Interplay between magnetism and structure in atomic-size Pd contacts: *Ab initio* studies

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We present *ab initio* study of the interplay between atomic structure and magnetic properties in palladium atomic-size contacts suspended between palladium electrodes. This study was motivated by recent controversy between Delin *et al.* [Phys. Rev. Lett. **96**, 079702 (2006)] and Alexandre *et al.* [Phys. Rev. Lett. **96**, 079701 (2006)] about possible onset of magnetism in palladium (Pd) contacts. Here, we elucidate the effect of atomic arrangement and structure relaxations revealed in contracted and elongated Pd contacts on their magnetic properties. Planelike and pyramidlike geometries for electrodes are studied. We demonstrate that palladium contacts exhibit magnetic properties distributed inhomogeneously within the contact for a wide range of distances between separated electrodes.

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Magnetic phenomena in metallic atomic-size nanocontacts (NC's) and nanowires (NW's) are one of the most challenging field of basic research and technological applications nowdays.[1–3] Recent progress in experimental techniques, such as the scanning tunneling microscope,[4] transmission electron microscope,[5] and mechanically controllable break junctions,[6] makes it possible to study metallic NC's, suspended between two electrodes, consisted of just a single metallic chain of few atoms or even one atom. The fabrication of these atomic-size structures opens an intriguing prospect to discover a new physical phenomena and their technological usage based on one dimension.[1–8] The quantum confinement of the electrons within atomic-size contacts and wires leads to the ballistic electronic transport with the conductance close to its theoretical one-dimensional limit $G_0 = 2e^2/h$. The occurrence of magnetism and its effect on quantized transport in different 3*d*, 4*d*, and 5*d* transition metal NC's and NW's have been extensively explored experimentally[3] and theoretically.[9,11,12] However, despite considerable progress in understanding the spin-polarized transport phenomena through NC's and NW's, their magnetic properties are still under debate, especially for systems of 4*d* and 5*d* elements which are normally nonmagnetic materials.[9,11–18] Recently, Rodrigues *et al.*[3] have studied experimentally the formation and the conductivity of Co, Pd, and Pt NW's at room temperature. The observed half-integer peaks in conductance suggest that the considered NW's exhibit magnetic behavior even at room temperature and without external magnetic filed. However, several works suggest that an appearance of the conductance similar to the fractional quantization or oscillations around this value can arise due to the presence of impurities or gas molecules in contamination process.[19] An important result of these works is that the magnetic states of nanocontacts are not related in a simple manner to their conductance. Various theoretical studies, mostly based on density functional theory, have been performed to explore the structural and conducting properties of NC's and NW's,[8,9,11–17,20–22] but only a few of them have been interested in studying the occurrence of magnetism in atomic contacts.[9,11,12,14–17]

There has been some controversy in the literature regarding possible onset of magnetism in Pd NC's and NW's. Palladium is one of the most intriguing and controversial material nowdays, which could exhibit magnetic properties for very small freestanding nanoclusters.[23–26] In the recent paper of Delin and co-workers,[14] the existence of magnetic ground states in palladium nanowires has been reported. Magnetism governed by Hund's rule has been predicted for infinitely long straight monatomic Pd wires with local magnetic moments of $0.7\mu_B$ and about $0.3\mu_B$ for a stretched short Pd chain suspended between bulk leads. An idealized structural geometries of nanocontacts were exploited in this work to explore the magnetic properties. These results are strongly differ from those obtained by Bahn and Jacobsen[16] where no magnetism was found in Pd nanowires. There has been some controversy between Delin *et al.*[27] and Alexandre *et al.*[28] about reliability usage of both generalized gradient approximation (GGA) and local density approximation (LDA) for the exchange-correlation functional to study magnetic properties of Pd nanowires. Meanwhile, it was shown in the recent paper of Stepanyuk *et al.*[15] that the three atomic Pd chains suspended between copper electrodes demonstrate metastable magnetic solution (that has only about 6 meV higher energy than nonmagnetic one) with the largest magnetic moment of $0.29\mu_B$. The metamagnetic behavior was revealed in the paper of Nautiyal *et al.*[9] where stable magnetic solution was obtained for infinite monatomic Pd wire with a large local magnetic moment of $0.53\mu_B$ per atom. It is believed that a strong inhomogeneous strain relaxations revealed in nanocontacts can cause magnetic fluctuations between different magnetic states.[15] To our knowledge, almost nothing is known about real atomic arrangement and geometries of Pd NC's. The study of their magnetism is still a challenge.

We present in this paper the results of *ab initio* calculations for short atomic Pd contacts suspended between palladium electrodes in a fully relaxed geometries. The elongated and contracted three atomic palladium chains are studied between two Pd(001) electrodes with planelike and pyramidlike geometries. We predict that the linear elongated palladium contacts exhibit magnetic properties with local magnetic moments distributed inhomogeneously within the

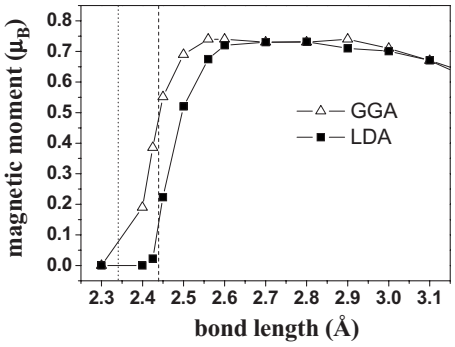

FIG. 1. Magnetic moment per palladium atom in infinite monatomic wire as a function of bond length. Vertical lines are linked to GGA (dashed) and LDA (dotted) equilibrium bond lengths.

chain. The interplay between atomic structure and magnetic properties of Pd contacts is discussed.

Our self-consistent electronic-structure calculations of Pd contacts have been performed by means of the projector augmented-wave technique[29] as implemented in VASP *ab initio* simulation code[30] based on the density functional theory. The GGA for exchange-correlation functional has been applied using Perdew-Wang'91 treatment.[31] In the context of recent discussions between Delin *et al.*[27] and Alexandre *et al.*[28] about reliability usage of GGA approximation, the LDA has been also used to study magnetic properties of Pd wires and contacts. Structural relaxations are performed via a quasi-Newton algorithm using the exact Hellmann-Feynman forces acting on ions. Pd contacts are modeled by the three-dimensional periodic tetragonal supercells with the palladium chains suspended between two semi-infinite palladium (001) slabs. Each chain is aligned along the z axis and separated from its images large enough along the x and y axes to avoid spurious interactions with them. The integration over Brillouin zone (BZ) is performed using the tetrahedron method with Blöchl corrections.[32] BZ sampling is performed using $4\times4\times1$ k-point mesh in Monkhorst-Pack grid.[33] A cutoff energy of 250 eV is used. The total energies of the whole supercells are converged up to 1 meV/atom, while the residual force acting on each atom is less than 0.01 eV/Å^2.

First, we discuss magnetic properties of infinitely long monatomic palladium wires. Pd wire is represented by five atomic chain aligned along the z axis. Figure 1 shows the results of spin-polarized calculations for infinite Pd monatomic wire as a function of the interatomic distance. Both the GGA and the LDA approximations demonstrate magnetic properties of Pd wires with the large local magnetic moments up to $0.75\mu_B$ per palladium atoms in the wide region of interatomic distances. The magnetic moment reaches rapidly its maximum for the interatomic distance of about 2.56 Å and then vanishes monotonically. Our results are consistent with those obtained by Nautiyal *et al.*[9] and Delin and co-workers[14] for infinite monatomic Pd wires. However, the estimated equilibrium GGA bond length value of 2.44 Å obtained via total energy minimization in our case differs from that obtained by Delin and co-workers (2.56 Å),[14] but it is in very good agreement with those reported by Nautiyal *et al.*[9] (2.44 Å) and Mokrousov *et al.* (2.47 Å).[10] Since these latter

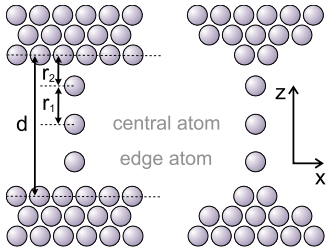

FIG. 2. (Color online) A schematic view of Pd chains suspended between (A) planelike and pyramidlike (B) electrodes considered in this work. r_1, distance between the central and the edge atoms; r_2, distance between edge atoms and electrodes; and d, distance between electrodes.

studies have been carried out in the same framework of theoretical approach as the one used by Delin and co-workers, the latter's enhanced bond length is unclear for us. Our theoretical studies predict the existence of magnetic solution for the ground state with local moment of about $0.5\mu_B$ per palladium atom in very good agreement with the calculations of Nautiyal *et al.*[9] and Delin and co-workers.[14] The occurrence of magnetism in infinite Pd monatomic wires has been discussed exploiting their electronic-structure properties.[14,34]

Now, we turn to our results obtained in GGA spin-polarized calculations for Pd contact suspended between Pd(001) electrodes. We consider Pd chains consisting of three atoms which have been observed experimentally for Pd contacts.[2,3] Two types of electrodes with planelike and pyramidlike geometrical structures (see Fig. 2) are considered in order to study the interplay between atomic structure and magnetic properties in atomic-size contacts. We present in Fig. 3 our results for optimized geometries obtained for Pd contacts as a function of the distance between electrodes. The calculations reveal not only changes of interatomic distances in Pd contacts but also the structural transition in the contacts. When the distance between electrodes increases, Pd contact behaves as a straight elongated chain, while during electrodes compression, it exhibits the transition from the linear to zigzag structure. Figure 3 also indicates that the

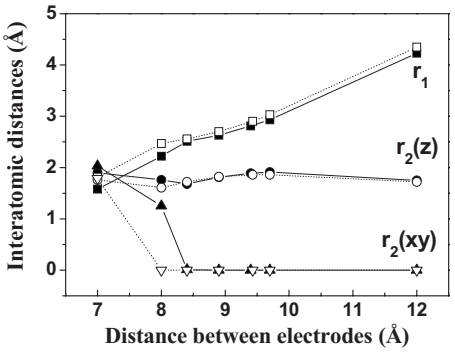

FIG. 3. The relaxed interatomic distances for Pd chains suspended between planelike (solid curves) and pyramidlike (dotted curves) electrodes as a function of interelectrodes distance. r_1, distance between the central and the edge atoms, and $r_2(z)$ and $r_2(xy)$ the projections of distance between edge atom and electrode on the z axis and xy plane, respectively.

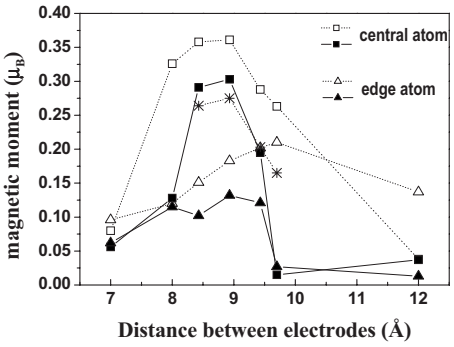

FIG. 4. Local magnetic moments calculated with GGA for the central and the edge palladium atoms in chains suspended between planelike (solid curves) and pyramidlike (dotted curves) electrodes as a function of interelectrodes distance. The star symbols represent the local magnetic moments calculated in LDA approximation for central palladium atom in chains suspended between pyramidlike electrodes.

structural transition occurs in Pd contact suspended between planelike electrodes for larger separation than between pyramidlike ones. This behavior can be explained by larger tension of the bond lengths between the edge and the central palladium atoms in the chains retained within pyramidlike electrodes (see Fig. 3). For example, our calculations reveal that for distance $d=8.0$ Å between electrodes, the bond length between the edge and the central palladium atoms in Pd chain (2.5 Å) is larger for pyramidlike electrodes than that obtained for planelike ones (2.2 Å). This difference shows that the chain suspended between planelike electrodes has already contracted bonds for $d=8.0$ Å with respect to its equilibrium bond length (2.44 Å) found for infinite wire and therefore exhibits earlier transition to zigzag configuration. We would like to point out a general trend of inhomogeneous relaxations of interatomic distances within Pd contact caused by different bondings of atoms. As can be seen in Fig. 3, the edge atoms in Pd contact strongly relax toward the electrodes, compensating the lack of interatomic interactions within the chain. These atoms have almost saturated bond lengths with electrodes. Such bond lengths are "rigid," since they are not varied over a whole range of electrodes separations. They are also shorter than bond lengths between the edge atoms and the central atom in palladium chain and increase monotonically under further elongation of the chain.

Our spin-polarized calculations predict the onset of magnetism for elongated Pd contacts. In Fig. 4, we present the distribution of local magnetic moments per atom in Pd chains as a function of the distance between electrodes. The stretching of Pd chains sets up the sizable local magnetic moments distributed inhomogeneously within the contact. A lower cohesion of central palladium atom in the chain, caused by a reduced coordination number, elongates easily the bond lengths between the central and the edge atoms during stretching. As a consequence, a local magnetic moment in the central atom increases rapidly to an upper limit of $0.36\mu_B$ at the bond length of 2.56 Å. The edge atoms have an almost saturated value of magnetic moment of about $0.15\mu_B$ which varies slowly due to strong interaction with electrodes. These results agree with previous spin-polarized calculations of Pd chain suspended between planelike copper electrodes, where the central atom of three atomic Pd chain attains a larger local magnetic moment up to $0.29\mu_B$ at practically the same bond length of 2.50 Å.[15] Our total energy calculations show that the magnetic solutions for Pd contacts suspended between Pd electrodes are lower in energy than nonmagnetic ones with an energy gain of about 0.003 eV/atom as a mean value over the electrodes separations. Our results are consistent with former studies of Delin and co-workers,[14] where a stable magnetic solution with a local moment of $0.3\mu_B$ per Pd atom has been found. We have found also that further stretching shows a clear tendency of Pd contact to vanish its magnetic properties at larger separations (above 9.4 Å). At this range of distances, magnetic states are still more stable than nonmagnetic ones, but the energy difference between magnetic and nonmagnetic solutions is rather small. This might lead to metamagnetic behavior of Pd contacts, i.e., the fluctuations between different states can occur.[15] Figure 4 shows that Pd contacts attain nonmagnetic states faster when they are suspended between planelike electrodes than between pyramidlike ones. It is seen that the magnetic moments of the central and the edge palladium atoms in the chain are suppressed already at the distance of about 9.7 Å between planelike electrodes, while these atoms have a still sizable moments ($0.26\mu_B$) in the chain between pyramidlike ones. We assume that Pd contact stretched to the distance of 9.7 Å between planelike electrodes can be already considered as the broken chain. The bond length between the central and the edge atoms in the chain exceeds 2.9 Å, which was ascribed as a breaking point for Pd contacts.[3,14] Almost saturated number of bonds of edge atoms at the proximity of planelike electrodes leads to a weaker bonding between the central and the edge atoms in the chain. This is not the case for palladium contacts stretched between pyramidlike electrodes, where a rather slow decay of magnetic moments has been observed (see Fig. 4). The structural transition in Pd chains from the linear to the zigzag atomic arrangement diminishes its magnetic properties due to increasing the number of interacting palladium atoms. Such a structural transition occurs earlier for the chain suspended between planelike electrodes than between pyramidlike ones. As a result, the magnetic properties of this chain vanish faster for larger separations of electrodes (see Fig. 4). The robust magnetic moments of Pd contacts obtained in our GGA calculations were also found in LDA ones. The local magnetic moments distributed inhomogeneously within Pd contacts were found by LDA spin-polarized calculations for elongated palladium chains (see Fig. 4). The LDA values of local magnetic moments in Pd chains are smaller than GGA ones due to a stronger interaction between palladium atoms in LDA approximation and exhibit a similar but faster decay with stretching of contacts. Thus, both the LDA and the GGA approximations predict the onset of magnetism in elongated Pd contacts.

In summary, we have demonstrated that contracted and stretched three atomic Pd chains, suspended between Pd(001) electrodes, undergo strong strain relaxations. We predict that the elongated Pd chains exhibit magnetic behavior over a wide range of the distances between electrodes.

We reveal an inhomogeneous distribution of the local magnetic moments within a chain driven by strain relaxations. The onset of magnetism in Pd chain is caused by the reduced dimensionality of the chain. The contraction of Pd chains leads to their structural transition from linear to zigzag atomic arrangement, which suppresses completely their magnetic behavior.

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[1] U. Landman *et al.*, Science **248**, 454 (1990); K. Terabe *et al.*, Nature (London) **433**, 47 (2005); J. Bettini *et al.*, Nat. Nanotechnol. **1**, 182 (2006).
[2] T. Matsuda and T. Kizuka, Jpn. J. Appl. Phys., Part 2 **45**, L1337 (2006).
[3] V. Rodrigues, J. Bettini, P. C. Silva, and D. Ugarte, Phys. Rev. Lett. **91**, 096801 (2003).
[4] H. Ohnishi *et al.*, Nature (London) **395**, 780 (1998); J. I. Pascual, J. Mendez, J. Gomez-Herrero, A. M. Baro, N. Garcia, and V. T. Binh, Phys. Rev. Lett. **71**, 1852 (1993).
[5] Y. Takai, T. Kawasaki, Y. Kimura, T. Ikuta, and R. Shimizu, Phys. Rev. Lett. **87**, 106105 (2001); V. Rodrigues and D. Ugarte, Phys. Rev. B **63**, 073405 (2001).
[6] C. Untiedt, A. I. Yanson, R. Grande, G. Rubio-Bollinger, N. Agrait, S. Vieira, and J. M. van Ruitenbeek, Phys. Rev. B **66**, 085418 (2002); R. H. M. Smit, C. Untiedt, G. Rubio-Bollinger, R. C. Segers, and J. M. van Ruitenbeek, Phys. Rev. Lett. **91**, 076805 (2003).
[7] V. M. García-Suarez, A. R. Rocha, S. W. Bailey, C. J. Lambert, S. Sanvito, and J. Ferrer, Phys. Rev. Lett. **95**, 256804 (2005).
[8] N. V. Skorodumova and S. I. Simak, Phys. Rev. B **67**, 121404(R) (2003); A. Grigoriev, N. V. Skorodumova, S. I. Simak, G. Wendin, B. Johansson, and R. Ahuja, Phys. Rev. Lett. **97**, 236807 (2006).
[9] T. Nautiyal, T. H. Rho, and K. S. Kim, Phys. Rev. B **69**, 193404 (2004).
[10] Y. Mokrousov, G. Bihlmayer, S. Heinze, and S. Blugel, Phys. Rev. Lett. **96**, 147201 (2006).
[11] M. Wierzbowska, A. Delin, and E. Tosatti, Phys. Rev. B **72**, 035439 (2005); A. Delin and E. Tosatti, *ibid.* **68**, 144434 (2003).
[12] J. Fernández-Rossier, D. Jacob, C. Untiedt, and J. Palacios, Phys. Rev. B **72**, 224418 (2005).
[13] N. Zabala, M. J. Puska, and R. M. Nieminen, Phys. Rev. Lett. **82**, 3000 (1999); O. A. Starykh and D. L. Maslov, *ibid.* **82**, 2999 (1999); N. Zabala, M. J. Puska, and R. M. Nieminen, *ibid.* **80**, 3336 (1998).
[14] A. Delin, E. Tosatti, and R. Went, Phys. Rev. Lett. **92**, 057201 (2004); A. Delin and E. Tosatti, J. Phys.: Condens. Matter **16**, 8061 (2004).
[15] V. S. Stepanyuk, A. L. Klavsyuk, W. Hergert, A. M. Saletsky, P. Bruno, and I. Mertig, Phys. Rev. B **70**, 195420 (2004); V. S. Stepanyuk, P. Bruno, A. L. Klavsyuk, A. N. Baranov, W. Hergert, A. M. Saletsky, and I. Mertig, *ibid.* **69**, 033302 (2004); R. Z. Huang, V. S. Stepanyuk, A. L. Klavsyuk, W. Hergert, P. Bruno, and J. Kirschner, *ibid.* **73**, 153404 (2006).
[16] S. R. Bahn and K. W. Jacobsen, Phys. Rev. Lett. **87**, 266101 (2001).
[17] K. Hirose, Y. Meir, and N. S. Wingreen, Phys. Rev. Lett. **90**, 026804 (2003).
[18] Y. Morigaki *et al.*, J. Appl. Phys. **88**, 2682 (2000).
[19] P. Jelinek, R. Perez, J. Ortega, and F. Flores, Phys. Rev. Lett. **96**, 046803 (2006); Sz. Csonka, A. Halbritter, and G. Mihaly, Phys. Rev. B **73**, 075405 (2006); Y. Qi, D. Guan, Y. Jiang, Y. Zheng, and C. Liu, Phys. Rev. Lett. **97**, 256101 (2006); N. V. Skorodumova, S. I. Simak, A. E. Kochetov, and B. Johansson, Phys. Rev. B **75**, 235440 (2007).
[20] T. N. Todorov and A. P. Sutton, Phys. Rev. Lett. **70**, 2138 (1993).
[21] H. Mehrez and S. Ciraci, Phys. Rev. B **56**, 12632 (1997).
[22] G. Rubio-Bollinger, S. R. Bahn, N. Agrait, K. W. Jacobsen, and S. Vieira, Phys. Rev. Lett. **87**, 026101 (2001).
[23] B. Sampedro, P. Crespo, A. Hernando, R. Litran, J. C. Sanchez Lopez, C. Lopez Cartes, A. Fernandez, J. Ramirez, J. Gonzalez Calbet, and M. Vallet, Phys. Rev. Lett. **91**, 237203 (2003); T. Shinohara, T. Sato, and T. Taniyama, Phys. Rev. Lett. **91**, 197201 (2003); R. Litrán, B. Sampedro, T. C. Rojas, M. Multigner, J. C. Sanchez-Lopez, P. Crespo, C. Lopez-Cartes, M. A. Garcia, A. Hernando, and A. Fernandez, Phys. Rev. B **73**, 054404 (2006); A. Hernando *et al.*, arXiv:cond-mat/0605496 (unpublished).
[24] Y. N. Kim *et al.*, J. Am. Chem. Soc. **126**, 8672 (2004).
[25] S. C. Hong, J. I. Lee, and R. Wu, Phys. Rev. B **75**, 172402 (2007).
[26] F. Aguilera-Granja, J. Ferrer, and A. Vega, Phys. Rev. B **74**, 174416 (2006).
[27] A. Delin, E. Tasatti, and R. Weht, Phys. Rev. Lett. **96**, 079702 (2006).
[28] S. S. Alexandre, M. Mattesini, and J. M. Soler, Phys. Rev. Lett. **96**, 079701 (2006).
[29] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[30] G. Kresse and J. Hafner, Phys. Rev. B **48**, 13115 (1993); G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[31] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
[32] P. Blöchl, O. Jepsen, and O. K. Andersen, Phys. Rev. B **49**, 016 223 (1994).
[33] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[34] D. Spišák and J. Hafner, Phys. Rev. B **67**, 214416 (2003).