Magnetism in Atomic-Sized 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, monoatomic wires, we find a spin moment of 0.7 $\mu_B$ per atom, whereas for short, monoatomic wires between bulk leads, the predicted moment is about 0.3 $\mu_B$ per wire atom. In contrast, a coaxial (6,1) wire was found to be nonmagnetic. The origin of the wire magnetism is analyzed.

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Magnetism at the nanoscale is an exciting emerging research field, of both basic and applied relevance. In future technology, when the electronic components will have become so tiny that quantum size effects will determine their functionality, 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 wire geometries [2]. 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. Monowires of Pd, i.e., wires consisting of a single line of atoms, have recently been observed by Rodrigues et al. [3]. We find magnetic moments as high as 0.7 $\mu_B$ per atom for infinitely long, straight, monatomic wires. Even short, three-atom Pd wire chains between bulk-like leads, are predicted to possess a magnetic moment around 0.3 $\mu_B$ per wire atom, whereas the bulk leads remain nonmagnetic. In contrast, thicker coaxial (6,1) wires were found to be nonmagnetic.

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 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 [4]. 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, in which all magnetic exchange splittings of the electronic bands vanish through motional narrowing. 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 [6] were performed with an all-electron full-potential linear muffin-tin orbital (FP-LMTO) basis set [6] together with a generalized gradient approximation (GGA) [7] to the exchange-correlation functional. A simpler local density functional [8] was also tested, giving results very similar the GGA. As a double check, some of the calculations were repeated using the linear augmented plane-wave code WIEN97 [9]. 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 wire direction.

The calculations were performed with inherently three-dimensional codes. Thus, the infinitely long, straight, isolated monowires, as well as the (6,1) coaxial wires, were simulated by regular arrays of well spaced nanowires. The short wire consisted of three atoms in a straight line attaching to thick planar slabs of close-packed bulk Pd. The bond length in the short wire was chosen to be 2.7 Å, as suggested by transmission electron microscope images of Pd monowires [3], and corresponds to a somewhat stretched wire. Convergence of the magnetic moment was checked with respect to k-point mesh size. The remainder of the magnetic moment has 5s character. At around 3.5 Å, the magnetic moment disappears completely, where the wire undergoes a metal-insulator transition, with the opening of a d s gap, fore-shadowing that of the noninteracting atoms.

For the long monatomic wire, the energy gain per atom due to spin polarization is around 25 meV at the equilibrium bond length 2.56 Å. For comparison, we mention that in bulk Ni the corresponding energy gain is around 40 meV, indicating that the Pd wire magnetism might actually exist not only at ultra-low temperatures. Antiferromagnetic Pd monowire configurations were also tested, and found to be energetically unstable compared to the ferromagnetic configuration. Our result differs from that of Bahn et al. [11] who found no magnetism in pseudopotential calculations for Pd monowires. It is 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 monowire magnetize? In the bulk, and also at surfaces, the Pd 4d band is too wide to provoke 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 wire 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 [12]. From the atomic perspective, as the distance between Pd atoms decreases, the increased interatomic hybridization causes the 4d band to become partially unfilled due to d → 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 wire compared to the bulk causes a narrowing of the 4d band, and the band width 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 4d band-narrowing argument, we can rationalize the existence of a magnetic state in the wire.

However, we have reason to believe that this explanation of the large magnetic moment in long Pd monowires is too simple, and that 4d 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 monowires in some detail.

Fig. 2 shows the magnetic moment per atom for the (infinitely) long Pd monowire, as a function of the bond length along the wire. The total magnetic moment rapidly reaches 0.7 μB at a bond length around 2.3 Å, and retains this magnetic moment over a long region. The steep rise at the onset of magnetism is almost entirely due to 4d polarization, which reaches a maximum of ~0.5 μB already at 26 Å and then decreases monotonically. The remainder of the magnetic moment has 5s character. At around 3.5 Å, the magnetic moment disappears completely, where the wire undergoes a metal-insulator transition, with the opening of a d s gap, fore-shadowing that of the noninteracting atoms.

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ation is different. The moment is large, and 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 the mechanism that triggers awake a strong Hund’s rule magnetic moment.

If the Pd monowire magnetism is to the most part due to 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) wire. As expected, it was found to be nonmagnetic, supporting the view that the magnetism in the Pd monowire 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 wire suspended between bulk Pd leads is substantially smaller than the moment of the long monowire moment; 0.3 \( \mu_B \) per wire atom compared to 0.7 \( \mu_B \). Due to the high complexity of the band structure for the short wire (not shown), it is not possible to single out band edges as responsible for triggering the Hund’s rule magnetism in the short-wire case. However, we find that the bulk leads affect the electronic structure in the short wire resulting in a wider 4\( d \) band than in the long wire, 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 wire. Rodrigues et al. 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 speculative explanation could entail some kind of spin reversal amid the nanowire. More theory work will be needed to address their data, explicitly including such elements as tips, spin structures, and temperature as well as their effects on the system’s conductance. We are currently working to address this issue.

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FIG. 1: Schematic drawing of the wire geometries addressed in this paper. From left to right: (6,1) coaxial wire; monowire; short monowire between bulk leads.
FIG. 2: Magnetic moment per atom as a function of bond length for a long, monatomic Pd wire. 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.)
FIG. 3: Scalar-relativistic Pd monowire band structures, along the wire direction. The Fermi energy is at zero. The upper panels shows the ferromagnetic calculation, and the lower panels the nonmagnetic calculation.
FIG. 4: Character-resolved scalar-relativistic band structure along the wire direction, for a nonmagnetic Pd wire with a bond length of 2.6 Å. The Fermi energy is at zero.