Growth, morphology, and structure of a monolayer thick GdFe₂ surface alloy

R. P. Williams,^{1,*} S. G. Alcock,² P. B. Howes,¹ and C. L. Nicklin^{2,†}

¹*Department of Physics and Astronomy, University of Leicester, University Road, Leicester LE1 7RH, United Kingdom*

²*Diamond Light Source, Chilton, Didcot, Oxon OX11 0DE, United Kingdom*

(Received 18 May 2016; published 15 August 2016)

The growth and structure of an ordered GdFe₂ surface alloy deposited on Mo(110) has been studied using *in situ* surface x-ray diffraction. Growth curves and reflectivity scans of varying ratios of Gd to Fe show how the two species intermix prior to alloy formation. After annealing to form the ordered surface alloy, in-plane x-ray diffraction data indicate that the Fe atoms are laterally displaced along the [001] or [00 $\bar{1}$] direction by 0.16 ± 0.02 Å from the long bridge site positions. Out-of-plane crystal truncation rod analysis reveals that the Gd atoms lie 3.40 ± 0.09 Å above the Mo(110) bridge site, an expansion of 22% relative to the expected hard sphere distance. This is significantly larger than observed in previous studies of the growth of pure Gd on Mo(110). Simple geometric changes are not able to account fully for this expansion and we propose that hydrogen incorporation during alloy formation may also contribute.

DOI: [10.1103/PhysRevB.94.075419](https://doi.org/10.1103/PhysRevB.94.075419)

I. INTRODUCTION

The growth of ultrathin magnetic films continues to be the subject of much research attention, motivated by possible applications for future magnetic recording devices. In order to study adsorbate driven interactions in pure thin film growth of rare earth–transition metal (RE-TM) alloys, it is important to choose a substrate that is not prone to alloying because rare earth elements are highly reactive and will readily intermix. Molybdenum and tungsten show little tendency to alloy and the (110) surface is ideal as it is the most close-packed crystal plane for the body-centered crystal.

Transition metal ferromagnetic single crystal films grown on fcc and bcc surfaces have been extensively studied. In particular, Gradmann *et al.* [1] reported on the epitaxial growth of Fe(110) on W(110) at 500 K using low energy electron diffraction (LEED) and Auger electron spectroscopy (AES), reporting that one monolayer (ML) of Fe grew pseudomorphically by Frank–van der Merwe (FM) layer-by-layer growth. Previous surface x-ray diffraction studies by Meyerheim, Popescu, and co-workers [2,3] of Fe on W(110) show pseudomorphic growth in the initial layers together with interlayer contractions and the onset of tensile stress with second layer formation. Additionally, they showed that for a thick (13 ML) film, satellite peaks can be attributed to a periodic arrangement of misfit dislocations. Tikhov *et al.* [4] studied Fe, Co, and Ni on a Mo(110) surface and found that for all cases pseudomorphic FM growth occurred at room temperature, island or Stranski-Krastanov (SK) growth at elevated temperatures while alloying was observed for thicker films at higher temperatures. However, up to 1 ML no alloying was found to occur even at the highest temperatures. They

also reported that in the case of Fe, structural rearrangements only occur towards the end of second monolayer formation. Malzbender *et al.* [5] found that the morphology of the first layer was independent of the flux of Fe, allowing a consistent monolayer structure to be formed on Mo(110) regardless of the deposition rate. Subsequent growth at low deposition rates resulted in multilayer formation while at higher rates, layer growth was partially preserved. Osing *et al.* [6] also show that at room temperature Fe grows pseudomorphically on Mo(110) via a strained layer-by-layer growth mode. However, in contradiction to other reports they show that at elevated temperatures (~ 700 K) island growth occurs on top of a partially Fe covered substrate (Volmer-Weber growth mode). It was suggested that this behavior was the result of either a density defect introduced by the miscut surface or due to alloying.

Rare earth metals continue to be widely studied as they exhibit unique properties as a direct result of their electronic configuration. In the case of Gd the 4*f* states contain seven unpaired electrons giving Gd the highest atomic magnetic moment of all known elements. Bulk Gd orders ferromagnetically at temperature below $T_c = 293$ K (where T_c is the Curie temperature). Gd surfaces have been reported to have an increased T_c , however the magnitude of this value is still debated with values ranging from an increase of 85 K over the bulk [7] down to no noticeable increase at all [8].

The adsorption of Gd on the Mo(110) and (112) surfaces has been previously studied by Nicklin *et al.* [9,10] and Waldfried *et al.* [11], respectively. Growth on the corrugated (112) surface results in a strained Gd overlayer that shows preferential domain growth along the [111] direction. The close packed (110) surfaces exhibit a large number of submonolayer structures generally described by a series of $(n \times 2)$ reconstructions with increasing coverage, and ending with a closed-packed hexagonal monolayer.

Compound alloys of 3*d* transition metals with 4*f* rare earth metals, e.g., GdFe₂, TbFe₂, and GdCo₂, are of intense technological importance because of their interesting magnetic effects. They can exhibit a high perpendicular uniaxial anisotropy in an amorphous and ferromagnetic structure, which is necessary in order to align the magnetization normal

*Now at AWE, Aldermaston, Reading, Berkshire, RG7 4PR, UK.

†chris.nicklin@diamond.ac.uk

to the film plane [12]. Crystalline alloys and especially TbFe_2 can exhibit a strong magnetocrystalline anisotropy resulting in an easy magnetization direction perpendicular to the film plane in thin film systems [13]. In devices this would allow for not only an enhanced writing density but also a high signal-to-noise ratio. Suits *et al.* [14] found that by altering the rare earth to transition metal ratio, both the Curie temperature and coercivity of alloys of Gd or Tb with Fe can be tuned over a wide range. Although there have been many studies of the magnetic and magnetostrictive properties of the bulk alloy materials, relatively little is still known about thin film properties.

Despite well documented studies on the growth and structure of Fe and Gd on surfaces, little has been reported on the ordered structure of the thin film alloy that can form between them. Notably, Getzlaff *et al.* [15–17] have reported the formation of ordered reconstructions of GdFe_2 on a $\text{W}(110)$ surface using LEED and scanning tunneling microscopy (STM). The first and second monolayer were found to grow pseudomorphically on the substrate. As a consequence the normally highly complex GdFe_2 atomic arrangement (C15 Laves phase [18–23]) is completely modified because of the influence of the substrate during growth.

X-ray diffraction is a well established tool for the study of surfaces and overlayer structures including the study of real time epitaxial growth [24–27] and surface reconstructions [28–34]. Here we describe the growth of 1 ML of GdFe_2 through careful evaporation calibration and derive both the in-plane and out-of-plane structure of the ordered alloy by analysis of surface x-ray diffraction data.

II. EXPERIMENTAL PROCEDURES

The measurements were carried out on beamline 9.4 of the synchrotron radiation source at Daresbury laboratory using a six circle x-ray diffractometer [35]. Radiation of wavelength $0.9 \text{ \AA}$ was selected using a channel cut $\text{Si}(111)$ monochromator. The scattered x-ray intensity was recorded using a liquid nitrogen cooled germanium detector that was mounted behind two sets of four-jaw slits to define the angular resolution.

The Mo sample (dimensions of $8 \times 8 \times 0.5 \text{ mm}$) was cut and polished to within 0.1° of the (110) surface and mounted inside the University of Leicester x-ray ultrahigh vacuum chamber [36]. The chamber was configured to allow for simultaneous deposition of Gd and Fe onto the Mo (110) surface via two independent Knudsen cell evaporation sources.

The Mo crystal was cleaned by flashing the sample to 2100 K in vacuum to get contamination levels of oxygen to below the detection limit using Auger electron spectroscopy (AES). A small carbon signal was always visible, but the formation of the submonolayer $n \times 2$ Gd structures (not stable on contaminated surfaces) indicated that this did not influence the growth. The base pressure of the system was $7 \times 10^{-11} \text{ mbar}$, which during co-evaporation rose to $7 \times 10^{-10} \text{ mbar}$. Gd and Fe growth rates were carefully characterized by monitoring growth oscillations on $\text{Mo}(110)$. This allowed the correct stoichiometric deposition rates to be set to grow GdFe_2 by simultaneous growth. The sample was flash cleaned as described above and then left to cool to room temperature

FIG. 1. The $\text{Mo}(110)$ surface. The unit cell vectors are shown as a_1 and a_2 . The reconstruction has a unit cell described by the vectors $a_1^r = a_1 + a_2$ and $a_2^r = 3a_1 - 3a_2$.

before each growth curve was recorded. The alloy structure was formed by annealing the sample at 470 K until the superstructure peaks appeared.

For the analysis, the atomic structure of the $\text{Mo}(110)$ surface is described by three base vectors a_i . The vectors are related to the conventional bcc unit cell by

$$a_1 = \frac{1}{2}[1\bar{1}1]_{\text{cubic}}, \quad a_2 = \frac{1}{2}[11\bar{1}]_{\text{cubic}}, \quad a_3 = [110]_{\text{cubic}}, \quad (1)$$

where

$$|a_1| = |a_2| = \frac{\sqrt{3}}{2}a_0, \quad |a_3| = \sqrt{2}a_0. \quad (2)$$

The reconstructed surface unit cell is shown in Fig. 1. It can be described by a vector translation of the substrate unit cell vectors a_1 and a_2 using the matrix shown below,

$$\begin{bmatrix} a_1^r \\ a_2^r \end{bmatrix} = \begin{bmatrix} 1 & 1 \\ 3 & \bar{3} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix}. \quad (3)$$

The surface was oriented using a laser to establish the optical surface followed by crystallographic alignment using bulk Bragg peaks. Growth oscillations were recorded by monitoring the x-ray reflectivity intensity as a function of time at the Mo antiphase position, which gives high sensitivity to layerwise epitaxial growth. Crystal truncation rods (CTRs) and fractional order rods (FORs) were measured using rocking scans, where the intensity is recorded while the sample is azimuthally rotated about the sample normal. Reflectivity measurements involved simultaneous scanning of the incidence and exit angles to keep them equal, while the surface normal remains horizontal. This corresponds to the well known θ - 2θ scan (θ is the x-ray incidence angle) that is sensitive only to the structure normal to the surface.

The integrated intensities were found by numerically integrating the peaks after background subtraction. The structure factor data were calculated from the integrated intensities

after correcting for the Lorentz factor, polarization factor, and the illuminated surface area. Symmetry equivalent reflections agreed within 5%.

We define one monolayer (ML) as the density of a single (110) layer of bulk molybdenum, 1.428×10^{19} atoms m^{-2} . Fe and Gd coverage is expressed in substrate units. Fe grows pseudomorphically and hence the first complete monolayer occurs at 1 ML. Gd has a larger atom size leading to completion of the first full layer at 0.62 ML, assuming that it forms hexagonally close packed (0001) planes.

Growth curves were recorded for a range of ratios of Gd:Fe, to establish the fluxes required to achieve the correct stoichiometry for GdFe_2 . Reflectivity scans were taken at single ML coverage for clean Mo, various ratios of pure Gd/Fe, and for the final structure. For the GdFe_2 structure, a total of 119 in-plane fractional order scans were recorded, which reduced to 43 after $p2mm$ symmetry averaging. The in-plane measurements were measured at a low value of perpendicular momentum transfer, making them highly sensitive to the lateral structure. Out-of-plane measurements included three integer order CTRs and six reconstructed surface FORs.

During data collection the (0.670.330.1) fractional order reflection was regularly scanned to monitor any surface degradation. The intensity did not decay significantly throughout the course of the experiment.

III. RESULTS

A. Growth calibration

It was necessary to first calibrate the individual growth rates of Gd and Fe and to establish how the film morphology developed as the ratio of the two fluxes was changed. Figure 2 shows room temperature growth oscillations [measured at the Mo antiphase condition ($l = 1$) of the specularly reflected x-ray beam] for varying ratios of Gd and Fe as a function of evaporation time. Additional reflectivity measurements were recorded for the flux ratios labeled (a)–(d) when the growth was interrupted at the monolayer completion point. These are shown in Fig. 3 together with fits to determine the atomic displacement heights above the Mo(110) surface and relative occupancies of Gd and Fe.

Figure 3(e) shows the reflectivity from the clean Mo(110) crystal, indicating a slight expansion of the surface layer (2.29 Å) in comparison to the bulk layer separation (2.23 Å). In the lower curve of Fig. 2 when growing a pure Fe film, the x-ray signal shows a small peak at 440 s which is attributed to the formation of the first monolayer (ML) followed by a larger peak at 900 s consistent with second layer completion. The fit to the reflectivity curve recorded for 1 ML of Fe and shown in Fig. 3(d) reveals 100% occupancy and a layer height of 2.15 ± 0.03 Å, consistent with the expected nearest-neighbor distances.

The deposition of pure Gd onto the Mo surface (Fig. 2 upper curve) shows an initial peak due to monolayer completion followed by a shoulder at 2 ML. These results are consistent with those of Nicklin *et al.* [9] who also report that subsequent growth tends to be disordered. As the proportion of Fe increases, the initial peak diminishes and the second peak becomes more apparent. The fit shown in Fig. 3(a) is consistent

FIG. 2. Growth curves for varying ratios of Gd to Fe.

with percentages of Gd and Fe within the monolayer of $78 \pm 2.5\%$ and $27 \pm 2.5\%$, respectively. This gives a total occupancy of $105 \pm 2.5\%$ for the first ML and indicates that the initial layer contains 5% extra atoms than expected, in agreement with similar findings by Nicklin *et al.* [9] for a pure Gd film.

The growth oscillations for approximately equal fluxes of Gd and Fe [Fig. 2(b)] extend up to at least 5 ML coverage, indicative of high quality layer by layer growth. The 1 ML reflectivity curve [Fig. 3(b)] is fitted with a model where the Gd lies 2.98 ± 0.03 Å above the Mo surface and the Fe sits at 2.00 ± 0.03 Å. This is the first indication that there may be some buckling at the interface, with the Gd sitting higher and the Fe lower than expected for a hard sphere model.

B. Growth curve fitting

The intensity oscillations that arise from layerwise growth can be modeled using kinematic scattering theory [37]. For a bulk terminated Mo(110) surface the scattering amplitude for the specular reflected beam is given by

$$A_{00l}^{\text{bulk}} = \frac{f^{\text{Mo}}}{1 - \exp(-\pi i l)}, \quad (4)$$

where f^{Mo} is the atomic scattering factor for molybdenum. If n layers of Gd or Fe with atomic scattering factor f^M ($M = \text{Gd or Fe}$) are grown on the surface, then the total scattering

FIG. 3. Fitted (solid red line) x-ray reflectivity curves for varying ratios of Gd to Fe at 1 ML coverage as shown in Fig. 2. The labels (a) to (d) correspond to the growth curves in Fig. 2 and (e) shows the reflectivity from the clean Mo(110) surface. Note that the intensity is plotted on a logarithmic axis and curves have been offset for clarity.

amplitude is the sum of each individual layer contribution added to that from the bulk thus,

$$A_{00l}^{\text{total}} = A_{00l}^{\text{bulk}} + \sum_n \theta_n f^M \exp \left[\frac{2\pi i l}{\sqrt{2}a_0} Z_n \right]. \quad (5)$$

Z_n is the height of the n th layer above the Mo surface and θ_n is the relative occupancy. An occupancy of $\theta_n = 1$ corresponds to a completely unreconstructed Mo(110) plane of 1.428×10^{19} atoms m^{-2} . As stated previously, Gd and Fe have theoretical occupancy limits of $\theta = 0.62$ and 1.00 , respectively.

A three level diffuse model [38] was used for the growth curve fitting. This model allows for the $(n+1)$ th layer to form before the n th layer is complete. A bilayer parameter S_n is included in the fitting procedure, which yields the percentage of next layer occupancy when the current layer is completed.

Figure 4 shows fits to the growth curves of pure Gd and pure Fe, deposited at a calibrated evaporation rate of 0.0023 ML s^{-1} . The fits to both curves give excellent results with a goodness of fit parameter χ^2 of 1.42 and 1.23 for Gd and Fe, respectively.

FIG. 4. Fitted growth curves for Gd (top) and Fe (bottom) deposited on Mo(110) at the calibrated rates for co-evaporation. The best fits are shown by the solid red line.

The Gd growth curve suggests an initial layer height of $Z_1 = 2.77 \pm 0.03 \text{ Å}$ above the Mo substrate layer, consistent with hard sphere positions if the Gd atoms are assumed to lie in long bridge positions. The growth of the second layer is predicted to have a $3 \pm 1\%$ occupancy when the first layer is complete and a height of $Z_2 = 3.59 \pm 0.09 \text{ Å}$ above the first. This second layer is also consistent with hard sphere positions indicating that Gd adopts its bulk lattice separation (3.63 Å).

The fit to the Fe growth curve gives layer heights of $Z_1 = 2.14 \pm 0.03 \text{ Å}$ and $Z_2 = 2.22 \pm 0.09 \text{ Å}$, consistent with pseudomorphic growth. The first layer height is as expected for a hard sphere approximation and almost identical to that from the fitted reflectivity curve [Fig. 3(d)], where $Z_1 = 2.15 \pm 0.03 \text{ Å}$. The bilayer parameter S_1 shows that the second layer is $8 \pm 1.5\%$ occupied when the first ML completes. The slight expansion of the second layer may be attributed to a small increase in film roughness after the first monolayer.

The growth curves and reflectivity scans [Figs. 3(a)–3(c)] for co-deposited films show how the addition of Fe

significantly changes the Gd growth dynamics. The Gd atoms sit highest when the occupancies of Gd and Fe are equal [Fig. 3(b)] and if a long bridge adsorption site is assumed then the Gd is expanded by approximately $8 \pm 1\%$. This could be caused by strain induced by the Fe atoms in the layer which are at a relatively low height of 2.00 ± 0.03 Å.

C. Structure determination

Structure determination of the ordered alloy reconstruction is achieved by comparing the measured structure factor amplitudes with model predictions. For a particular reflection, the structure factor is given by

$$F_{hkl} = \sum_j f_j \exp\left(\frac{-B_j q^2}{16\pi^2}\right) \exp[2\pi i(hx_j + ky_j + lz_j)], \quad (6)$$

where the sum extends over all atoms j in the unit cell, f_j is the atomic scattering factor, q is the momentum transfer, and x_j , y_j , and z_j are the atomic positions expressed as fractions of the unit cell parameters a_1 , a_2 , and a_3 , respectively. B_j is the isotropic Debye-Waller factor and has the same value for symmetry equivalent atoms. It is given by

$$B_j = 8\pi^2 \langle u_j^2 \rangle, \quad (7)$$

where $\langle u_j^2 \rangle$ is the mean square vibrational amplitude. Reflections with small perpendicular momentum transfer ($l \sim 0$) are insensitive to the z coordinate and are used to establish the in-plane structure. Out-of-plane atomic positions are determined from CTR and FOR rod scans, recorded as a function of l . This combined data set is therefore able to reveal the full three-dimensional structure.

1. In-plane data set

A total of 119 fractional order reflections were recorded. Each one was analyzed by fitting a Lorentzian curve to find the background, with subsequent numerical integration to calculate the intensity and derive the structure factor. The correlation length was found to be 150 Å from a fit to the $(-0.33 \ 0.33 \ 0.1)$ reflection, which had a full width half maximum (FWHM) of 1.109 deg. The reflections were averaged using $p2mm$ symmetry and the structure factors $|F_{hko}|$ are estimated by averaging the measured amplitudes $|F_{hk0.1}|$ and $|F_{\bar{h}\bar{k}0.1}|$. The latter is equivalent by Friedel's rule to $|F_{hk0.1}|$. This averaging reduces the data set to 43 unique fractional order reflections.

The first step to solve the structure involved calculating the in-plane electron density by direct methods using the FS98 code of Marks [39,40]. This approach clearly gave one dominant family of results as shown in Fig. 5 which was used as a starting point to model the data with established fitting software [41,42]. Initial refinement involved calculating an autocorrelation function of the electron density (Patterson map) from the fractional order reflections. This reveals interatomic correlations defined only by the reconstructed surface and not the underlying bulk.

Figure 5 shows a contour plot of the Patterson map next to the direct methods result. The Patterson map shows strong positive peaks at the corners of the unit cell and in the central

FIG. 5. Electron density map from the direct methods (left) and the Patterson function autocorrelation map from the in-plane fractional order reflections (right).

position together with weaker autocorrelation peaks around the central peak. The map indicates high symmetry in the structure and by comparison with the results of Getzlaff *et al.* [15] it is likely that the strongest interatomic vectors are due to Gd-Gd correlations while the vectors to the weaker peaks result from the Fe (from either Gd or other Fe atoms). A surface structure model was created that was consistent with these interatomic vectors, prior to parameter optimization.

The measured and calculated best fit model structure factors for all of the in-plane fractional order reflections are tabulated in the Supplemental Material [43]. The best fit model gives a fit with $\chi^2 = 1.64$ which results from allowing relaxation

FIG. 6. In-plane model showing the hard sphere model on the left, and the best fit model on the right. Atoms 1 move in the $[001]$ directions and atoms 2 in the $[00\bar{1}]$ direction.

FIG. 7. Intensity profiles of (a) the (11l) CTR, (b) the (10l) CTR, and (c) the (00l) reflectivity. The circles represent the experiment data with the hard sphere (model B) fits shown by the dashed blue curves and the best fit (model A) by the solid red curve. Model C is shown by the dotted green curves and represent the bulk continuation model [surface atoms follow the Mo(110) planes].

of the iron atoms relative to the model suggested by Getzlaff *et al.* [15] which has a fit index of $\chi^2 = 8.8$ when unrelaxed.

The in-plane models are shown in Fig. 6 with the unrelaxed model on the left and the best fit model on the right. The best fit was achieved using a four parameter least squares fit, including an arbitrary scale factor, Debye-Waller factor

FIG. 8. Out-of-plane model comparison. The original model as found by Getzlaff *et al.* is shown above with the best fit model below. Both the in-plane and out-of-plane atomic displacements are indicated.

for Gd ($B_{\text{Gd}} = 0.65 \pm 0.06 \text{ \AA}^2$), Debye-Waller factor for Fe ($B_{\text{Fe}} = 0.54 \pm 0.1 \text{ \AA}^2$), and Fe atom displacements in the [001] direction. The Fe atoms are displaced by $0.16 \pm 0.02 \text{ \AA}$ with Fe atoms labeled 1 moving in the [001] direction and atoms labeled 2 in the $[00\bar{1}]$ direction. One caveat is that here we have compared the alloy growth on Mo(110) with the published data on W(110), which have the same structure and very similar lattice constants (3.142 and 3.155 Å, respectively). Similar adsorbate reconstructions are known to form on both samples for pure Gd growth or pure Fe growth, but we cannot rule out any subtle effects that would lead to slight differences in the alloy structure formed on the two substrates.

2. Out-of-plane data set

The earlier analysis of growth curve and reflectivity scans provide some limited information about the structure perpendicular to the surface. To provide a full picture it is necessary to include CTR scans which are sensitive to lateral and perpendicular ordering in addition to the registry with the substrate. FOR scans, where the scattering is purely from the surface reconstructed layer, are also sensitive to effects such as buckling within the layer. The profiles along three CTRs and six FORs were recorded and the (10l) and the (01l) CTRs were combined by $p2mm$ symmetry averaging. Error bars are calculated as for the in-plane data set, taking systematic and statistical errors into account and never exceeding 10%. All models of the out-of-plane structure used the relaxed Fe atomic positions from the in-plane analysis.

The integer order rod profiles are shown in Fig. 7. Model C is a bulk continuation model, where the surface Gd and Fe atoms are fixed at a height corresponding to the Mo(110) spacing ($\frac{a_0}{\sqrt{2}}$). A χ^2 value of 23.89 for the (11l) CTR and 19.43 for the (10l) CTR clearly indicate that some atomic displacements must be applied to this model. Model B was formed by calculating the expected hard sphere positions of the Gd and Fe atoms. The in-plane data and previous reports [15–17,44,45] indicate that the Gd and Fe atoms sit in, or

FIG. 9. Fractional order rods scans the give information above the surface only and not with the registry with the bulk. The best fit is given by the solid red line. For comparison the hard sphere model (blue dashed line) and bulk continuation (dotted green line) are also shown.

close to, a long bridge site, with Gd at 2.76 Å and Fe at 2.08 Å above the topmost Mo layer. Model B gave χ^2 values of 5.58 for the $(10l)$ CTR, 16.08 for the $(11l)$ CTR, and 13.84 for the reflectivity $(00l)$ scan.

The solid lines in Fig. 7 show the best fit model (model A), in which the Gd and Fe vertical displacements were allowed to vary independently. The Gd is found to sit 22% higher than calculated for the long bridge hard sphere position, at 3.40 Å

TABLE I. Atomic displacements of Gd and Fe atoms in the reconstructed unit cell for two models, the best fit model A and hard sphere model B. The χ^2 value of the two CTRs and reflectivity for both models are shown.

	Model A (best fit)			Model B (hard sphere)		
	x_A	y_A	z_A	x_B	y_B	z_B
Gd	0.000	0.000	0.264	0.000	0.000	0.123
Gd	0.500	0.500	0.264	0.000	0.000	0.123
Fe	0.500	0.183	0.000	0.500	0.183	-0.050
Fe	0.000	0.317	0.000	0.000	0.317	-0.050
Fe	0.500	0.817	0.000	0.500	0.817	-0.050
Fe	0.000	0.683	0.000	0.000	0.683	-0.050
(10l) χ^2	= 1.99			5.58		
(11l) χ^2	= 1.93			16.08		
(00l) χ^2	= 2.82			13.84		

above the Mo(110) surface. Using this model, the χ^2 values reduced to 1.99 for the (10l) and 1.93 for the (11l) CTRs and 2.82 for the specular (00l) rod. The out-of-plane atomic displacements are illustrated in Fig. 8.

Further support for the best fit model is derived from the FOR data, shown in Fig. 9. The fit is significantly improved when the expanded Gd positions are used as opposed to the hard sphere model. The rods show intensity modulations,

especially for the $(2/3 \ 1/3 \ l)$ and $(4/3 \ 2/3 \ l)$ rods with a periodicity of four reciprocal lattice units, which result from the variation of atomic heights. Model C, the bulk continuation model where there is no such height variation, has been included (green dotted curve) as it does not show the observed periodicity. The final in-plane and out-of-plane atomic positions are given in Table I.

IV. DISCUSSION

The height of the Gd atoms ($3.40 \text{ \AA}$) above the Mo(110) surface is significantly expanded relative to the calculated long bridge position and also much larger than previously reported [9] for 1 ML of pure Gd ($2.74 \text{ \AA}$). Analysis of a film with the same stoichiometry but recorded at room temperature [Fig. 3(b)] also showed a much lower atomic height for the Gd of $2.98 \text{ \AA}$. We propose that the room temperature film is likely to consist of phase separated regions of pure Gd and Fe, which intermix when annealed to form the ordered alloy with the resulting expansion of the Gd. It is likely that the in-plane reorganization of the Fe atoms, together with some relaxation of the outer Mo layer, can explain some of this expansion. The Fe atoms move away from the high coordination long bridge positions, which will then force the Gd atoms higher to accommodate the changing Fe height. Simple geometric arguments suggest that such compressive stresses within the film could account for about half of the observed expansion. It is unclear what else may drive the expansion and we have considered that magnetic coupling effects between the Gd and Fe atoms, although weak, may have an influence. However, we believe that it is more likely that hydrogen is being incorporated into the structure when the film is being annealed. The x-ray diffraction is not directly sensitive to the very weak scattering from hydrogen but is to any secondary effect of exposure such as Gd layer expansion. The rare earth elements are known to be very prone to hydride formation and indeed it has been observed to expand the lattice in deliberately hydrogenated epitaxial Gd films [46] by the order of 11%. Similar expansions have been observed in compounds of $\text{GdNiH}_{3.2}$ relative to the parent GdNi compound [47]. Although these effects have been observed in thicker films, it is likely that the monolayer film will also be highly susceptible to hydrogen incorporation. Another origin of the expansion could be distortion as the alloy tries to adopt the structure of the bulk alloy C15 Laves phase where there is significant buckling between the Gd and Fe atoms along the high symmetry (e.g., $\langle 111 \rangle$) planes. Thicker films will adopt the bulklike phase and it is likely that for thinner films there will be a balance of the surface mediated and the intralayer adsorbate interactions that is likely to result in partial distortion of the interface.

V. SUMMARY

Surface x-ray diffraction has been used to establish the three-dimensional structure of the GdFe_2 alloy grown on a Mo(110) surface. The co-evaporation of Gd and Fe at various ratios showed that the Gd height varied depending on the amount of Fe that was present. The expansion is greatest for approximately equal occupancies of Fe and Gd. Annealing at a temperature of 470 K led to formation of

FIG. 10. The final three-dimensional model. A: Plan view with unit cell indicated. B: Side view. C: Details showing the bond lengths.

the alloy structure. A series of in-plane and out-of-plane x-ray diffraction measurements were recorded to identify the three-dimensional structure. Analysis of the in-plane data indicates that the Fe atoms are laterally displaced by 0.16 ± 0.02 Å relative to the model of Getzlaff *et al.* [15]. The out-of-plane data show that the Gd atoms sit at 3.40 ± 0.09 Å above the Mo surface, higher than expected from the room temperature growth curve results. This is an expansion of $22 \pm 3\%$ over the favored long bridge hard sphere position. The Fe atoms sit at 2.23 ± 0.05 Å, slightly higher than

expected for the long bridge position (2.08 Å), due to the lateral in-plane displacement. The movement of the Fe atoms raises the Gd atoms into higher sites but cannot alone explain the $22 \pm 3\%$ expansion which we suggest may also be due to hydrogen incorporation during the annealing, required to form the ordered surface alloy. Figure 10 shows the final three-dimensional model of the GdFe_2 structure with the bond lengths shown in part C. The symmetry equivalent bond lengths are grouped together and the high symmetry is clearly visible.

-
- [1] U. Gradmann and G. Waller, *Surf. Sci.* **116**, 539 (1982).
 - [2] H. L. Meyerheim, D. Sander, R. Popescu, J. Kirschner, P. Steadman, and S. Ferrer, *Phys. Rev. B* **64**, 045414 (2001).
 - [3] R. Popescu, H. L. Meyerheim, D. Sander, J. Kirschner, P. Steadman, O. Robach, and S. Ferrer, *Phys. Rev. B* **68**, 155421 (2003).
 - [4] M. Tikhov and E. Bauer, *Surf. Sci.* **232**, 73 (1990).
 - [5] J. Malzbender, M. Przybylski, J. Giergiel, and J. Kirschner, *Surf. Sci.* **414**, 187 (1998).
 - [6] J. Osing and I. Shvets, *J. Magn. Magn. Mater.* **198**, 734 (1999).
 - [7] E. D. Tober, F. J. Palomares, R. X. Ynzunza, R. Denecke, J. Morais, Z. Wang, G. Bino, J. Liesegang, Z. Hussain, and C. S. Fadley, *Phys. Rev. Lett.* **81**, 2360 (1998).
 - [8] C. S. Arnold and D. P. Pappas, *Phys. Rev. Lett.* **85**, 5202 (2000).
 - [9] C. L. Nicklin, M. J. Everard, C. Norris, and S. L. Bennett, *Phys. Rev. B* **70**, 235413 (2004).
 - [10] C. Nicklin, Ph.D. thesis, University of Leicester, 1993.
 - [11] C. Wladfried, P. Dowben, O. Zeybek, T. Bertrams, and S. Barrett, *Thin Solid Films* **338**, 1 (1999).
 - [12] J. Daval and B. Bechevet, *J. Magn. Magn. Mater.* **129**, 98 (1994).
 - [13] T. Morishita, Y. Togami, and K. Tsushima, *J. Phys. Soc. Jpn.* **54**, 37 (1985).
 - [14] J. Suits, R. Rugar, and C. Lin, *J. Appl. Phys.* **64**, 252 (1988).
 - [15] R. Pascal, M. Getzlaff, H. Tödter, M. Bode, and R. Wiesendanger, *Phys. Rev. B* **60**, 16109 (1999).
 - [16] M. Getzlaff, R. Pascal, and R. Wiesendanger, *Surf. Sci.* **566**, 236 (2004).
 - [17] M. Getzlaff, R. Pascal, H. Todter, M. Bode, and R. Wiesendanger, *Appl. Surf. Sci.* **142**, 543 (1999).
 - [18] K. Buschow, *Rep. Prog. Phys.* **40**, 1179 (1977).
 - [19] D. Bull and D. Ross, *J. Alloys. Comp.* **293**, 296 (1999).
 - [20] D. Thoma, K. Nibur, and K. Chen, *Mater. Sci. Eng. A* **329**, 408 (2002).
 - [21] K. Aoki, H. Li, M. Dilixiati, and K. Ishikawa, *Mater. Sci. Eng. A* **449**, 2 (2006).
 - [22] C. Zhang, Z. Zhang, S. Wang, and H. Li, *Solid. State. Commun.* **142**, 477 (2007).
 - [23] K. Hachiya and Y. Ito, *Elec. Acta* **53**, 224 (2007).
 - [24] M. Finney, C. Norris, and P. Howes, *Surf. Sci.* **277**, 330 (1992).
 - [25] E. Vlieg, A. W. Denier van der Gon, J. F. van der Veen, J. E. Macdonald, and C. Norris, *Phys. Rev. Lett.* **61**, 2241 (1988).
 - [26] S. Mozley, C. Nicklin, M. James, P. Steadman, C. Norris, and M. Lohmeier, *Surf. Sci.* **331**, 961 (1994).
 - [27] C. Nicklin, C. Norris, P. Steadman, J. Taylor, and P. Howes, *Physica B* **221**, 86 (1996).
 - [28] N. Jones, C. Norris, C. L. Nicklin, P. Steadman, S. Baker, A. Johnson, and S. Bennett, *Surf. Sci.* **409**, 27 (1998).
 - [29] G. Charlton, P. B. Howes, C. L. Nicklin, P. Steadman, J. S. G. Taylor, C. A. Muryn, S. P. Harte, J. Mercer, R. McGrath, D. Norman, T. S. Turner, and G. Thornton, *Phys. Rev. Lett.* **78**, 495 (1997).
 - [30] S. de Vries, W. Huisman, P. Goettkindt, M. Zwanenburg, S. Bennett, I. Robinson, and E. Vlieg, *Surf. Sci.* **414**, 159 (1998).
 - [31] M. Finney, C. Norris, P. Howes, and R. van Silfhout, *Surf. Sci.* **291**, 99 (1993).
 - [32] N. Jones, C. Norris, C. Nicklin, P. Steadman, J. Taylor, A. Johnson, and C. McConville, *Surf. Sci.* **398**, 105 (1997).
 - [33] M. Lohmeier, H. van der Vegt, R. van Silfhout, and E. Vlieg, *Surf. Sci.* **275**, 190 (1992).
 - [34] E. Vlieg, A. van der Gon, J. van der Veen, J. Macdonald, and C. Norris, *Surf. Sci.* **209**, 100 (1988).
 - [35] J. Taylor, C. Norris, E. Vlieg, M. Lohmeier, and T. Turner, *Rev. Sci. Instrum.* **67**, 2658 (1996).
 - [36] C. L. Nicklin, J. S. G. Taylor, N. Jones, P. Steadman, and C. Norris, *J. Synchrotron Radiat.* **5**, 890 (1998).
 - [37] C. Norris, *Philos. Trans. R. Soc.* **344**, 557 (1993).
 - [38] M. Everard, Ph.D. thesis, University of Leicester, 2004.
 - [39] E. Landree, L. Marks, P. Zschack, and C. Gilmore, *Surf. Sci.* **408**, 300 (1998).
 - [40] C. Gilmore, L. Marks, D. Grozea, C. Collazo, E. Landree, and R. Twisten, *Surf. Sci.* **381**, 77 (1997).
 - [41] http://www.esrf.eu/computing/scientific/joint_projects/ana-rod/index.htm.
 - [42] E. Vlieg, *J. Appl. Crystallogr.* **33**, 401 (1999).
 - [43] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.94.075419> for a comparison between the calculated best fit in-plane structure factors and the measured data.
 - [44] E. Clementi, D. Raimondi, and W. Reinhardt, *J. Chem. Phys.* **38**, 2686 (1963).
 - [45] B. Vainshtein, V. Fridkin, and V. Indenbom, *Structure of Crystals*, 3rd ed. (Springer-Verlag, Berlin, Heidelberg, 1995).
 - [46] P. Tessier, D. Fruchart, and D. Givord, *J. Alloys Compd.* **330–332**, 369 (2002).
 - [47] Y. Yaropolov, A. Andreenko, S. Nikitin, S. Agafonov, V. Glazkov, and V. Verbetsky, *J. Alloys Compd.* **509**, Supplement 2, S830 (2011).