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Onset of room temperature ferromagnetism by plastic deformation in three paramagnetic pure metals

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ABSTRACT

This work shows that plastic deformation may trigger a spontaneous magnetization at ambient temperature in pure paramagnetic metals such as zirconium, titanium and magnesium. Subsequent strain relaxation by annealing leads to a decrease of the permanent magnetization. We propose that the lattice distortions associated with dislocations promote the emergence of ferromagnetism at the nanometric scale. Evidence for this explanation is the simultaneous observation, in pure Zr, which in the undeformed state exhibits Pauli paramagnetism, of a decrease in the susceptibility and of the absolute value of the magnetization at high fields with increasing deformation.

The search for magnets with high Curie temperatures (T_c) is of great practical interest. However, room temperature ferromagnetism is a rare phenomenon [1,2]. Only four pure elements, namely Fe ($T_c = 1043$ K), Co ($T_c = 388$ K), Ni ($T_c = 627$ K), and Gd ($T_c = 289$ K), exhibit this behavior. Ferromagnetism in itinerant electron systems, as is the case for delocalized electrons of metals, is achieved when at the energy band both the exchange interaction, J, and the density of states at the Fermi level, $N(E_F)$, are high enough to obey the Stoner criterion, $JN(E_F) > 1$ [1,2]. Under this condition both spin sub-bands are unequally populated and, thus, a net magnetic moment at temperatures below T_c is spontaneously induced. Since 1935, when room temperature ferromagnetism was discovered in Gd [3], no other pure elemental room temperature magnets have been identified. This paper demonstrates how room temperature ferromagnetism may be induced in classic paramagnetic pure metals subjected to sufficient levels of strain.

We start with commercially pure (CP) rolled and annealed α-Zirconium (99.98% purity), purchased from Haines & Maassen, Bonn, Germany, in the form of $(5.2 \times 140 \times 200)$ mm^3 rolled slabs. The average grain size is 17 μm. Disks of 10 mm diameter and 1 mm in thickness were machined out of the as-received slabs and were then strained at room temperature ($T/T_m \approx 0.14$) by the simultaneous application of compression and shear in a constrained high pressure torsion (HPT) die-set [4] using a pressure of 6 GPa and 10 full rotations of the anvil (at an approximate speed of 1 rpm). The final thickness of the processed disks was approximately 0.8 mm. The equivalent true strain imposed (ε), which is a function of the disk radius (r), is given by the following equation [4]:

$$\varepsilon = \ln\left(\frac{2\pi N \cdot r \cdot h_0}{h^2}\right) \quad (1)$$

where h_0 and h are, respectively, the initial and final thicknesses of the disk, and N denotes the number of anvil turns.

The magnetic behavior of pure Zr in the as-received condition and after HPT severe straining to ε ~ 6 (r ~ 3.5 mm) was measured using a Quantum Design Physical Property Measurement System vibrating sample magnetometer (PPMS-VSM), with a maximum field of 2 T, on encapsulated samples. The room temperature hysteresis loops corresponding to the as-received and to the severely strained pure Zr are compared in Fig. 1(a). As expected, the undeformed pure Zr is paramagnetic ($\chi_m = 1.2 \times 10^{-6}$ emu/gOe). However, deformation clearly gives rise to the emergence of a ferromagnetic component. It has been reported earlier that HPT processing of pure Zr under similar conditions to those utilized in the present study may lead to the stabilization of different volume fractions of the ω and β-Zr phases under ambient conditions [5,6]. However, all pure Zr allotropic phases are known to exhibit a paramagnetic behavior [7] and therefore the observed emergence of ferromagnetism cannot be attributed to the presence of the ω and β phases in the deformed specimens. The observed increase in the Fe content in the deformed sample due to contamination from the HPT anvils (Table 1) can also be ruled out as the cause for the emergence of ferromagnetism. Indeed, it can be clearly seen in Fig. 1(a) that in the deformed Zr sample, exhibiting magnetic hysteresis at low fields, the

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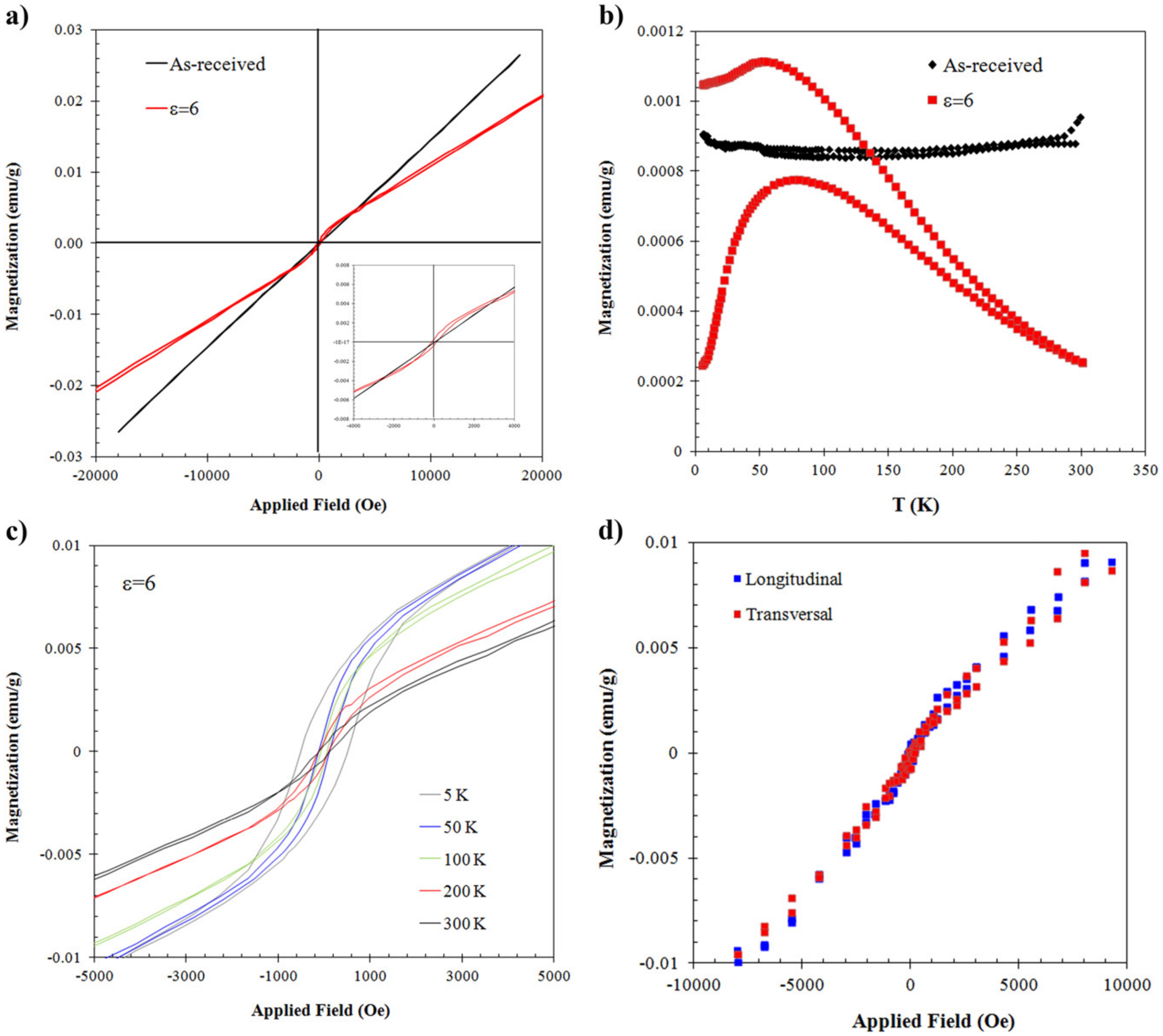

Fig. 1. Magnetic behavior of pure Zr in the undeformed state and after HPT processing using 6 GPa and 10 anvil turns (N = 10, ε ~ 6). (a) Room temperature behavior; (b) variation of the magnetization with temperature at 100 Oe; (c) variation of the hysteresis loops corresponding to the HPT processed sample with temperature; (d) magnetic behavior of the HPT processed sample along two perpendicular directions.

high field paramagnetic susceptibility becomes approximately 40% lower than that corresponding to the undeformed sample. If the hysteresis were due to Fe impurities they should be almost saturated under fields of 2 T. Thus, the experimentally observed 40% decrease of the paramagnetic susceptibility would mean that the impurities (with negligible susceptibility) constituted approximately 40% of the sample mass, which seems illogical. Furthermore, the absolute value of the magnetization at high fields is 40% higher for the undeformed sample. This observation further rules out any relevant contribution of Fe impurities introduced by the HPT anvil, given that their contribution should be the opposite one (i.e., their presence should result, instead, in an overall increase in the value of the magnetization at high fields).

Table 1
Chemical composition (ppm) of the pure Zr in the undeformed state and after HPT processing using 6 GPa and N = 10 at room temperature up to strains of ε ~ 6.

	K	Na	Fe	Cu	P	Ti	Zn	Cr	Mg	S	Zr
As-received	137	20	214 ± 55	14	78	21	10	14	5	6	Bal.
ε ~ 6	77	37	611 ± 47	382	12	33	133	35	2	70	Bal.

Fig. 1(b) illustrates, furthermore, the thermal independence of the magnetization of the undeformed Zr, a clear manifestation of Pauli paramagnetism and, consequently, of the direct dependence of its susceptibility on the density of states at the Fermi level. A very different thermal dependence of the magnetization, with a typical contribution of localized magnetic moments, was measured in the deformed Zr samples. Finally, Fig. 1(c) illustrates the hysteresis cycles corresponding to temperatures ranging between 5 K and 300 K and Fig. 1(d) shows the magnetic behavior along two perpendicular directions. From the latter it can be inferred that there is no magnetic anisotropy. This seems consistent with the fact that, at such high strains, the distribution of strain-induced defects is in general rather homogeneous [4]. In summary, the data in Fig. 1 clearly prove that, in the deformed pure Zr, in some regions there is an increase the paramagnetic susceptibility, sometimes reaching the onset of ferromagnetism, whereas other regions must undergo a strong decrease of the susceptibility. Both effects can be nicely related with the tensile and compressive stress fields associated to dislocation cores, which would have opposite contributions to the local density of states. Indeed, a common feature of metals deformed severely at temperatures well below their melting point, such as the pure