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Reply to the Commentary on "Graphite and its hidden superconductivity"

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I appreciate very much the time our colleague Forgan took to read my manuscript and write his comment on the exposed Physics and interpretation of experimental results. It is surely not easy to find somebody that provides such a detailed report. There is no doubt that the subject of the manuscript remains highly controversial and most of the community does not simply believe in the existence of high or low temperature superconductivity in non-intercalated graphite. After working for nearly 13 years with this material, I had the opportunity to deal with all kind of transport, magnetic and band structure data and revise part of the interesting history of this material. My personal experience related to the defect-induced magnetic order in graphite discovered more than 10 years ago (a phenomenon that one finds nowadays in a large number of compounds) and the (over)skepticism the whole community had at that time showed me (once more) that in natural sciences one should not always accept the opinion of the majority.

Before replying to Forgan's comment, I would like to tell you a short story. Six years ago and after independent colleagues proved using different experimental methods that one can have magnetic order in graphite due to defects or non-magnetic ad-atoms like hydrogen, a speculative explanation on the magnetic data published in the year 2000 [1] (59), I decided that it was time to check whether the claim of superconductivity in graphite at extraordinarily high temperature could be real or not. The first unexpected hint came by chance, when I took one HOPG sample from Advanced Ceramics company and asked the responsible of a dual beam microscope to take a look at the interior with the low-energy transmission electron microscope option that machine had. What we saw at that time were well defined quasi two-dimensional interfaces inside the samples. I had no idea about the origin of those interfaces and whether they could influence the transport properties or not. Years later I found that these interfaces had been recognized before [2] (8) but nobody apparently payed attention on their possible influence on measurable properties. It was the systematic change in the absolute value of the resistivity as well as in its temperature dependence with the thickness of that kind of HOPG samples [3,4] (7,10) that helped me clarify some inconsistencies found in the graphite literature and provided us with a hint of where superconductivity, if at all, could be hidden.

In the reply, I will try to describe and emphasize important details of the experimental evidence that were not, apparently, taken into account or simply just overseen in Forgan's comment. I reply to Forgan's comment in the order of appearance, copying at the beginning of each issue part of the corresponding paragraph to help the reader. With

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the same purpose, I have included citations at the end of the reply. In case the citation was already in the manuscript I wrote it with its corresponding number in parentheses, at least the first time I cite it.

(1) "This bulk property and many others, such as the de Haas van Alphen effect in large samples [1] have been understood in general terms [2] as a consequence of a semi-metallic band-structure [3] since 1960."

Reply: I believe the graphite story is an example that shows that sometimes a "democratic" experimental fact and its possible "democratic interpretation" do not assure correctness. In this case, such a "democratic consent" can have a rather negative influence in the development of science, more dangerous than a wrong interpretation or an experiment carried out incorrectly. The cited de Haas - van Alphen as well as the Schubnikov - de Haas (SdH) oscillations in the magnetoresistance of graphite were taken as evidence for the existence of a finite Fermi surface and understood in terms of an anisotropic 3D band structure with coupling constants between C-atoms obtained from fitting experimental data. Those data, e.g., those SdH oscillations, were assumed to represent the ideal defect-free graphite structure. However, systematically done measurements on thin graphite flakes [5] (11), as well as the influence of irradiation in the SdH oscillations [6] (9), already indicate that the oscillations found in some bulk samples do not correspond to ideal graphite. Graphite samples, independently of their size but without interfaces, do not show any oscillations in the magnetoresistance (even in its derivative) at low temperatures. For such samples, these SdH oscillations can be observed after producing defects (i.e., after increasing the carrier density in some regions of the sample) [6] or by applying a large enough electric field [7].

(2) "I now turn to the various sections of the paper. In section II, there is an account of strong magnetoresistance effects. Similar effects have also been observed in bismuth [4] and have a very interesting explanation [4] in terms of the semi-metallic properties of graphite and bismuth, so there is no need to propose a superconducting explanation for this."

Reply: One can start arguing against the explanation of the (magnetic field driven) Metal-Insulator-Transition (MIT) proposed in that paper [8] (26) in Forgan's report taking into account the large (about 6) number of free parameters and the inconsistency of the proposed explanation with the nearly linear field dependence of the resistance observed at low temperatures in ordered graphite. On the other hand, one could argue that those critical points are of rather technical nature that do not touch the main idea of the proposed explanation. However, there is a more serious problem with the "interesting explanation" based on the assumed electronic band structure of Bernal graphite: As I wrote in my review, the MIT is not observed when the graphite sample has no interfaces. That is to say, the "democratically observed" metallic-like temperature dependence of graphite samples is simply not intrinsic of ideal graphite [3, 4, 9] (7,10,12). Therefore, the explanation used in [8] to understand apparent "intrinsic properties" of Bernal ideal graphite is actually not applicable. The MIT as well as the metallic-like temperature dependence of graphite samples is related to the existence of interfaces, or other lattice defects, and this matches the forthcoming explanations of other effects in the review. If one does not realize or accept this fact discussed at the beginning of the review, one loses an important part of evidence.

Regarding the MIT found also in bismuth in that paper [8]: it is important to remark that in that work [8], no information about the internal structure of the measured Bi sample was given and whether interfaces were there or not. This is important because, as graphite, interfaces in Bi samples can have superconducting properties at temperatures even above 10 K [10–14] (-,-,90,-,91), although pure Bi bulk is not a superconductor. This interface effect in both semimetals seems to be more than a simple coincidence.

(3) "In section III, a tiny hysteresis in magnetoresistance is described. Two comments are relevant here: the author notes that the sign of the hysteresis is opposite to that expected for a superconductor and limits himself to stating that the data provide "striking hints that granular superconductivity is at work in some regions of these samples". This is hardly definitive proof."

Reply: Certainly, a definitive proof for the existence of granular superconductivity only through an anomalous magnetoresistance hysteresis loop is not. However, if we put all the pieces of the puzzle together, the proposed interpretation does not appear like a simple coincidence. The evidence of an anomalous hysteresis in the magnetoresistance measured in graphite flakes and its enhancement with constrictions leave not so many possibilities of interpretation. Note that the hysteresis appears in the temperature region where the resistance shows a metallic-like temperature dependence. Coincidentally, it is in this temperature region where we observe the field driven MIT. This experiment can be easily reproduced in all graphite flakes that show such a maximum in the resistance vs. temperature, if one has a measurement system with a 10^{-5} relative error in the measurement of the resistance and good temperature stability. A hysteresis in the magnetoresistance is evidence for magnetic entities that remain pinned or for example, magnetic anisotropy observed in ferromagnets. Typical ferromagnetic hysteresis loops in the magnetoresistance have been observed in graphite flakes [15] (46) as well as in bulk graphite after proton irradiation [16] (22). These facts do not speak for an origin of the anomalous hysteresis observed in [17, 18] (38,42) in terms of ferromagnetism. Similar anomalous hysteresis in the magnetoresistance were observed in granular superconductors [19–21] (39,40,41) and explained in terms of Josephson-coupled superconducting grains [19].

(4) " Section IV is headed "Direct evidence for Josephson behaviour". This quotes data ... and the fact that magnetic fields could increase, decrease or have no effect on the voltages observed, also cast great doubt on the Josephson interpretation."

Reply: Indeed, the currents used here were small simply because high currents shift the observed transitions systematically to lower temperatures [22] (45) and this fact should be taken as evidence in the direction of superconductivity, actually. It is also correct that no measurement of a strictly zero resistance state has been shown in [22] just because in such measurements and due to the finite sensitivity one cannot measure zero resistance, this is actually obvious. However, the estimate of the minimum measured resistance given in the comment is not quite correct. Upon sample and at low enough temperature, the voltage noise around zero voltage measured at 1 μA is ±5 nV, or ±5 mΩ for samples with a resistance at high temperature of the order of 100 Ω. It should be clear that upon Josephson coupling and the characteristics of the superconducting patches at the interfaces, thermal fluctuations may affect the zero average value. To verify that a zero resistance state is possible one needs to show that currents remain for a sufficiently large time by measuring, for example, the magnetic moment of a ring where a superconducting current flows, as it has been done recently using graphite flakes embedded in alkanes [23] (94). Hopefully, new experiments in this direction will clarify the situation.

Such sharp transitions in the measured voltage vs. temperature do not appear to be simply possible from wrong contacts or anisotropic current distributions. In particular, when the whole $I-V$ behavior is compatible with the one expected from Josephson-coupled regions within the interfaces. That an anisotropic current distribution can exist in the graphite lamellae is especially true in the case the contacts are localized at the corners of the lamellae, i.e., in a Van de Pauw configuration, as it has been clearly stated in the review and in [22] (45). In this case, the simple model used to fit the $I-V$ curves takes explicitly into account the anisotropic arrangement. The negative resistance behaviour was observed only in that case but not for the usual linear electrode arrangement [22], as expected. It seems to be more than a simple coincidence that the same equation with only the critical Josephson current as free parameter is sufficient to interpret the $I-V$ curves measured in very different configurations. Finally, one can convince oneself about the relationship between interfaces and the observed transitions simply by measuring a lamella without interfaces but with the same anisotropy of graphite and with similar contacts.

Forgan correctly pointed out the striking magnetic field effects on the $I-V$ and $V(T)$ at constant current. The effect of a magnetic field on the $I-V$ characteristics is as expected only for large (thick) samples and in the same field region (a few kOe) where the field suppresses the metallic-like behaviour, i.e., the MIT. At fields higher than several Tesla, one observes a reentrance in the $I-V$ curves at low currents, i.e., the resistance starts to decrease with field [22]. This effect in the resistance has already been reported in 2003 [24] (48) and its interpretation remains open. Again, this effect is related to the existence of the interfaces and it does not appear to be a simple artefact of anisotropic current distribution or contact problems.

(5) "In response to [6], a colleague repeated

their measurements as an undergraduate project [7]. Their clear conclusion was that if the correct diamagnetic background slope (that obtained at large fields) is subtracted, then the hysteresis corresponds to a tiny ferromagnetic component. However, if a slightly different background is chosen, the hysteresis loops look somewhat like the response of a granular superconductor."

Reply: The arbitrariness of the diamagnetic background subtraction has been taken into account in the description of the results in [25, 26] (58,29) and, indeed, the appearance of the hysteresis can be changed subtracting different backgrounds. Although I do not know the results from the undergraduate project, I would like to emphasize a few details and the difference of the results in [25, 26] with those one expects from a simple ferromagnetic response.

There are two methods one can use without the need of any background subtraction to obtain the true magnetic response of the sample. The first one is to measure the remanent magnetic moment (i.e., at zero field) after cycling the sample to a maximum field strength, see Fig. 3 in [25] or Fig. 10 in [26]. In general, for a ferromagnetic sample and from the measurements of the minor loops at low fields one obtains a remanence M_r that increases following the Rayleigh law, i.e., $M_r \propto H^n_{\mathrm{max}}$, with H_{max} the maximum applied field strength and $n \sim 1 \ldots 1.5$, see [27]. The measurements done in graphite powders and HOPG samples with interfaces do show, however, a within error nearly zero remanence up to a temperature dependent critical field $h^J_{c1}(T)$ [25, 26].

One could still argue that a critical field may also appear through magnetic domain pinning or magnetic anisotropy response in any ferromagnetic inclusions that exist in the graphite powder. In this case, one can use a second method to measure the difference between field cooled (FC) and zero-field cooled (ZFC) temperature dependent magnetic moment $m(T)$. A finite positive difference between $m_{FC} - m_{ZFC}$ can be taken as due to pinning of magnetic entities, superconducting vortices or magnetic domains in ferromagnets, for example. Let us assume that the hysteresis seen in [25] is due to a ferromagnetic response with a saturation field $H_s \sim 1$ kOe. In this case, the difference $m_{FC} - m_{ZFC}$ would increase with field reaching a maximum at a field $H \lesssim H_s$, but then it should decrease to zero sharply at higher fields. This experiment can be easily carried out using, for example, a real ferromagnet as micro or nano particles of magnetite, which upon size and sample preparation can show saturation fields of this order. However, this is not the behaviour reported in [25] (see Fig. 6 in the Supporting Information of that article). This difference, after reaching a minimum or plateau at ~ 1 kOe, increases again steadily up to the maximum applied field of 7 T. It seems difficult to find a ferromagnetic material that shows a hysteresis in field that does not saturate but increases steadily with field of the order or higher than 7 T. We have repeated this kind of experiments in different graphite powders from the same source as used in [25] and this behaviour is well reproducible and it does not appear compatible with a ferromagnetic response. Measurements with ferromagnetic small particles embedded in disordered carbon show clearly different behavior from that reported in [25, 26], as expected.

Regarding Forgans's comment, and I quote, "There are many possible reasons (both real and due to experimental artifacts) why measurements on a sample taken on heating and cooling might disagree", one can test the SQUID system and convince oneself about its limits and sensitivity, using different samples, as HOPG samples without interfaces [26] or just amorphous carbon powder or ferromagnetic particles in a non magnetic matrix, etc., and check whether similar behavior for the $m_{FC} - m_{ZFC}$ is observed using exactly the same SQUID sequence. The results we obtain from all those samples provide us with the necessary confidence.

Let us assume now that the undergraduate students cited by Forgan measured indeed a hysteresis of ferromagnetic nature. If it is due to magnetic impurities, then this can be firstly proved through elemental analysis and the behaviour of the remanence and the difference $m_{FC} - m_{ZFC}$ must be different from the one of a granular superconductor. But, what if this ferromagnetic response is not due to magnetic impurities but it is due to graphite itself due to, for example, hydrogenation through the water treatment? Note that hydrogen may trigger magnetic order in graphite, as shown recently through measurements using three different experimental methods as XMCD [28], magnetization and the anisotropic magnetoresistance

[29] (56). The hysteresis curves of ferromagnetic graphite reported in those works as well as in several other independent reports show, however, saturation fields of the order of a few kOe, without any opening of the hysteresis at higher fields, and a small remanence in contrast to the nearly square hysteresis loops found in [25]. Thus, the usual ferromagnetic behaviour of graphite does not seem to be compatible with the reported observations in [25, 26].

Nevertheless, if the ferromagnetic response is due to the treatment the undergraduate students did to the graphite powder, and vanishes after pressing the powder (see Fig. 4(c) in [25]), that means that it may come from interfaces between grains or grain surface near region. In this case, it should be taken seriously, spending more time on its characterization. One should not take for granted that magnetic order in any graphite or carbon-based sample is due to impurities and not something intrinsic. There is enough evidence about defect-induced magnetism in graphite, due to vacancies as well as due to hydrogen (for a short review see [30] and refs. therein). It is even possible that some interfaces in graphite show magnetic order or even that both phenomena, superconductivity and magnetism, appear and a mixture of both signals is observed. I would like to cite one sentence written in the conclusion of the work in [31] (21) where the flat band at the interfaces between Bernal and rhombohedral graphite structures is proposed as the origin for the high temperature superconductivity: "In general, flat bands are susceptible to instabilities with respect to some other ordered states; for example, a magnetic state could also be possible." Evidently, if both phenomena occur at the interfaces or surface of graphite, the situation will get more interesting but difficult from the experimental point of view. Unless one can prove that the ferromagnetic hysteresis is due to impurities, one should not take this kind of evidence offhandedly.

(6) "We see in [6] that the hysteresis at 300 K is essentially the same as that at 5 K. We bear in mind that by assumption the superconductivity is confined to an atomic layer, and that the higher the Tc of a superconductor the shorter the coherence length. These two together ensure that thermal fluctuations (which are already very noticeable at T $\sim$ 100 K in cuprate materials) would be huge for any room temperature graphite superconductivity [9]. Thermal fluctuations would greatly reduce vortex pinning and magnetic irreversibility at room temperature, contrary to what is observed."

Reply: A possible answer to this comment might be that the superconductivity at graphite interfaces has not only a ten times larger critical temperature but also ten times larger activation energies as in cuprate materials. In fact, in [25, 26] not only a ten times larger critical Josephson fields (within the interpretation given in that paper), but also a larger pinning potential barrier than in cuprates have been estimated from the time relaxation measurements. In this case, the effect of thermal fluctuations should not affect substantially the sample response between 5 K and 300 K. It is rather premature to speculate based on usual *s*-wave (or *d*-wave) pairing equations. If it is true that the magnetic field makes this interface superconductivity robust then the equations used for conventional and cuprates superconductors will not be applicable.

Forgan speculates that the coherence length should be very small. Should it really be small? The usual estimate of the coherence length is based, in general, on the Ginzburg-Landau theory. Whether this is applicable in the case of superconductivity at graphite interfaces has to be seen. We note that a direct measurement of the coherence length is not possible. The use of the proximity effect or the change of the critical temperature with sample size are possible experimental methods one can take to estimate the coherence length, if the upper critical field cannot be measured. If one uses the variable sample size method on the interfaces found in graphite, one observes indeed a systematic decrease of the Josephson critical temperature measured at a fixed current, decreasing the width of the interfaces, i.e., the thickness of the TEM lamellae, behaviour measured recently in more than eight samples of the same HOPG batch (same interface density) [32]. This size dependence may provide also a hint to understand the differences in the behavior of large and small samples, i.e., for SQUID or transport measurements.

It is still too early to answer whether recent theories [31, 33] (21,93) can explain quantitatively the observed behaviour. Note that, according to the last theoretical work [33], the nature of granular superconductivity that may exist at interfaces is not as simple as in usual Josephson-coupled localised superconductor grains in a normal matrix. The size of the effective region that influences the observed Josephson behaviour may be larger than the intrinsic coherence length.

(7) "I cannot give an overriding simple explanation for all the different results reported in Esquinazi's paper, but neither can the author."

Reply: This is obviously true (for both) and I fully agree. Taking into account that the Physics of interfaces in graphite is a subject starting just now and that nobody has tried to make them systematically, it is natural that we need time. Taking the example of the cuprates and the time needed to clarify some, not all, open issues, nobody should be surprised that we do not have "an overriding simple (why simple?) explanation" at the moment.

[1] Y Kopelevich, P Esquinazi, J Torres, S Moehlecke, *Ferromagnetic- and superconducting-like behavior of graphite*, J. Low Temp. Phys. **119**, 691 (2000).

[2] M Inagaki, *New Carbons: Control of Structure and Functions*, Elsevier (2000).

[3] J Barzola-Quiquia, J L Yao, P Rödiger, K Schindler, P Esquinazi, *Sample size effects on the transport properties of mesoscopic graphite samples*, Phys. Status Solidi A **205**, 2924 (2008).

[4] N García, P Esquinazi, J Barzola-Quiquia, S Dusari, *Evidence for semiconducting behavior with a narrow band gap of Bernal graphite*, New J. Phys. **14**, 053015 (2012).

[5] Y Ohashi, K Yamamoto, T Kubo, *Shubnikov - de Haas effect of very thin graphite crystals*, In: Carbon'01, An International Conference on Carbon, Pag. 568, The American Carbon Society, Lexington, KY, United States, (2001).

[6] A Arndt, D Spoddig, P Esquinazi, J Barzola-Quiquia, S Dusari, T Butz, *Electric carrier concentration in graphite: Dependence of electrical resistivity and magnetoresistance on defect concentration*, Phys. Rev. B **80**, 195402 (2009).

[7] A Ballestar, J Barzola-Quiquia, S Dusari, P Esquinazi, R R da Silva, Y Kopelevich, *Electric field induced superconductivity in multigraphene*, arXiv:1202.3327 (2012).

[8] X Du, S W Tsai, D L Maslov, A F Hebard, *Metal-insulator-like behavior in semimetallic bismuth and graphite*, Phys. Rev. Lett. **94**, 166601 (2005).

[9] B C Camargo, Y Kopelevich, S B Hubbard, A Usher, W Böhlmann, P Esquinazi, *Effect of structural disorder on the quantum oscillations in graphite*, (unpublished). In this work the authors show that in certain HOPG samples (SPI) of high grade, the density of interfaces is much lower than in, for example, Advanced Ceramics HOPG ZYA samples. In this new HOPG samples basically no SdH oscillations are found and the temperature dependence of the resistance shows a semiconducting behavior with saturation a low temperatures. (2013).

[10] D V Gitsu, A F Grozav, V G Kistol, L I Leporda, F M Muntyanu, *Experimental observation of a superconducting phase with $T_c \simeq 8.5$ K in large-angle bismuth bicrystals*, JETP Lett. **55**, 403 (1992).

[11] F M Muntyanu, L I Leporda, *Restructuring of the energy spectrum in large angle bismuth bicrystals*, Phys. Solid State **37**, 298 (1995).

[12] F Muntyanua, A Gilewski, K Nenkov, J Warchulska, A Zaleski, *Experimental magnetization evidence for two superconducting phases in Bi bicrystals with large crystallite disorientation angle*, Phys. Rev. B **73**, 132507 (2006).

[13] F M Muntyanu, A Gilewski, K Nenkov, A J Zaleski, , V Chistol, *Fermi-surface rearrangement in Bi bicrystals with twisting superconducting crystallite interfaces*, Phys. Rev. B **76**, 014532 (2007).

[14] F Muntyanua, A Gilewski, K Nenkov, A Zaleski, V Chistol, *Superconducting crystallite interfaces with T_c up to 21 K in Bi and Bi-Sb bicrystals of inclination type*, Solid State Commun. **147**, 183 (2008).

[15] J Barzola-Quiquia, P Esquinazi, *Ferromagnetic- and superconducting-like behavior of the electrical resistance of an*

inhomogeneous graphite flake, J. Supercond. Nov. Magn. **23**, 451 (2010).

[16] P Esquinazi, J Barzola-Quiquia, D Spemann, M Rothermel, H Ohldag, N García, A Setzer, T Butz, *Magnetic order in graphite: Experimental evidence, intrinsic and extrinsic difficulties*, J. Magn. Magn. Mat. **322**, 1156 (2010).

[17] P Esquinazi, N García, J Barzola-Quiquia, P Rödiger, K Schindler, J L Yao, M Ziese, *Indications for intrinsic superconductivity in highly oriented pyrolytic graphite*, Phys. Rev. B **78**, 134516 (2008).

[18] S Dusari, J Barzola-Quiquia, P Esquinazi, *Superconducting behavior of interfaces in graphite: Transport measurements of microconstrictions*, J. Supercond. Nov. Magn. **24**, 401 (2011).

[19] L Ji, M S Rzchowski, N Anand, M Thinkam, *Magnetic-field-dependent surface resistance and two-level critical-state model for granular superconductors*, Phys. Rev. B **47**, 470 (1993).

[20] Y Kopelevich, C dos Santos, S Moehlecke, A Machado, *Current-induced superconductor-insulator transition in granular High-T_c Superconductors*, arXiv:0108311 (2001).

[21] I Felner, E Galstyan, B Lorenz, D Cao, Y S Wang, Y Y Xue, C W Chu, *Magnetoresistance hysteresis and critical current density in granular $RuSr_2Gd_{2-x}Ce_xCu_2O_{10-\delta}$*, Phys. Rev. B **67**, 134506 (2003).

[22] A Ballestar, J Barzola-Quiquia, T Scheike, P Esquinazi, *Evidence of Josephson-coupled superconducting regions at the interfaces of highly oriented pyrolytic graphite*, New J. Phys. **15**, 023024 (2013).

[23] Y Kawashima, *Possible room temperature superconductivity in conductors obtained by bringing alkanes into contact with a graphite surface*, AIP Advances **3**, 052132 (2013).

[24] Y Kopelevich, J H S Torres, R R da Silva, F Mrowka, H Kempa, P Esquinazi, *Reentrant metallic behavior of graphite in the quantum limit*, Phys. Rev. Lett. **90**, 156402 (2003).

[25] T Scheike, W Böhlmann, P Esquinazi, J Barzola-Quiquia, A Ballestar, A Setzer, *Can doping graphite trigger room temperature superconductivity? Evidence for granular high-temperature superconductivity in water-treated graphite powder*, Adv. Mater. **24**, 5826 (2012).

[26] T Scheike, P Esquinazi, A Setzer, W Böhlmann, *Granular superconductivity at room temperature in bulk highly oriented pyrolytic graphite samples*, Carbon **59**, 140 (2013).

[27] S Kobayashi, S Takahashi, T Shishido, Y Kamada, H Kikuchi, *Low-field magnetic characterization of ferromagnets using a minor-loop scaling law*, J. Appl. Phys. **107**, 023908 (2010).

[28] H Ohldag, P Esquinazi, E Arenholz, D Spemann, M Rothermel, A Setzer, T Butz, *The role of hydrogen in room-temperature ferromagnetism at graphite surfaces*, New J. Phys. **12**, 123012 (2010).

[29] J Barzola-Quiquia, W Böhlmann, P Esquinazi, A Schadewitz, A Ballestar, S Dusari, L Schultze-Nobre, B Kersting, *Enhancement of the ferromagnetic order of graphite after sulphuric acid treatment*, Appl. Phys. Lett. **98**, 192511 (2011).

[30] P Esquinazi, W Hergert, D Spemann, A Setzer, A Ernst, *Defect-induced magnetism in solids*, IEEE Transactions on Magnetics **49**, 4668 (2013).

[31] N B Kopnin, M Ijäs, A Harju, T T Heikkilä, *High-temperature surface superconductivity in rhombohedral graphite*, Phys. Rev. B **87**, 140503 (2013).

[32] A Ballestar, *Superconductivity at graphite interfaces*, Ph.D. Thesis, University of Leipzig, (unpublished).

[33] W A Muñoz, L Covaci, F Peeters, *Tight-binding description of intrinsic superconducting correlations in multilayer graphene*, Phys. Rev. B **87**, 134509 (2013).