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Magnetic properties of epitaxial gadolinium hydride films

P. Tessier[a,*], D. Fruchart[a], D. Givord[b,1]

[a]*Laboratoire de Cristallographie, CNRS, 25 avenue des Martyrs, BP166 38042, Grenoble Cedex 9, France*
[b]*Laboratoire Louis Néel, CNRS, 25 avenue des Martyrs, BP166 38042, Grenoble Cedex 9, France*

Abstract

Epitaxial gadolinium films were synthesized by pulsed laser deposition on a molybdenum layer itself grown on a sapphire substrate. These films exhibit high structural order, as shown by RHEED and X-ray diffraction. The structure of hydrogenated films were also studied. The magnetic properties of gadolinium and gadolinium hydride were measured in a vibrating sample magnetometer at temperatures ranging from 10 K to room temperature. Unexpectedly, films hydrogenated at 0.5 MPa for 30 min remain partly ferromagnetic. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Gadolinium films; Magnetic properties; X-ray diffraction; RHEED

1. Introduction

Metal hydrides are the subject of intense research activity for energy storage applications [1]. More recently they have attracted interest because of the dramatic change in optical transmission that occur upon hydrogen absorption in rare-earth thin films protected by a palladium protective layer. 'Switchable mirrors' can be fabricated where the optical transmission follows hydrogen pressure [2] or the voltage in a thin electrochemical cell [3]. The metal–semiconductor transition in these systems was related to the creation of low-energy bonding states which take electrons down from the conduction band. It is natural to wonder how magnetism that strongly depends on the valence band states is affected in such systems. One would expect interactions between magnetic moments to switch from a RKKY-type to a dipolar interaction. We therefore undertook a study of the magnetic properties of thin films in the Gd–H system. Gd is a ferromagnetic metal ($T_C = 293$ K) with large magnetization at low temperatures, theoretically 7.5 μ_B per atom at absolute zero. The hydride GdH_2 is antiferromagnetic ($T_N = 18.5$ K) [4]. Furthermore, in order to provide more precise information, we attempted making epitaxial films of gadolinium.

2. Experimental procedure

We synthesized our films by pulsed laser deposition according to the procedure previously described in Ref. [5]. We used a ultra-high vacuum chamber equipped with a quartz microbalance for deposition rate calibration. The pressure was close to 2×10^{-11} Torr prior to and 10^{-10} Torr during deposition. A frequency-doubled Nd–Yag laser was used at an average power close to 1 W and defocalisation of about $f/5$. Sapphire (Al_2O_3) single-crystal substrates were thoroughly cleaned prior to being annealed 1 h at 800°C. Pure metallic targets were used. Deposition was first done on a test substrate which was repeatedly analyzed by Auger spectroscopy inside the ultra-high vacuum apparatus until the deposited layer was free of oxygen or other impurities. At specific times, reflection high energy electron diffraction (RHEED) was performed to verify the quality of the films (roughness, crystallographic orientation). The acceleration voltage of the electron beam used for RHEED was 10 kV.

A 50 Å thick molybdenum (110) was first deposited at 200°C. It was subsequently heated up to 800°C and cooled. This considerably improved the structural quality and reduced the roughness of the films as evidenced by the narrowing of the RHEED streaks. The purpose of the Mo buffer is to prevent oxidation of gadolinium during annealing. Gadolinium (50 Å) was deposited at 200°C, heated, usually up to around 600°C, and cooled. As in the case of the Mo layer, heat treatment greatly enhanced structural quality. The growth of the Gd layer occurred along the (001) axis. Deposition was resumed at room temperature.

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*Corresponding author. Present address: Nano Technologies Inc., c/o Institut de Recherche d'Hydro-Québec, 1790 boul. Lionel-Boulet, Varennes, Québec, J3X 1S1, Canada.

[1] Present address: Laboratoire National des Champs Magnétiques Pulsés (LNCMP), Institut National des Sciences Appliquées de Toulouse, 135, avenue de Rangueil, 31077 Toulouse Cedex 4, France.

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After Gd deposition was completed, the film was again heat-treated at 600°C. Films of Gd thickness between 400 and 800 Å were made. Finally, a 100 Å Pd protective layer was deposited, which proved to be polycrystalline. This is not a concern since its role was to prevent oxidation while permitting the passage of hydrogen to the gadolinium layer. No oxidation was observed even after several months.

Hydrogenation was done by exposing the films to 0.5 MPa of pure hydrogen at room temperature for 30 min. As-deposited and hydrogenated films were characterized by X-ray diffraction using Fe Kα radiation. Magnetization curves were measured at 10, 100, 200 and 290 K at fields up to 6.5 T in a vibrating sample magnetometer (VSM). A Mo 50 Å/Pd 100 Å film was used to subtract any signal other than that of gadolinium.

3. Results and discussion

The X-ray diffraction pattern of an as-deposited Mo 50 Å/Gd 600 Å/Pd 100 Å film is shown at the top of Fig. 1. An extremely sharp and strong sapphire peak (exceeding the scale of the graph) is clearly seen close to 48°. Its intensity relative to other peaks tend to vary significantly since its sharpness makes it very sensitive to any minor misalignment of the sample in the diffractometer. Only peaks corresponding to the (001) axis of the hexagonal Gd structure are visible, (002) at 39° and (004) at 84°. A small peak at 37° may be attributed to GdH_2 (111) and a even smaller one around 36° could be fcc pure gadolinium, which has the same type of structure as the Gd sublattice of GdH_2. The broad and faint peak at 51° corresponds to the most intense reflection of both molybdenum and palladium.

Upon hydrogenation, the Gd peaks shift to lower angles as the plane spacing increases to accommodate hydrogen atoms (centre part of Fig. 1). This result indicates that the gadolinium lattice expanded perpendicular to the substrate while retaining its epitaxial relationships to the Mo layer. The sapphire peak is unchanged, but a companion peak associated with Fe Kβ radiation is seen in this case at 44°. The Gd peaks are those of the GdH_3 phase whose Gd sublattice is the same type of structure as pure gadolinium. By visual inspection of the hydrogenated films, we noted an increased optical transmission compared to the as-deposited films.

During the course of our experiments we found that hydrogenated films would decompose over several hours or days. The GdH_3 phase slowly transformed into GdH_2. The X-ray pattern of the decomposed film is shown at the bottom part of Fig. 1. Some GdH_3 is still visible. Upon transforming to GdH_2 the structure has to go through extensive rearrangment of the planes, since it must change from the ABABAB stacking of the hexagonal phase to the ABCABC stacking of the face-centred cubic phase. A highly twinned structure is expected in the decomposed films. It is possible to revert to the GdH_3 phase by hydrogenating the films again. In fact we repeated this operation several times, each time going from GdH_3 to GdH_2 and back. The rate of transformation of the hydrogenated films to the decomposed state appeared to accelerate over time, showing that some hysteresis phenomenon gradually decreased.

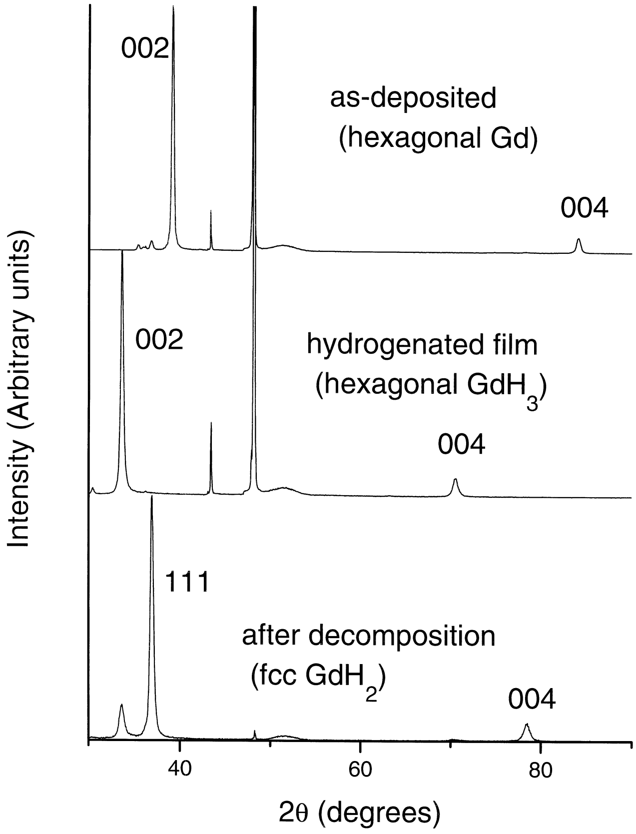

Fig. 1. X-ray diffraction patterns of an as-deposited film (top), a hydrogenated film (center) and a film after decomposition (bottom).

4. Magnetic properties

Fig. 2 shows magnetization loops performed at 10, 100, 200 and 290 K on an as-deposited film. The curves are typical of a soft ferromagnetic metal. The light slope at high fields may be due to some hydrogen contamination during storage of the film, as seen by X-ray diffraction (Fig. 1). The same magnetization loops for a hydrogenated film is shown in Fig. 3. A surprising feature is the persistence of a ferromagnetic signal up to 290 K and, seemingly, above room temperature. By using a linear fit of the curves at high field, we have extracted the saturation magnetization of the ferromagnetic part and plotted it in Fig. 4. The ferromagnetic signal drops between 10 and 100 K but remains almost constant as the temperature is raised

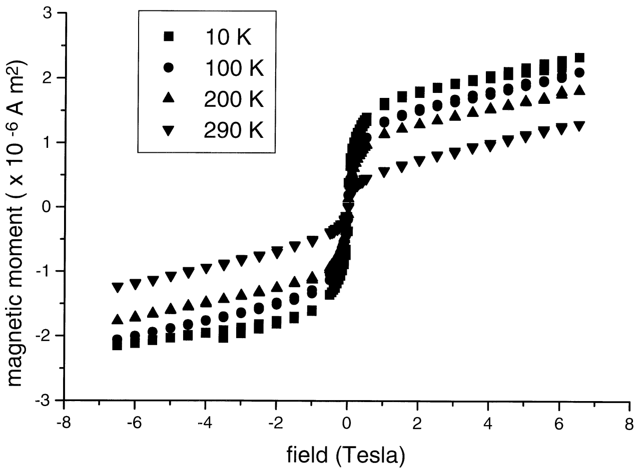

Fig. 2. Magnetization curves for an as-deposited film.

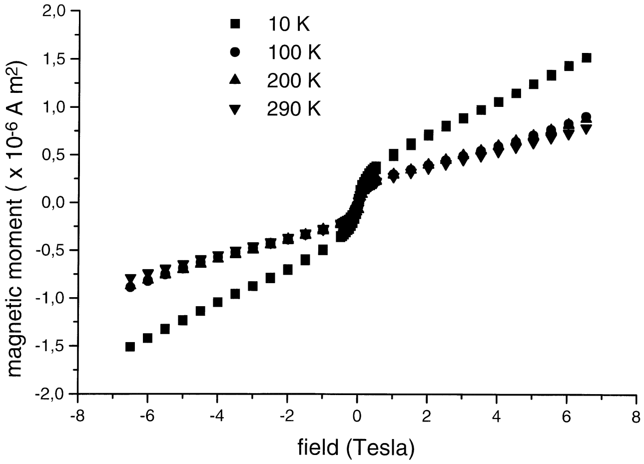

Fig. 3. Magnetization curves for a hydrogenated film.

further. The magnetic susceptibility exhibits a similar behaviour (Fig. 5).

As we explained in the previous section, these hydrogenated films decomposed over time. The magnetization curves of such a decomposed film are shown in Fig. 6. In this case, the ferromagnetic signal vanishes between 10 and 100 K (Fig. 7), while the magnetic susceptibility at high field varies somewhat less than that of the hydro-

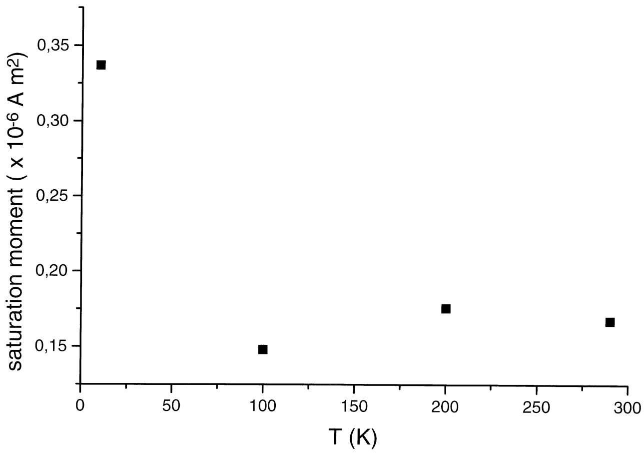

Fig. 4. Saturation moment for a hydrogenated film.

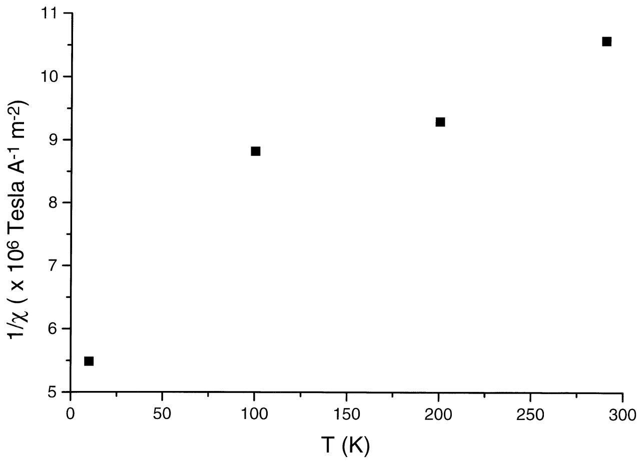

Fig. 5. Inverse of the susceptibility for a hydrogenated film.

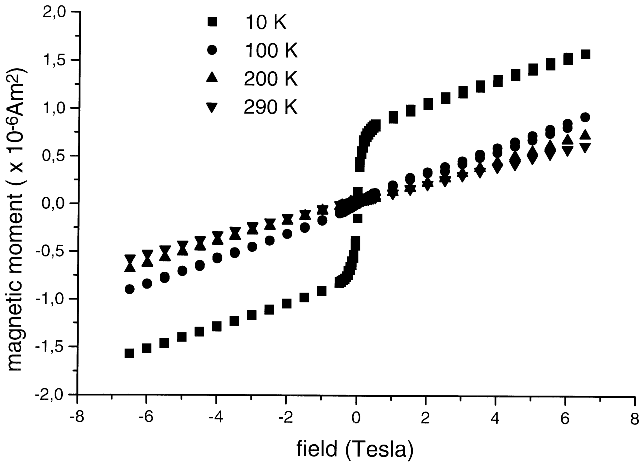

Fig. 6. Magnetization curves for a decomposed film.

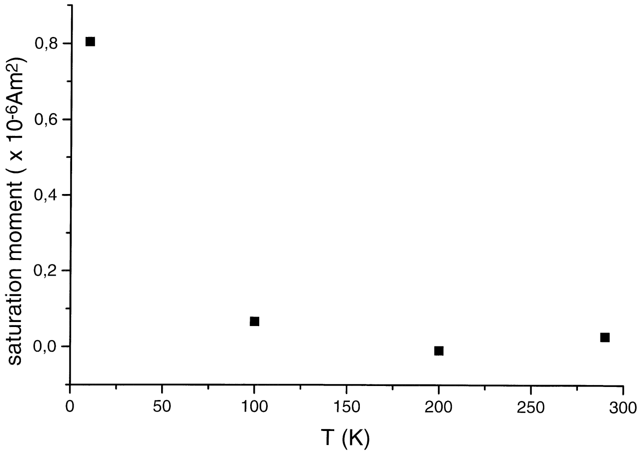

Fig. 7. Saturation moment for a decomposed film.

genated film. It is consistent with antiferromagnetic ordering. We are confronted by a paradoxical situation where, of two materials with different hydrogen concentrations, that containing more hydrogen exhibits a ferromagnetic component to a much higher temperature.

Our hypothesis to explain this situation is the hydrogenated film contains some amount of pure (hydrogen-free) gadolinium. It is known from several studies on hydride multilayers [6] that at the interface with a non-absorbing metal (in our case molybdenum), several layers of hydrogen storage sites in a hydrogen-absorbing metal will remain empty. In our case, we assume that epitaxial stress also plays a strong role. To explain the fact that pure Gd is not observed in the X-ray diffraction pattern of hydrogenated films (Fig. 1), we have carried out numerical calculations of simulated X-ray patterns of a GdH_3 film having uncharged layers. The calculation is done for a 600 Å film with varying amounts of pure Gd (Fig. 8). What we find is that significant amounts (up to approximately 20%) of pure Gd can be present without producing noticeable X-ray peaks. We cannot go as far as establishing a quantitative relationship between the X-ray simulation and the magnetic measurements, but we are confident that they support our hypothesis. Other facts can contribute to lowering the X-ray signal from pure Gd: strain, out-of-phase contribution from disconnected areas of Gd phase and so on.

In the decomposed film, the pure Gd has absorbed some hydrogen (GdH_ϵ), giving a strong ferromagnetic signal but having a low Curie temperature. At the same time GdH_3 has transformed to GdH_2 which is responsible for the antiferromagnetic contribution to the magnetization curves. The fact that the ferromagnetic signal at 10 K is so strong could be due to proximity effects between the two phases. Such a proximity effect was already discussed in terms of low temperature interaction of ferromagnetic and antiferromagnetic regions [7]. The difference in composition of the GdH_ϵ phase between the hydrogenated and decomposed films might be related to a higher interfacial energy between GdH_2 and Gd than between GdH_3 and Gd, because of the symmetry-breaking of the three-fold axis of the face-centered cubic structure of GdH_2 (one of four) which are not perpendicular to the interface. Looking back at the saturation magnetization of the hydrogenated film (Fig. 4), the decrease between 10 and 100 K suggests that a small amount GdH_ϵ is also present.

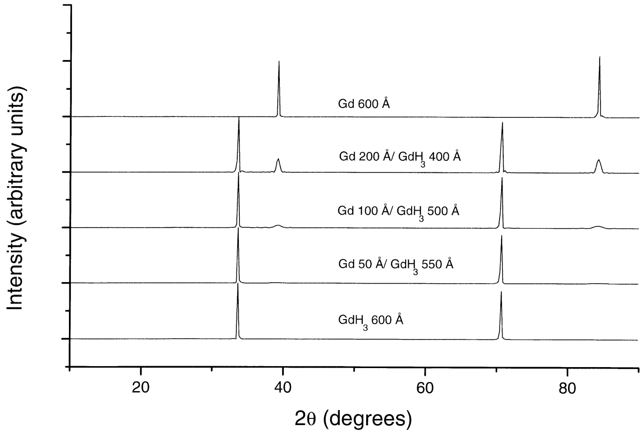

Fig. 8. Simulated X-ray diffraction patterns of a 600 Å (initial thickness) film for different thickness of uncharged gadolinium, from 0 (bottom) to 600 Å (top), and corresponding thickness of GdH_3.

5. Conclusion

We have studied the structural modifications in epitaxial gadolinium films upon hydrogenation. Protected by a palladium cap layer, the films readily absorb hydrogen, forming mainly GdH_3, but then slowly decomposing. The decomposed films contain mostly GdH_2. Subsequent hydrogenation reverses the transformation and it is possible to alternate reversibly between the hydrogenated and decomposed states. The hydrogenated film remains ferromagnetic up to room temperature, a fact tentatively explained by the presence of a hydrogen-poor phase whose small domain size prevents its detection by X-ray diffraction.

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