Magnetism in Atomic-Size Palladium Contacts and Nanowires

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We have investigated Pd nanowires theoretically, and found that, unlike either metallic or free atomic Pd, they exhibit Hund's rule magnetism. In long, monostrand nanowires, we find a spin moment of $0.7\mu_B$ per atom, whereas for short, monostrand nanowires between bulk leads, the predicted moment is about $0.3\mu_B$ per nanowire atom. In contrast, a coaxial (6,1) nanowire was found to be nonmagnetic. The origin of the nanowire magnetism is analyzed.

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Magnetism at the nanoscale is an exciting emerging research field, of both basic and applied relevance. For a future spin-based technology working in the quantum-mechanical regime, an understanding of nanomagnetic phenomena will be crucial; yet, relatively little is currently understood about how magnetism arises and how it affects the properties of metals at the nanoscale.

Systems of special interest are nanowires and atomic-sized nanocontacts. The low dimensionality of such systems causes specific physical phenomena to appear, for example quantized ballistic conductance [1] and helical nanowire geometries [2,3]. These phenomena interplay with the possible presence of magnetism in the nanosystem, especially of a genuine Hund's rule magnetic order parameter. Here, we report theoretical studies of emerging magnetism in Pd nanowires in various geometries (see Fig. 1). Monostrand nanowires of Pd, i.e., nanowires consisting of a single straight line of atoms, have recently been observed by Rodrigues *et al.* [4]. We find magnetic moments as high as $0.7\mu_B$ per atom for infinitely long, straight, monostrand nanowires. Even short, three-atom Pd nanowire chains between bulklike leads are predicted to possess a magnetic moment around $0.3\mu_B$ per nanowire atom, while the bulk leads remain nonmagnetic. In contrast, thicker coaxial (6,1) nanowires are predicted to be nonmagnetic.

We have assumed that the ultimately thin wires are straight, with equidistant atoms. For monatomic wires not attached to leads, one could imagine more complicated wire geometries, such as zigzag configurations, or Peierls distortions [5] leading to dimerization, trimerization, or multimerization. However, when suspended between leads, local minima or saddle points of the string tension should be considered instead of those of the energy, since they alone will in quasiequilibrium correspond to long-lived, or "magic" nanowires [3]. In Au, the zigzag deformations do not survive the string tension, and the same would happen, if they existed, in Pd. Thus, we conclude that zigzag distortions do not exist in the systems addressed here. With regards to Peierls dimerization, trimerization, or multimerization distortions, they should lead to insulating nanowires.

Of course, thermal fluctuations, very large in a nanosystem, will generally act to destroy static magnetic order in the absence of an external field. There are nonetheless two different fluctuation regimes: slow and fast. Slow fluctuations transform a nanomagnet to a superparamagnetic state, where magnetization fluctuates on a long time scale between equivalent magnetic valleys, separated, e.g., by anisotropy-induced energy barriers. If the barriers

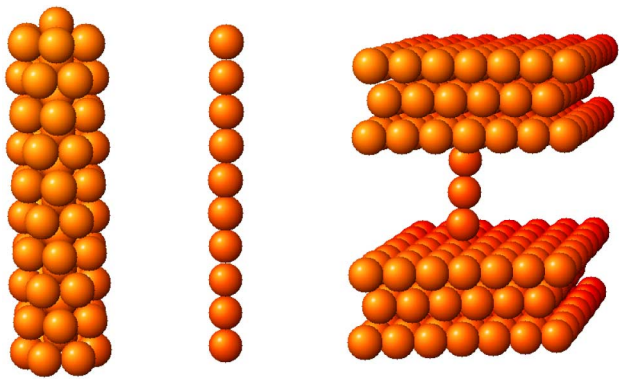

FIG. 1 (color online). Schematical drawing of the nanowire geometries addressed in this Letter. From left to right: (6,1) coaxial nanowire; monostrand nanowire; short monostrand nanowire between bulk leads.

are sufficiently large, the nanosystem spends most of the time in a single magnetic valley, and will for many practical purposes behave as magnetic. We may under these circumstances be allowed to neglect fluctuations altogether, and to approximate (as we will do here) the calculated properties of the superparamagnetic nanosystem with those of a statically magnetized one. Experimentally, evidence of one-dimensional (1D) superparamagnetism with fluctuations sufficiently slow on the time scale of the probe has been reported in Co atomic chains deposited at Cu surface steps [6]. At the opposite extreme—a situation reached, for example, at high temperatures—the energy barriers are so readily overcome that the magnetic state is totally washed away by fast fluctuations, leading to a conventional paramagnetic state. A complete description of this high entropy state is beyond scope, but a conventional $T = 0$ nonmagnetic, singlet solution of the Kohn-Sham electronic structure equations can be used in its place, at least as a crude approximation.

The present density functional calculations [7] were performed with an all-electron full-potential linear muffin-tin orbital (FP-LMTO) basis set [8] together with a generalized gradient approximation (GGA) [9] to the exchange-correlation functional. A simpler local density functional [10] was also tested, giving results very similar to the GGA. As a double check, some of the calculations were repeated using the linear augmented plane-wave code WIEN2K [11]. None of these calculations assume any shape approximation of the potential or wave functions. We performed both scalar-relativistic calculations, and calculations including the spin-orbit coupling as well as the scalar-relativistic terms. In the calculations involving the spin-orbit interaction, the spin axis was chosen to be aligned along the nanowire direction.

The calculations were performed with inherently three-dimensional codes. Thus, the infinitely long, straight, isolated monostrand nanowires, as well as the (6,1) coaxial nanowires, were simulated by regular arrays of well spaced nanowires. The short nanowire consisted of three atoms in a straight line attached to thick planar slabs of close-packed bulk Pd. The bond length in the short nanowire was chosen to be 2.7 Å, as suggested by transmission electron microscope images of Pd monostrand nanowires [4], and corresponds to a somewhat stretched nanowire. Convergence of the magnetic moment was checked with respect to k-point mesh density, Fourier mesh density, tail energies, nanowire-nanowire vacuum distance, and bulk thickness. In the calculations, spin-orbit coupling was seen to have only a minor effect on the results, in contrast to the situation for 5d metals [12].

Figure 2 shows the magnetic moment per atom for the (infinitely) long Pd monostrand nanowire, as a function of the bond length along the nanowire. The total magnetic moment rapidly reaches $0.7\mu_B$ at a bond length around 2.3 Å, and retains this magnetic moment over a long

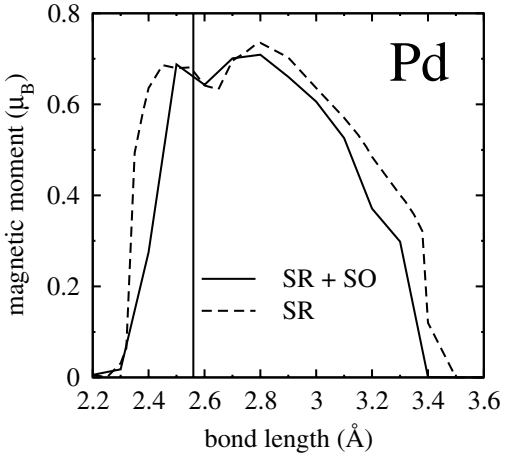

FIG. 2. Magnetic moment per atom as a function of bond length for a long, monostrand Pd nanowire. The vertical line points out the equilibrium bond length. (SR + SO = calculation including spin-orbit coupling and scalar relativistic terms; SR = calculation including scalar relativistic terms but not spin-orbit coupling).

region. The steep rise at the onset of magnetism is almost entirely due to 4d polarization, which reaches a maximum of $\sim 0.5\mu_B$ already at 2.6 Å and then decreases monotonically. At $\sim$3.5 Å, the magnetic moment disappears completely, where the straight nanowire undergoes a metal-insulator transition, with the opening of a ds gap, foreshadowing that of the noninteracting atoms. Experimental data [4], as well as a negative curvature of energy versus length for spacings above $\sim$2.9 Å suggest, however, that the nanowire has already broken due to excessive string tension well before large bond lengths in themselves provoke a metal-insulator transition.

For the long monostrand nanowire, the energy gain per atom due to spin polarization is around 12 meV (spin-orbit coupling included) at 2.56 Å, which is the bond length minimizing the total energy. For comparison, we mention that in bulk Ni the corresponding energy gain is around 40 meV, indicating that the Pd nanowire magnetism might actually exist not only at ultralow temperatures. Antiferromagnetic Pd monostrand nanowire configurations were also tested, and found to be energetically unstable compared to the ferromagnetic configuration. Our result differs from that of Bahn *et al.* [13] who found no magnetism in pseudopotential calculations for Pd monostrand nanowires. It seems possible that the disagreement could arise in this very borderline case due to the different methods used, in which case we would tend to trust our all-electron approach better.

Why does the Pd monostrand nanowire magnetize? In the bulk, and also at surfaces, the Pd 4d band is slightly too wide to sustain spin polarization. In the atom, on the other hand, Pd forms a singlet with a completely filled 4d shell. Thus, the limiting cases are all nonmagnetic and the strong Hund's rule magnetism in the nanowire appears

rather unexpected. However, the borderline case of Pd magnetism is demonstrated by the fact that certain clusters are predicted to have a magnetic ground state [14]. From the atomic perspective, as the distance between Pd atoms decreases, the increased interatomic hybridization causes the 4*d* band to become partially unfilled due to $d \rightarrow s$ transfer, and thus symmetry breaking through spin polarization becomes possible. Hund's rules make it reasonable to assume that spin polarization will also be energetically favorable. From the bulk perspective, the reduction of the number of nearest neighbors in the nanowire compared to the bulk causes a narrowing of the 4*d* band, and the bandwidth may become sufficiently small that the gain in exchange energy due to spin polarization is larger than the increase in kinetic energy. Thus, using this 4*d* band-narrowing argument, we can rationalize the existence of a magnetic state in the nanowire.

However, we have reason to believe that this explanation of the large magnetic moment in long Pd monostrand nanowires is too simple, and that 4*d* band narrowing is not the only mechanism at work, but that the one-dimensionality of the system is crucial. We will illustrate this point by analyzing the band structure of the long Pd monostrand nanowires in some detail.

Figure 3 shows the band structure of the Pd monostrand nanowire for several different bond lengths, as it goes from insulator, to ferromagnet, to paramagnet, for decreasing bond length. There are six orbitals to consider, two $s + d_{z^2}$ orbitals, two (d_{xz}, d_{yz}) orbitals, and two $(d_{xy}, d_{x^2-y^2})$ orbitals, as illustrated in Fig. 4. The two $s + d_{z^2}$ orbitals give rise to the two bands with highest dispersion. Of these, the band with mostly *s* character has an electron band edge close to the Fermi level at Γ, and the *d* character dominated one has a hole band edge close to the Fermi level at the zone boundary *A*. Next, we have the two (d_{xz}, d_{yz}) orbitals, which are degenerate and have a band edge close to the Fermi level at Γ. Finally, the two $(d_{xy}, d_{x^2-y^2})$ orbitals form a flat band situated between 0.5 and 1 eV below the Fermi level.

The $(d_{xy}, d_{x^2-y^2})$ band lies far below the Fermi level with both spins completely occupied, and gives no contribution to magnetism. The spin moment is related to the $s + d_{z^2}$ and (d_{xz}, d_{yz}) bands, which have a high dispersion, and display one-dimensional band edges close to the Fermi level at Γ and *A*. In the magnetic regime, i.e., from 2.3 Å to 3.5 Å, these three band edges all are nearly degenerate in energy and close to the Fermi level. This accidental feature of the long Pd monostrand nanowire band structure dramatically increases the density of states, with divergent Van Hove singularities close to the Fermi level. A spin splitting of these band edges can thus lower the total electron band energy, somewhat analogous to a band Jahn Teller, or a Peierls instability effect. Interestingly, for bond lengths of ~2.8 Å or more, even the *s*-dominated band edge at Γ is spin split around the Fermi level.

The fact that the Stoner stability criterion against magnetism is necessarily violated leading to a magnetized nanowire when a band edge approaches to the Fermi level is universal. It was pointed out earlier by Zabala *et al.* [15]

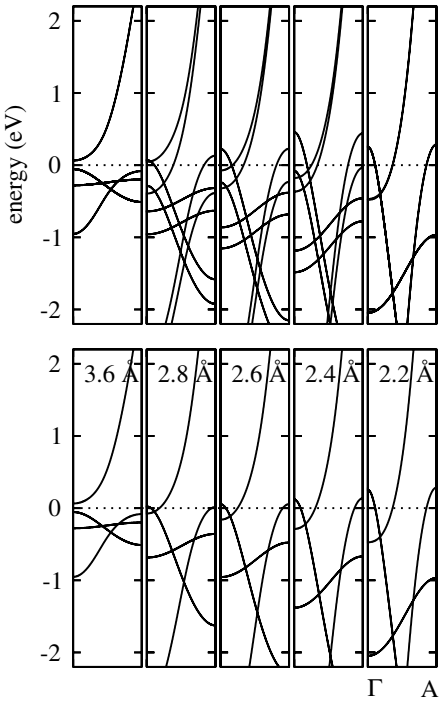

FIG. 3. Scalar-relativistic Pd monostrand nanowire band structures, along the nanowire direction. The Fermi energy is at zero. The upper panels show the ferromagnetic calculation, and the lower panels the nonmagnetic calculation.

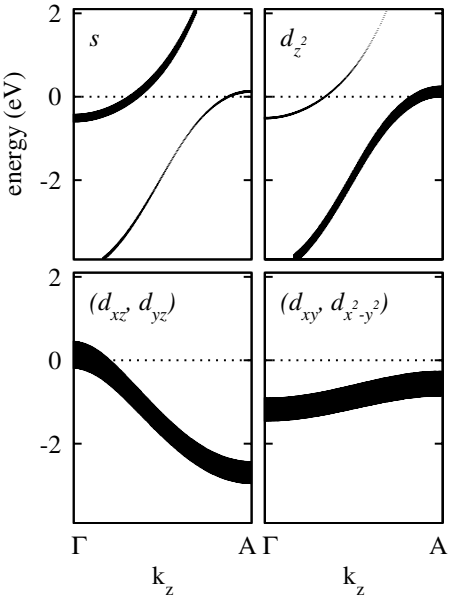

FIG. 4. Character-resolved scalar-relativistic band structure along the nanowire direction, for a nonmagnetic Pd nanowire with a bond length of 2.6 Å. The Fermi energy is at zero.

and demonstrated in explicit calculations for aluminum nanowires [16,17]. However, for a simple sp metal, such as Al, the ensuing 1D magnetism implies rather small moments supported by a very weak exchange interaction. Consequently, those moments will readily be washed away by fluctuations. In the Pd case, the situation is different. Here, we expect a robust superparamagnetic state for temperatures not too high, transformable to a genuine magnetic state under an external field. The 1D singularities — in scattering terms the relevant band edge singularities correspond to standing waves, here of $s + d_{z^2}$ and (d_{xz}, d_{yz}) electrons and holes — provide here merely a mechanism to trigger awake a strong Hund's rule magnetic moment, based on the strong exchange interaction of the d electrons.

If the Pd monostrand nanowire magnetism is mainly triggered by a 1D scattering phenomenon, it should disappear or at least become much smaller when the number of nearest neighbors becomes large. To test this assertion, we, as already mentioned, also performed calculations for a two-layer coaxial (6,1) nanowire. As expected, it was found to be nonmagnetic, supporting the view that the magnetism in the Pd monostrand nanowire is, to a large extent, a 1D phenomenon. This 1D magnetism in Pd proves nevertheless to be remarkably robust, as it survives even down to three-atom chains suspended between nonmagnetic leads.

The magnetic moment in the short-nanowire suspended between bulk Pd leads is substantially smaller than the moment of the long monostrand nanowire moment; $0.3\mu_B$ per nanowire atom compared to $0.7\mu_B$. Because of the high complexity of the band structure for the short nanowire (not shown), it is not possible to single out individual band edges as responsible for triggering the Hund's rule magnetism in the short-nanowire case. However, we find that the bulk leads affect the electronic structure in the short nanowire resulting in a wider $4d$ band than in the long nanowire, which in turn reduces the magnitude of the magnetic moment.

In summary, we predict that ultimately thin Pd nanowires, both short and long, exhibit a spin-polarized ground state. The resulting superparamagnetic state of the nanowire should show up in the ballistic conductance in the form of a strong and unusual magnetic field and temperature dependence as well as spin polarization of the current through the nanowire. Rodrigues *et al.* [4] recently measured the charge conductance of Pd nanocontacts and found features in the conductance histogram above as well as below one conductance quantum $G_0 = 2e^2/h$. The existence of features below G_0 is intriguing since it seems to suggest that the s-dominated band crossing the Fermi level is spin split around the Fermi level, a situation our calculations do predict for a stretched wire with bond length of $\sim$2.8 Å or larger. Another speculative explanation of the low conductance could entail some kind of spin reversal amid the nanowire [18]. More theory work will be needed to address their data, explicitly including such elements as tip form, spin structures, impurities [19], and temperature as well as their effects on the system's conductance. We are currently working to address some of these issues.

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