Emergence of magnetism in bulk amorphous palladium

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Magnetism is a macro-manifestation of quantum phenomena due mainly to the spin and the orbital momentum of the electrons. In materials science magnetism can exhibit short- and long-range behavior giving rise to different properties in the bulk: paramagnetism, diamagnetism, ferromagnetism, etc.¹. Magnetism in palladium has been the subject of much work and more speculation²-⁴. Bulk palladium in its crystalline form is paramagnetic with a high magnetic susceptibility¹. First principles simulations of palladium under pressure² and palladium nanoclusters³ have generated interest to scrutinize its magnetic properties. Here we report another possibility: Palladium may become an itinerant ferromagnet in the amorphous bulk phase at atmospheric pressure. Atomic palladium is a d¹⁰ element, whereas bulk crystalline Pd is a d¹⁰-x(sp)x material; this, together with the possible presence of “unsaturated bonds” in amorphous materials, may explain the remnant magnetism reported herein. Properties of the amorphous counterpart have been little studied and consequently this is terra ignota that must be explored since the ample range of applications in geophysics, engineering, in transmission and generation of electric power, in magnetic recording, etc. demands a better knowledge of the phenomenon. In this work, we present and discuss magnetic effects in bulk amorphous palladium.

Motivated by these considerations, in this work we investigate the effect of topological disorder in the electronic and magnetic properties of samples of bulk palladium at zero kelvin. We propose that atomic disorder in solid palladium (amorphous samples) could generate magnetism since this
disorder would induce an unbalance in the number of nearest neighbours, locally creating a variation of unsaturated bonds leading to a net spin and consequently to a net magnetic moment. This, together with the creation of holes in the corresponding d band, due to the spilling over of electrons unto the s and p bands may contribute to magnetism. We have performed ab initio calculations and the results indicate that magnetism may appear in a-Pd: Palladium may become an itinerant ferromagnet in the amorphous bulk phase at atmospheric pressure and at $T = 0$ K.

To computationally generate amorphous structures of palladium we use a method developed by our group that has given good results for several materials; this is the undermelt-quench approach. This approach allows the generation of disorder in an otherwise unstable crystalline structure, (isodense to the stable one) by heating it to just below the melting temperature of the real material. In this manner, a disordered sample is created and then an optimization run is carried out to release stresses and let the sample reach local equilibrium; these samples resemble quite accurately the amorphous phase of the material considered5-7. A variation of this approach consists in doing molecular dynamics on an unstable specimen at a given constant temperature, under or over the melting point of the real material. The optimization (relaxation) run then ensues. For Pd we did precisely this on a supercell with 216 atoms, and generated, using ab initio techniques, three amorphous structures whose Pair Distribution Functions (PDFs or g(r)) are presented in Fig. 1. The bimodal structure of the “second” peak typical of amorphous metallic elements can be observed and that we herein identify as the “elephant” peaks (see inset) due to the resemblance to the profile of the elephant swallowed by a snake in the western children’s story Le petit prince by Antoine de Saint-Exupéry8.

Fig. 1 | Three Pair Distribution Functions (PDFs) for ab initio simulated amorphous palladium. The initially unstable supercell used contains 216 atoms and the inset depicts the elephant peaks8 typical of amorphous metallic elements. The average is solid grey.

The supercells were amorphized using three independent, but similar, processes; the results indicate that the final structures, determined through the PDF, are essentially the same. For a
discussion of the parameters used in the undermelt-quench approach we refer the reader to the Methods section. The molecular dynamics (MD) procedure was performed at a temperature of $T = 1,500 \text{ K}$, during 300 steps for a total duration of 1.5 ps. The evolution of the energy per atom during this process is depicted in Fig. 2a. The evolution of the energy per atom during geometry optimization (GO) is shown in Fig. 2c. Here the maximum number of steps was set to 1,000 to make sure it would adequately relax. The energy systematically diminishes until an arrangement of atoms in local equilibrium is reached.

![Energy per atom as a function of steps of MD.](image)

**Fig. 2** | Molecular dynamics and geometry optimizations for the three palladium supercells. a, Energy per atom as a function of steps of MD. b, Average magnetic moment per atom as a function of the MD steps. c, Energy per atom as a function of the GO steps. d, Average magnetic moment per atom per step of GO. The inset details the behaviour in the first 100 steps.

To investigate the magnetic properties, we ran both the MD and GO processes with unrestricted spin, so the magnetism would evolve freely and acquire a value congruent with a minimum energy structure. Figures 2b and 2d reflect the evolution of the average magnetic moment per atom, in Bohr magnetons $\mu_B$, as a function of the number of steps of MD and GO, respectively. The magnetic moment per atom begins to manifest in the first 50 steps of MD and increases until the end of the run, Fig. 2b. Afterwards, it increases somewhat during the GO process and tends to a
constant value, Fig. 2d. The inset shows details of the first 100 steps of GO. The average magnetic moment tends to 0.45 $\mu_B$ per atom.

How can we be sure that the PDFs obtained do represent the amorphous structure of bulk palladium and that therefore the average magnetic moment obtained corresponds to the amorphous phase? We could argue that since our previous results$^5$-$^7$ are very close to the experimental ones, the PDFs that we report in this work should be adequate to describe $\alpha$-Pd; however, since to our knowledge nobody has experimentally produced the pure amorphous phase, we decided to validate our topological findings by using some experiments reported in the literature. Experimentalists have found PDFs for amorphous palladium-silicon alloys: $\alpha$-Pd$_{85}$Si$_{15}$$^9$, $\alpha$-Pd$_{82.5}$Si$_{17.5}$$^{10}$ and $\alpha$-Pd$_{81}$Si$_{19}$$^{11}$, so we first compare the total PDFs they report for the alloys with our simulated PDF for the pure; Fig 3a, where the similarities can be observed. We next compare, in Fig. 3b, our simulation with the experimental result by Masumoto et al.$^{12,13}$ for a Pd-Pd partial; the agreement is spectacular. For reference purposes the peaks that describe the atomic positions in crystalline Pd ($\lambda$-Pd) are also presented. The simulated PDF for the pure is the average value displayed in Fig. 1. A more detailed study of $\alpha$-PdSi alloys is in the making (I.R. et al. Manuscript in preparation).

Fig. 3 | Comparison between total and partial experimental and simulated (solid grey) PDFs. a, Total PDF for the simulated $\alpha$-Pd and for the experimental $\alpha$-PdSi alloys. b, Total PDF for the simulated $\alpha$-Pd, partial Pd-Pd obtained by Masumoto et al.$^{12}$ and PDF for the crystalline structure. The agreement between our simulation and the experiment by Masumoto and coworkers (as reported in ref$^{13}$) is impressive.

But what about the magnetic properties discovered in our simulations? Is this topological structure indicative of some exciting, non-expected electronic or magnetic properties of $\alpha$-Pd? If we calculate the number of nearest neighbours (nn) by integrating the area under the first peak of the radial distribution function, we could infer that something is going on since it is smaller than 12, the number of nn in the crystalline fcc phase. This together with the overflow of electrons from the $d$ shell to the $sp$ shells may be an indicator of an unexpected behavior. However, since identifying unambiguously the cutoff value to calculate the nn in amorphous metals is a controversial subject$^{13}$ we opted for a complementary, direct approach, in a manner similar to our previous calculations on bismuth$^{14,15}$, and obtained the densities of electronic states with $\alpha$ spins and with $\beta$ spins to see if
they indicate a net magnetic moment, and they do, Fig. 4a. For this we used CASTEP\textsuperscript{16} in the suite of codes of Materials Studio\textsuperscript{17} as described in the Methods section.

Our electronic calculations indicate that the overflow of electrons invoked for crystalline Pd exists also in the amorphous 5s, 5p and 4d states, 4d\textsuperscript{10-x} (5s5p)\textsuperscript{x}; however, we claim that the spin band splitting in the absence of a magnetic field will be more preponderant in \(\alpha\)-Pd than in \(\chi\)-Pd and that the energy balance \(\Delta E = K (1 - UN(E_F))\) [with \(K = (\frac{1}{2})N(E_F)\) \(\delta E^2\) and \(U = \mu_0\mu_B^2\lambda\) (see ref\textsuperscript{1} p. 145)] will now be \(\Delta E = K (1 - UN(E_F) - Vf_B)\) where \(V\) indicates the contribution to the magnetic splitting of the unsaturated bonds \(f_B\) in the amorphous, because of Hund’s rule. This heuristic argument would lead us to a modified Stoner criterion for the stability of the amorphous palladium magnetic phase: \([UN(E_F) + Vf_B] \geq 1\), and the spontaneous ferromagnetism is possible for smaller values of \(UN(E_F)\).

**Fig. 4** | Calculated densities of states for our three ab initio simulated supercells of \(\alpha\)-Pd. \(\alpha\), for \(\alpha\) and \(\beta\) spins; a non-zero magnetism appears when the two types of spins are contrasted, indicating a net magnetic moment. \(\beta\), for the non-magnetic state, the number of unpaired electrons is set equal to zero at the start of an energy calculation (single point). The average of the three results is solid grey. The insets show the details at the Fermi level.

To quantify our results, we resort to calculating the traditional Stoner criterion \(UN(E_F) \geq 1\) for spin band splitting by first evaluating the areas under the spin-up and spin-down curves in Fig. 4a and then mapping these results onto a free-electron parabola to obtain the unbalance at the Fermi energy, \(\delta E\). Once we have these evaluations and the total density of states at the Fermi level for the non-magnetic state, 1.78 states eV\textsuperscript{-1} spin\textsuperscript{-1} atom\textsuperscript{-1}, Fig. 4b, then we obtain an average value of \(UN(E_F) = 1.42\) that satisfies the Stoner criterion and leads to a negative \(\Delta E = -0.02\) eV atom\textsuperscript{-1} (see the Extended Data section). This indicates that the magnetic state is more stable than the non-magnetic. The 1.42 value should be compared to those found for iron 1.43\textsuperscript{18}, or nickel 2.03\textsuperscript{18}, or even crystalline palladium 0.78\textsuperscript{18} so the validity of our results can be assessed.

Evidently, no calculation can force a material to behave in a certain manner, so the final judge is the experiment, needed to scrutinize the hitherto poorly known electronic, magnetic, vibrational, etc. properties of pure and alloyed non crystalline (amorphous and defective) metallic systems.
Recent experimental advances, commented in Ref\textsuperscript{19}, discuss the possibility of obtaining pure amorphous metals and these efforts may well be the beginning of a whole new field.

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Author Contributions R.M. Valladares, A.A. Valladares and A. Valladares conceived this research project. A circumstantial result by I. Rodriguez led us to a state of incredulousness followed by critical analysis, benchmarking and acceptance of the findings reported herein; all authors participated in these stages. The first draft of the paper was written by A.A. Valladares and all others contributed to the enrichment of subsequent versions.

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FIGURE LEGENDS

Fig. 1 | Three Pair Distribution Functions (PDFs) for ab initio simulated amorphous palladium. The initially unstable supercell used contains 216 atoms and the inset depicts the elephant peaks typical of amorphous metallic elements. The average is solid grey.

Fig. 2 | Molecular dynamics and geometry optimizations for the three palladium supercells. a, Energy per atom as a function of steps of MD. b, Average magnetic moment per atom as a function of the MD steps. c, Energy per atom as a function of the GO steps. d, Average magnetic moment per atom per step of GO. The inset details the behaviour in the first 100 steps.

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METHODS

The computational tools utilized are contained in the suite of codes Materials Studio\textsuperscript{16,17}. In particular, to perform the molecular dynamics and the geometry optimization, and to calculate the electronic and magnetic properties of \(\alpha\)-Pd, the code CASTEP was used\textsuperscript{16}. A crystalline palladium supercell of 216 atoms was constructed with diamond symmetry (unstable) and with the experimental crystalline density of 12.0 g/cm\(^3\); this instability allowed the undermelt-quench process to generate amorphous supercells, as mentioned in refs\textsuperscript{5-7}. The cell underwent three different and independent molecular dynamics (MD) processes and once they were complete the three resulting structures were subjected each to a geometry optimization (GO) procedure starting with a total spin of 93, 96 and 97 \(\mu_B\), respectively, the results generated by the MD procedure. The evolution of the energy and of the spin is shown in Figs. 2 in the main text. Figs. 2a and 2c are the results for the energy evolution whereas Figs. 2b and 2d are for the spin. Figs. 2a and 2b are for the MD processes and Figs. 2c and 2d are for the GO.

For the NVT molecular dynamics the following approximations were used. The PBE XC-functional with a zero spin initially; an electron energy convergence tolerance of \(2 \times 10^{-6}\) eV with a convergence window of 3 consecutive steps; a cutoff energy of 260 eV to generate the plane-wave basis to represent the 2160 electrons (10 per atom) distributed in 1297 bands (217 empty); a process at 1,500 K using a thermal bath controlled by a Nose-Hoover thermostat, with a time step of 5 fs during 300 steps, for a total duration of 1.5 ps and a Pulay mixing scheme. To optimize the MD process, the palladium ultrasoft pseudopotential, Pd\_00PBE.usp, included in the Materials Studio (MS) suite of codes was the choice.

For the geometry optimization the following parameters were employed. The minimization of the energy of the structure was performed with the density mixing method under the Pulay scheme; the functional PBESOL and the relativistic treatment according to Koelling-Harmon included in the MS suite; the energy cutoff for the plane waves was set to 300 eV; the 2160 electrons (10 per atom) were distributed in 1353 bands (226 empty). The initial spin was the output of the MD results: 93, 96 and 97 \(\mu_B\); an electron energy convergence tolerance of \(1 \times 10^{-6}\) eV with a convergence window of 2 consecutive steps and a smearing of 0.1 eV; the geometry energy tolerance used was \(1 \times 10^{-5}\) eV; the force tolerance used was \(3 \times 10^{-2}\) eV/Å; the displacement tolerance used was \(2 \times 10^{-3}\) Å and the geometry stress tolerance was set to \(5 \times 10^{-2}\) GPa.

To corroborate our results, we did some testing as follows. We calculated the average energy per atom, magnetic and non-magnetic, and we found that the non-magnetic value was -797.418 eV/atom and for the magnetic structure was -797.438 eV/atom. The magnetic structure is more stable and the difference of 0.02 eV/atom is of the order of the results calculated for some silicon phases, 0.016 eV/atom in going from silicon diamond, the stable phase, to hexagonal diamond\textsuperscript{20}. Once we found that bulk amorphous palladium was magnetic we did some \textit{ab initio} computational calculations for the crystalline unit cells of nickel (fcc) and iron (bcc), both with zero spin and with non-zero spin initially, using the same code (CASTEP) and the same parameters utilized for the palladium jobs, to test our results and procedures. When the initial spin was zero, our code and our approach led to non-magnetic results for both materials; this suggested that a magnetic trigger may be needed. When values of spin of 1 and 2 \(\mu_B\) per atom were assigned to nickel and 1 and 4 \(\mu_B\) to iron, the energy optimization run gave a net magnetic moment of 0.68 \(\mu_B\) per atom of nickel, for both runs, and 2.47 \(\mu_B\) per atom of iron, for both runs. Compare these results to experiment: 0.61 \(\mu_B\) per atom for Ni\textsuperscript{21} and 2.22 \(\mu_B\) per atom for Fe\textsuperscript{22}. We did something similar for a unit cell of gold and found no magnetism with or without an initial magnetic trigger. We also ran amorphous 216-atom supercells of copper and platinum, with and without an initial magnetic trigger, and found no remnant magnetism. This indicates that if our procedure is applied to all these materials it leads to results that are expected. We conclude that these results validate our findings for amorphous palladium.
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To quantify the Stoner criterion, \( UN(E_F) \geq 1 \), for the spontaneous spin band splitting we need to obtain the product \( UN(E_F) \) from our computer results. So, first we start from the equation for the total energy change between the magnetic and non-magnetic states \( \Delta E \) (see ref\(^1\) p. 146):

\[
\Delta E = \frac{1}{2} N(E_F) (\Delta E)^2 \left[ 1 - UN(E_F) \right],
\]

where \( N(E_F) \) is the non-magnetic result (obtained by setting the number of unpaired electrons equal to zero at the outset of an energy calculation) and \( \delta E \) is the difference between the highest energies for the magnetic and non-magnetic free electron gas. Hence the product \( UN(E_F) \) becomes

\[
UN(E_F) = 1 - \frac{2\Delta E}{N(E_F)(\delta E)^2}.
\]

To calculate \( \delta E \) we first obtain the value of the proportionality constant \(\alpha\) in the density of states for the free electron gas in three dimensions \( N(E) = \alpha \sqrt{E} \) by requiring that the integral from the bottom of the band to the Fermi level of the non-magnetic states integrates to 10 states eV\(^{-1}\)atom\(^{-1}\).

\[
\int_{0}^{E_F} N(E_F) dE = \int_{0}^{E_F} \alpha \sqrt{E} dE = 10,
\]

where the Fermi energy for the average of the non-magnetic states is \( E_F = 7.87 \) eV as seen in Fig. 4b and the proportionality constant is \( \alpha = 0.68 \) eV\(^{-\frac{1}{2}}\).

Next we evaluate the areas under the spin-up and spin-down curves in Fig. 4a, and then map them onto the free electron parabola to obtain the unbalance at the Fermi energy, \( \delta E \), to finally calculate \( UN(E_F) \). The results are given in the Table above.

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### Table 1. Energy, magnetism and Stoner parameter for the three palladium amorphous supercells studied.

| System       | Total energy per atom (eV) | Average Magnetic moment (μB) | \( \Delta E \) (eV) | \( \delta E \) (eV) | \( UN(E_F) \) |
|--------------|----------------------------|------------------------------|---------------------|---------------------|----------------|
|              | Magnetic                   | Non-magnetic                 |                     |                     |                |
| a-Pd\(_{100}\)-I | -797.4391                  | -797.4178                    | 0.45                | -0.021              | 0.22           | 1.50           |
| a-Pd\(_{100}\)-II | -797.4323                  | -797.4178                    | 0.45                | -0.015              | 0.23           | 1.31           |
| a-Pd\(_{100}\)-III | -797.4427                  | -797.4189                    | 0.44                | -0.024              | 0.23           | 1.50           |
| Average      | -797.4380                  | -797.4181                    | 0.45                | -0.020              | 0.23           | 1.42           |