Magnetic Phase Diagram of Epitaxial Dysprosium

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We have determined the magnetic phase diagram of Dy as a function of expitaxial strain ε, applied field H, and temperature T. Y_xLu_{1-x} alloys were employed as templates to clamp the films at selected strains. The separate roles of epitaxial clamping and strain are identified for the first time. There is a clearly defined transition as the strain is changed at low temperature from the clamped helical phase to the ferromagnetic phase. The transition is modeled by a linear coupling treatment of the magnetoelastic strains.

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Recent publications emphasize that magnetic phase diagrams may be tuned by epitaxy [1]. The effects are expected to be the largest when a phase transition is accompanied by a large magnetoelastic strain. The strain energy alters the energy balance among alternative phases when the magnetic material is prevented from changing shape by its epitaxial clamping to a substrate. A separate effect is the epitaxial strain ε caused by interfacial atomic registry between the substrate and the magnetic film (pseudomorphic strain). All the energies change smoothly with the strain and this modifies the phase diagram further. The effects of clamping and strain have not been separated in previous research. Here we explore the magnetic phase diagram of epitaxial dysprosium, which undergoes large magnetostrictive strains $\sim$0.5% at $T_c = 85$ K in the bulk material, where the antiferromagnetic (H: helical) to ferromagnetic (F) phase transition occurs [2]. hcp Dy is of particular interest because basal plane epitaxy on Y, which causes a 1.6% expansion of the Dy basal plane, completely suppresses the F phase, owing to clamping and/or strain [3]. However, a metastable magnetized phase in Dy/Y superlattices can be induced by a 5 kOe field applied below 15 K [3]. In contrast, epitaxy on Lu, which compresses the a and b axes by 2.4%, doubles the Dy T_c [1,4]. A related observation for Dy/Lu superlattices is that the spontaneous orthorhombic distortion of the Dy basal plane in the F phase, present in pure Dy, is sufficiently strong to distort the surrounding Lu lattice as well [1]. These striking epitaxial effects add special interest to the study of clamped Dy epilayers.

To examine the effects of magnetostrictive clamping and strain separately we have grown c axis Dy single crystals 50 Å thick on selected substrates. The methods of molecular beam epitaxy employed here start from 1000 Å each of Mo(110), then Y(0001), freshly grown on sapphire ($11\bar{2}0$), and are described elsewhere [3]. The high quality of the resulting crystals is documented there (see also below). It is known that Dy films thicker than 100 Å undergo some inelastic strain relief so that the properties depend on the film thickness. In the present case the thickness was limited to 50 Å. An initial 1500 Å of template material was prepared before the Dy growth, and the same template material was regrown as a 100 Å thick cap directly on the Dy, in order to double the clamping strength and best establish the chosen pseudomorphic strain. For this purpose Y_xLu_{1-x} alloys were selected. These tune the Dy basal plane from an expansion of $\varepsilon = 1.6\%$ for $x = 1$ to a compression of $\varepsilon = -2.4\%$ for $x = 0$. In practice alloys with $0.2 < x < 0.8$ were used together with results for the pure metal templates [3,4]. Earlier results for Dy on Er [5] and pure bulk Dy [2,6] provide further relevant information.

Figure 1 presents an x-ray Bragg scan for the case of the sample with $x = 0.65$, which is typical for the materials employed here. The Bragg scan width shows that the coherence length is 500 Å along the growth direction; the observed mosaic spread is $\sim$0.2°. The observations point to crystals of sufficiently high structural quality that the magnetic behavior is expected to be insensitive to any remaining structural defects.

Magnetization measurements on these materials were carried out using a commercial SQUID magnetometer.

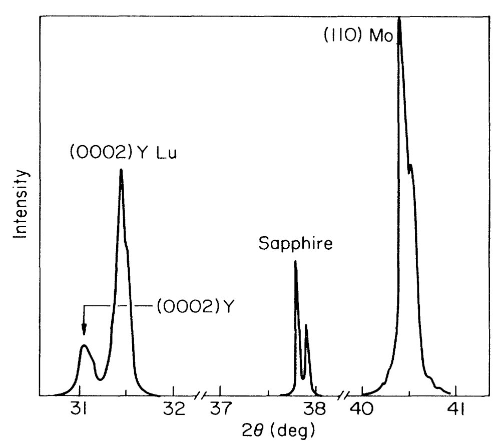

FIG. 1. X-ray Bragg scan of $(Y_{0.65}Lu_{0.35})_{1500Å}/Dy_{50Å}/(Y_{0.65}Lu_{0.35})_{100Å}$ sandwich film grown along the [0001] direction. The coherence length of the alloy is $\sim$500 Å. Bragg peaks for the sapphire substrate, the Y buffer, and the Mo buffer are also shown.

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The experiments were designed to determine the field and temperature dependent magnetic behavior of Dy clamped at different basal plane strains. Helimagnetic ordering occurs near the bulk Néel temperature $T_N = 175$ K in all the present materials, and is thus very insensitive to the epitaxial strain ε. Strong but differing magnetizations were observed in field-cooled and zero-field-cooled measurements, much as in earlier studies of Sc [7], Y [3], and Lu [4] templates. These nonequilibrium characteristics arise from thin film constraints on the accessible magnetic domain structures. The ferromagnetic transition was probed using the field-cooled magnetization with results shown for the template alloy with $x = 0.4$ in Fig. 2. At temperatures above the zero field critical temperature T_c, the field dependent magnetization curves thus deduced exhibit discernible slope changes. These determine the variation of H_c with T for $H > 0$ at that particular value of the basal plane strain ε. The slope change that occurs at lower fields, before the rapid rise, pertains to the collapse of the spiral phase. Its midpoint is defined for the present purpose as H_c.

At still higher fields a second slope change occurs at H_f, before the magnetization saturates. Magnetic and neutron scattering measurements have not yet been able to establish for pure Y and pure Lu templates whether this is a regime of mixed F and H phases or a fan configuration derived from a distorted helix similar to that observed at high fields above ~ 130 K in pure Dy [2].

Open circles in Fig. 3 show the locus of H_c as a surface depending on the temperature T and on the basal plane strain ε, defined by the alloy template. The smoothed behavior is indicated by solid lines. In completing the figure, use has been made of published results for Dy grown on Y and Lu templates [3,4], indicated by solid data points. Results for Dy on Er above the T_c of Er are also shown by solid points near $\varepsilon = 1\%$ [5]. The figure makes clear that the magnetism is insensitive to ε near $\varepsilon = 1.6\%$ (pure Y template) and $\varepsilon = -2.4\%$ (Lu). A rapid transition from H_c large to zero near $\varepsilon = 0$ marks the helical to ferromagnetic phase transition induced here by changing ε. Accordingly, T_c (for $H_c = 0$) rises rapidly to ~ 85 K near $\varepsilon = 0$ and, for $0 < \varepsilon < -2\%$, it changes almost linearly with ε.

It is an important observation that $H_c(T)$ for the H to F transition of pure Dy is quite similar to that for Dy on Y_xLu_{1-x}. The behavior of pure Dy is shown by a thick line near $\varepsilon = 0$ in Fig. 3. Without question it lies close to the surface in Fig. 3 derived from the use of alloy templates. In the first place, the combined observations suggest that the process mapped by the surface in Fig. 3 must be similar to the well-studied magnetization observed for pure Dy, in part through fan states. Second, as bulk Dy magnetizes it undergoes a tetragonal γ distortion ε_γ along the direction of the magnetization **M** in the basal plane, and a tetragonal α distortion ε_α along the c axis. A natural expectation is that epitaxy modifies both ε_γ and ε_α through the effects of clamping and interfacial registry. Figure 3 clearly establishes that the *strain* ε associated with misfit does have a profound effect in tuning the film across its magnetic phase diagram. However, the *clamping* caused by epitaxy causes surprisingly little change of the phase diagram. The fact that pure Dy behaves very much like epitaxial Dy near $\varepsilon = 0$ in Fig. 3 is one demonstration that clamping alone has no large effect. Further evidence is that the variation of T_c with ε for $\varepsilon \leq 0$ coincides with the known dependence of T_c on uniaxial stress in bulk Dy (broken line in Fig. 3) [6] when converted to an ε dependence using the hydrostatic pressure dependence. The linear behavior is also consistent with the ε

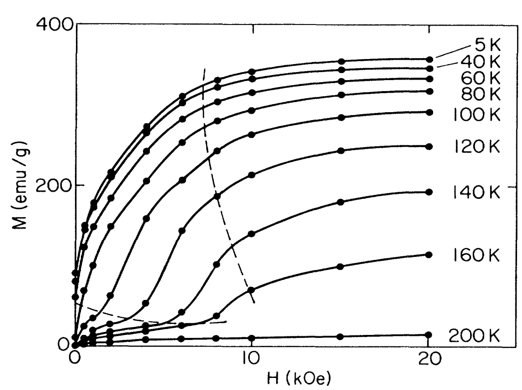

FIG. 2. Field dependent magnetization curves for the field-cooled $(Y_{0.45}Lu_{0.55})_{1500\text{Å}}/Dy_{50\text{Å}}/(Y_{0.45}Lu_{0.55})_{100\text{Å}}$ at various temperatures. The magnetic field was applied along one of the a axes in the growth plane. Note that above $T_c = 90$ K, the magnetization exhibits a low field anomaly at H_c before its rapid rise to saturation. The critical fields H_c and H_f are indicated by dashed lines.

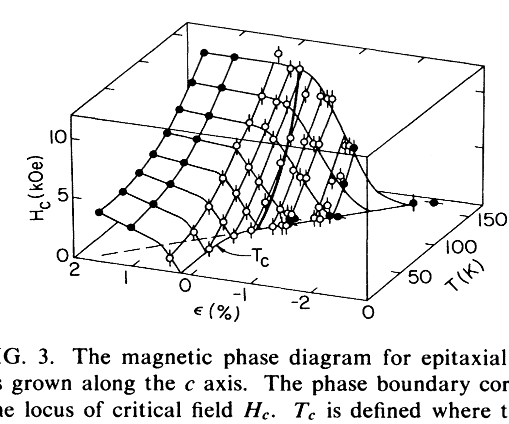

FIG. 3. The magnetic phase diagram for epitaxial Dy thin films grown along the c axis. The phase boundary corresponds to the locus of critical field H_c. T_c is defined where the phase boundary intersects the T-ε plane at zero field. The open circles are data points from this research on $(Y_xLu_{1-x})_{1500\text{Å}}/Dy_{50\text{Å}}/(Y_xLu_{1-x})_{100\text{Å}}$ sandwich films, and the closed circles are obtained from Refs. [3–5]. The smoothed behavior is indicated by solid lines. The dashed line through the nearly linear part of the T_c curve indicates the equivalent bulk uniaxial behavior [6].

dependence of T_c obtained from observations for Dy partially relaxed on Lu [4]. The behavior is different for $\varepsilon > 0$ where a transition takes place and T_c deviates from the linear behavior of the strained but unclamped bulk Dy and drops rapidly to zero. These first observations of the separate effects of clamping and epitaxial strain on the magnetic phase diagram lead us to the unexpected conclusion that, while strain causes large changes, the effect of clamping is quite small particularly for $\varepsilon \leq 0$. Any model discussion of $H_c(T)$ must include the observed transition in the ε dependence where the effect of clamping seems to change drastically.

In what follows we describe mechanisms by which magnetostrictive strains may be favored even in thin epitaxial films that are clamped by the surrounding material. Our purpose is to explain why clamping has an unexpectedly small effect on the Dy phase transitions and how it can appear to have an ε dependent transition. All the ordered phases of Dy consist of ferromagnetic basal planes stacked in an ordered sequence. In the helical phase the moment is rotated from one a axis to the next between successive planes to yield a magnetic spiral with typical period 10 planes and wave vector $q \sim 0.1$ Å^{-1}. The ferromagnetic phase is the same except that $q = 0$. In the bulk this phase is accompanied by magnetostriction in the form of one tetragonal strain, $\varepsilon_\gamma = \frac{1}{2}(\varepsilon_{11} - \varepsilon_{22})$, about the a axis of the basal plane along which the moment points, and a second tetragonal strain along c, namely, $\varepsilon_\alpha = \frac{1}{3}(2\varepsilon_{33} - \varepsilon_{11} - \varepsilon_{22})$. Here we discuss two alternative $q = 0$ phases: one with anisotropic magnetostriction and the other lacking anisotropy. Our discussion of spontaneous strain treats only ε_γ because Fig. 3 indicates that the isotropic basal plane strain $\varepsilon = \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22})$ is fully clamped in the thin film, in order that epitaxial strain can tune Dy through the different phases. To proceed we assume for simplicity that the Dy surface planes are fully clamped to their YLu neighbors, with no interfacial slip, and that Y_xLu_{1-x} and Dy have similar enough elastic constants to be treated as identical. In a more complete publication we will show that these simplifications do not alter the character of the conclusion so reached.

The two $q = 0$ phases of interest here differ in that one undergoes a tetragonal distortion about the direction of magnetization and the other does not. We compare the two energies by expanding the energy about the symmetrical configuration in powers of the strain ε_γ and retain the lowest relevant terms. Figure 4 shows a magnetic domain of the distorted phase occupying the full thickness d of the magnetic layer for an in-plane dimension l. We assume that, as observed in Dy/Lu superlattice [1], the epilayer minimizes its γ strain energy by breaking into tetragonal domains so arranged that the mean strain vanishes. In each domain the magnetization lies along one of the easy orientations. It is reasonable to represent the electronic energy E_e of magnetization as linearly coupled to the tetragonal magnetostrictive strain coordinate

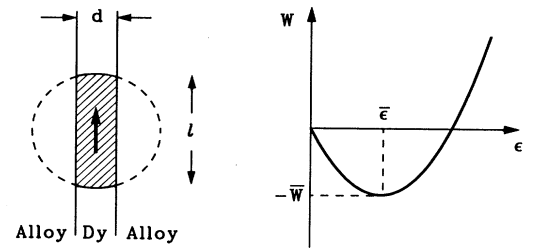

FIG. 4. Schematic diagram of a magnetic domain (left) in an epitaxial film. It occupies the full thickness of the magnetic layer, d, for a dimension l in the growth plane. Nonuniform elastic fields due to magnetostriction must extend $\sim l$ into the nonmagnetic bulk. The resulting energy of the film as modeled in the text is shown to the right.

ε_γ it produces in the pure bulk. Thus $E_e = -a\varepsilon_\gamma l^2 d$, in which $l^2 d$ is the domain volume and a for Dy is a constant that depends smoothly on ε. Any distortion of the film over an area with typical dimension l must create nonuniform elastic fields extending $\sim l$ into the bulk. The lattice energy for $l \gg d$ is therefore $E_l = b\varepsilon_\gamma^2 l^3$, in which l^3 is the volume and b is an elastic constant. When the energy $W = (E_e + E_l)/l^2$ per unit area is now minimized, as shown in Fig. 4, to obtain the equilibrium strain $\bar{\varepsilon}_\gamma$ and energy $\overline{W}$ for a distorted phase relative to the undistorted system, one finds

$$\bar{\varepsilon}_\gamma = \frac{a}{2b}\frac{d}{l}, \quad \overline{W} = -\frac{a^2}{4b}\frac{d^2}{l}.$$

This relaxation energy $\overline{W}$ must be augmented to include an added domain boundary energy per unit area given by $E_d = cd/l$, with c the surface energy, to yield the total energy difference between the distorted and undistorted magnetized phases as

$$\overline{W}_t = \left[c - \frac{a^2 d}{4b}\right]\frac{d}{l}. \tag{1}$$

The conclusions we draw from this model are now simply stated. Equation (1) shows that the distorted phase is preferred when $a^2 > 4bc/d$. This means that the electronic energy is reduced by more than the combined elastic and domain boundary energies. In this case $\overline{W}_t$ is negative and the energy is least when l is small, with $l \sim d$ the lower limit of the model. When, in contrast, a is small and the coefficient in brackets is then positive, the *unstrained* phase is stable. $\overline{W}_t$ is now positive, at least for l very large. Investigation of the film thickness d predicted by this model will clearly be of future interest.

The very similar behaviors of unconstrained bulk Dy and epitaxial Dy for $\varepsilon \leq 0$ in Fig. 3 present a challenging puzzle identified above. How is it possible that clamping-fails to cause substantial changes of the critical field? The problem is largely resolved if, as predicted above from Eq. (1), the epitaxial layer distorts into domains of size comparable with the magnetic layer thickness d. This reduces the distortion of the nonmagnetic clamping material to a minimum, and therefore disturbs the bulk phase relationships least. The ε dependence of the constants $a(\varepsilon)$, $b(\varepsilon)$, and $c(\varepsilon)$ can cause the "unstrained" phase with large domains to be preferred for $\varepsilon > 0$, as discused above, and consequently the observed transition occurs near $\varepsilon = 0$.

The domain size of 300 Å observed for Dy/Lu superlattices remains substantially larger than the magnetic layer thickness typically of $d = 50$ Å employed in the earlier work [1]. This must be reconciled with the present model discussion. In the case of superlattices, however, the lattice distortion is favored by the proximity of neighboring magnetic layers. The penalty in energy for deforming neighboring Lu blocks is, in effect, shared between two Dy layers. That a cooperative effect of this type does indeed take place is detected experimentally by the observation that an interaction between Dy moments in successive layers results from this elastic coupling [1]. It seems reasonable that smaller domains may be necessary to minimize the energy in the present study of isolated layers. The similarity with bulk Dy indicates that the domain boundary energy may not be important.

In summarizing this research from a broader perspective we note first that by systematically tuning the epitaxial strain we have been able to explore the magnetic phase diagram of epitaxial Dy over a range of 4% in basal plane strain. These methods make it possible to interrelate the behaviors observed previously both in isolated epitaxial systems and in the pure material. The procedure promises widespread utility for other materials in both scientific and technical applications. For the specific case of Dy we have confirmed the very wide range of magnetic behavior accessible in the epitaxial system, ranging smoothly from a doubling of T_c to the complete suppression of ferromagnetism. Our results are unambiguous in establishing that the magnetic phase diagram is tuned almost entirely by the choice of the basal plane strain ε. Lattice clamping of the tetragonal magnetostriction in the basal plane appears to have a relatively small effect on the magnetic behavior. This is observed even when the elastic energy is comparable in magnitude to the electronic and magnetic energy differences in the phase transition. The magnetization measurements presented here do not afford an unambiguous identification of the mechanism responsible for this unexpected result. However, a modeling of the behavior shows that a distorted ferromagnetic phase like that of the bulk can remain favored even for a fully clamped film, provided that it deforms into small domains that minimize the clamping energy.

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