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Magnetism in Gd–W films*

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Vapor condensation techniques are useful to prepare magnetic alloys whose components have low or even negligible equilibrium mutual solubility. In this work, one of these techniques—sputtering—was used to obtain $\mathrm{Gd}_x\mathrm{W}_{1-x}$ alloys whose magnetic properties were investigated as a function of the Gd atomic concentration x. Gadolinium and various Gd-based alloys are promising materials for magnetic refrigeration and this was one of the motivations for this study. The $\mathrm{Gd}_x-\mathrm{W}_{1-x}$ films were sputter deposited from Gd and W targets with x ranging from 0 to 1 as determined by x-ray energy-dispersive spectroscopic analyses. X-ray diffraction patterns indicate that crystalline structures were formed at low and high Gd concentrations, while at intermediate concentrations, the films were amorphous. Magnetization measurements, performed as a function of temperature and with static and alternating applied fields, reveal a spin glasslike behavior in all the W-containing samples for temperatures below the freezing temperature T_f. For low and intermediate Gd concentrations, and for $T > T_f$, the films were paramagnetic, while a ferromagnetic phase was observed in the Gd–W alloy of the highest Gd content. The magnetocaloric effect was investigated from the magnetization isotherms M versus H, from which the isothermal magnetic entropy variation ΔS_M as a function of T, for the removal of an applied field of 50 kOe, was determined. It was observed that the maximum value of ΔS_M for each ΔS_M versus T curve and the temperature at which these maxima occur, are strongly dependent on x. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2838462]

I. INTRODUCTION

Gadolinium-containing magnetic materials have been intensively investigated. The high atomic moment of Gd may be responsible for the relatively high magnetic susceptibility in the material, which is usually appropriate for various applications such as magneto-optical devices[1] and magnetic refrigeration.[2] Pronounced magnetocaloric effects (MCEs) have been observed in various Gd alloys such as Gd–Si–Ge,[3,4] Gd–Tb–Si,[5] and Gd–X (X=Tb,Zn,Y).[6] An important detail in the MCE of Gd-based alloys stems from the Curie temperature T_C of Gd which is nearly 293 K, implying that it is possible to prepare Gd-containing materials with T_C around that of Gd, very promising in magnetic refrigeration starting at ambient and near-ambient temperatures.

In this paper, the magnetic properties and the MCE of $\mathrm{Gd}_x\mathrm{W}_{1-x}$ films are investigated as a function of the Gd atomic concentration x. Since Gd and W have a negligibly small mutual solubility in the equilibrium state, a vapor quenching technique—sputtering—has been used to synthesize the Gd–W alloys. Since the thicknesses of the films are equivalent to hundreds of atomic monolayers, the magnetic behaviors usually observed in films of a few monolayers thick[7,8] are not seen in this work. X-ray diffractometry was used for the structural investigation, while the magnetization and other magnetic parameters (susceptibility, Curie–Weiss and freezing temperatures) were obtained from measurements of the magnetic moment of the samples as a function of temperature and applied static and alternating fields. Special attention was given to the MCE of the films, represented by the curves ΔS_M versus T, where ΔS_M is the isothermal magnetic entropy change due to the removal of a high magnetic field and T is the temperature. While the temperature, T_h, corresponding to the maximum of the ΔS_M versus T curve for the Gd ($x=1$) film is similar to that for bulk polycrystalline Gd,[9,10] widely different T_h values were observed for the $\mathrm{Gd}_x\mathrm{W}_{1-x}$ films. To the best of our knowledge, this is the first investigation on the MCE of the Gd–W system.

II. EXPERIMENTAL

Films were obtained by magnetron sputtering from separate Gd and W targets by using Ar at a flow rate of 25 SCCM (SCCM denotes cubic centimeter per minute at STP) as the sputtering gas. The chamber base pressure was about 1×10^{-5} Pa. Silicon (001) slabs were used as substrates. Depositions were carried out with the substrate holder at room temperature. Film thicknesses d were in the range of 200–500 nm measured by using a high resolution profile meter. The film masses were determined by using the Gd and W atomic proportions, their respective bulk densities, atomic masses, and film volumes.

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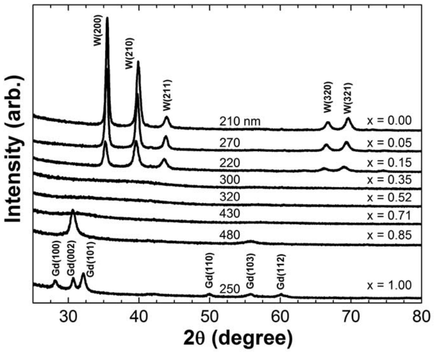

FIG. 1. Grazing incidence angle x-ray diffraction patterns of Gd_xW_{1-x} films for various Gd concentrations. The film thicknesses are indicated in each pattern.

Grazing incidence angle x-ray diffraction was employed to investigate the crystalline structure of the films by using the Cu $K\alpha$ radiation (0.154 518 nm). The Gd atomic concentrations were determined by using x-ray energy-dispersive spectroscopic analysis.

A superconducting quandum interference device magnetometer was used to measure the magnetic moment of the films as a function of temperature and applied field. The data were corrected for the magnetic moments of the substrate and sample holder. The magnetization data were collected by using the zero field cooled (ZFC) and FC procedures. In the former, the sample temperature was lowered without the magnetic field down to 4 K. Subsequently, the magnetic field was applied, the temperature was raised to 300 K, and the magnetic moment was measured in 2 K steps. For the FC procedure, the sample was cooled down to 4 K under an applied field of 200 Oe, while the magnetic moment was measured every 2 K. Alternating-field susceptibility measurements were performed in a physical property measurement system equipment at four different frequencies of the driving field, without an static applied field. The MCE was studied for the removal of an applied field of 50 kOe. The ΔS_M versus T curves were determined from sets of magnetization isotherms obtained for each sample at discrete temperature intervals according to a calculation procedure outlined by Pecharsky and Gschneidner.[9]

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction patterns of the various Gd_xW_{1-x} films, for x in the range of 0–1. The cubic lattice (Pm-$3n$) of the W ($x=0$) film clearly appears in the indexed diffractogram. For the low Gd concentration samples ($x=0.05$ and 0.15), only the W expanded lattice ($\Delta V/V \sim 2\%$) is observed due to the Gd contribution.

Amorphous films were observed for larger x values (0.35, 0.52, and 0.71). According to the phenomenological theory of Egami and Waseda[11] for binary alloys, large diameter differences in the atomic radii of the constituent atoms enhance the formation of an amorphous state. Thus, the relatively large atomic radius difference between Gd (0.174 nm) and W (0.142 nm) is probably the most important ingredient for the observed amorphism.

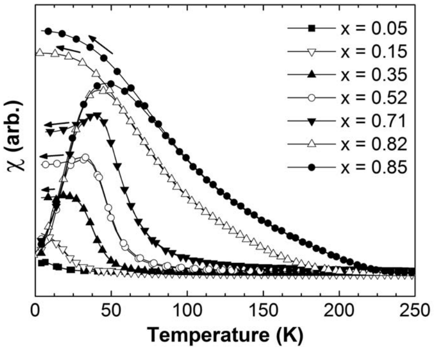

FIG. 2. ZFC and FC magnetic susceptibilities (arbitrary units) as a function of temperature for Gd_xW_{1-x} samples at various Gd concentrations. The FC branch at low temperature is indicated by an arrow. For higher temperatures, the FC and ZFC curves coincide.

The formation of the Gd structures is suggested in the $x=0.85$ sample patterns through the two broad peaks, probably Gd (002) and (103) observed if one uses the hexagonal closed packed structure of Gd ($P63/mmc$) identified in the $x=1$ pattern.

The susceptibility χ obtained by FC and ZFC procedures, for the samples with x in the range of $0.05 \leqslant x \leqslant 0.85$ is plotted in Fig. 2 as a function of temperature, between 2 and 250 K. The χ values were obtained for an applied field of 200 Oe. The low temperature χ peak of the ZFC branch of each curve reveals the spin glasslike behavior of the films, as it will be discussed later. The FC branch is also typical of spin glasses, as it strongly diverges from the ZFC plot near the freezing temperature T_f. For $T > T_f$, the films with x in the range of $0.05 \leqslant x \leqslant 0.71$ are paramagnetic.

From plots of χ^{-1} versus T, the Curie–Weiss temperature θ_c was obtained for all the films for which $0.05 \leqslant x \leqslant 1$ from extrapolation of the linear portions of the curves to $\chi^{-1}=0$. Figure 3 shows the Curie–Weiss temperatures, thus, obtained as a function of x. From the figure, θ_c slowly increases for low and medium values of x but abruptly increases for $x > 0.71$, implying that the sample for $x=0.85$ bears a ferromagnetic phase. Although significant, this phase is not unique in the film, since, as previously outlined, a spin glasslike behavior is revealed in all samples with x in the range of $0.05 \leqslant x \leqslant 0.85$.

To demonstrate the spin glasslike behavior of the Gd–W

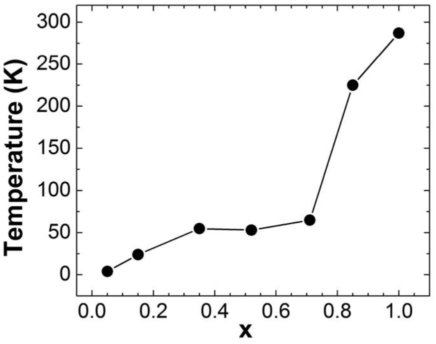

FIG. 3. Curie–Weiss temperature as a function of x for the Gd_xW_{1-x} samples.

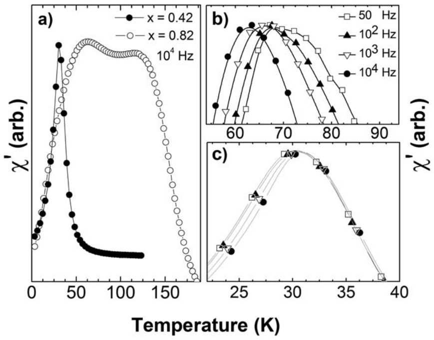

FIG. 4. Real part of the ac susceptibility of $Gd_{0.42}W_{0.58}$ and $Gd_{0.82}W_{0.18}$ films as a function of temperature for the driving field frequency of 1×10^4 Hz and zero static applied field (a). Expanded view of the susceptibility peaks for various driving field frequencies for the $Gd_{0.82}W_{0.18}$ low temperature peak (b) and $Gd_{0.42}W_{0.58}$ single peak (c).

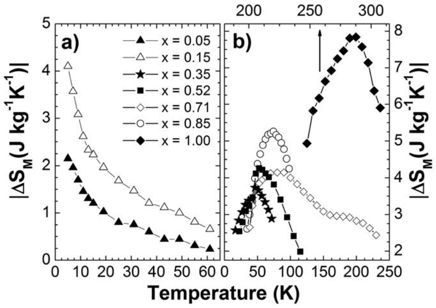

FIG. 5. Absolute value of the magnetic entropy change of Gd_xW_{1-x} per kg of film as a function of temperature for the removal of a 50 kOe magnetic field. The temperature scale (Kelvin) for the Gd sample ($x=1$) is indicated by an arrow.

films, we performed ac susceptibility experiments in samples of high ($x=0.82$) and intermediate ($x=0.42$) Gd concentrations. The measurements were made as a function of temperature, at four different frequencies of the alternating driving field. The results are shown in Fig. 4 for χ', the real part of the susceptibility. Each χ' versus T curve exhibits a peak at the freezing temperature [Fig. 4(a)] but the plot for the $Gd_{0.82}W_{0.18}$ alloy shows another peak at a higher temperature, indicating a ferromagnetic transition. For spin glass systems, the χ' versus T curves shift with driving frequency,[12] and this shift can be quantified by the ratio $\Delta T_f/[T_f\Delta(\log \nu)]$, where ΔT_f is the freezing temperature change when the frequency varies from ν_i to ν_f and $\Delta(\log \nu)=\log \nu_f-\log \nu_i$.[13] From the data of Figs. 4(b) and 4(c), the ratio $\Delta T_f/[T_f\Delta(\log \nu)]$ is calculated yielding 0.02 and 0.004, respectively. Such low values are typical of spin glasses. However, it is interesting to note that for single domain noninteracting magnetic particles, the χ' versus T curves bear close similarity with those of Fig. 4. In such particle systems, the Arrhenius law, $\nu=\nu_0 \exp[-E_a/k_BT]$, where ν is the flipping frequency of the particle moment, E_A is the anisotropy energy of a single particle, k_B is the Boltzmann constant, and ν_0 is the frequency constant, is obeyed. However, if we use the data of Fig. 4 to make plots of the Arrhenius law, we get completely unphysical values such as a negative E_A from Fig. 4(b) and $\nu_0 \approx 10^{100}$ Hz from Fig. 4(c). These results rule out the possibility that fine Gd magnetic particles, if they really exist in the Gd–W alloys, significantly contribute to their magnetic behavior.

Figure 5 shows the absolute value of the magnetic entropy change $|\Delta S_M|$ as a function of T, for the Gd–W alloys, for the removal of a 50 kOe applied field. As can be seen, the temperature, T_h, at which the highest $|\Delta S_M|$ values occur for each sample, $|(\Delta S_M)_h|$, widely varies with the Gd concentration. As x is increased, T_h exhibits a nearly monotonical increase from 5 K (lowest Gd concentration sample) to nearly 280 K (Gd film). Furthermore, an abrupt increase in T_h is indicated in the figure as x varies from 0.85 to 1.0. It is interesting to note that the $|(\Delta S_M)_h|$ values for the $Gd_{0.05}W_{0.95}$ sample are comparable to those for the Gd_xW_{1-x} samples with $x=0.85$, 0.52, and 0.35, despite its much lower Gd concentration. The results of Fig. 5 suggest that Gd–W films can be useful in magnetic refrigeration, as their dependence of ΔS_M on T can be tailored according to the alloy composition.

IV. CONCLUSIONS

The Gd–W films produced in this work bear crystalline structures and/or an amorphous state, depending on the Gd concentration. All of the W-containing films exhibit a spin glasslike behavior at cryogenic temperatures. If x is in the range of $0.05 \leq x \leq 0.71$, the films are paramagnetic for $T > T_f$, while a ferromagnetic phase is observed for $x > 0.82$. The maximum entropy change for the sample with the lowest Gd concentration is comparable to that for samples of much higher Gd concentration. As the Gd concentration in the alloys changes from $x=0.05$ to 1.0, the temperatures at which the highest $|\Delta S_M|$ values occur range from 5 to 280 K.

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