g was used). Interestingly also in this case the memory effect analyzed above is observed. Note that these measurements were

performed in the Rigaku Smartlab powder X-ray diffractometer (Cu K- α , $\lambda = 0.154$ nm) under vacuum values below 7 Pa (approximately 2.5 Pa) in the temperature range from 140 K to 300 K.

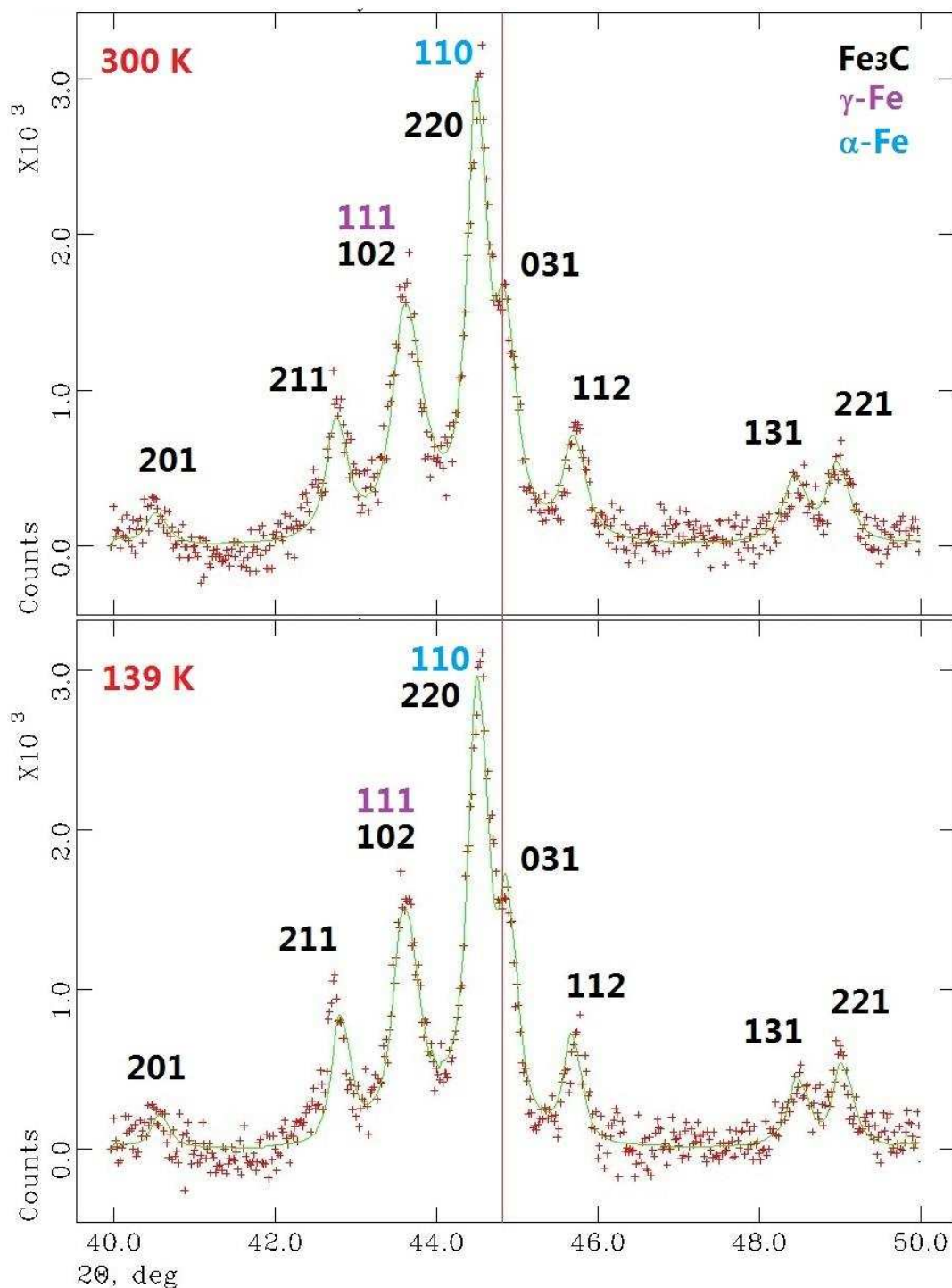


Figure Supp. 15: T-dependent experimental XRD pattern (red line) and Rietveld refinement (green line) of as grown CNTs partially filled with Fe_3C crystals measured at 300 K and 139 K (see Fig. Supp.14). Note the shift of the 031 peak of Fe_3C toward higher values of 2θ degrees. Instead due to the limited 131 peak-resolution at 300 K (probably due to collection time being shorter than the case of Fig.Supp.3), the 131 peak-shift could not be clearly evaluated for this sets of

measurements.

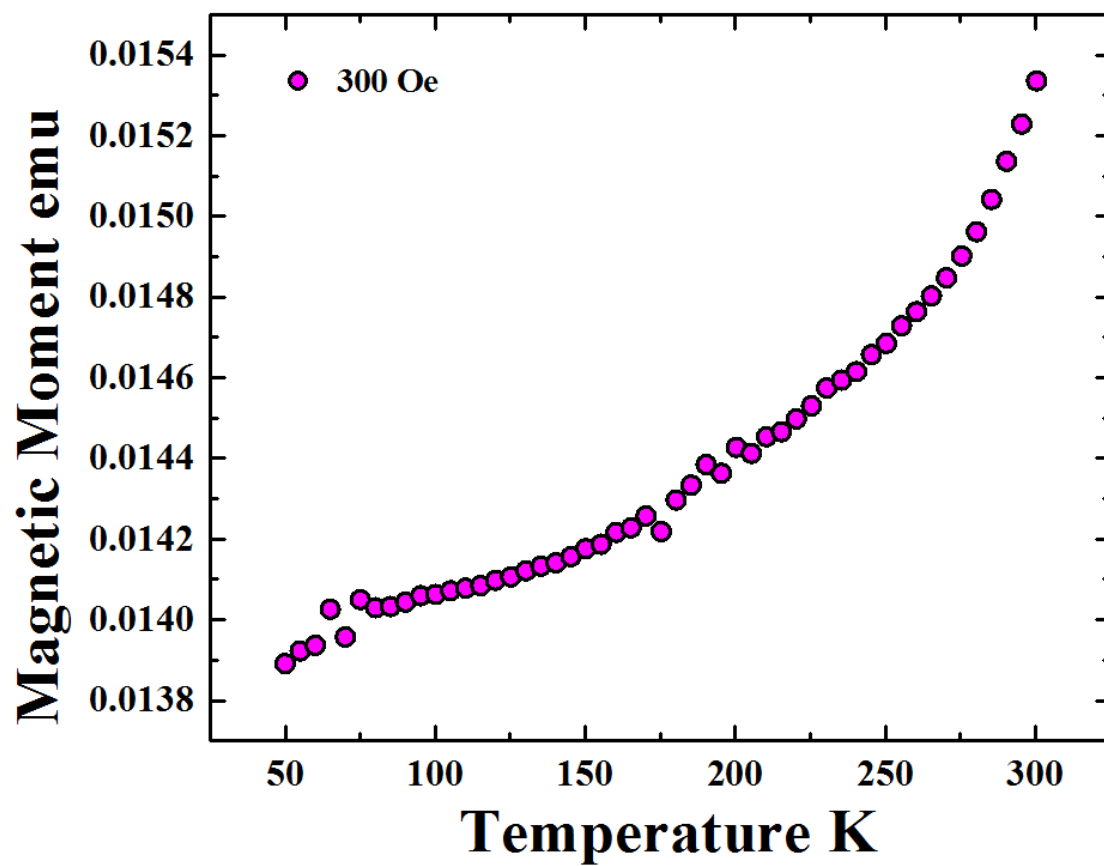


Figure Supp. 16: T-dependent zero field cooled measurement of the magnetization. The used field was 300 Oe.

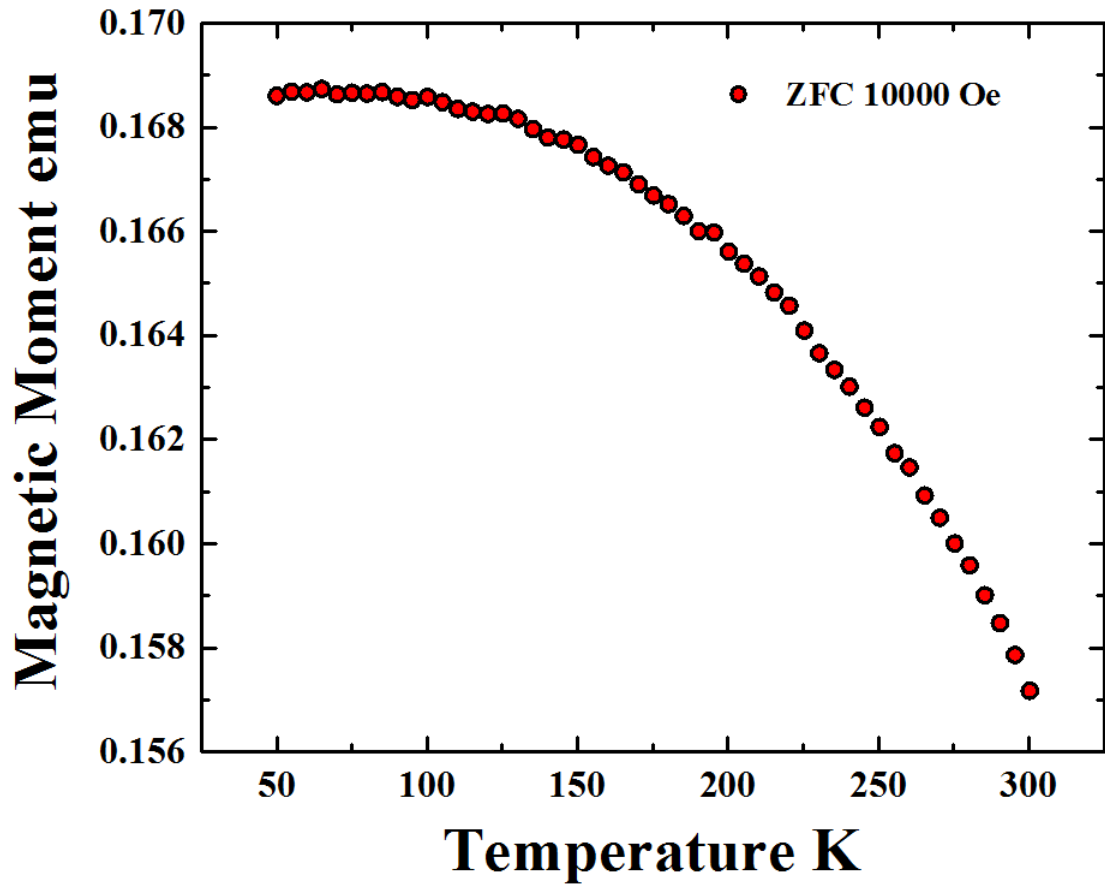


Figure Supp. 17: T-dependent zero field cooled measurement of the magnetization. The used field was 10000 Oe.