Eur. Phys. J. B **40**, 499–504 (2004)
DOI: 10.1140/epjb/e2004-00286-6

THE EUROPEAN PHYSICAL JOURNAL B

Defects in graphite may be magnetic and magnetostrictive as revealed by scanning tunneling microscopy

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Received 12 February 2004 / Received in final form 25 May 2004
Published online 24 September 2004 –

Abstract. We use scanning tunneling microscopy to measure magnetic field induced strains in highly oriented pyrolytic graphite. This is done by using a scanning tunneling microscope with some magnetic components, which however do not produce an observable response within our resolution in the case of pure (99.999%) paramagnetic or diamagnetic metals (at the low field strengths applied). We study also ferromagnetic metals with this method for comparison. We find a relatively large (similar to that of permalloy) magnetostrictive response of graphite for the low applied field. The data shows saturation of the strain and also that the strain observed is localized and is not the cumulative strain from the mounted edge of the sample to the position of measurement, implying that volume is not conserved with the strains. We believe that the observed strains correspond to a signal of a ferromagnetic material and in this case may be due to the defects observed on the graphite planes.

PACS. 68.37.Ef Scanning tunneling microscopy (including chemistry induced with STM) – 75.80.+q Magnetomechanical and magnetoelectric effects, magnetostriction – 81.05.Uw Carbon, diamond, graphite

In the last several years, the search for, and study of new magnetic materials has witnessed substantial growth. This is due to the technological importance of such materials as well as their interesting potential properties [1–3]. Materials comprised of carbon are of special interest, such as polymerized fullerine [4] and highly oriented pyrolytic graphite (HOPG) [5]. From the purely scientific standpoint, ferromagnetism in systems containing exclusively p- and s-electrons, such as materials comprised of the light elements (C, H, N, O, S) is a topic that challenges current assumptions that such ferromagnetism is only possible in materials containing metallic $3d$ and $4f$ elements. Poor reproducibility, insufficient characterization of the impurity concentration and the relatively low quality of graphite samples in the past, however, may have contributed to the conclusion that for magnetic polymers most of the claimed high-temperature ferromagnetism in magnetic ion-free compounds in the past ended up being of extrinsic origin [6]. Despite the controversy, there has been some very interesting research done recently into the possible magnetic properties of HOPG. In particular, there have been a variety of experiments conducted where ferromagnetic-like signals in HOPG that were not due to the presence of impurities were detected [5,7]. Though the perfect graphene layer does not show ferromagnetic instabilities [8], the electronic structure of the graphite π-system differs considerably for carbons within the graphite sheet as opposed to those at its edges [9,10]. Edge states may, therefore, lead to an increase in the density of states at the Fermi level, and if such edge states occur at a high enough density, a ferromagnetic spin polarization may result.

Characterization techniques complementing those utilized so far can bring the possibility of metal-free carbon ferromagnets further toward fruition. One such technique is the measurement of the magnetostriction of the sample in mention. Magnetostriction occurs in ferromagnetic materials and results in a change in the dimensions of the specimen when a magnetic field is applied, which is usually on the order of a few parts per million (ppm) [11–13]. We have recently developed a novel method to measure magnetostriction of specimens using Atomic Force Microscopy (AFM) and an electromagnet, positioned around the sample during measurement [14]. The method allows the direct observation of magnetically induced unidirectional topographic changes in the samples' dimensions in a profoundly illustrative manner. Strains as small as 5×10^{-8} have been observed on metallic wires, and the topographic data clearly shows the mechanism of magnetostriction in the nanometer regime. In this study, we perform similar

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measurements on HOPG surfaces using Scanning Tunneling Microscopy (STM), (STM provides a much improved resolution compared to AFM), and the same experimental setup as in our AFM observations. If HOPG is indeed ferromagnetic, magnetic fields must induce a strain that is detectable at nanometer or sub-nanometer scales.

The experiment was conducted with a Dimension 3100 Scanning Probe Microscope (SPM), and a Nanoscope IV Controller. Scanning tunnelling microscopy was performed in the air (ex situ) using PtIr probes. The magnetic field was applied parallel to the sample plane with a laboratory-designed and constructed electromagnet with a 12 mm gap. Field strengths were up to 480 Oe, measured with a DTM-133 Digital Teslameter at the sample plane, while the programmable DC power supply current could apply the magnetic field for the time interval required to within <0.1 Oe. Specimens were cut from a $12\times12\times2$ mm sample of ultra-high purity (99.999%) commercial monochromator-grade HOPG, from Advanced Ceramics. Dimensions of specimens were 6 mm × 2 mm, and glue was applied to 2 mm along one end, leaving a 4 mm × 2 mm portion free. Scanning was preformed always along the direction of the long axis (x-direction), where the magnetoelastic shift was observed. The mounting of the sample was not arbitrary. Magnetic field induced strain (MFIS) studies on organic specimens are, to our knowledge, absent from the literature. Since the only comparable reference system for this type of measurement at this time is that of ferromagnetic wires, we have duplicated the conditions of measurement for reference purposes. Once the magnetic response of HOPG is confirmed, we seek to observe how that response is similar or not to that of ferromagnetic wires.

The magnetostriction observations with the STM were done on *step sites* because of their abundance on the HOPG surface, because they represent high-contrast topographic boundaries, ideal for the precise observation of magnetoelastic displacements at the lower end of the nanometer scale. In addition, comparisons of MFIS values at two different defect sites along the long axis of the sample can confirm if magnetization of graphite produces strains dependent on the tip's position with respect to the mounted edge of the sample. In other words, is the strain a local event or the sum of local strains from the mounted edge to the placement of observation (STM tip position)? If the strain is independent of position then the system does not change its total shape, but deforms only locally. This in turn would imply that volume conservation during MFIS on pyrolytic graphite does not occur. It would also strengthen the view that strains are locally caused by defect structures.

First, we perform experiments with Ni that allow us to illustrate how the method works with a well known ferromagnetic material. In wires such as Ni, the strain effect is very straightforward. The top two AFM images of Figure 1 depict 600 nm scans of the Ni wire surface. The wire was 8 mm long, with 2 mm mounted with cyanoacrylic glue on the sample holder, leaving 6 mm Ni wire resting freely on the sample holder surface. The left-hand image shows a feature of the Ni surface without a magnetic field applied. In the top right hand image of Figure 1, the scan shows where the 250 Oe field was applied (i.e. the white arrow pointing *left*). The whole scan field shifts to the left with a distinct horizontal line indicating the displacement. As long as the magnetic field remains constant, scanning continues from the new position without degradation in the image. When the field is turned off the effect exhibits precise reversibility. In other words, the scan field shifts back to the exact position before the magnetic field was applied. In the corresponding image of Figure 1 (top right), this is shown with the white arrow pointing to the *right*. Thereafter, scanning again continues in a stable manner.

Measurements were performed to prove that the effect is not an artifact of the microscope, or due to mechanical vibration of the sample and/or microscope system, by using samples with no observable magnetic response. That is to say, we used a reference material that we know does not show magnetostriction in our resolution scale. The results are shown in the lower left-hand image of Figure 1, which shows a 200 nm scan of a Pt wire surface, scanned at the tip of the 12 mm wire. Two millimetres at the other end of the wire were mounted with cyanoacrylic glue on the specimen holder, leaving 10 mm free to expand and/or contract under the influence of the applied magnetic field. The image was taken with a high-contrast colour scale to make even the smallest displacement detectable. When a 250 Oe field was applied, no motion was detected. Although the smallest measurable displacement with the AFM was around 0.5 nm [14], displacements <0.5 nm can be recognized by the disturbance in the scan line(s) where the shift occurs.

Sample preparation for the case of HOPG has been done in the same manner as with metallic wires. Measurements were taken with the field direction parallel to the long axis of the sample. Figure 2 shows sample images of a step site without and with the application of a 480 Oe magnetic field. The top left image shows a 25 nm scan of the area (with three step features) where the field was applied. The aforementioned image is zoom of a the area depicted in the top left insert showing a 200 nm scan of the same step feature. This particular scan was taken at 2 mm from the glued portion of the specimen. The step feature resolved at 25 nm is depicted at the top right of Figure 2 in a three-dimensional rendering for greater clarity. The same feature, although not the same exact position (see diagram at lower left portion of Figure 2 with corresponding caption), is shown at the lower portion of Figure 2. The image is, furthermore, rendered in three dimensions with the magnetic field applied several times during the scan. We can clearly see the differences between the figures with and that without the applied field. The magnetic field was applied several times during the scan at regular time intervals, and as can be seen in Figure 2 (bottom) the shift is reproducible through the whole topographic scan range. In the latter image, point A indicates the step position before field application, while point B shows the shifted topography. Along the same line, the white arrow indicates the direction of the displacement. In

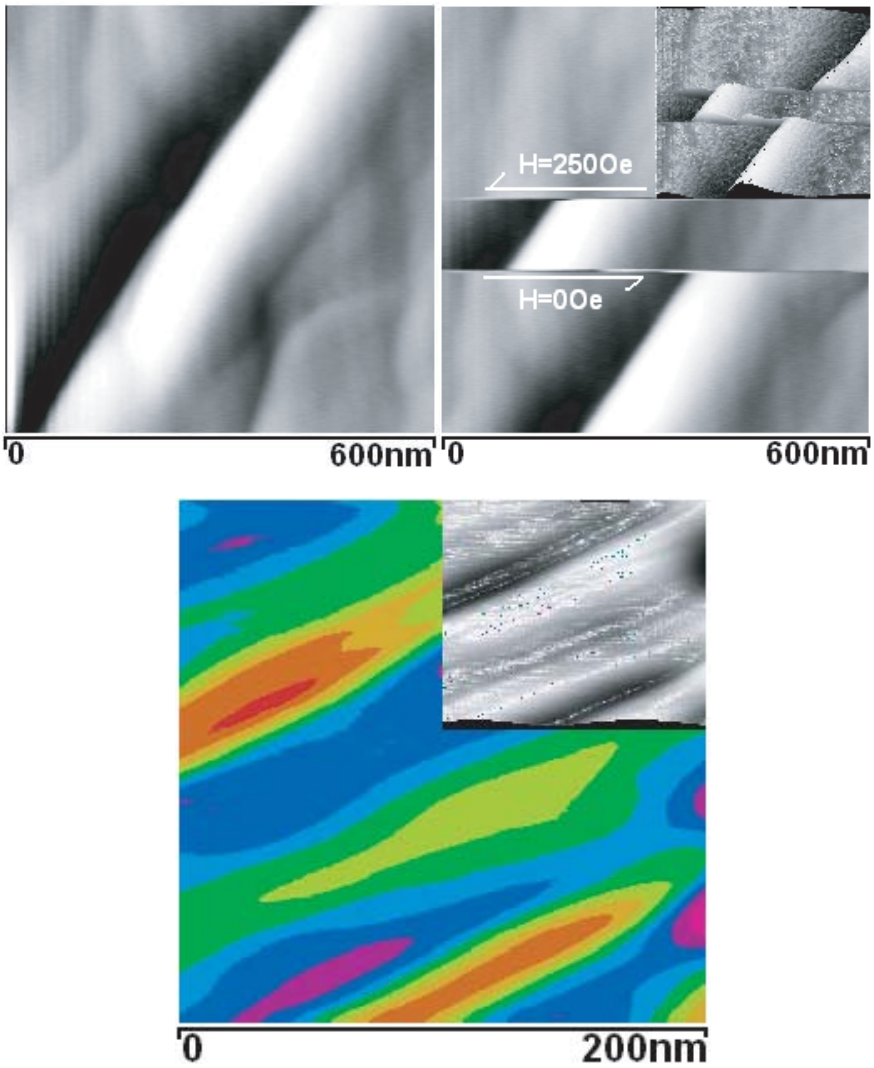

Fig. 1. Top: Two 600 nm scans of the Ni wire surface. Specimen dimensions and mounting details are given in the text. The left-hand image shows the Ni surface without magnetic field application. In the top right hand image of Figure 1, the scan shows where the 250 Oe field was applied and subsequently removed. The insert at the upper right-hand corner shows the same scan in a three-dimensional rendering. Bottom: A 200 nm image of a Pt wire surface (also described in text). The image was taken with a high-contrast colour scale for clarity. In the scan there are no recognizable displacements, despite the repetitive magnetic field applications (H = 250 Oe). This is reaffirmed in the 3D rendering of the image inserted at the top right-hand corner of the Pt scan.

the same manner as in ferromagnetic wires, when the field is turned off, the topography returns to the same position (point A), indicated by the second white arrow. The average displacement was measured at about 3 nm with a max 20% deviation from this value for all the measurements taken at this particular site. The magnetostriction values observed are approximately a third and a hundredth of those of permalloy and Ni respectively, i.e. very weak, but detectable.

Figure 3 shows a plot of the measured displacement Δl (in nanometers) vs. the strength of the applied field H (in Oe), for a magnetic field direction parallel to the long dimension of the graphite specimen. The plot shows that magnetostriction saturation is reached around 100 Oe, while the magnetoelastic response with increasing field strength has a similar pattern to permalloy $Ni_{79}Fe_{21}$ and Ni wires, (i.e., rapidly decreasing to a saturation value of about 1.75 nm). Overall, however, scans were taken at various positions within a 1 mm^2 area (around a point 4 mm from the glue boundary) on the sample, and the results varied from about 1.5 to about 3 nm for the same field strength of 480 Oe. From the two sets of measurements taken (Figs. 2 and 3) we deduce that the strain values do not increase the farther we are from the mounted edge, nor are the strain values decreased closer to the mounted edge. This behavior is contrary to the MFIS responses of ferromagnetic wires, and has been confirmed with repeated measurements around the sample, which are not shown here. The results imply that *the magnetoelastic strains do not conserve volume as happens in many materials and in*

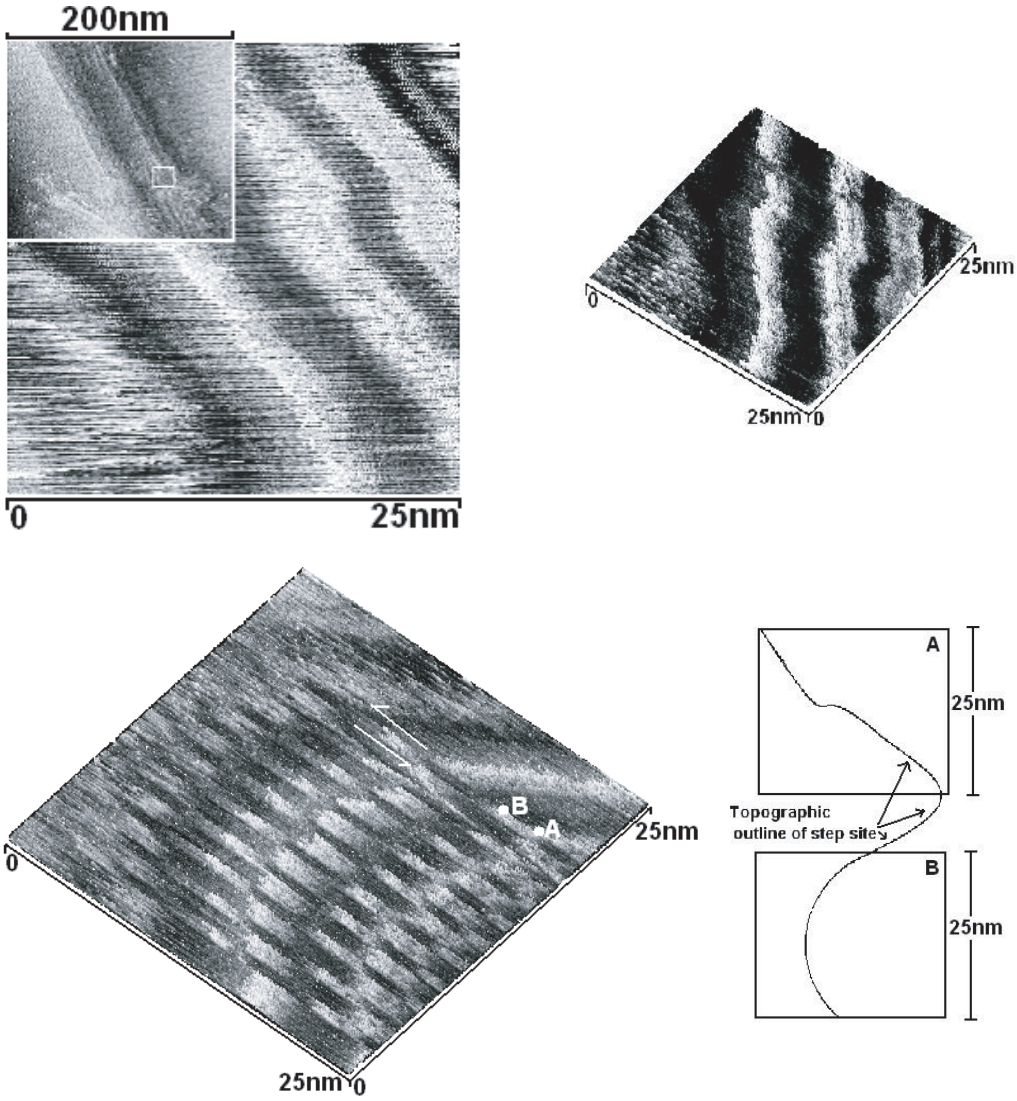

Fig. 2. Top: shows sample images of a step site without and with the application of a 480 Oe magnetic field. The top left image shows a 25 nm scan of the area where the field was applied. The image is zoom of a the area depicted in the top left insert showing a 200 nm scan of the same step feature. The step feature resolved at 25 nm is depicted at the top right of Figure 2 in a three-dimensional rendering for greater clarity. Bottom left: A 25 nm scan of the same feature with a 480 Oe magnetic field applied several times during the scan. Bottom right: diagram explaining the change in step orientation that shows the approximate locations of the scan areas (indicated as squares A and B). "A" represents the scan area for the area scanned without the applied field and "B" the area where the field was applied (the tip was withdrawn and approached again, which accounts for the slight shift in the site area scanned). The zig zag shape of the step itself (which seems straight in the 200 nm scan shown at the insert) has, therefore, resulted in an apparent change in the step orientation, which is not due to drift or artifacts.

particular should happen with materials that show ferromagnetism. On the other hand, the finding that the strain reaches saturation at a given field strength, after a rapid increase in the strain value with increasing field up to that saturation value, is comparable to similar effects observed on ferromagnetic wires.

It is well known that the perfect graphene planes do not hold magnetic moments. They are, in fact diamagnetic, exhibiting 10^{-9} or less magnetostriction, which is beyond the reach of our precision. The data and the magnetism presented here can be understood in terms of the defects of the HOPG. Indeed, there is a very high occurrence of defects observable under the optical microscope. In particular, steps on the HOPG surface are fractures in the graphene layer where the triangular symmetry is broken, resulting in a sp^2-sp^3 hybridization mix. This, in turn, results in dangling bonds that generate magnetic moments that can be exchange coupled, either by direct coupling, since the atoms are very near together or by indirectly mediated KKRY interactions. The situation then is that patches of material become ferromagnetic or paramagnetic. Magnetization measurements [5,7] show that only

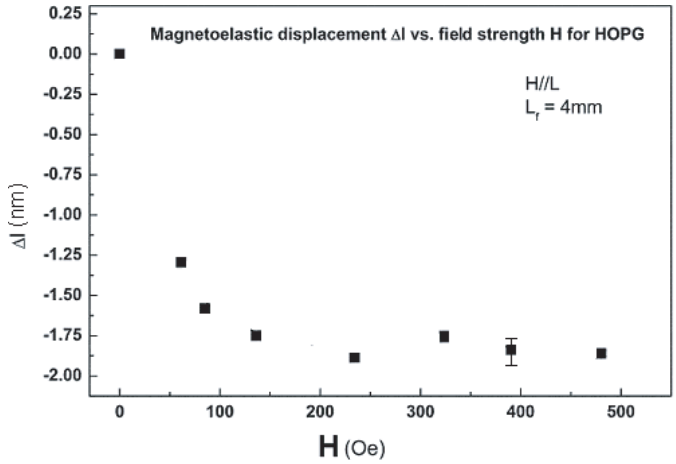

Fig. 3. Top: plot of the measured displacement Δl (in nanometers) vs. the strength of the applied field H (in Oe), for an HOPG sample where the magnetic field direction was parallel to the long dimension of the specimen. The site measured was 4 mm from the glued portion of the sample (measured at the glue boundary). Saturation is reached around 100 Oe in this case.

10^{-3}–10^{-4} of the atoms in the sample behave magnetically, showing very weak magnetization and a very high critical temperature, (greater than 1000 K). The magnetic patches are high temperature ferromagnets but only a relatively small number of patches and atoms of the total HOPG surface are truly magnetic. The density and coupling of these broken bonds, furthermore, varies from site to site. It is, therefore, expected that the magnetization, and hence the magnetostriction of HOPG with defects also varies from site to site on the sample, indicating a non-uniform effect, as well as a wide variation of the critical temperature varying from one patch to another. This is in strong contrast to the homogeneous ferromagnetic metal wires where the strain is applied globally throughout the specimen and the displacement is a function of the wire's length. The pattern is clearly observed in our experiments, as well, since our probe is a local one and the displacements vary due to the magnetic heterogeneity of the sample.

It should be noted that the results presented here may be possibly extrapolated onto organic compounds where defects cause breaking of bonds, resulting in the creation of localized magnetic moments, just like in the mechanism described for graphene planes that can be coupled by a direct or indirect exchange mechanism. In addition, the mechanism described here is not unique for defects in graphite. Namely, Cu clusters created from a sol-gel solution [15] have also exhibited ferromagnetism. The fact that non-ferromagnetic materials can, under certain conditions, exhibit magnetic properties is exemplified by considering that nanocontacts made of (ferromagnetic) Ni have shown up to 300% magnetoresitance [16], while nanocontacts of Cu wires also show large values of magnetoresitance, up to 70% [17]. This implies that small Cu contacts, perhaps through reactions with oxygen, become magnetic. The above is an example how phenomena (such as magnetostriction) cannot always be macroscopically generalized from nano-scale information, and that when working in this region what happens in the large part of the bulk material may not be very relevant for the characterization of new desired properties. As we mentioned above, organic compounds combining with local probes, as the STM described here, can open many doorways of exploration and technological development through their examination of local behavior at the nanoscale.

In conclusion, the experiment was dedicated to the measurement of the magnetostriction of ultra-pure (99.999%) HOPG under applied magnetic fields directed parallel to the long axis of the sample, using in-air STM with 0.2 nm resolution. We have performed tests comparing the effect with results on magnetic and nonmagnetic metallic wires to confirm that the displacement is not due to mechanical effects, inadequate clamping or the motion of the sample. The magnetoelastic displacements observed in the scans occur in the same fashion as with ferromagnetic wires. The fact that displacements are taking place under an applied field clearly implies that the sample has a nonzero magnetization. We interpret the data in terms of defects occurring on the graphite surface. These defects break the sp^2 triangular symmetry, giving magnetic moments that can be exchange coupled. Other evidence for attributing the magnetostrictive behaviour of HOPG to a local mechanism (defects) is the characteristic that the straining mechanism of HOPG does not conserve volume, as the strain values differ from place to place in the sample without dependence on position relative to the sample's mounted edge. Defects as intrinsic sources of magnetic behaviour may open new avenues for the study of the magnetic properties of organic compounds.

This work has been supported by the Spanish DGICyT.

References

1. *Science and Technology of Nanostructures Materials*, edited by G.C. Hadjipanayis, G.A. Prinz (Plenum, New York, 1991)
2. P. Grünberg, S. Dimocritov, A. Fuss, R. Schreiber, J.A. Wolf, S.T. Purcell, J. Magn. Magn. Mater. **104-107**, 1734 (1992); B. Heinrich, Z. Celinski, J.F. Cochran, W.B. Muir, J. Rudd, Q.M. Zhong, A.S. Arrot, K. Myrtle, J. Kirschner, Phys. Rev. Lett. **64**, 674 (1990)
3. Qi Pan, R.D. James, J. Appl. Phys. **87**, 4702 (2000)
4. T. Makarova, B. Sundqvist, R. Höhne, P. Esquinazi, Y. Kopelevich, P. Scharff, V.A. Davydov, L.S. Kashevarova, A.V. Rakhmanina, Nature **413**, 716 (2001)
5. P. Esquinazi, A. Setzer, R. Höhne, C. Semmelhack, Y. Kopelevich, D. Spemman, T. Butz, B. Kohlstrunk, M. Lösche, Phys. Rev. B **66**, 24429 (2002)
6. J.S. Miller, Adv. Materials **4**, 298 (1992); J.S. Miller, Adv. Materials **4**, 435 (1992)
7. P. Esquinazi, R. Höhne, K.-H. Han, A. Setzer, D. Spemann, T. Butz, Carbon **42**, 1213 (2004)

8. J. Gonzalez, F. Guinea, M. Vozmediano, Phys. Rev. B **63**, 134421 (2001)
9. K. Nakada, M. Fujita, K. Wakabayashi, K. Kusakabe, Czechoslovak J. Phys. **96**, 2429 (1996)
10. K. Kusakabe, K. Wakabayashi, M. Igami, K. Nakada, M. Fujita, Molecular Crystals and Liquid Crystals Science and Technology Section A- Molecular Crystals and Liquid Crystals **305**, 445 (1997)
11. S. Chikazumi, *Physics of Ferromagnetism* (Oxford University Press, 1999)
12. E. Du Tremolet de Lacheisserie, *Magnetostriction* (CRC Press, Boca Raton, FL. USA, 1993)
13. A. del Moral, *Magnetostriction: Basic Principles and Materials* (IOP Publications, Bristol, 2003)
14. A.C. Papageorgopoulos, H. Wang, C. Guerrero, N. Garcia, J. Magn. Magn. Mater. **268**, 198 (2004)
15. N. Garcia, P. Crespo, A. Hernando, C. Bovier, J. Serughetti, E. Duval, Phys. Rev. B **47**, 570 (1993)
16. N. García, M. Muñoz, Y.-W. Zhao, Phys. Rev. Lett. **82**, 2923 (1999)
17. D.M. Gillingham, C. Muller, J.A.C. Bland, J. Phys: Condens. Matter **15**, L291 (2003)