Magnetic and Structural Properties of Single-Crystal Rare-Earth Gd-Y Superlattices

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The first coherent, single-crystal, magnetic rare-earth superlattices of Gd-Y were grown by metal molecular-beam epitaxy. X-ray structural analysis showed that the superlattices have a composition modulation of two atomic-layer-sharp interfaces with the modulation amplitude approaching 100%. The magnetic properties are consistent with a model in which the central Gd layers in each array behave like ideal ferromagnetic thin films even for as few as five atomic layers. The two interfacial Gd layers at the sides appear not to order ferromagnetically and have a susceptibility χ_g independent of the number of atomic layers.

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The magnetic properties of surfaces and thin films are of continuing interest. There have been a number of recent attempts to observe[1,2] and to calculate[3,4] variations in the magnetic behavior resulting from the breaking of the bulk symmetry at a surface or interface. One approach to the carrying out of such studies is through the synthesis of superlattices composed of alternating regions of magnetic and nonmagnetic components (Cu-Ni,[5,6] Mo-Ni,[7] Fe-V,[8,9] Tm-Lu[10]). Many rare-earth metals have similar crystal structures with a close lattice-constant match. Therefore, formation of coherent superlattices is highly probable.[10] Furthermore, the magnetic moments of rare-earth ions are well localized and the indirect exchange interaction is long range through the conduction electrons. Isolated arrays of moments which vary both in thickness and in separation can be synthesized as a model system for investigation of two-dimensional magnetism, intermagnetic layer coupling, and antiferromagnetic-ferromagnetic lockin transitions.[10]

The discovery that single-crystal films of yttrium can be grown epitaxially on sapphire with an intervening Nb buffer layer has led to the synthesis of the first high-quality, single-crystal, inter–rare-earth superlattices.[11] In this Letter we report the synthesis and magnetic and structural properties of a series of Gd/Y superlattice crystals. This system was chosen because the Gd ion has a spin-only moment with $S=\frac{7}{2}$ and $L=0$, and bulk Gd is a simple ferromagnet ($T_C=292$ K) with weak anisotropy. The magnetic results on Gd-Y multilayers with Gd varying from 5 to 21 atomic layers are consistent with a model in which the Gd layers in the middle of each array have the simple ferromagnetic structure observed in the bulk. The two interfacial Gd layers have a different, nonferromagnetic spin structure. This picture is in accord with the x-ray structural analysis which indicates that the interface between (essentially) pure Gd and Y regions is only two atomic layers thick. Such sharp boundaries achieved in this work are approaching those observed in semiconductor superlattices. It is expected that similar results can be obtained with other rare earths because of their similar crystal-chemical nature.

The superlattice crystals were prepared in a metal molecular-beam epitaxial deposition system operating at a low pressure of 3×10^{-11} Torr during growth.[11] The sensitive flux detection and fast loop control maintained the deposition rate constant to within 2%. The epitaxial growth was monitored and optimized with *in-situ* reflection high-energy electron diffraction (RHEED). The superlattice crystals were grown on sapphire $(11\bar{2}0)$ and we first deposited a Nb(110) buffer layer and then a Y(0001) seed layer. The Nb buffer layer eliminated chemical reactions between the rare earths and the sapphire and provided an atomically smooth surface for the epitaxial growth of the Y seed layer. The RHEED patterns clearly showed that one monolayer of Y wets the Nb completely, and by fifty atomic layers an atomically smooth Y single crystal is obtained. The epitaxial relations obtained from subsequent x-ray studies are $[\bar{1}11]\mathrm{Nb}\|[0001]\mathrm{Al_2O_3}$ and $[1\bar{1}0]\mathrm{Nb}\|[10\bar{1}0]\mathrm{Y}$. The buffer and seed layers were grown at 900°C and 700°C, respectively, and then the Gd-Y superlattice was grown at 220°C in order to minimize interdiffusion.

The structure and coherence of Gd-Y superlattices with respective numbers of atomic layers $(n,m)=(21,21)$, (10,11), and (5,5) were determined from x-ray diffraction analysis by use of techniques described previously.[12] Typical high-resolution scans through the (0002) and (0004) Bragg reflections of the $(10,11)\times80$ samples are shown in Fig. 1. The full widths at half maximum (FWHM) of the rocking curves are $\Delta\theta_\perp=0.16$ and $\Delta\theta_\parallel=0.23$ (Fig. 1 inset). The linewidths are $\Delta q_c=0.0025$ Å^{-1} (0002) and 0.0039 Å^{-1} (0004), and $\Delta q_a=0.0041$ Å^{-1} $(10\bar{1}0)$ and 0.0063 Å^{-1} $(20\bar{2}1)$. Here instrumental resolution is $\Delta q=0.0014$ Å^{-1} from the $(11\bar{2}0)$ $\mathrm{Al_2O_3}$ (FWHM in units of $2\pi/d$). The samples are single crystals with some strain broadening and with coherence lengths of several thousand angstroms. The composition modulation was determined by fitting of the integrated in-

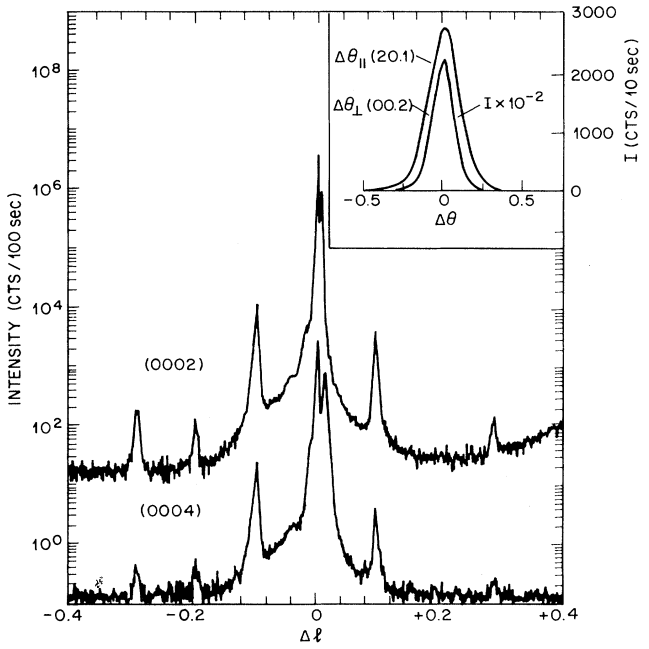

FIG. 1. High-resolution longitudinal scans around Bragg peaks (00.2) and (00.4) of a $(10,11)\times 80$ multilayer. Δl's are in units of $2\pi/d$. The intensity scales for (00.4) scans are displaced by two decades for clarity. The inset shows the rocking curves of (00.2) and (20.1).

tensities of the (0002), (0004), and (0006) reflections and their harmonics up to $\pm$fifth or $\pm$seventh order depending on wavelength. The amplitude of the interplanar spacing modulation was calculated from the elastic constants with the assumption of a coherent structure. With the Poisson contraction or expansion the difference in spacings along the c axis is reduced from 0.9% for the pure elements to 0.72% for the superlattices. The Gd composition in layer N for one wavelength was approximated by

$$c(N)=\tfrac{1}{2}c_0[\mathrm{erf}((N_{\mathrm{Gd}}+2N)/N_I)+\mathrm{erf}((N_{\mathrm{Gd}}-2N)/N_I)],$$

where N_{Gd} and N_I are the number of atomic layers of Gd and the interface thickness, respectively, and c_0 is the maximum Gd concentration. These three parameters plus a scale factor were refined by minimization of the weighted R factor[13] for the 20-30 observed intensities. In all cases N_I was found to be 3.5 atomic layers, which means that the compositional profile goes from 90% to 10% Gd in about two atomic layers. c_0 was essentially unity except at the shorter wavelengths where the interfacial regions begin to overlap [$c_0=0.83$ for (5,5)].

The magnetizations per gram of Gd in the superlattices as a function of the applied field (σ-H loops) were measured at 25 K with a vibrating-sample magnetometer (0–15 kOe). The magnetization curves for all the samples measured closely follow the behavior expected for an ideal thin film with weak anisotropy, namely a square loop for H in the plane of the film ($H_{\parallel}$), and a linear dependence of σ on H for field less than the saturation magnetization ($4\pi M_0$) applied perpendicular to the plane ($H_{\perp}$). An example of a σ-H loop is shown in Fig. 2 for a (5,5) sample with a coercive force in the plane of only 25 Oe. The small remanence for $H_{\perp}$ seen in Fig. 2 is an indication that some unspecified imperfections in this film keep $\sigma_{\perp}$ from reaching zero at $H_{\perp}=0$ as would be the case for an ideal thin film. This film is actually an exception to all the other multilayers studied. Samples with larger N_{Gd} show the expected linear dependence of $\sigma_{\perp}$ on $H_{\perp}$, with $\sigma_{\perp}=0$ when $H_{\perp}=0$. The slight decrease in $\sigma_{\parallel}$ for $H_{\parallel}$ less than 1 kOe is attributed to the magnetocrystalline anisotropy of Gd which at 25 K gives an easy cone of magnetization 32° away from the c axis.[14]

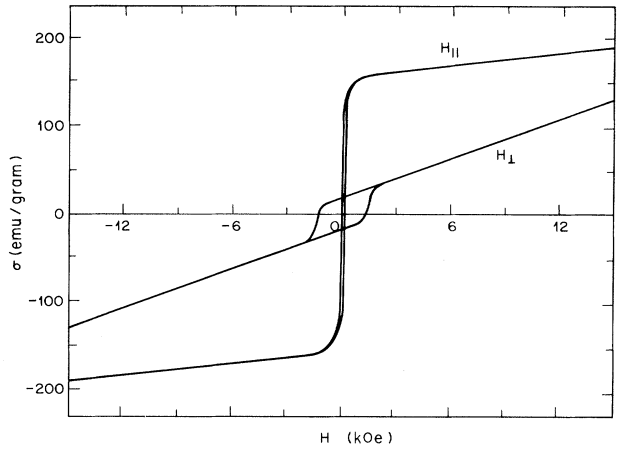

FIG. 2. The magnetization curves at 25 K for **H** parallel and **H** perpendicular to the film plane of a $(5,5)\times 80$ multilayer.

Using the usual definition of $\sigma(0)$ as the extrapolation on the high-field data for $H_{\parallel}$ back to zero field, we obtain $\sigma(0)$ for the (5,5) sample to be 154 emu/g, which is about 60% of the bulk Gd moment, $\sigma_{\mathrm{Gd}}=268$ emu/g. Furthermore, the $\sigma_{\parallel}$ data in Fig. 2 show a linear rise with applied field, and by 15 kOe, the maximum measuring field, this linear rise has produced an increase of moment of $\Delta\sigma(15)\equiv\sigma(15)-\sigma(0)=36$ emu/g. For all the superlattices measured, the general trend is that $\sigma(0)$ increases and $\Delta\sigma(15)$ decreases with increasing N_{gd}. These results are summarized in Figs. 3(a) and 3(b), where $\sigma(0)$ and $\Delta\sigma(15)$ are plotted as functions of $1/N_{\mathrm{Gd}}$. Clearly for $0\leq 1/N_{\mathrm{Gd}}\leq 0.2$ both $\sigma(0)$ and $\Delta\sigma(15)$ vary linearly with $1/N_{\mathrm{Gd}}$.

This systematic variation of $\sigma(0)$ and $\Delta\sigma(15)$ with N_{Gd} can be explained on the basis of a model which assumes that in the middle of each Gd array there are

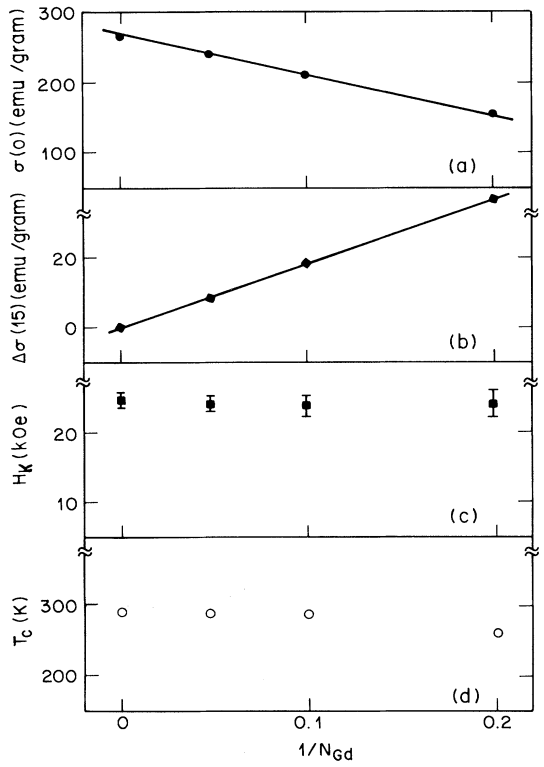

FIG. 3. (a) The magnetization $\sigma(0)$ at zero field, 25 K, (b) the increment of moment at 15 kOe, $\Delta\sigma(15)$, (c) the anisotropy field H_K, and (d) the Curie temperature T_C, as functions of $1/N_{Gd}$ in (n,m) multilayers.

$N_{Gd}-X$ layers of Gd that exhibit, at least at low temperature, the properties of the bulk material. On either side of this center region there exists an interfacial region at least $X/2$ layers thick. This interfacial region is taken to be not ferromagnetic and is characterized by a susceptibility χ_g and, hence, a moment $\sigma_{int}=\chi_g H$. Accordingly, the total moment in the plane is described by

$$\sigma(H)=\sigma_{Gd}\left[1-\frac{X}{N_{Gd}}\right]+\chi_g H\frac{X}{N_{Gd}}.$$

Obviously, then,

$$\sigma(0)=\sigma_{Gd}[1-X/N_{Gd}],$$

and

$$\Delta\sigma(15)=\sigma(15)-\sigma(0)=\chi_g(1.5\times10^4\ \text{Oe})\frac{X}{N_{Gd}}.$$

If X and χ_g are, as assumed in the model, independent of N_{Gd} these equations yield both the observed linear dependence of $\sigma(0)$ and $\Delta\sigma(15)$ on $1/N_{Gd}$ and the correct intercepts at $1/N_{Gd}=0$. The best fit to our experimental data gives $X=2.2\pm0.2$ layers and $\chi_g=(5.5\pm0.5)\times10^{-3}$ emu/(g Oe). The fact that the X and χ_g values vary only slightly among superlattices of substantially different wavelengths adds support to the validity of our model in the description of this magnetic system. Furthermore, the thickness of the interfacial layers as deduced from the present model is in good agreement with independent structural analysis by x-ray diffraction.

In order to ascertain whether the films consisting of $N_{Gd}-X$ magnetic Gd layers indeed retain ideal thin-film behavior it is necessary to substract the contributions of the interface layers from the experimental σ-H loops. For $H_{\parallel}$ this contribution is simply $\chi_g H(X/N_{Gd})$. The contribution for $H_{\perp}$ is deduced to be $\chi_g H(X/N_{Gd})(1+4\pi\rho\chi_g)^{-1}$, in which a correction for the demagnetization field is made. In addition, χ_g is assumed to be isotropic, and the density (ρ) of the interface layer is taken to be that of bulk Gd. After application of these corrections to the σ-H loops for both $H_{\parallel}$ and $H_{\perp}$ the magnetization curves are extrapolated to high fields for the determination of H_K, the effective anisotropy field. In this case H_K is defined to be the value of $H_{\perp}$ at which $\sigma_{\perp}$ equals $\sigma(0)$. For an ideal thin film the anisotropy arises only from shape effects and $H_K=4\pi M_0$. As seen in Fig. 3(c) the value of H_K remains nearly constant at 24 ± 2 kOe independent of the value of N_{Gd}. The fact that the measured H_K is to a very good approximation equal to the saturation moment of Gd (27 kG) supports our model of the central $N_{Gd}-X$ layers behaving like an ideal Gd thin film. It should be noted that if the correction to $\sigma_{\perp}$ from the finite susceptibility of the interfacial regions is not applied, a slight reduction in the H_K value will result. For the (5,5) sample H_K, at most, decreases to 21 kOe.

The temperature dependence of the magnetic moment was measured by both the vibrating-sample magnetometer and the Faraday method. In general σ vs T is similar to the behavior seen in bulk Gd. The Curie temperature (T_C) was determined from Arrott plots[15,16] (σ^2 vs H/σ at constant T), which were linear over the field range used, 2.6 to 12.8 kOe. As shown in Fig. 3(d), T_C remains close to the bulk value of 292 K, and only for the (5,5) film is T_C reduced to 264 K. This 10% depression of T_C is consistent with the T_C expected for Gd-Y alloy[17] with the composition obtained from the x-ray analysis ($c_0=0.83$). In contrast, our homogeneous $Gd_{50}Y_{50}$-alloy film orders antiferromagnetically at 180 K as in the bulk alloy.[17]

In conclusion, after subtraction of the contribution of the interfacial layers, the observed low-temperature magnetic properties of single-crystal superlattices of Gd-Y are consistent with the properties of bulk Gd even for Gd arrays thin as five atomic layers. It is quite remarkable that, for all films considered here, the central region behaves like an ideal thin film for both $H_{\parallel}$ and $H_{\perp}$, independent of N_{Gd}. For $N_{Gd}=5$,

this region is only three atomic layers thick. The good agreement of H_K with $4\pi M_0$ obtained in this work has, in general, been seen only in much thicker films. Since the interfacial layers have a zero ferromagnetic moment, the spins of these layers could be rotated with respect to the central region in such a manner as to take an antiferromagneticlike arrangement. Indeed, many of the heavy rare-earth metals and alloys have spiral spin structures in which the ferromagnetic planes are rotated successively to give rise to antiferromagnetism. Further experiments are planned to resolve the magnetic structure by x-ray and neutron-scattering techniques.

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