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Tuning the magnetic properties of pure hafnium by high pressure torsion



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ABSTRACT

This work demonstrates that room temperature (RT) ferromagnetism might be triggered in pure hafnium (Hf), a classic paramagnet, by severe plastic deformation (SPD) via high pressure torsion (HPT). The origin of this phenomenon is elucidated by a combined approach including density functional theory (DFT) calculations and transmission electron microscopy (TEM). In particular, it is shown that the elastic lattice distortions induced in pure Hf as a consequence of grain refinement down to the nanocrystalline regime by HPT lead to the development of a new monoclinic crystalline structure that exhibits a spontaneous magnetization at RT. DFT calculations are utilized to prove that local stretching of the original pure Hf hexagonal close packed (hcp) lattice along specific pyramidal directions, due to the presence of internal stresses in the deformed nanostructure, may give rise to the emergence of the monoclinic phase, which is endowed with a net magnetic moment. An excellent agreement is found between DFT calculations and experimental TEM observations, which provide a first evidence of the presence of the pure Hf monoclinic crystal lattice. This work shows that SPD may constitute a viable, yet widely unexplored, strategy to tune the magnetic properties and, in particular, to induce RT ferromagnetism in bulk non-magnetic metals.

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1. Introduction

Room temperature ferromagnets are critical to a wide range of applications in key industrial sectors including energy generation and storage, electronics, biomedicine, and transport [1]. The emergence of spontaneous spin ordering in metals is achieved, according to the Stoner criterion [2,3], when the product of the density of states at the Fermi level, $N(E_F)$, and the exchange interaction, J , is greater than 1. Unfortunately, only a handful of pure metallic materials (Fe, Co, Ni, Gd) exhibit room temperature ferromagnetism [4,5]. The vast majority of metals are considered non-magnetic (paramagnetic or diamagnetic) since, although they

can be weakly magnetized in the presence of an external field, their magnetization vanishes once the field is withdrawn [6].

Attempts to trigger ferromagnetism in diamagnetic and paramagnetic metals and alloys without altering their chemical composition must devise alternative ways to modify permanently their electronic properties. This has been accomplished only in a few cases and mostly at a local scale. Sampedro et al. [7] have reported RT ferromagnetism in 2.4 nm size twinned Pd nanoparticles, a phenomenon that was attributed to lattice distortions in the vicinity of the twin boundaries. Similarly, Crespo et al. [8] observed RT ferromagnetism in thiol capped 1.2 nm size Au nanoparticles due to the presence of 5d localized holes generated through Au–S bonds. Finally, Al Ma'Mari et al. [9] have demonstrated that it is possible to overcome the Stoner criterion at RT in 2 nm thick copper films interfaced with C_{60} molecular layers. It has recently been shown that bulk RT ferromagnetic behavior may be induced in

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paramagnetic metals such as titanium, zirconium and magnesium by straining [10]. The origin of this phenomenon remains, however, widely unknown.

Elastic strain engineering (ESE) has been recently put forward as an efficient method to design materials with unprecedented properties [11]. This methodology exploits the fact that nanostructured materials such as thin films, nanowires, nanoparticles, bulk nanocomposites, and atomic sheets can withstand anomalously high non-hydrostatic (e.g., tensile or shear) stresses, and are thus able to sustain much larger elastic strains than in bulk, coarse grained, form. The dramatic alterations of the elastically strained crystal structures with respect to their relaxed counterparts lead to the emergence of unique functional properties. For example, it has recently been shown that inhomogeneous elastic strain can be utilized to tune the bandgap of an initially homogeneous monolayer membrane of MoS₂, allowing it to capture a broader range of the solar spectrum, and thus increasing its potential for photovoltaic devices [12,13]. It has also been demonstrated by first-principles calculations that ESE can be a very useful tool to control the bandgap and, thus, the electronic and optical properties of zigzag BN nanoribbons [14], thus increasing their applicability in electronic, piezoelectric, photovoltaic, and opto-electronic devices. Furthermore, elastic strain can also be utilized to enhance the properties of known ferroic oxides, to convert oxides that are neither ferroelectric nor ferromagnetic in their unstrained state into ferroelectrics, ferromagnets or multiferroic materials, or to create new tunable microwave dielectrics with outstanding performance [15]. Strain has also been widely utilized with great commercial success in Si technology to enhance the carrier mobility [16], as well as to boost the chemical reactivity and the electrocatalytic properties of metal and oxide surfaces [17], or to alter the lattice parameter and, thus, the electronic states, of semiconductor nanowires [18]. Finally, it has recently been shown [19] that, under an applied load which leads to elastic strains slightly larger than 5%, it is possible to increase the superconducting transition temperature and the critical magnetic field of kilogram scale Nb nanowires embedded in a metallic matrix. The potential of ESE to design materials with singular functional properties is still largely unexplored. In particular, to date, no studies have applied this methodology to tune the magnetic behavior of metals.

Pure Hafnium is a transition metal belonging to Group IV of the periodic table. Under equilibrium conditions it exhibits a hcp lattice (α) at 100 kPa (1 atm) and 298 K. This phase undergoes a wide range of solid state phase transformations when subjected to high temperatures and high pressures [20]. In particular, upon heating, hcp Hf transforms into a body centred cubic (bcc) structure (β) at 2016 K before reaching the melting temperature. With increasing isostatic pressure, at RT, hcp Hf transforms into a simple hexagonal lattice (ω) at 30–35 GPa and into a bcc lattice at 70 GPa [21]. Recent work [22] has shown that a face centred cubic (fcc) form of pure Hf can be stabilized by high energy milling of powders. This was accompanied by a lattice expansion of about 6%. To our knowledge, no other pure Hf crystalline structures have been reported so far.

This paper reports how pure hcp Hf can be partially transformed by severe straining into a monoclinic phase that exhibits RT ferromagnetic behavior. Several samples of the original, coarse grained, material, were processed at RT by HPT using a pressure of 6 GPa and 5 anvil turns. The resulting nanostructures, which are shown to exhibit a ferromagnetic component, are exhaustively characterized by TEM. DFT calculations are then utilized to gain further insight about the source of the emerging ferromagnetism, which is found to be originated by the elastic strains induced in the nanocrystalline processed pure Hf as a consequence of the high density of interfaces. This work provides solid evidence of the

possibility of tuning the magnetic behavior of metals by severe straining.

2. Experimental procedure

Polycrystalline pure Hf (99.7% purity, Table 1) was purchased in the form of a 10 mm diameter round bar. Disks with a thickness of 1 mm were sliced out of the as-received bar and were then severely strained at 298 K by high pressure torsion (HPT) [23]. An unconstrained setup, consisting of a bottom anvil with a flat surface, where the sample is placed, and a top anvil that exerts a pressure on the specimen and, subsequently, rotates a predetermined number of turns, was utilized. A pressure of 6 GPa and 5 full rotations of the anvil (at an approximate speed of 1 rotation per minute) were applied. The final thickness of the deformed samples was approximately 0.2 mm. The equivalent true strain imposed (ϵ), which is a function of the disk radius (r), is given by the following equation [22]:

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

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

The magnetization curves of the as-received and deformed pure Hf were measured between RT and 5 K using a Physical Property Measurement System vibrating sample magnetometer (PPMS-VSM) and a Magnetic Property Measurement System (MPMS-SQUID), both from Quantum Design, with a maximum field of 5 T. Measurements of the magnetic behavior were carried out in 3 mm-diameter and 200 μm -thick foils punched out of the disks processed by HPT. In particular, the center of the foils was approximately located, respectively, at r values of 0.025 mm and 3.5 mm. At these points, according to equation (1), the corresponding true strains are, respectively, ~ 3 and ~ 8 . These foils were subsequently annealed at 1273 K for 5 h and their RT magnetization curves were also measured.

The microstructure of the as-received and annealed samples was examined by scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) using a field emission gun SEM (Helios NanoLab 600i, FEI) equipped with an HKL EBSD system, a CCD camera and the Channel 5.0 data acquisition and analysis software package. EBSD measurements were conducted at an accelerating voltage of 15 kV and 2.7 nA. The average grain size values were calculated by the linear intercept method from SEM and EBSD maps in the normal direction to the disk surfaces. Sample preparation for EBSD included mechanical mirror-polish using first diamond pastes of increasingly finer particle sizes and then a colloidal silica slurry finishing. Final surface finishing was carried out by electropolishing using a solution of 90% perchloric acid and 10% acetic acid and a voltage of 20 V. The nanostructure of the deformed specimens was analyzed by transmission electron microscopy using a 200 kV Talos F200X (FEI) microscope. With that purpose, the foils that were utilized for magnetic characterization, corresponding to strains of ~ 3 and ~ 8 , were mechanically thinned to about 100 μm followed by electrochemical polishing to electron transparency at RT in a Struers Tenupol-5 double-jet twin electropolisher using a solution of 90% perchloric acid and 10% acetic acid

Table 1

Chemical composition (ppm) of the pure Hf in the as-received state and after HPT processing using 6 GPa and $N = 5$ at RT up to strains of $\epsilon \sim 8$.

	Ca	K	P	S	Pd	W	Zr	Ag	Pt	Fe	Hf
As-received	–	–	–	67	75	1585	1187	19	16	142	Bal.
$\epsilon \sim 8$	17	208	178	47	90	1647	1234	32	8	207	Bal.

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