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Abstract

Ferromagnetically-filled carbon nanotubes have been recently considered important candidates for application into data recording quantum disk devices. Achievement of high filling rates of the ferromagnetic materials is particularly desirable for applications. Here we report the novel observation of carbon nanotubes continuously filled along the capillary with unusual μm-long faceted Fe_3C nanowires. Anomalous magnetic features possibly due to strain effects of the crystal facets are reported. Magnetization measurements revealed unusual stepped magnetic hysteresis-loops at 300 K and at 2 K together with an anomalous decrease in the coercivity at low temperature. The observed unusual shape of the hysteresis is ascribed to the existence of an antiferromagnetic transition within or at the boundary of the ferromagnetic facets. The collapse in the coercivity value as the temperature decreases and the characteristic width-enhancement of the hysteresis with the field increasing appear to indicate the existence of layered antiferromagnetic phases, possibly in the strain-rich regions of the nanowire facets. Zero field cooled (ZFC) and field cooled (FC) magnetic curves evidenced presence of magnetic irreversibilities, an indicator of a possible spin-glass-like behavior induced by competing antiferromagnetic and ferromagnetic interactions. Characterization performed with low temperature XRD measurements, further revealed a slight variation in the average Fe_3C unit cell parameters, suggesting the absence of additional unit-cell volume induced ferromagnetic transitions at low temperature.

Introduction

Molecular clusters behaving as single molecular magnets are typically able to show quantum tunnelling of magnetization at low temperatures [1-9] due to a ground state with a giant spin and an easy-axis of magnetization. These properties are different with respect to those measured in typical nano-ferromagnetic systems [10-16] where, owing to a large number of spins (10^5-10^8), the observation of quantum tunnelling is not trivial [16-31]. Interestingly Wernsdorfer et al., showed that 5 types of stepped-hysteresis loops could be obtained in the case of ferromagnetic nanoparticles [16]. It was also shown that the magnetization reversal of a single ferromagnetic nanoparticle could be described by thermal activation over a single-energy barrier [17]. However, in agreement with the predicted cross-over temperature [18-19] (T = 20 mK), no quantum effects were reported. Observation of staircase-like hysteresis loops has been reported also in diluted magnetic semiconductors, examples of these systems include (In, Mn)As at low temperatures. In these systems formation of multiple magnetization jumps have been generally attributed to the depinning processes of magnetic domain walls [36]. Also, the formation of unusual magnetization steps, so-called Barkhausen jumps, has been reported in the presence of structural defects which strongly affect the magnetization process [33-35]. These effects have been recently observed in the specific cases of iron carbide/iron interfaces [35] and polycrystalline α-Fe-filled materials encapsulated within carbon nanotubes (CNTs) [33].

Possible influence of Kondo effects in such phenomena has been also excluded in recent Seebeck-studies [32].

Differently from these examples, other types of stepped hysteresis loops have been reported to arise in materials where coexistence of superparamagnetic- and ferromagnetic-single-domain- grains is present [37-40]. Existence of such magnetic phenomena has been also reported in conditions of: I) coexistence of two magnetic components with contrasting coercivities, II) relatively high ratios of the coercivity remanence to coercive force and III) low coercivity components as large fraction of the total volume of the magnetic grains [37-40].

Additionally, the values of magnetic moment for certain types of ferromagnetic crystals (i.e. iron carbide Fe_3C) have been reported to change under certain conditions of unit cell volume contraction [28, 41-44]. Interestingly, observation of temperature-driven structural transitions in CNTs filled with Fe_3C nano-crystals was reported in a recent work by Boi et al. [41]. In that study, temperature dependent X-ray diffraction (T-XRD) measurements from 12 K to 298 K and Rietveld refinement analyses revealed a cooperative reversible 2θ-shift in both the 002 peak of the graphitic CNTs-walls and the 031 and 131 peaks of the encapsulated Fe_3C nano-crystals, evidencing a contraction in the average unit-cell volume of Fe_3C with the decrease of the temperature [41]. Unusual variation of the magnetization with temperature and applied field in CNTs films containing a large quantity of Fe_3C were also reported by Karmakar et al. by SQUID magnetometry [43] and attributed to exchange bias effects resulting from magnetic interaction with secondary γ-Fe -phases (inside the CNTs) [43].

Appearance of butterfly shaped signal in the magnetization hysteresis has been also indicated as a hint to ferrimagnetism (see Mihalik et and Wollan et al. in ferrimagnetic oxide-based materials ($NdMn_{1-x}FexO_{3+\delta}$) and [(1—x)La, xCa]$MnO_3$ systems [45,46]). Unusual hysteresis shapes were reported also by Hellwig et al. in presence of an antiferromagnetic-coupling effect between ferromagnetic multilayers [48].

In this work we report the novel observation of anomalously stepped hysteresis loops exhibiting a temperature-induced collapse in the magnetic coercivity parameter, in multiwall carbon nanotubes (MWCNTs) filled with faceted long ferromagnetic Fe_3C nanowires (diameter of 40-60 nm and length of 1-5 micrometres).

The encapsulated nanowires were found to exhibit a unit-cell with averagely large atomic-parameters a = 0.5109243 nm, b = 0.6765692 nm, c = 0.4543652 nm and an average volume of 0.15706 nm^3.

The observed magnetic phenomenon is ascribed to the possible existence of layered antiferromagnetic interactions at the defective grain boundaries of the Fe_3C-facets (created by the fast cooling) within the μm-long faceted nanowires. The change in the coercivity parameters with the decrease of the temperature from 300 K to 2K cannot be explained on the basis of previous works on Fe-filled nanotubes. The appearance of such strained faceted features (as revealed by high resolution transmission electron microscopy (HRTEM)) in the encapsulated nanowires and the observed Fe_3C-unit cell reduction, as revealed by T- XRD and Rietveld refinements, implies instead the possible formation of ferromagnetic-antiferromagnetic interfaces at low temperature. Zero field cooled (ZFC) and field cooled (FC) magnetic curves highlighted the presence of magnetic irreversibilities, an indicator of a possible spin-glass-like behavior induced by competing antiferromagnetic and ferromagnetic interactions.

The observed small variation in the average Fe_3C unit cell parameters, as extracted by Rietveld refinements, further suggest the absence of unit-cell volume induced magnetic moment transitions [28].

Experimental

MWCNTs filled with Fe_3C nanowires (diameter of 40-60 nm) were produced by sublimation and pyrolysis of ferrocene and dichlorobenzene mixtures (40 mg of ferrocene were mixed with one drop of dichlorobenzene). A quartz tube reactor of 1.5 m and an Ar flow rate of 11 ml/min were used. The samples were cooled down with cooling times of 10-20 min by removing the furnace along a rail system (quench). Different sublimation temperatures were used (the value of sublimation temperature was measured within the area occupied by the ferrocene-containing quartz boat, within the quartz tube reactor), and the pyrolysis temperature was 990 °C. The duration of each reaction was 10 minutes. Fe_3C filled carbon nano-onions (CNOs) were produced for comparative purposes, following the method reported in ref.47. Different average unit-cell volumes (determined via Rietveld refinement of the XRD patterns) were obtained for the MWCNTs depending on the used sublimation temperature: 0.15528 nm^3 with 630-700 °C; 0.15608 nm^3 with 530-600ºC; 0.15706 nm^3 with 460-530 °C and 0.15778 nm^3 with 360-460 °C. Note that the observed effect was then found to vanish for larger quantities of ferrocene (i.e. ~ 100- 200 mg), owing to the increase of the overall CNTs-diameter and systematic differences in the carbon to metal ratios within the pyrolyzed vapor. A 200 kV American FEI Tecnai G2F20 HRTEM and a Philips X'pert Pro MPD powder X-ray diffractometer (Cu K-$\alpha_{1,2}$, λ =0.15418 nm) were employed for the crystal characterization. The magnetic characterization was performed at 300 K with a vibrating sample magnetometry 2.5 Tesla electromagnet East Changing 9060 by using a magnetic field of 13000 Oe and at 2 K with a Quantum Design Superconducting Quantum Interference Device by using the magnetic field of 10000 Oe. T-XRD measurements were performed on a PANalytical Empyrean powder X-ray diffractometer, equipped with a primary Johansson monochromator (Cu K-α_1, λ =0.15406 nm), an Oxford Cryosystems PheniX cryostat operating under vacuum below 10-2 Pa, and a X'celerator linear detector. Measurements were collected from 12 K to 298 K (12 K, 20 K, 30 K, 40 K, 50 K, 60 K, 70 K, 80 K , 90 K, 100 K, 120 K, 140 K, 160 K, 180 K, 200 K, 220 K, 240 K, 260 K, 280 K and 298 K). See also ref. [49] for comparative SQUID magnetometry measurements on Fe_3C filled CNOs, in absence of nanowire facets.

Results and Discussion

A typical example of MWCNTs completely filled with a Fe_3C nanowire is shown in the transmission electron micrograph of Fig.1A. It is interesting to notice that a variation in the volume distribution of the Fe_3C crystal along the MWCNT-core is present with the formation of unusually faceted atomic lattice periodicities characterized by repeated dark and bright contrasts within individual encapsulated nanowires. A typical XRD measurement confirming the presence of Fe_3C in the sample is shown in Fig.2. The Fe_3C phase was identified by the 210, 002, 201, 211, 102, 220, 031, 112, 131, 221 and 122 reflections. The unit cell parameters determined via Rietveld refinement were:
a = 0.5109243 nm, b = 0.6765692 nm, c = 0.4543652 nm (unit cell volume of 0.15706 nm^3). Detailed HRTEM measurements revealed further a high detail of the Fe_3C crystal-lattice. As shown in Fig.1B and Figs.3,4 slight variations in the lattice parameters could be probed in different regions of the encapsulated carbide nanowires. In the inset of Fig.1C, the reduced Fourier transform allowed to identify the 100 (cyan circles) and 001 (yellow circles) lattice planes of Fe_3C with space group Pnma corresponding to the spacings of approximately 0.51 nm and 0.45 nm respectively.

Presence of unusual hysteresis loops, characterized by a characteristic width-enhancement with the field increasing was revealed in the room-temperature magnetization vs applied field hysteresis (see rose-colored hysteresis Fig. 5A and B) of a powdered-sample comprising many randomly oriented filled MWCNTs as those shown in Fig.1. Two steps were identified at approximately 492 Oe, 22.4 emu/g, and at -460 Oe, -22.9 emu/g. A saturation magnetization of 109 emu/g and a coercivity of 850 Oe were measured.

The hysteresis loop was further measured also at 2K (see Fig.5A and 5B, dark magenta hysteresis). These measurements revealed a temperature-induced shift in the step-position together with an increase in the length parameter of each step. The two anomalously long step-features were found at 96.6 Oe, 37 emu/g and at -100 Oe, -37 emu/g. The length of each step was found to be 58-62 emu/g. An extremely low coercivity of 100 Oe and a higher saturation magnetization of 120 emu/g were also measured at low temperature. We can immediately notice that these properties are very different with respect to those reported at 0.2 K by Wernsdorfer et al. [16]. Also, the observed trend is significantly different with respect to that measured by Boi et al. in non-faceted Fe_3C filled CNOs in ref.49, where a progressive increase in the coercivity parameter with the decrease of the temperature was found.

Stepped hysteresis loops have been reported also in the case of single-molecule magnets [1,9], nanomagnets [25-26], FeC crystals and Fe/Sm multilayers [20-27]. However due to the large number of atomic periodicities comprised in the Fe_3C nanowires, the temperature of observation and the unusual dynamics of coercivity decrease, the origin of the observed step features is not attributable to quantum tunnelling of magnetization effects or the possible presence of a wasp-waisted hysteresis loops. Instead, given the presence of strained regions in the encapsulated nanowires, the formation of ferromagnetic/antiferromagnetic interfacial features is possible [48]. Comparing the observed hysteresis in Fig.5B with those observed in antiferromagnetically-coupled ferromagnetic multilayers, a similarity in the shape of the hysteresis is noticeable [48]. Additional investigation of this magnetic transition was considered by employing ZFC and FC methods to extract the variation of the magnetic moment with temperature. Fig.6 shows the ZFC and FC magnetization vs temperature signals acquired from 2K to 300K at the field of 300 Oe. It is important the notice the existence of a spin-glass-like behavior in both the analyzed portions of the filled CNTs in Fig.6A-B, which may be an indicator of competing ferromagnetic and antiferromagnetic ordering within the same sample [50-51].

Further investigation of the possible existence of T-induced structural variation in the Fe_3C unit-cell volume was considered by employing T-XRD and Rietveld refinements. These Rietveld refinements were performed on the same dataset acquired in ref.41 for CNTs filled partially/or continuously with Fe_3C. Repeated Rietveld refinements were performed on a narrower 2θ region (from 39º to 50º 2θ) of the XRD patterns with respect to the refinements reported in reference [41], allowing for a more accurate estimation of the unit-cell volume parameters.

Plots showing the variation of the 100, 010 and 001 Fe_3C axis values are shown in Fig.7A-H (on CNTs partially and continuously filled with Fe_3C), and plots showing the unit-cell volume parameters are shown in Figs.7D,H (see typical examples in ESI Fig.1 and ESI Fig.2). Note that this more accurate estimation of the unit-cell volume indicates a contraction of 0.52% in the continuously filled CNTs case (Fig.7D) and of 0.06% in the partially filled CNT case (Fig.7H). The unit cell volume appears to slightly decrease with the decrease of the temperature. Note however that the observed volume change is not comparable to that required for the observation of significant transitions in unit-cell magnetic moment values [28].

In order to further verify this interpretation, additional comparative measurements were then performed on Fe_3C filled CNOs produced according with the method reported in ref.47 (see Fig.8 for typical TEM images) in a comparable temperature range (see also supp. Materials in ref.49 for comparative magnetization measurements). As shown in Figs.9-11 also in this case a weak contraction in the average unit cell volume of Fe_3C and in the graphitic c-axis of the CNOs was found with the decrease of the temperature, with a small Fe_3C unit cell volume change of 0.27%.

This observation appears to confirm the above interpretation and suggests the absence of Fe_3C unit cell induced magnetic moment transitions at low temperature in these types of materials. Instead, a crucial role in the appearance of the observed stepped magnetization hysteresis appears to be taken by the faceted morphology of the nanowires. This observation is confirmed by direct comparison with other magnetization measurements performed in non-faceted Fe_3C-filled CNOs, reported in ref.49; indeed, in this latter CNO-case an opposite trend involving a significant increase of the coercivity parameter with the decrease of the temperature was found.

Conclusions

In conclusion in this work we have shown that MWCNTs filled with Fe_3C nanowires can show unusual stepped-like hysteresis loops due to strain induced variation of the Fe_3C nanowire volume. The origin of the observed stepped hysteresis was attributed to existence of antiferromagnetic-coupling in ferromagnetic faceted-interfaces. These findings open new avenues towards investigation of antiferromagnetism in faceted Fe_3C filled CNTs systems for application in magnetic devices.

Conflicts of interest

There are no conflicts of interest to declare

Acknowledgments:

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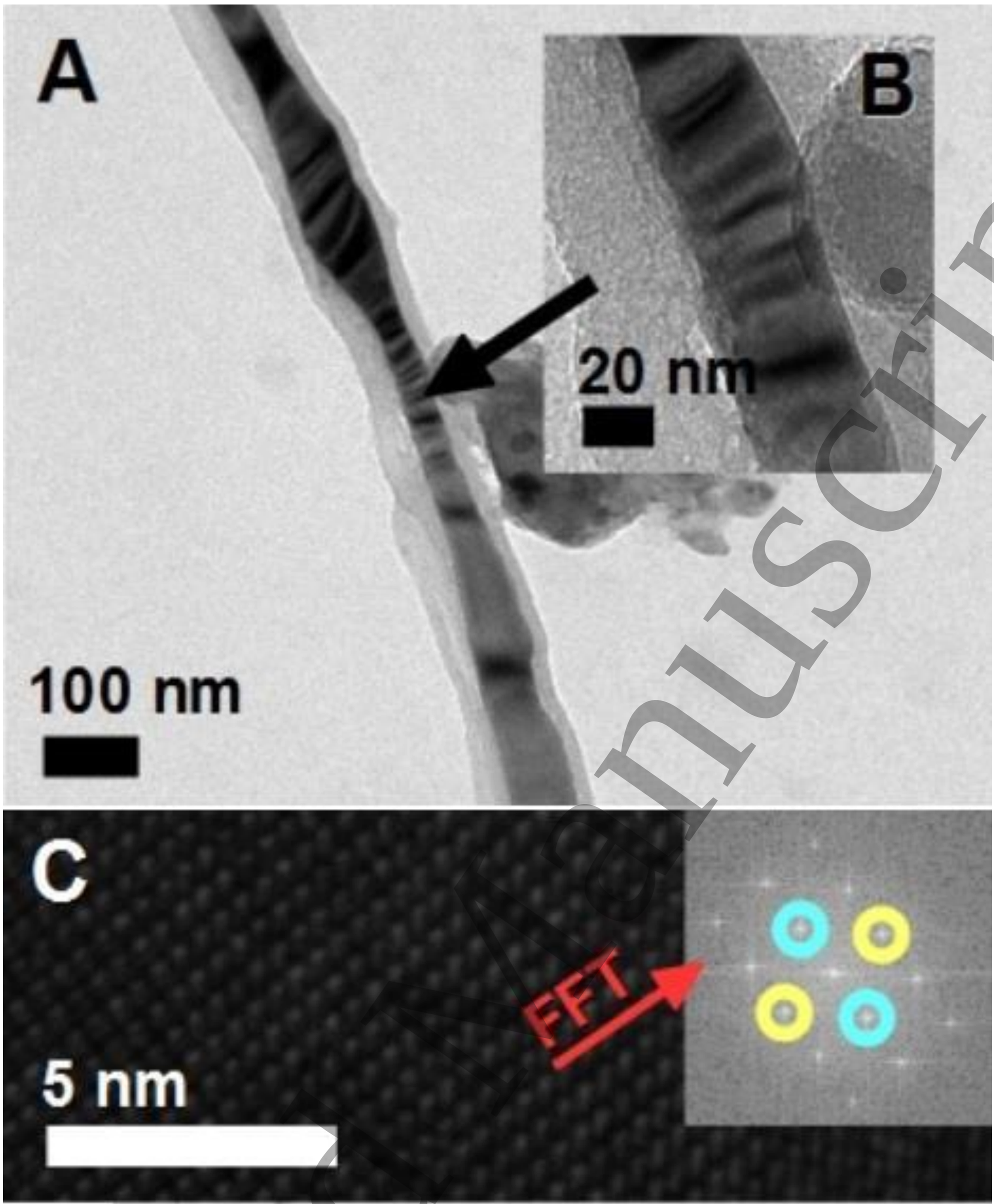

Figure 1: TEM (A-B) and HRTEM (C) micrographs of a typical Fe_3C crystal encapsulated inside a MWCNT. The inset in C shows the reduced Fourier transform of the lattice (see text for lattice indexing).

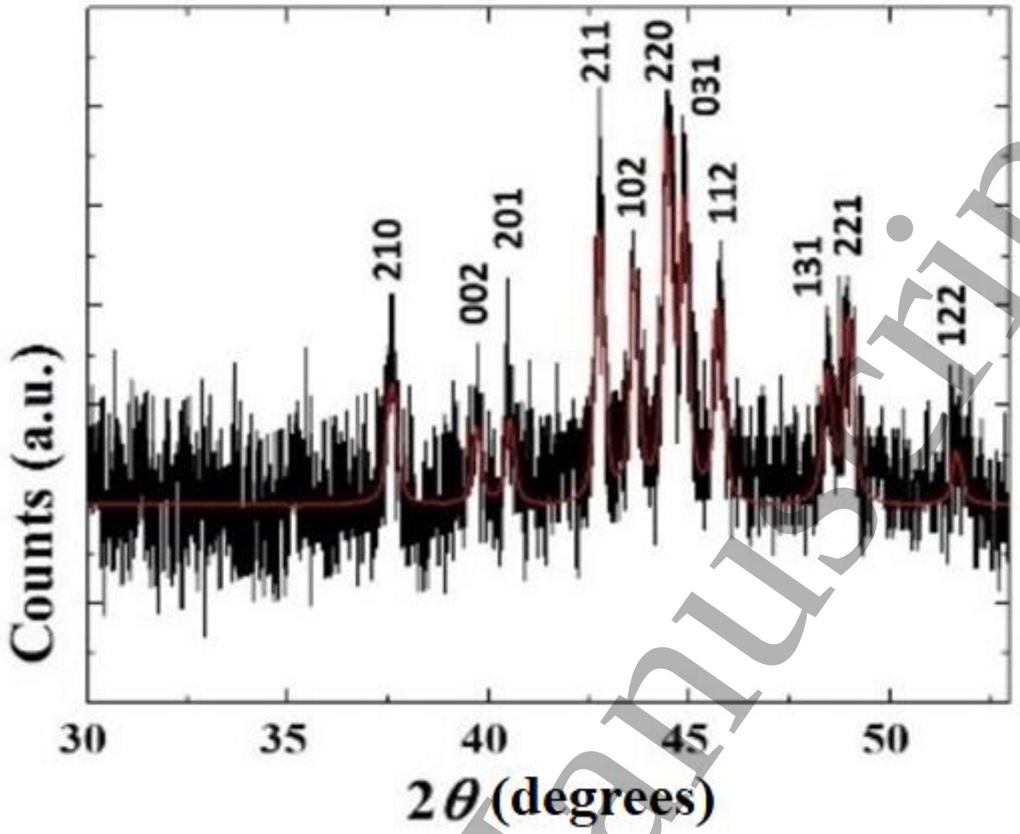

Figure 2: XRD pattern (acquired at ~ 298 K) of a typical powder sample of MWCNTs filled with Fe_3C (unit cell volume of 0.15706 nm^3). The red line represents the Rietveld refinement of the measured data (black line). Each peak is indicated with the corresponding lattice reflection

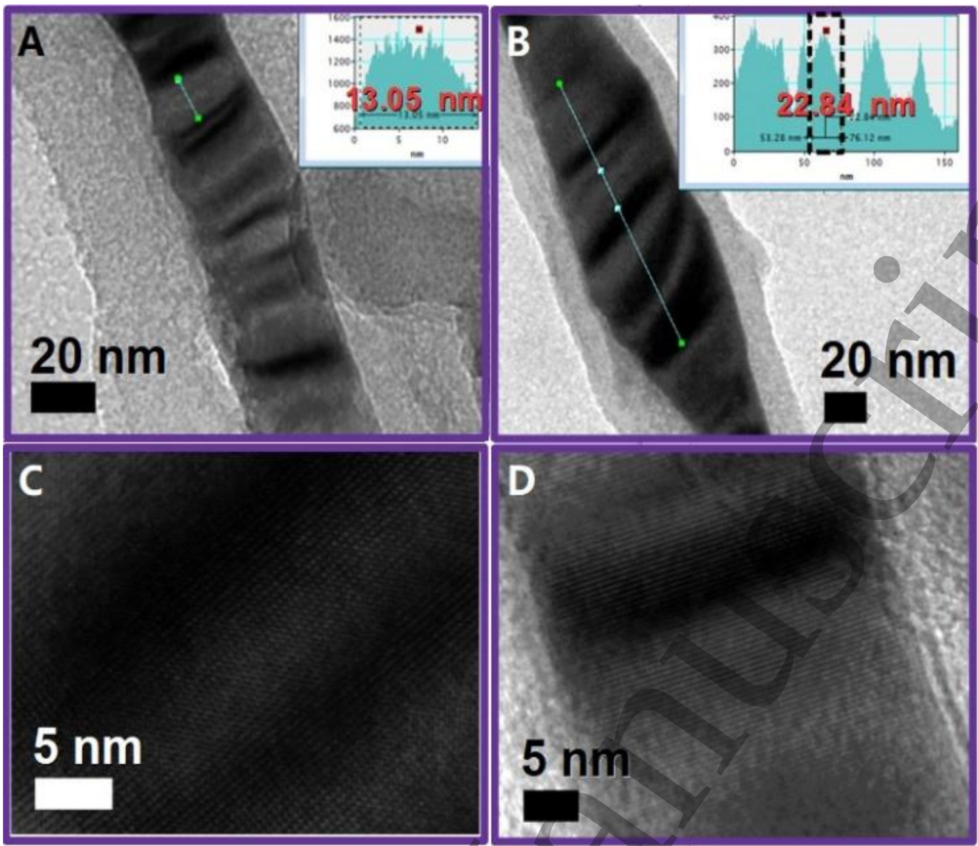

Figure 3: In A HRTEM micrograph of typical faceted Fe_3C crystal inside a MWCNT. The inset profile analysis shows the size of a selected faceted-like area of the nanowire where a variation in the unit cell volume is found. Note the presence of repeated bright and dark areas implying existence of strain in the nanowire lattice, which could be at the origin of the formation of antiferromagnetic regions in the sample. In B HRTEM micrographs of another area of a typical Fe_3C crystal inside the MWCNT. The inset profile analysis shows the size of a selected faceted-like area of the nanowire where a variation in the unit cell volume is found. Note also in this case the presence of repeated bright and dark areas implying existence of strain in the nanowire lattice. In C and D HRTEM micrographs showing other examples of faceted Fe_3C crystals inside a MWCNT with atomic resolution.

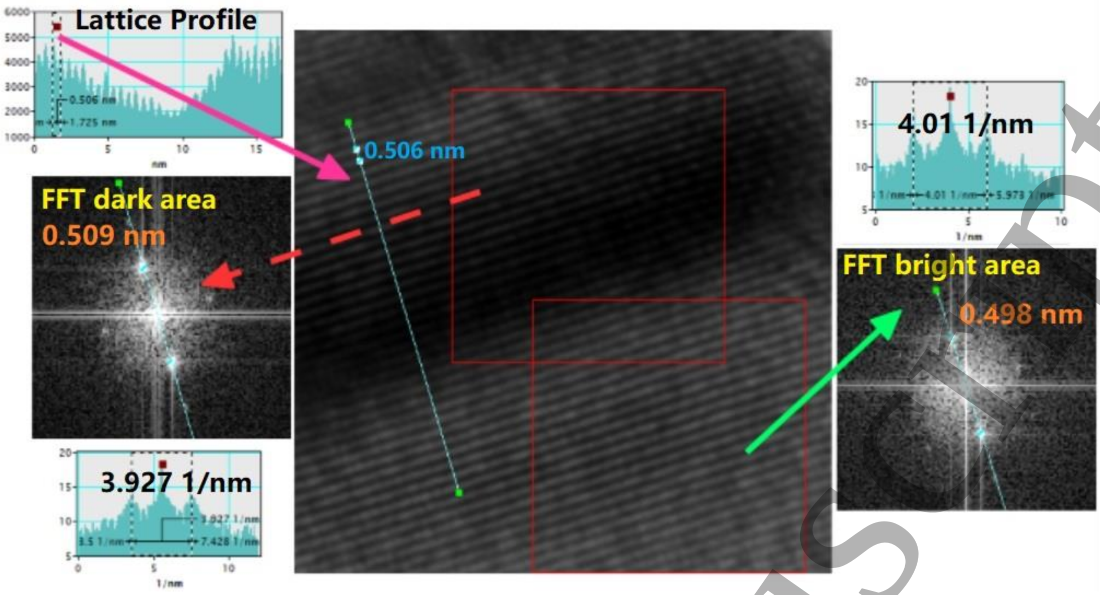

Figure 4: Profile analyses of the Fe_3C nanowire. Note the variation of the lattice parameters in the dark region (which represents a zone of nanowire bending) from the value of 0.498 nm to the value of 0.509 nm. Such lattice variation along the nanowire volume implies possible presence of multiple magnetic contributions to the observed hysteresis, as a consequence of nanowire localized lattice-stress in the faceted areas. Possible strain-induced formation of antiferromagnetic-ferromagnetic interfaces due to the fast cooling used in the experimental methods is suggested.

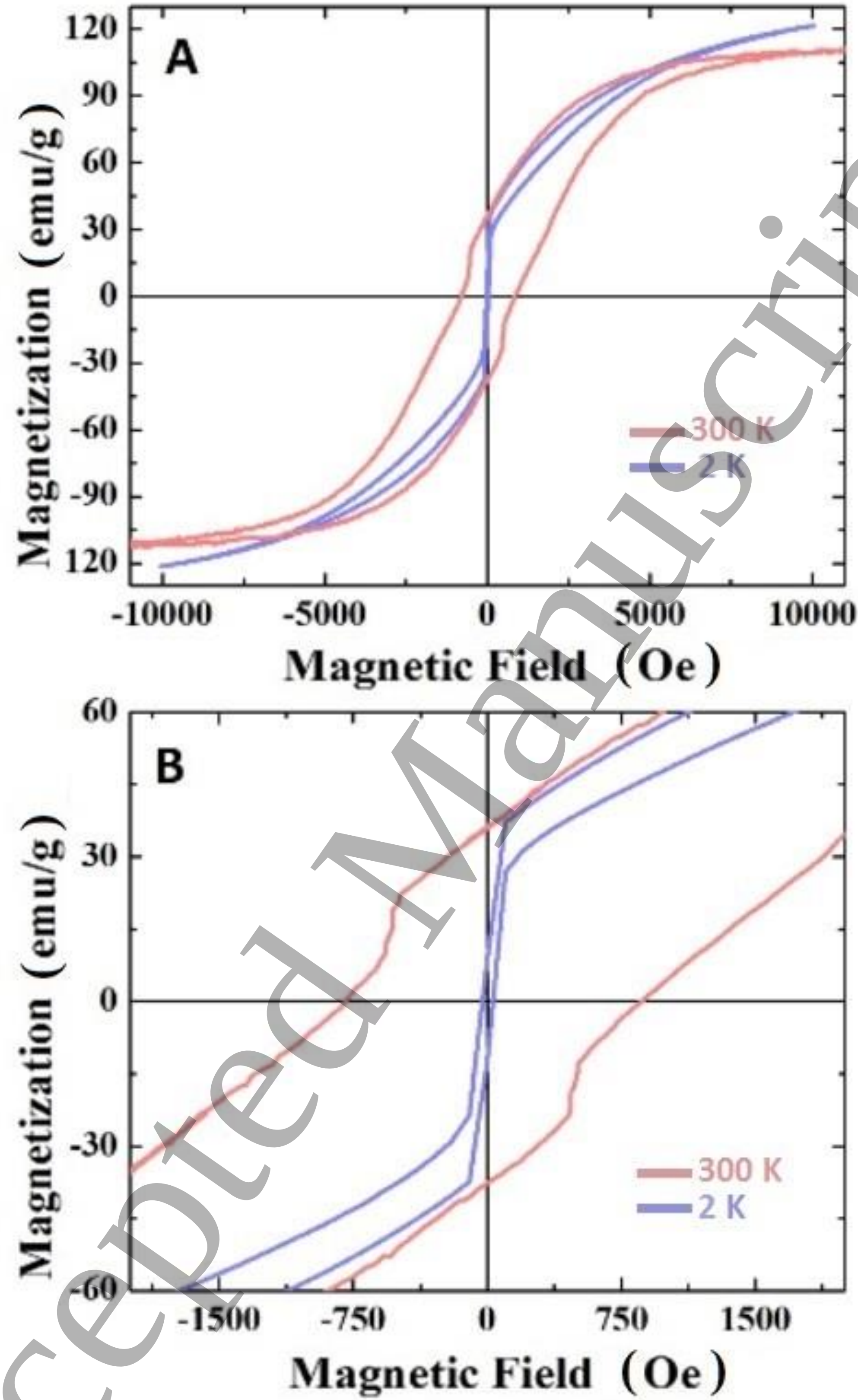

Figure 5: In A, ferromagnetic hysteresis acquired at 300 K (red-line) and 2 K (blue-line) from a powder of MWCNTs filled with Fe_3C nanowires with average unit cell volume of 0.15706 nm^3 as determined via Rietveld refinement methods. The unusual collapse in the coercivity at low temperature is shown in B with a higher detail.

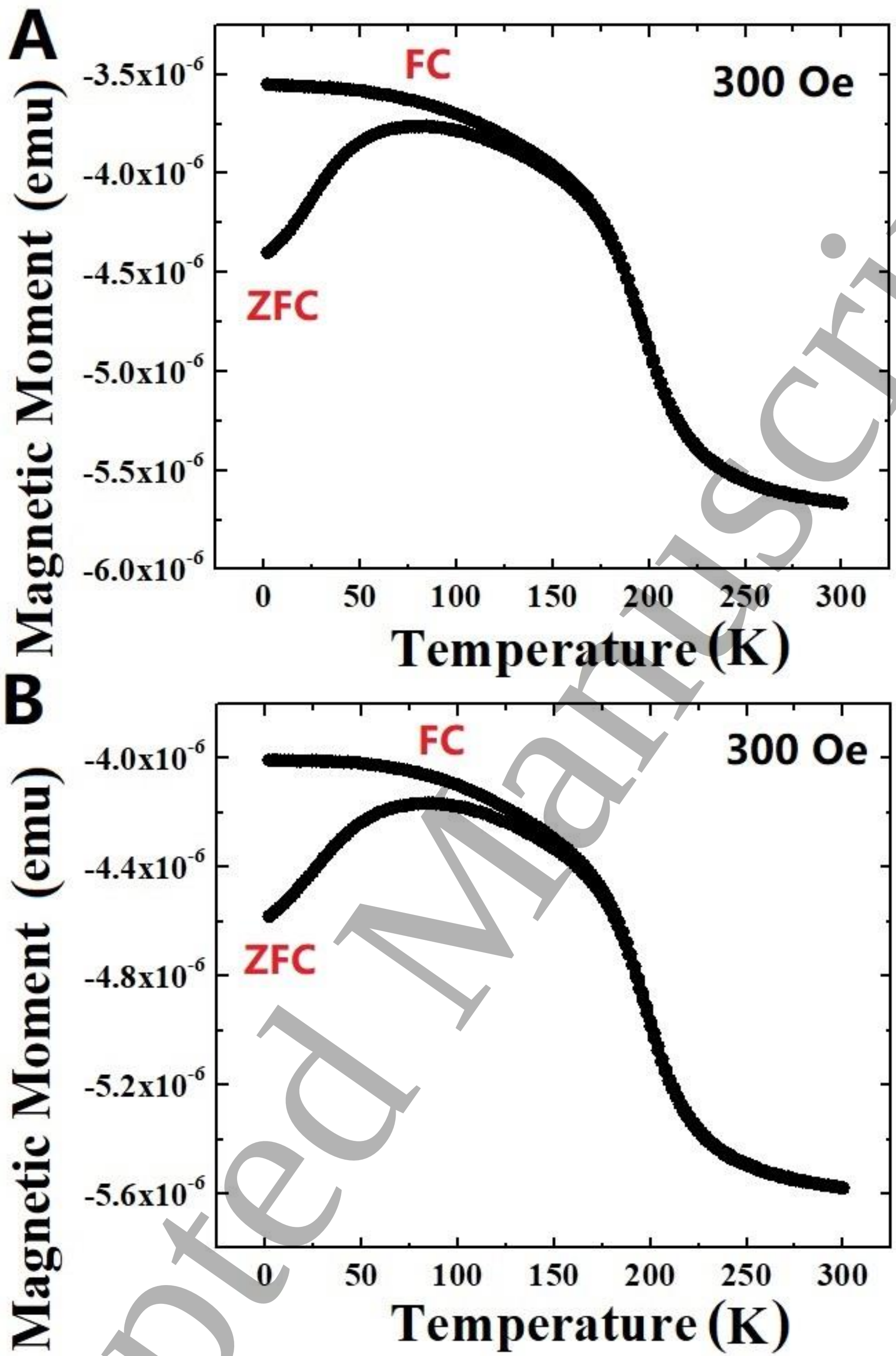

Figure 6: ZFC and FC magnetic curves in A and B, acquired from two different portions of the filled CNTs product. At ~70K it is noticeable the presence of a spin-glass-like behaviour possibly arising from competing ferromagnetic and antiferromagnetic interactions. It is also important to highlight the presence of a negative magnetic moment within all the temperature range.

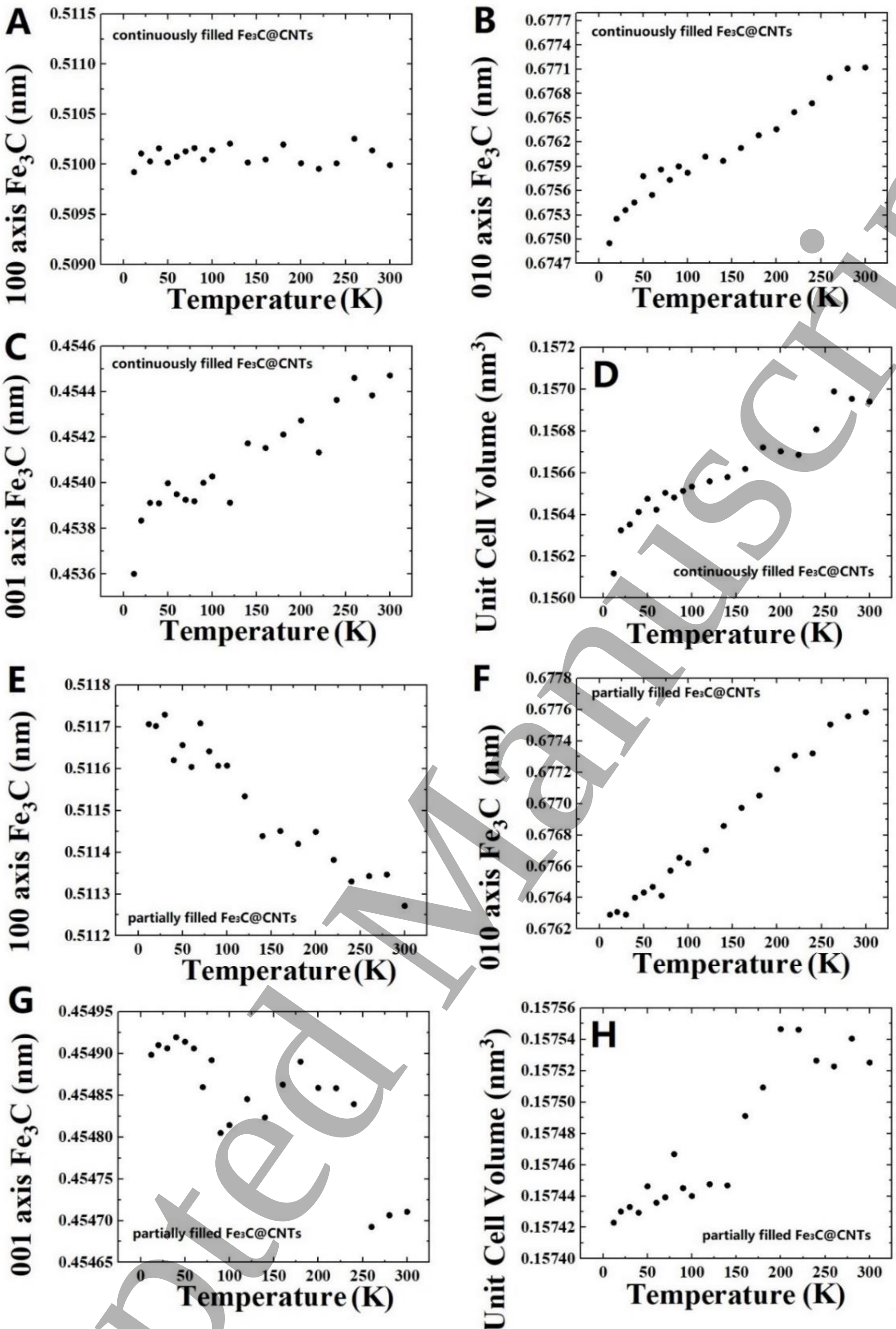

Figure 7: Plots showing the variation of the 100, 010, 001 axis values and of the unit-cell-volume of Fe_3C nanowires encapsulated continuously (A-D) and partially (E-H) inside the CNTs. This was determined via repeated Rietveld refinements performed on a narrower 2θ region of the XRD patterns reported in ref. 41. The improved quality of the refined data allowed for a more accurate estimation of the unit cell volume variation which appears to slightly decrease with the decrease of temperature in both cases. Note however that the observed change in unit cell volume values is not comparable to that required for the observation of significant transitions in magnetic moment values, as indicated in ref. [28,29]

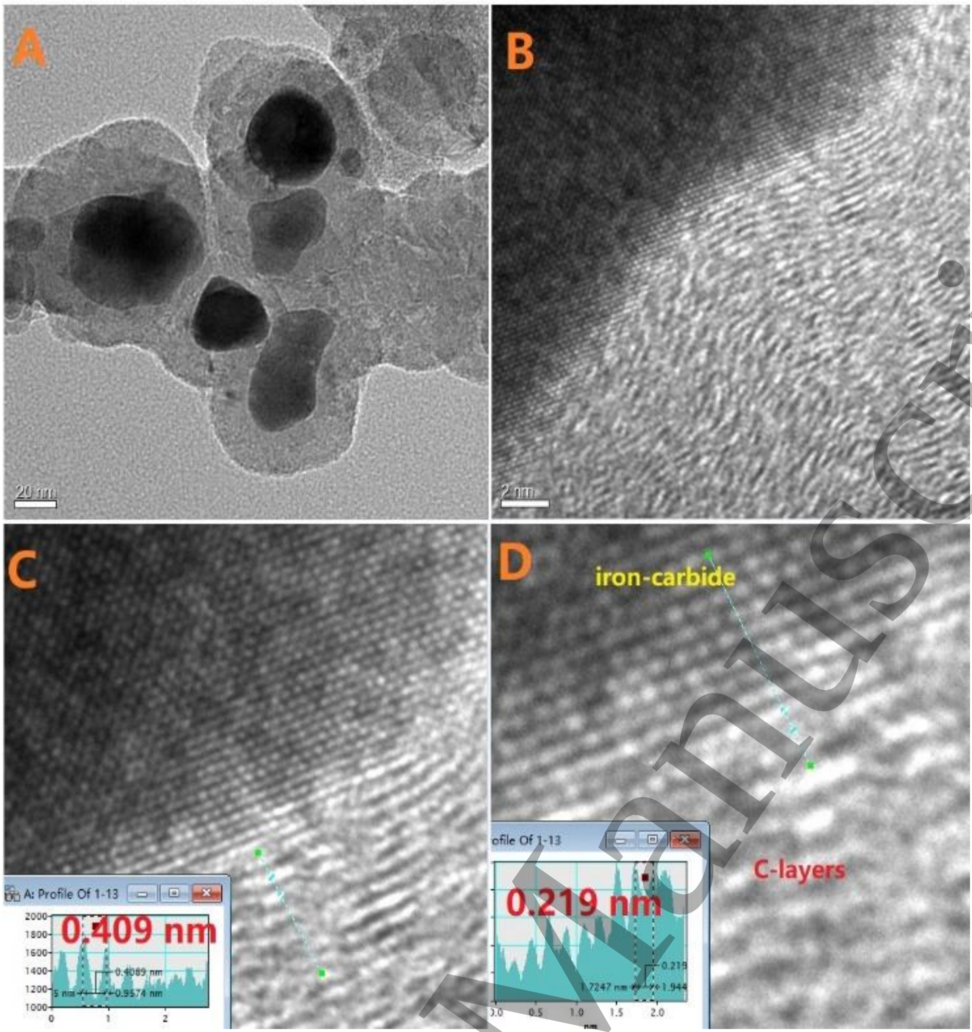

Figure 8: TEM micrograph shows the cross sectional of Fe_3C@CNOs. In (D), the detail interface region of the Fe_3C crystals and C layers is shown.

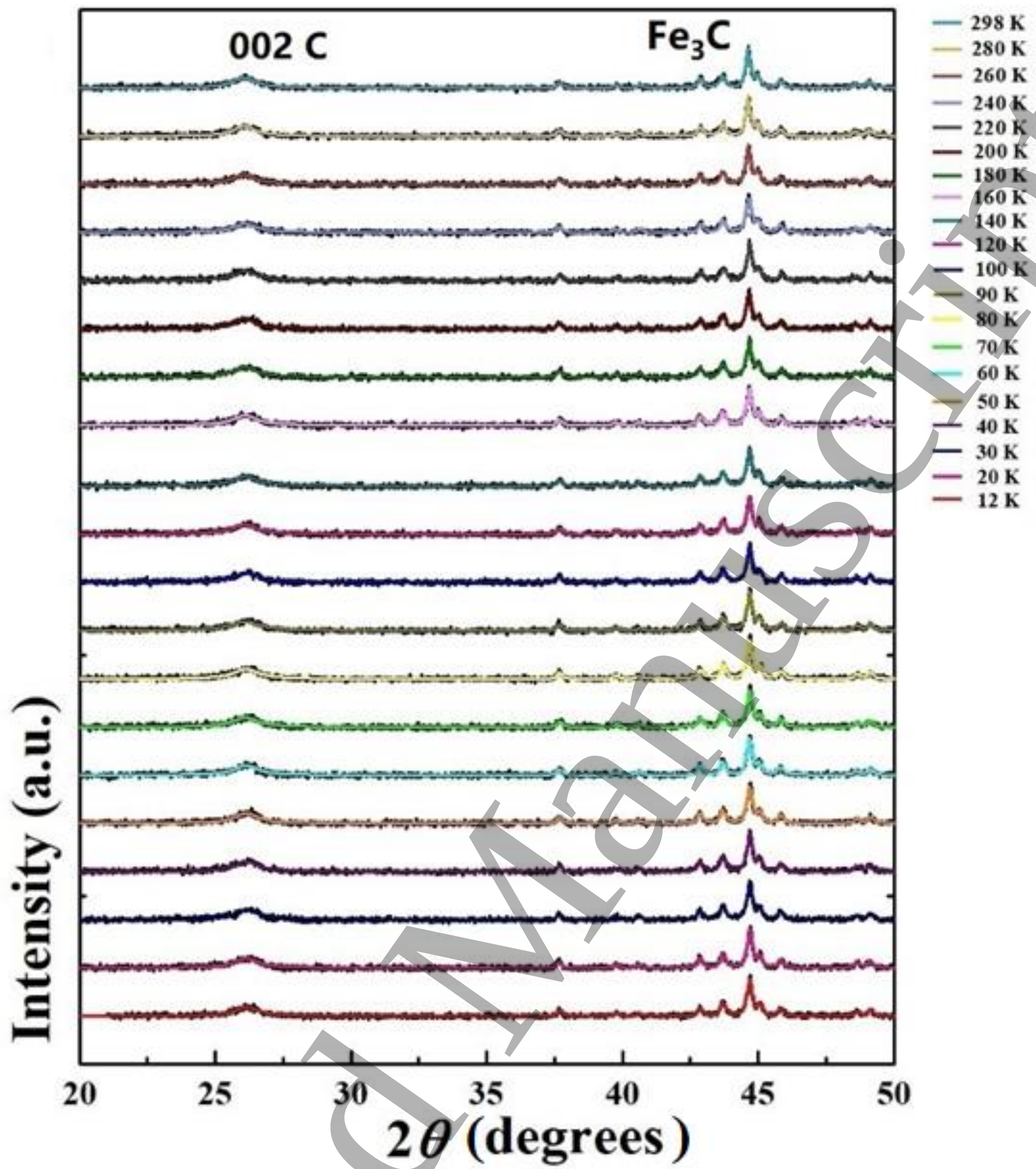

Figure 9: XRD patterns and Rietveld refinements (colored lines) in the temperature range from 12K to 298 K for the specific case of Fe_3C filled CNOs.

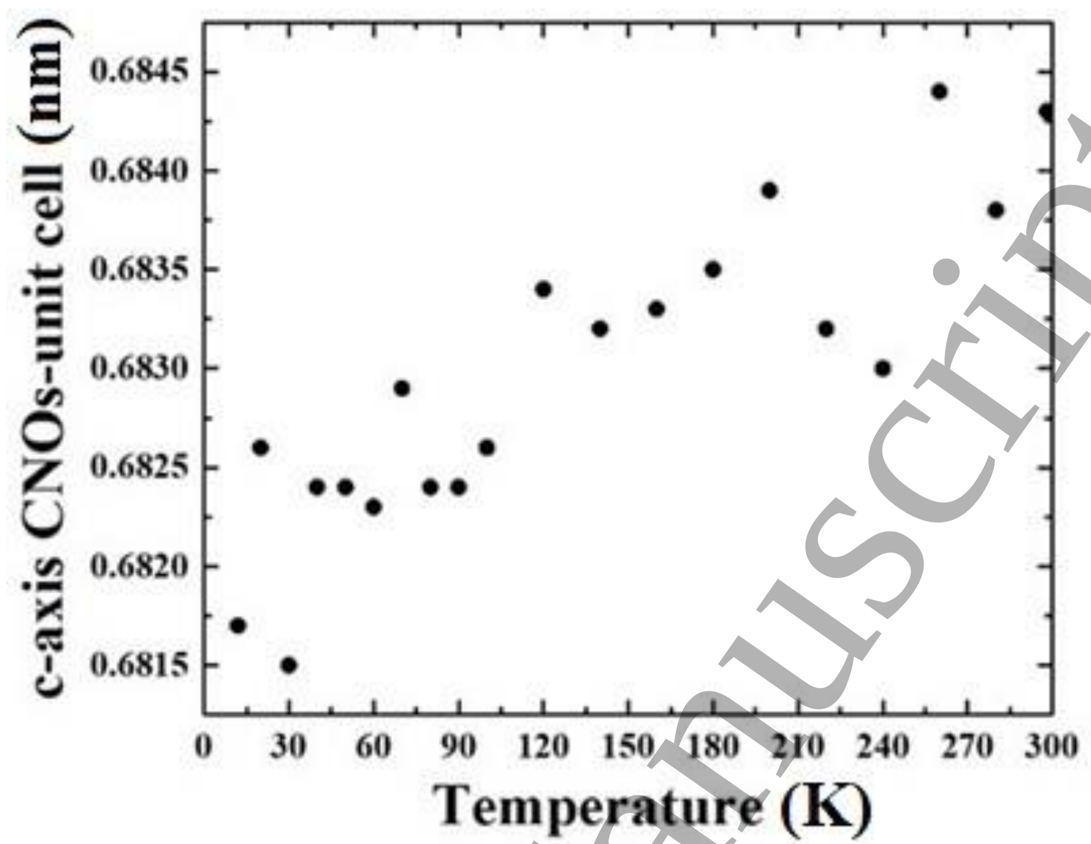

Figure 10: Plot showing the variation of the unit cell c-axis of CNOs as a function of the change of the temperature from 12K to 298 K. A contraction effect similar to that observed in ref. 41 is observed, with decreasing temperature.

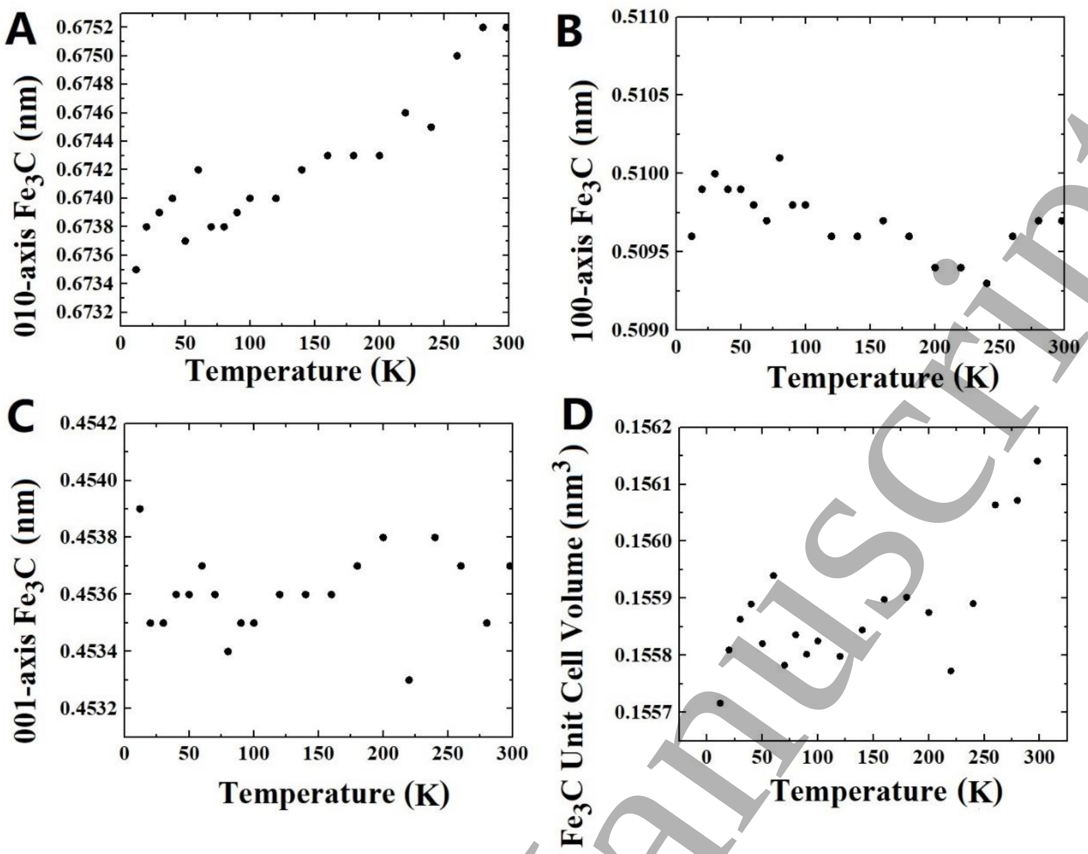

Figure 11: Plot showing the variation of the unit cell (010), (100), (001) axis and calculated unit cell volume of Fe_3C filled CNOs by the change of the temperature from 12K to 298 K. A 0.32% average unit cell volume change is shown in (D) in the temperature range from 12K to 298K.