Reply to "Comment on 'Imaging the atomic orbitals of carbon atomic chains with field-emission electron microscopy' "

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In our recent paper [I. M. Mikhailovskij, E. V. Sadanov, T. I. Mazilova, V. A. Ksenofontov, and O. A. Velicodnaja, Phys. Rev. B **80**, 165404 (2009)], we have presented evidence for field emission from individual orbitals of self-standing carbon chains, which can be used for real-space imaging of the end-atom orbitals with a field-emission electron microscope (FEEM). In this reply to the preceding Comment, we refer to the issues brought up there, which concern the viewpoint that the observed spontaneous mutual transformations of FEEM patterns have been attributed to the ligand-induced symmetry breaking by calling attention to the role of hydrogen atoms unavoidable in most nanostructured carbon materials.

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In our recent publication,[1] we have presented experimental evidence that ultrahigh-resolution field-emission electron microscopy (FEEM) can be used for direct imaging of orbitals of the end atoms in self-standing carbon atomic chains, which are anchored on a polyacrylonitrile (PAN)–derived carbon nanofiber. The overwhelming majority of carbon atoms gives rise to singlets and doublets of bright spots as it is expected for *s*- and *p*-like states. In the preceding comment,[2] the authors presented *ab initio* calculations within the framework of the density-functional theory, which were found to be in satisfactory agreement with the FEEM patterns.

We interpreted the FEEM patterns using the representation of linear carbon chains by expanding the wave function on the basis of a set of the Bessel functions of order n multiplied by the azimuthal phase factor $\exp(\pm in\varphi)$, where φ is the azimuthal angle around the chain axis.[1] The FEEM patterns corresponded to the squared eigenfunctions for the angular momentum or a linear combination of the first terms in the expansion. This approach is similar to the waveguide model of the FEEM images of multimolecular structures put forward by Komar and Komar.[3,4] The authors of the Comment remarked that $n=1$ does not imply the existence of angular nodes. We agree with this remark. However, the calculated maps of the squared wave function that correspond to the doublet FEEM patterns [see Figs. 4b and 4d of our original paper] were obtained, as in Ref. 3, using a real part of the azimuthal phase factor, i.e., $\sim\cos(n\varphi)$. Unfortunately, we did not specify that properly in the paper.

Another important question concerning the interpretation of the FEEM images of carbon atomic chains was raised in the Comment.[2] Manini and Onida showed that the type of the FEEM pattern of carbon atoms depends on the hybridization of the anchored end of the chain. They claimed that the electron current could induce the transformation of quantum states by exciting a jump of the atomic chain attaching point, such as those revealed under the beam in high-resolution electron microscopes. A symmetry-breaking perturbation in self-standing atomic chains is determined by changing the hybridization of the C atom at the anchored end of the chain from sp^2 to sp^3. The FEEM patterns in Ref. 1 did not show any noticeable shifts accompanying the symmetry breaking. That may be due to insufficient spatial resolution of the method. For the self-standing linear atomic chain anchored at the graphite parabolic tip, the determination accuracy of the location of the atomic chain attaching point depends on the radius of the supporting graphite parabolic tip lying typically within the micrometer or submicrometer range. In this range, the local FEEM resolution is correspondingly limited to several nanometers, so that, in contrast to the high-resolution electron microscopy and field ion microscopy techniques,[5–7] subnanometer scale jumps of the atomic chain attaching point cannot be observed directly. Nevertheless, a detailed analysis of the obtained FEEM micrographs of anchored atomic chains has revealed a few cases of jumps of image spots accompanied by mutual transformation of singlets and doublets.

The FEEM images shown in Fig. 1 illustrate a spontaneous doublet-to-singlet pattern transformation and a jump of image spots at a voltage of 340 V. The arrowheads point to the inconspicuous microspot on the FEEM screen, which serves as a reference mark. The arrow in Fig. 1(b) shows the direction and length (about 10 nm) of the image spot shift corresponding to the jump of the atomic chain attaching point. Hence, the proposed in Ref. 2 mechanism of the trans-

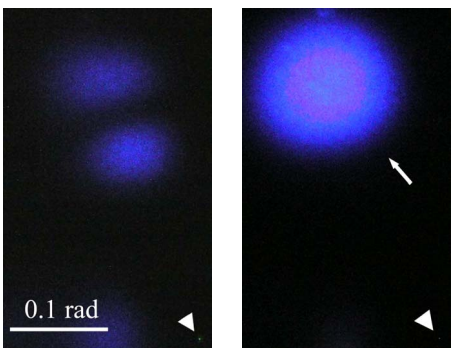

FIG. 1. (Color online) Field emission images of the end atom of carbon chain (a) before and (b) after spontaneous transformation of the FEEM pattern at constant voltage (340 V); arrow indicates the in-plane displacement of the image pattern.

formation of quantum states of the end atoms in carbon atomic chains seems to be consistent with our FEEM observations. The available data show that the transformation frequency is a slowly increasing function of the current. It increases by less than 2 orders of magnitude as the emission current rises from 1 pA to 100 nA. Hence, the observed jumps of the atomic chain attaching point are not associated with the direct momentum transfer from the electrons (knock-on mechanism[5]). The hybridization change of the C atom in graphitic nanocarbons from sp^2 to sp^3 can also be due to absorption of hydrogen atoms with the breaking of a π bond and production an additional σ bond.[8,9] The atom-by-atom analysis of a number of different nanocarbons by atom probes[10] has revealed a high concentration of hydrogen in these materials.

Mass spectrometric analyses of the PAN-derived carbon fibers performed with a tomographic three-dimensional atom probe (3DAP) (Ref. 11) have revealed a large amount of hydrogen ions H^+, which correspond to the dissociation of field-evaporated hydrocarbon ratio of hydrogen atoms to that of carbon equal to 0.083 ± 0.010.[12] 3DAP analyses were carried out in vacuum of 10^{-8} Pa at a temperature of 70 K. The hydrogen mass line in the spectrum (Fig. 2) can be unequivocally identified and reproduced. There are signals just above that of H^+ ions between 1.00 and 1.15 amu. In a time-of-flight spectrum, if a charged cluster ion dissociates within the acceleration region, then the lighter dissociated particle will appear in the low-energy tail of its mass line.[13] The low-energy tail of the mass peaks in Fig. 2 clearly indicates the occurrence of clusters near the specimen surface: $C_nH^{+m} \rightarrow C_n^{+m-1} + H^+$. The lack of H_2^+ mass line in the spectrum shown in Fig. 2 indicates that the H^+ ions arise essentially from field ionization of hydrogen atoms or dissociation of field-evaporated hydrocarbon clusters. Surface diffusion of hydrogen atoms on sp^2 bonded carbon nanostructures to the atomic chain attaching point might occur even at very low temperature thanks to quantum tunneling.[9,14] Additional heating microregions of carbon parabolic specimens near the chain-attaching point can be due to a field electron emission of high density (up to 10^{12} A m^{-2}). As a result of an increased mobility of hydrogen atoms, changing the hybridization of atoms in the attaching points from sp^2 to sp^3.

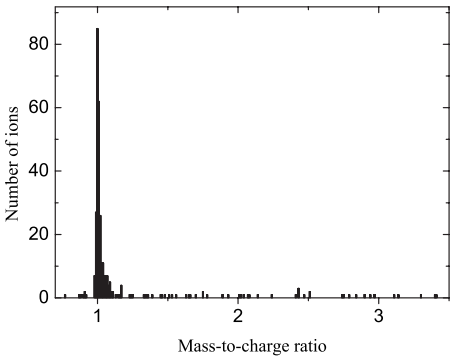

FIG. 2. Hydrogen atoms detected in a 3DAP mass spectrum of a PAN-derived carbon fiber.

In summary, motivated by the issues raised in the Comment, we present here the experimental data on spontaneous mutual transformations of FEEM patterns and mass spectrometric analyses of the carbon fibers performed with the tomographic atom probe. Our original paper, the Comment, and this Reply show that proposed mechanism of the transformation of the quantum states of the end atoms in carbon atomic chains by Manini and Onida seems to be consistent with the FEEM observations. A more detailed comparison of the experimental and theoretical results requires careful analysis of the limit on the resolution of FEEM images due to the wave nature of the electron beyond the frames of simple uncertainty arguments, including possible interference effects.[15]

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[1] I. M. Mikhailovskij, E. V. Sadanov, T. I. Mazilova, V. A. Ksenofontov, and O. A. Velicodnaja, Phys. Rev. B **80**, 165404 (2009).
[2] N. Manini and G. Onida, Phys. Rev. B **81**, 127401 (2010), the preceding Comment.
[3] A. P. Komar and A. A. Komar, Zh. Tekh. Fiz. **31**, 231 (1961) [Tech. Phys. **6**, 166 (1961)].
[4] A. P. Komar and A. A. Komar, Zh. Tekh. Fiz. **32**, 867 (1962) [Tech. Phys. **7**, 634 (1963)]; A. P. Komar and V. P. Savchenko, Fiz. Tverd. Tela (Leningrad) **7**, 759 (1965) [Sov. Phys. Solid State **7**, 606 (1965)].
[5] C. Jin, H. Lan, L. Peng, K. Suenaga, and S. Iijima, Phys. Rev. Lett. **102**, 205501 (2009).
[6] A. Chuvilin, J. C. Meyer, G. Algara-Siller, and U. Kaizer, New J. Phys. **11**, 083019 (2009).
[7] V. A. Ksenofontov, T. I. Mazilova, I. M. Mikhailovskij, E. V. Sadanov, O. A. Velicodnaja, and A. A. Mazilov, J. Phys.: Condens. Matter **19**, 466204 (2007).
[8] C. Srinivasan and R. Saraswathi, Curr. Sci. **97**, 302 (2009).
[9] C. P. Herrero and R. Ramírez, Phys. Rev. B **79**, 115429 (2009).
[10] O. Nishikawa, Y. Ohtani, K. Maeda, M. Watanabe, and K. Tanaka, J. Vac. Sci. Technol. B. **18**, 653 (2000).
[11] B. Radiguet, D. Blavette, N. Wanderka, J. Banhart, and K. L. Sahoo, Appl. Phys. Lett. **92**, 103126 (2008).
[12] N. Wanderka and I. M. Mikhailovskij, private communication.
[13] T. T. Tsong, *Atom-Probe Field Ion Microscopy* (Cambridge University Press, Cambridge, England, 1990).
[14] S. Cazaux and A. G. G. M. Tielens, Astrophys. J. **575**, L29 (2002).
[15] G. L. Martin and P. R. Schwoebel, Surf. Sci. **601**, 1521 (2007).