Comment on "Magnetism in Atomic-Size Palladium Contacts and Nanowires"

Based on density functional calculations, Delin *et al.* [1] conclude in a recent Letter that monoatomic wires of Pd are ferromagnetic at the calculated equilibrium separation of the atoms. However, we conclude that the functional used by Delin *et al.* [namely, generalized gradient approximation (GGA)] is not appropriate for the problem at hand since it artificially favors magnetism to the extent that, if applied to bulk fcc Pd, it would give a ferromagnetic ground state instead of a paramagnetic one.

Magnetism is very sensitive to the interatomic separation especially in Pd which is a paramagnetic metal close to a volume dependent nonmagnetic-magnetic transition [2]. Since in the case of monoatomic wires there is no experimental determination of the equilibrium distance between the atoms, we have carried out several monostrand calculations to assess the sensitivity of the theoretical results to different approximations. We have first used the SIESTA code [3], with norm-conserving pseudopotentials and well-converged parameters and basis sets of atomic orbitals. Within the GGA [4] to exchange and correlation we, like Delin *et al.* [1], find that the infinite monostrand has a finite magnetic moment of $\sim 0.7\mu_B$/atom, with an energy 12 meV/atom below the paramagnetic solution [Fig. 1(b)]. However, within the local density approximation (LDA) [5], the calculated atomic separation is 6% shorter and the ground state is paramagnetic [Fig. 1(a)]. We have calculated the equilibrium lattice constant and ground state of bulk fcc Pd, using both LDA and GGA, to assess their reliability for Pd. Within the LDA we find [Fig. 2(a)] a paramagnetic ground state and a lattice constant of 3.89 Å, in agreement with both the experimental values and previous LDA calculations [2]. However, the GGA gives a lattice constant of 3.99 Å, with a finite magnetic moment of

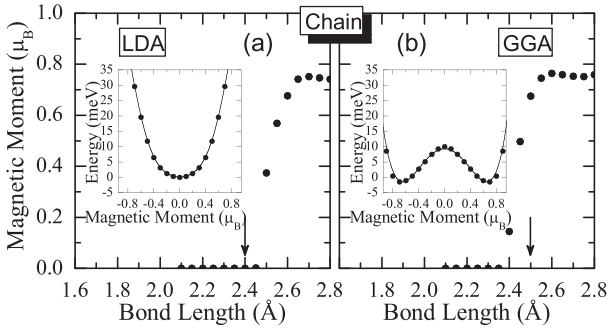

FIG. 1. Magnetic moment vs interatomic distance for an infinite linear monostrand of Pd, obtained with SIESTA. Panels (a) and (b) are for the LDA and GGA approximations, respectively. The insets indicate the variation of the total energy with magnetic moment at the equilibrium distances, indicated by arrows in the main figures.

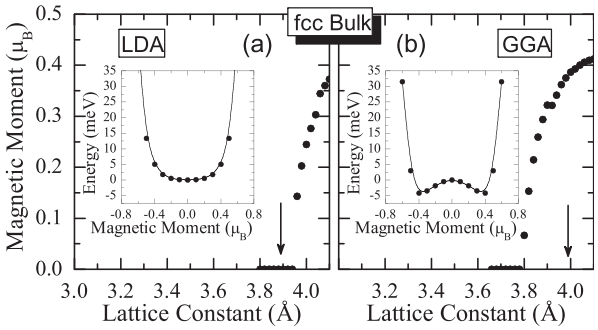

FIG. 2. Same as Fig. 1 for bulk fcc palladium.

$\sim 0.4\mu_B$/atom and an energy 4.5 meV/atom below the paramagnetic phase [Fig. 2(b)]. We obtain very similar results for bulk Pd with the pseudopotential plane wave program VASP [6] and with the all electron augmented plane wave code WIEN2K [7]: while the LDA gives a lattice constant and an electronic state in agreement with experiment, with the GGA the lattice constant is larger and the system is ferromagnetic. These results clearly indicate the need to carry out further investigations before a conclusion is reached concerning the magnetic properties of Pd in its various forms.

We would like to thank E. Anglada and O. Paz for their technical assistance. Work supported by Spain's MEC Grants No. BFM2002-10510-E and No. BFM2003-03372.

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Received 10 May 2005; published 22 February 2006
DOI: 10.1103/PhysRevLett.96.079701
PACS numbers: 75.75.+a, 73.22.−f, 75.50.Cc

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